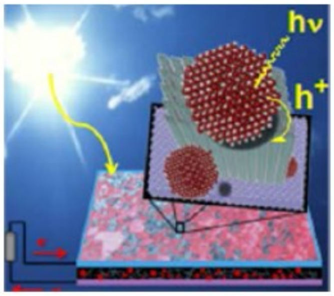
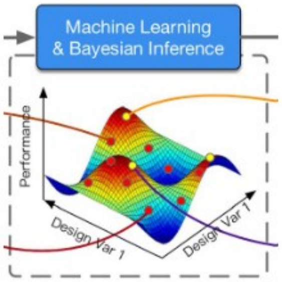
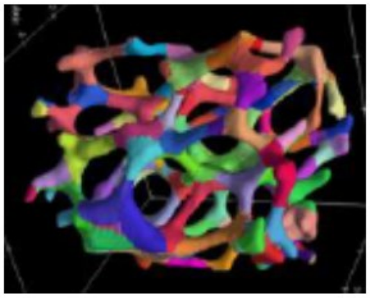
Materials Genome Initiative

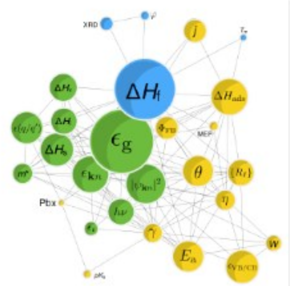
Accelerating Materials Research

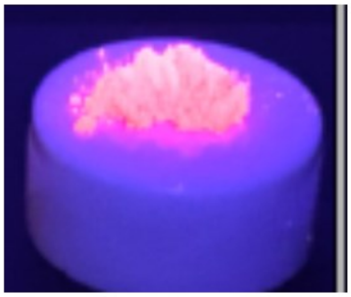
Fourth Principal Investigator Meeting

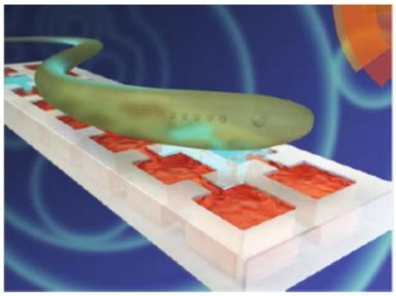


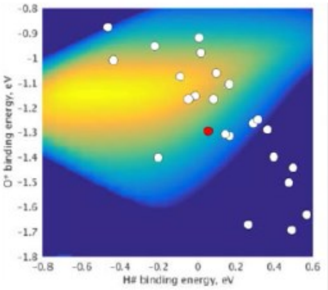


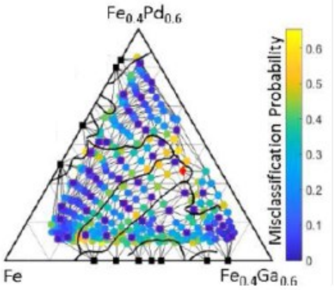


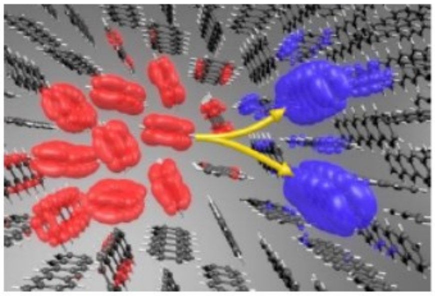












AIR FORCE RESEARCH LABORATORY

DEPARTMENT OF ENERGY
UNITED STATES OF AMERICA

NIST

NSF

March 26-27, 2018 – College Park, MD

On the Cover

Top left: Transfer of photogenerated holes from a quantum dot to an $M_xV_2O_5$ nanowire, a central step in redox photocatalysis. (Watson)

Top center: A data-centric approach for accelerating the design of future nanostructured polymer and composite systems includes the use of machine learning and Bayesian inference. (Brinson)

Top right: Results from 3D grain mapping of open-cell aluminum foam. (Spear)

Middle left: A systematic survey of the computational literature reveals a wide range of accessible performance factors, which can be categorized into thermodynamic (blue), photovoltaic (green), and electrocatalytic (yellow) parameters. (Dabo)

Middle center: Emission from fluorescent dyes in solid state is normally quenched. However, the bright emission seen in solution can be rescued by hierarchical organization into small-molecule ionic lattices. (Flood)

Middle right: A microfluidic reaction-diffusion network designed to produce a spatiotemporal pattern equivalent to an eel's neural network that controls swimming. (Fraden)

Bottom left: Computational analysis of descriptors and trends for water-gas shift on Au nanoparticles supported on doped substrates. Contours denote rates predicted from theoretical scaling relationships, while open circles correspond to particular dopants. (Greeley)

Bottom center: The autonomous phase mapping system utilizes physics, theory, physics databases, and instrument control to rapidly identify a ternary phase map for the Fe-Ga-Pd material system. (Kusne)

Bottom right: Ab initio many-electron calculations revealed a new mechanism (via a purely Coulomb process) for decay of a singlet exciton (red) into two triplet excitons. Predicted decay rate into two triplets of opposite center-of-mass momentum in solid pentacene is in good agreement with experiment. (Louie)

Foreword

This volume documents the proceedings of the Materials Genome Initiative (MGI) Principal Investigator (PI) meeting that was held March 26-27, 2018 in College Park, Maryland. The meeting convened MGI-related efforts at the National Science Foundation (NSF), the Department of Energy (DOE), the National Institute of Standards and Technology (NIST), and the Air Force Research Laboratory (AFRL). The meeting was co-chaired by Drs. Gregory Payne and William Bentley (University of Maryland – College Park).

The interagency MGI is intended to shorten the time required to transition new materials from discovery to deployment. It strives to combine advanced synthetic, experimental, and computational tools with digital data in an iterative fashion leading to validated software, curated software, curated data, and targeted synthesis. Further information on MGI is available at www.MGI.gov, including the MGI Strategic Plan released in December 2014. The Strategic Plan highlights four sets of goals of the MGI:

(1) Leading a culture shift in materials-science research to encourage and facilitate an integrated team approach;
(2) Integrating experiment, computation, and theory and equipping the materials community with advanced tools and techniques;
(3) Making digital data accessible; and
(4) Creating a world-class materials-science and engineering workforce that is trained for careers in academia or industry.

The meeting brought together PIs from NSF's Designing Materials to Revolutionize and Engineer our Future (DMREF) program, NSF's Material Innovation Platforms (MIPs), DOE's Computational Materials and Chemistry Science Centers, DOE's Energy Materials Network (EMN), and MGI-related efforts at NIST, Air Force, and other federal agencies. The meeting provided a venue for scientists to present and exchange information about their research activities, foster new ideas, establish collaborations, and discuss future research directions. It also aided NSF, DOE, NIST, and AFRL in assessing the needs of this research community and in charting future programmatic directions.

PIs were asked to submit an abstract and to prepare a poster to represent their project. Several projects were selected for oral presentation. Drs. Linda Sapochak (NSF) and Chuck Ward (AFRL) provided introductory remarks from the MGI Subcommittee regarding preparation for the tenth anniversary of the MGI. Sessions on the first day centered on how interactions among academia, national, and federal laboratories can be fostered and how centers/platforms can provide focal points for MGI-related research. Break-out sessions in the afternoon of the first day addressed key challenges across the materials spectrum. The second day opened with a panel discussion focused on the development of the next generation workforce. This was followed by two sessions that addressed topics of contemporary interest in MGI: 1) implementing data-driven materials research, and 2) progressing along the materials development continuum. Both days concluded with a poster session.

The MGI strategic plan recognizes that a key challenge to achieving its vision involves making digital data accessible. This will require combining data from experiment and computation into a searchable materials data infrastructure and encouraging researchers to make their data available to others. In order to address the MGI vision of enabling discovery, development, manufacturing, and deployment of advanced materials at least twice and at a fraction of the cost as is possible through traditional methods, it is necessary to lower the barriers to moving technology along the Materials Development Continuum. To facilitate this, opportunities for partnerships among fundamental research teams, applied research programs, and industrial partners should be made available.

The 2018 MGI PI meeting thus included a competition for supplemental funding for DMREF teams in order to encourage them to collaborate with federal MGI partners and industry in order to either advance the data aspects of their projects or to move fundamental technologies along the Materials Development Continuum. A pamphlet describing interagency collaborative opportunities was distributed to PIs at the beginning of the meeting. White Papers were due two weeks after the conference (April 9, 2018). Twenty seven (27) supplements were funded for a total of $2,695,607. Funds were provided by NSF's Directorate of Mathematical and Physical Sciences (MPS) Divisions of Materials Research (DMR) and Mathematical Sciences (DMS) and Office of Multidisciplinary Activities (OMA) and Directorate of Engineering (ENG) Divisions of Civil, Mechanical and Manufacturing Innovation (CMMI) and Chemical, Bioengineering, Environmental and Transport Systems (CBET).

We thank all the meeting participants for their active contributions in sharing their ideas and research accomplishments. We recognize the DMREF Management team for their insightful contributions before, during, and after the meeting. We also thank Anne Anonsen for her outstanding work in all aspects of the meeting organization and Jinyang Li for her valuable assistance with the meeting Abstracts and this Proceedings Booklet.

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Abstracts

Agenda

UNIVERSITY OF MARYLAND

Materials Genome Initiative Principal Investigators Meeting

Principal Investigators Meeting | March 26-27, 2018
The Hotel at the University of Maryland

MONDAY, MARCH 26TH

7:00 AM	Registration, Continental Breakfast
8:20 AM	Welcome, Laurie Locascio (University of Maryland)

PREPARING FOR A DECADE OF ACCELERATED MATERIALS RESEARCH

8:30 AM	Introductory Remarks from MGI Subcommittee — Linda Sapochak (NSF), Chuck Ward (AFRL)

HOW CAN INTERACTIONS AMONG ACADEMIA, NATIONAL, AND FEDERAL LABORATORIES BE FOSTERED?

9:00 AM	Opportunities for Collaboration among MGI-related Activities *Chair: Linda Sapochak (NSF)*
9:00 AM	Bruce Garrett (DOE-BES), "Computational Materials Science and Chemistry Centers"
9:15 AM	Richard Vaia (AFRL), "Research Priorities at the Air Force Research Laboratory"
9:30 AM	Eric Miller (DOE-EERE), "Energy Materials Network"
9:45 AM	Eric Lin (NIST), "Materials Data Resources, Modeling Software, and Tools"
10:00 AM	Panel & Open Discussion
10:30 AM	Break, Poster Setup
11:00 AM	Daryl Hess (NSF): Cyberinfrastructure for Sustained Scientific Innovation (CSSI)

HOW CAN CENTERS/PLATFORMS PROVIDE FOCAL POINT FOR MGI-RELATED RESEARCH?

11:10 AM	Resources in MGI *Co-chairs: Chuck Ward (AFRL), Ram Seshadri (University of California - Santa Barbara)*
11:10 AM	Tyrel McQueen (Johns Hopkins University), "PARADIM: Platform for the Accelerated Realization, Analysis and Discovery of Interface Materials"
11:20 AM	Vin Crespi (Pennsylvania State University), "2DCC: 2D Crystal Consortium"
11:30 AM	Ilja Siepmann (University of Minnesota), "Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials"
11:45 AM	E. Begum Gulsoy (Northwestern University), "CHiMaD: Center for Hierarchical Materials Design"
12:00 PM	Panel & Open Discussion
12:30 PM	Working Lunch Report on DMREF 2D Materials & Devices Data White Paper Competition (Eva Campo, NSF)

HOW IS THE MGI ADDRESSING KEY CHALLENGES ACROSS THE MATERIALS SPECTRUM?

1:30 PM ***Breakout Sessions: Recent Progress and Future Directions in MGI-related Research***

1) Polymers and Biomaterials

Co-chairs: Andrey Dobrynin (University of Akron), John D. Tovar (Johns Hopkins University)

1:30 PM Greg Payne (University of Maryland), "Thin Film Biofabrication for Integrated Bio-electronics"
1:45 PM Michael Webb (University of Chicago/ANL), "Machine-learning Enhanced Modeling, Characterization, and Discovery of Soft Materials"
2:00 PM Kevin Dorfman (University of Minnesota), "Computationally-driven Design of Advanced Block Polymer Nanomaterials"
2:15 PM Maneesh Gupta (AFRL), "Marine Biopolymers with Tunable and Responsive Mechanical Properties"
2:30 PM Karen Wooley (Texas A&M University), "Interface-promoted Assembly and Disassembly Processes for Rapid Manufacture and Transport of Complex Hybrid Nanomaterials"
2:45 PM Panel & Open Discussion

2) Catalysts and Catalytic Processes

Co-chairs: Ismaila Dabo (Pennsylvania State University), David Watson (SUNY-Buffalo)

1:30 PM Andreas Heyden (University of South Carolina), "Design and Discovery of Multimetallic Heterogeneous Catalysts for a Future Biorefining Industry"
2:00 PM Hendrik Heinz (University of Colorado), "Design and Testing of Nanoalloy Catalysts in 3D Atomic Resolution"
2:15 PM Laura Gagliardi (University of Minnesota), "Inorganometallic Catalyst Design"
2:30 PM Jeff Greeley (Purdue University), "Design of Multifunctional Catalytic Interfaces from Firsts Principles"
2:45 PM Panel & Open Discussion

3) Structural Materials

Co-chairs: Robert Hull (Rensselaer Polytechnic Institute). Katherine Faber (CalTech)

1:30 PM Tresa Pollock (University of California – Santa Barbara), "Accelerating the Design and Synthesis of Multicomponent, Multiphase Metallic Single Crystals"
1:45 PM Katsuyo Thorton (University of Michigan), "The PRISMS Center Framework: An Integrated Multi-Scale Capability for Accelerated Predictive Materials Science"
2:00 PM Ashley Spear (University of Utah), "Novel 3D Experiments, Simulations, and Optimization for Accelerated Design of Metallic Foams"
2:15 PM Jason Hattrick-Simpers (NIST), "Combining High-throughput Experimentation and Machine Learning to Discover new Functional Amorphous Alloys"
2:30 PM Mike Groeber (AFRL), "Challenges in the Digital Materials Enterprise: Structural Materials Examples"
2:45 PM Panel & Open Discussion

4) Correlated Materials (Beyond DFT)

Co-chairs: Brian Moritz (SLAC), Kyungwha Park (Virginia Tech)

1:30 PM	Gabi Kotliar (Rutgers University), "Towards Theoretical Spectroscopy and Material Design of Strongly Correlated Materials"
1:45 PM	Paul Kent (ORNL), "Predictive Calculations for Correlated Materials"
2:00 PM	Warren Pickett (University of California – Davis), "Designing Insulating Topological Insulators"
2:15 PM	Ed Barnes (Virginia Tech), "Ab initio Design of Quantum Molecular Magnets for Information Applications"
2:30 PM	Aldo Romero (West Virginia University), "Search for Magneto-Electronic Complex Fluoride-based Interfaces with Novel Properties"
2:45 PM	Jianwei Sun (Tulane University), "SCAN Meta-GGA: An Accurate, Efficient, and Physically Sound Density Functional for Wide Classes of Materials"
3:00 PM	Panel & Open Discussion

5) Electronic/Photonic Materials, Processes, and Devices

Co-chairs: Ruth Pachter (AFRL), John Anthony (University of Kentucky)

1:30 PM	Dabdeep Jena (Cornell University), "Extreme Bandgap Semiconductors"
1:45 PM	Steve Louie (University of California – Berkeley), "Ab initio Theory and Computation of Multiple-Particle Correlated Excitations in Materials: Trions and Biexcitons"
2:00 PM	Barry Dunietz (Kent State University), "Post-Marcus Theory and Simulation of Interfacial Charge Transfer Dynamics in Organic Semiconductors"
2:15 PM	Giulia Galli (University of Chicago), "Interoperability of Advanced Sampling and Electronic Structure Codes and Data Reproducibility"
2:30 PM	Meredith Reed (ARL)
2:45 PM	Panel & Open Discussion

6) Materials and Chemical Processes for Energy

Co-chairs: Randy Snurr (Northwestern University), Inga Ulusoy (Michigan State University)

1:30 PM	Eric Toberer (Colorado School of Mines), "Computationally Driven Targeting of Advanced Thermoelectric Materials"
1:45 PM	Koblar Jackson (Central Michigan University), "FLOSIC - Efficient Density Functional Calculations without Self-interaction"
2:00 PM	Amin Salehi-Khojin (University of Illinois – Chicago), "Operation of Lithium-oxygen Batteries with Long Cycle Life in a Realistic Air Atmosphere"
2:15 PM	Priya Vashishta (University of Southern California), "Materials Genome Innovation for Computational Software (MAGICS)"
2:30 PM	Hai-Ping Cheng (University of Florida), "Exploring Multi-functional Molecular Electronic Materials"
2:45 PM	Panel & Open Discussion

MONDAY, MARCH 26TH CONTINUED

3:30 PM	Poster Session & Networking with Refreshments (Odd Number Posters)
5:30 PM	Fuel Cell Toyota Mirai on Display
6:00 PM	Campus Tour (Optional)
	Dinner on your own.

TUESDAY, MARCH 27TH

8:00 AM	Continental Breakfast
8:30 AM	Breakout Session Reports
9:30 AM	**Developing the Next Generation Workforce (Panel Discussion)** *Chair: Alexis Lewis (NSF)*
	Katsuyo Thorton (University of Michigan) Ray Arroyave (Texas A&M University)
10:00 AM	Break

HOW CAN DATA-DRIVEN RESEARCH ACCELERATE MATERIALS DISCOVERY AND DEVELOPMENT?

10:30 AM	Implementing Data-Driven Materials Research *Co-chairs: James Rondinelli (Northwestern University), Dane Morgan (University of Wisconsin)*
10:30 AM	Shyue Ping Ong (University of California – San Diego), "Harnessing the Materials Project for Data-driven Materials Design"
10:45 AM	Elsa Olivetti (MIT), "Data Mining for Predictive Synthesis"
11:00 AM	Debra Audus (NIST), "Enabling Polymer Informatics through Database Creation"
11:15 AM	Matt Miller (CHESS), "Extracting Real Time Material Evolution Information as a Synchrotron Using Machine Learning Methods"
11:30 AM	Benji Maruyama (AFRL), "Autonomous Research of Carbon Nanotube Processing"
11:45 AM	Efthimios Kaxiras (Harvard University), "Machine Learning for Materials: What We Can Learn from Machines"
12:00 PM	Panel & Open Discussion
12:30 PM	Working Lunch Renewal Proposals in DMREF (John Schlueter, NSF)

HOW CAN MATERIALS DISCOVERY ADVANCE TOWARD DEVELOPMENT?

1:30 PM	Progressing along the Materials Development Continuum *Chair: John Schlueter (NSF)*
1:30 PM	Barry Johnson (NSF-IIP)

TUESDAY, MARCH 27TH CONTINUED

1:45 PM	Geoff Brennecka (Colorado School of Mines), Dan Potrepka (ARL), David VanHeerden (Materion), "IAB: Piezoelectrics"
2:00 PM	Volker Sorger (George Washington University), "I-corps: 2D Metal Dichalcogenides"
2:15 PM	Michael Mills (The Ohio State University), "GOALI: Superalloys"
2:30 PM	Ravi Chandran (University of Utah), Tony Sanders (Ortho Development Corp.), "GOALI: Ti-B-X Materials"
2:45 PM	**Panel & Open Discussion**
	Eric Toberer (Colorado School of Mines), "IAB: Thermoelectrics"
	George Rodriguez (Exxon Mobil), "GOALI: Additives for Novel Polymer Morphology and Performance"
	Viktor Podolskiy (University of Massachusetts – Lowell), "I-corps: Composite Photonics"
	Amar Flood (Indiana University), "I-corps: Fluorescent Dyes and Pigments"
	Karen Wooley (Texas A&M University), "I-corps: Natural Product-based, Mechanically-diverse Degradable Engineering Materials"
	Richard Vaia (AFRL), "Manufacturing USA"
3:30 PM	Poster Session & Networking with Refreshments (Even Number Posters)
5:30 PM	Meeting Adjourns

Breakout Session Reports

Polymers and Biomaterials

Session Chairs:
Andrey Dobrynin (University of Akron) and John D. Tovar (Johns Hopkins University)

The area of polymers and biomaterials has seen tremendous transformation during the last ten years. In particular, with the introduction of the MGI initiative, the field has accelerated the discovery of hierarchical, self-healing, adaptive, and biomimetic materials targeted for applications in energy transduction, tissue engineering, repair and regeneration, genetic manipulation of cells, drug delivery, multidimensional sensing, and additive manufacturing.

Building on this success, the following areas of research should be pursued in the MGI context: (1) self-replicating/adaptive materials; (2) design of materials out of equilibrium; (3) polymer based energy harvesting materials; (4) materials for active transport; and (5) time programmable materials. These areas of research will become a source of new technologies addressing societal needs in health, energy, and sustainability. The following MGI-related grand challenges were identified by the panel:

- Develop multiscale modeling/simulation tools to explore soft materials and polymer assembly/performance across time and length scales.
- Develop computational tools capable of pinpointing critical regimes impactful for materials functions in order to narrow the search in the parameters' space.
- Create and maintain searchable databases to fill in the gaps in existing tabulated data that will provide information on materials chemistry, dispersity, morphology, processing history, properties, etc.
- Develop the depository and format of the open source software for integration amongst commercial instruments to standardize data outputs for cataloging, data storage and data search.
- Develop strategies for data driven polymeric materials and biomaterials design.
- Develop tools for nondestructive characterization of polymeric materials and biomaterial across time and length scales to establish correlations with functions and failure.

Catalysts and Catalytic Processes

Session Chairs:

Ismaila Dabo (Pennsylvania State University) and David Watson (SUNY-Buffalo)

Speakers/panelists. The session highlighted progress in the application of atomistic models and of uncertainty-quantification techniques to accelerate the discovery and development of new catalysts. Each speaker underscored the need to go beyond idealized models of catalytic surfaces and tackle the complexity of catalytic nanostructures and multi-component catalysts taking into account the influence of the support and surrounding gas/liquid environment.

Andreas Heyden (University of South Carolina) presented on the computational design of multimetallic catalysts with a focus on the water-gas shift reaction. A combined top-down and bottom-up approach was applied to identify the active sites of Pt/TiO_2 catalysts. Key to this approach was the evaluation of the uncertainties arising from various DFT approximations by external comparison with experimentally measured activities or by internal comparison between different DFT functionals.

Hendrik Heinz (University of Colorado) discussed the application of interatomic force fields and large-scale simulations to explain how the adsorption of molecular species on alloy nanoparticles can promote the growth of active facets for the oxygen reduction reaction (ORR). These models were shown to predict the surface structure of metallic nanoalloys in close agreement with experimental maps of local composition and local strain. The importance of accounting for environmental effects (temperature, pH, solvent) was also emphasized.

Laura Gagliardi (University of Minnesota) presented on the theory-guided design of metal-organic framework (MOF) catalysts for natural gas conversion. In addition to the problem of predicting catalytic activity as a function of structure and composition, the speaker explained the challenges associated to predicting the stability of MOF catalysts and their ability to be synthesized. The need to develop beyond-DFT first-principles methods for accurately describing of electronic structure of MOF-supported transition-metal catalysts was also highlighted.

Jeff Greeley (Purdue University) presented on the design of multifunctional catalytic interfaces with a focus on overcoming the limitations imposed by volcano plots (Sabatier's principle) and scaling relations. Metal/metal-oxide interfaces were shown to offer new opportunities in the design of bifunctional catalysts for the water-gas shift reaction. Recent developments in the use of experimental data to find computational descriptors of catalytic activity were also discussed.

Panel discussion and feedback. A pervasive theme of the speakers' talks and the panel discussion was that the integration of theory and experiment, as it pertains to the design of catalysts and catalytic processes, is challenging but has the potential to accelerate the discovery of catalysts and the elucidation of active-site structures and catalytic mechanisms.

Challenges. Challenges associated with integrating theory and experiment were identified and discussed. First, experimental data will never be "perfect." Experimental data sets are complicated by limitations or gaps in data, uncertainties, and the fact that data pertaining to a given catalyst architecture or catalytic process are often obtained by multiple researchers or research teams, which can complicate comparisons. Computational models must be developed within this context.

Second, challenges associated with determining and modeling the structures of active sites were discussed. Computational scientists on the panel emphasized that improvements in the accuracy of structural information pertaining to active sites of catalysts and catalyst-support architectures would facilitate modeling. Structural evolution of active sites during catalysis can further complicate both measurements and predictions. Additionally, computationally-designed catalyst structures may not be stable or experimentally accessible.

Challenges pertaining to computational modeling include the variation of properties with the computational model used to predict them, the difficulty in ascertaining when a model system is sufficiently refined to yield reliable results, and the long-term sustainability of computational tools and databases. The need to move beyond density functional theory was discussed.

Open questions. The panel and attendees discussed the potential of machine learning and the interpretability of machine-learning models with respect to catalysis. The relevance of machine learning, and the choice of appropriate data-science model, for catalysis-associated data were discussed with regard to the relatively sparse data available. It was left as an open question whether catalysis is a big-data-relevant field.

The next level. Several themes were identified that have the potential to advance catalysis-related research to the next level. The targeted synthesis of catalyst constructs with well-controlled active-site structures would facilitate and accelerate computations. Improved data curation and the standardization of data from multiple sources would streamline experimental and theoretical research and promote cross-disciplinary communication. Finally, the movement away from idealized active sites in computational modeling, towards the improved modeling of interfaces and environmental effects, would increase the applicability of computational modeling to real-world catalyst systems.

Structural Materials

Session Chairs:
Robert Hull (RPI) and Katherine Faber (Caltech)

This break-out summary is organized around four themes identified by the workshop organizers:

1) *Identify specific examples of how MGI research has accelerated the discovery of new materials or development of new tools, processes, or devices within this field.*
2) *What is needed to take research in this field to the next level?*
3) *How is data science and applied mathematics being integrated into research projects?*
4) *Where does the field stand with respect to the challenges identified for this field in the MGI Strategic Plan?*

1. Examples of how MGI research has accelerated discovery of new materials or development of new tools, processes, or devices within the field.

In this section we summarize the progress summarized in the excellent presentations given by the five presenters in the break out.

1.a Discovery of New Materials: Development of Cobalt-based Alloys (Tresa Pollock, UCSB)

Motivated by the improvement in efficiency in gas turbine engines, this research explores multicomponent alloy space for new superalloys which would allow for 150 °C increase in operating temperatures. The work has included both new computational approaches and design methodologies for multilayer coatings and multicomponent solidification. New experimental characterization tools enhance verification efforts; these include tri-beam tomography and photo-stimulated luminescence spectroscopy coupled to high throughput ion plasma deposition.

1.b Development of New Tools: Center for PRedictive Integrated Structural Materials Science – PRISMS (Katsuyo Thornton, University of Michigan)

The PRISMS Center has made significant progress in the development of open source software including real space DFT, statistical mechanics, phase diagram generation (in conjunction with CALPHAD), phase field models, crystal plasticity and continuum plasticity. These can be integrated with external codes, such as Fourier space DFT, dislocation dynamics and atomistic models. This integrated system allows for tackling multi-scale phenomena in structural materials. The Center also operates The Materials Commons, a platform for organizing, collaborating, publishing and sharing research data.

1.c. Accelerated Design of Metallic Foams (Ashley Spear, University of Utah)

A DMREF/GOALI program for open-cell investment-cast metal foams is focused on multiscale deformation and characterization using X-ray computed tomography. These experiments are integrated with simulations of synthetic foams and are used to identify both processes and structures for optimized performance. The collaborations with industry allow for validation and enable transition to commercialization.

1.d Iterative Machine Learning-High Throughput Experimental Platform for Discovery of Novel Amorphous Alloys (Jason Hattrick-Simpers, NIST)

A machine learning model has been developed to identify new metallic glasses. From 24-million ternary alloys, the machine learning algorithm predicts nearly 75,000 potential metallic glasses. Results from the machine learning model are compared to other predictive models (Yang Model; Efficient Packing Model) for amorphous alloys. High throughput experiments are chosen which involve contradiction of the three models, which can then be used to improve machine learning.

1.e Digital Materials Enterprise (Michael Groeber, Air Force Research Lab)

The Digital Materials Enterprise is an integrated system of experimental tools to 'digitize' materials structure/function, data process algorithms to structure and reduce materials data, quantitative metrics to 'compress' material representation, instantiation tools to 'decompress' material realizations and simulation tools to encode material performance. Three case studies were provided to demonstrate progress in the Digital Materials Enterprise: metal additive manufacturing process understanding and optimization; impact damage in polymer matrix composites; and probabilistic approach to fatigue in micro-textured titanium.

2. What is needed to take research to the next level?

Break-out participant responses can be partitioned into three areas: research and development related, personnel related and suggestions for funding agencies. For R&D-related suggestions, investigators see the value of machine learning, but suggest that it could benefit from greater incorporation of physics and chemistry into models. The connections between experiments and modeling should continue to be developed. Finally, greater efforts in automation of data collection and its incorporation into sharable databases would streamline and accelerate research. From the personnel perspective, materials students could profit from more experience in data analytics. Both students and seasoned researchers need to be encouraged and trained to share data with the materials community.This could be accomplished with supplementary information in publications, or with MGI-related data repositories. Agencies are encouraged to design and support more agile funding models, particularly for short term projects.

3. How is data science and applied mathematics being integrated into research projects?

As evidenced by the presentations in the break out session, and in the workshop broadly, this aspect of MGI is advancing by leaps and bounds, with numerous examples of how data analytics, machine learning, artificial intelligence, and control theory are being coupled ever more closely to experiment and modeling. Specific examples include the guided discovery of amorphous metals, Bayesian analysis of optimal design in metallic foams, coupling of data analytics with high throughput synthesis and analysis, the development of multiple data bases and repositories of materials properties with rapidly increasing buy-in from the community, and meshing of experiment, simulation and data analytics across multiple length and time scales. Some challenges identified during the break-out discussions included the development of robust ontologies for materials processing, the need for increasing collaboration between materials researchers and computer / data scientists, better integration between the major materials data bases that are emerging, and the need for more robust structures for integrating materials processing data into data bases.

4. Where does the field stand with respect to the challenges identified for this field in the MGI Strategic Plan?

Specific elements of the strategic plan for "lightweight and structural materials" in the 2014 MGI strategic plan (www.mgi.gov) that were addressed were:

4.a Demonstrate the ability to fully characterize the microstructure of one cm^3 within one week.

Depending on the meaning of "fully characterize" the consensus of the break-out group was that with 3D resolution of tens of nm, and with full voxelation the state of the art is that currently ~ 1 mm^3 could currently be structurally analyzed in this time frame. It was emphasized in the discussions that rather than attempting to meet this target by "brute force" a more relevant approach – and consistent with the spirit of MGI – is the development of algorithms for intelligent sparse voxel sampling, and methodologies for definition of representative volumes (the latter also being highlighted in the 2014 plan).

4.b Develop analytical tools for efficient extraction of process-structure-property links from large datasets

The break-out group perceived different approaches in realizing this target, ranging from ever-increasing speed in data processing from improved hardware, algorithms or methods adapted to this task (such as cognitive computing), to the disparate challenges of organization of structured versus unstructured data. The major challenge / opportunity was recognized as the need to better engage the computer science community by collaborating to define the relevant questions as constituting cutting edge research for that community.

The overarching conclusion of the break out discussions was that the strategic plan is already somewhat outdated - this was perceived as a very positive conclusion, as it shows the rapid progress of the MGI vision in this field.

Correlated Materials

Session Chairs:
Brian Moritz (SLAC) and Kyungwha Park (Virginia Tech)

. The Correlated Materials breakout session featured six speakers:

- **Gabi Kotliar** "Towards theoretical spectroscopy and material design of strongly correlated materials"
- **Paul Kent** "Predictive Calculations for Correlated Materials"
- **Warren Pickett** "Designing Insulating Topological Insulators"
- **Ed Barnes** "Ab initio Design of Quantum Molecular Magnets for Information Applications"
- **Aldo Romero** "Search for Magneto-Electronic Complex Fluoride-based Interfaces with Novel Properties"
- **Jianwei Sun** "SCAN Meta-GGA: An Accurate, Efficient, and Physically Sound Density Functional for Wide Classes of Materials"

These talks focused on different aspects of ab initio materials modeling, current progress and challenges. Some of the most important challenges can be summarized as follows. There is a need to develop techniques that treat dynamic as well as static correlations to predict spectroscopic information for validation by experiment. This comes with a trade-off between computational cost and accuracy, which requires the design of long wavelength, more heuristic models and embedding schemes to perform computations more cost effectively. In order to become truly predictive, one needs to significantly reduce the amount of empiricism needed to account for materials synthesis variability. Especially for 3d-transition metal materials, errors can be significant and capturing unconventional behavior likely requires beyond-mean-field methods. To design and test models for molecular qubit states for quantum computing, with numerous intrinsic and extrinsic issues such as spin-orbit and hyperfine interactions, strong correlations, and substrate coupling and cross-talk, requires the refinement of new methods to assist experimental implementation. Growth conditions and geometric effects play a significant role and subtle materials synthesis differences can impact ab initio predictions for materials, including ferroelectrics. What are the limitations of many of these methods? How far can one push different approximations for various materials?

To achieve broader adoption, many of these techniques require significant simplification and the development of tutorials and training exercises with real research examples. A more significant connection and interaction between experimentalists and theorists, with predictions for more physical properties and real-world use cases, will foster broader adoption and help to better refine the models and methods.

There were some broad themes covered in the panel discussion.

How is data/computer science and applied math being integrated into research projects?

Materials specific, correlated materials research doesn't necessarily lend itself to data intensive, machine learning the way that it may be applied in other subfields. However, computer science and applied math still have a significant role to play. The design of more accurate functionals, thinking of those in the SCAN project, requires a lot of input from mathematics and applied math to develop a framework that satisfies certain exact constraints. Applied math certainly has a role to play in designing and implementing non-local corrections. Simplifying the codes and making them freely available to the community in a user-friendly package will require computer science expertise. More importantly, making these techniques and codes scalable, with efficient performance at exascale, requires a significant interaction between the domain scientists and computer science and applied math experts.

What is needed to take research in this field to the next level?

To move research to the next level, the panel hit on a number of key issues. Interaction with experimentalists and access to the best-quality experimental data to use as input will improve our theoretical descriptions, in particular details on the electronic structure and other properties. Echoing a common theme, next level research will require cheaper, more efficient computational methods, while still maintaining high accuracy for strongly correlated materials (again thinking of the SCAN project). This will undoubtedly require significant input from computational scientists to make codes efficient at the exascale. Of course no one enjoys having theoretical predictions that don't match empirical results. Often these are unpublishable results, but provide important constraints on the applicability of different computational schemes. Having some way of disseminating this information as a guide for other researchers can help to speed progress in the field. In addition, open and honest benchmarking between different codes and techniques (as has been done in other correlated materials research, as with the Simons Foundation studies) allows researchers in the field to better understand both the strengths and limitations of various methods. Finally, we need open channels of communication between experimentalists and other theorists, especially those engaged in research using different methodologies – quantum Monte Carlo (QMC) and density matrix renormalization group (DMRG), uniquely designed to treat the inherent many-body problem of correlated materials.

Electronic/Photonic Materials, Processes, and Devices

Session Chairs:
Ruth Pachter (AFRL) and John Anthony (University of Kentucky)

The five speakers at the electronic/photonic materials, processes, and devices session have outlined perspectives on the accomplishments of the MGI, experimentally (Jena), theoretically and computationally (Louie, Dunietz, Galli), and in an integrated approach (Reed).

1. Debdeep Jena (Cornell University) discussed 'Extreme Bandgap Semiconductors'. The speaker demonstrated that the MGI has led to excellent teaming, which enabled addressing a combination of properties in design of large bandgap semiconductors. For example, the team reported recently on the successful use of molecular beam epitaxy to grow and integrate niobium nitride (NbN)-based superconductors with the wide-bandgap family of semiconductors—silicon carbide, gallium nitride (GaN) and aluminum gallium nitride (AlGaN) (see Yan, R.; Khalsa, G.; Vishwanath, S.; Han, Y.; Wright, J.; Rouvimov, S.; Katzer, D. S.; Nepal, N.; Downey, B. P.; Muller, D. A., GaN/NbN epitaxial semiconductor/superconductor heterostructures. *Nature* **2018**, 555 (7695), 183).

2. Steve Louie (University of California-Berkeley) discussed 'Ab initio Theory and Computation of Multiple-Particle Correlated Excitations in Materials: Trions and Biexcitons'. The speaker, who pioneered prediction of excitations in solids by many-body perturbation theory, recently applied the approach to two-dimensional materials (Ye, Z.; Cao, T.; O'Brien, K.; Zhu, H.; Yin, X.; Wang, Y.; Louie, S. G.; Zhang, X., Probing excitonic dark states in single-layer tungsten disulphide. *Nature* **2014**, 513 (7517), 214-8), and demonstrated the importance of further fundamental theoretical developments through the MGI. The speaker reported on important computational developments to predict trions and biexcitons, which have implication in development of quantum materials.

3. Barry Dunietz (Kent State University) discussed 'Post-Marcus theory and simulation of interfacial charge transfer dynamics in organic semiconductors'. The speaker demonstrated, for example, the utility in using theoretical predictions for design principles development, whereby fluorination is utilized to achieve high charge mobilities, which is a key parameter in development of organic semiconductors (see recent work (Maiti, B.; Schubert, A.; Sarkar, S.; Bhandari, S.; Wang, K.; Li, Z.; Geva, E.; Twieg, R. J.; Dunietz, B. D., Enhancing charge mobilities in organic semiconductors by selective fluorination: a design approach based on a quantum mechanical perspective. *Chemical Science* **2017**, 8 (10), 6947-6953).

4. Giulia Galli (University of Chicago) discussed 'Interoperability of advanced sampling and electronic structure codes and data reproducibility'. The speaker described a new direction in computational development of interoperable and reproducible multiscale software, an imports component of the MGI, as described for example in Sevgen, E.; Giberti, F.; Sidky, H.; Whitmer, J. K.; Galli, G.; Gygi, F.; de Pablo, J. J., Hierarchical coupling of first-principles molecular dynamics with advanced sampling methods. Journal of Chemical Theory and Computation 2018, 14 (6), 2881-2888.

5. Meredith Reed (ARL) described programs in computationally-driven research at ARL, and successes thereof, consistent with the vision of the MGI. In the speaker's research (see Chung, R. B.; Garrett, G. A.; Enck, R. W.; Sampath, A. V.; Wraback, M.; Reed, M. L., Optical polarization switching in semipolar (202$\bar{1}$) InGaN multiple quantum wells induced

by strain engineering. Applied Physics Letters 2017, 111 (23), 231107/1-231107/4), experimental work was integrated with k··p modeling for mechanistic understanding.

The panel discussion raised a number of points to be considered as the MGI turns 8 in 2019.

1. To enable rational design of electronic and photonic materials, an important success of the MGI has been in bringing to the fore the significance of computational materials science, including multiscale methods to model realistic materials and environments, combined with experimental validation.

   However, although the MGI led the way towards important advances in electronic/photonic materials research, major challenges persist.

- Inclusion of machine learning/artificial intelligence/data science in the computational, experimental and integrated research of electronic/photonic materials, is an important part of the MGI, and progress has been made, yet this area is still in its infancy. Efforts to include these approaches are to be highly encouraged in all aspects of the material's life cycle, including for design of new/improved materials, processing and manufacturing.

- Accuracy in prediction of materials properties at the electronic/atomic scale, which are important for the development of electronic/photonic materials, including multiscale electromagnetic modeling, is still lacking.

- Validation of theoretical predictions for an experimental set-up that involves complex materials/environments is often lacking because proper validation of theory requires synthesis/ characterization on "model" material problems, but which may not lead to high-impact publishable experimental results.

2. The MGI led to teaming between experimental and computational groups in electronic and photonic materials research, which introduced experimentalists to the concept of a computationally-informed approach for problem solving, and enabled theorists to better understand the experiments.

   However, although examples of materials design by computation, validated by experiment, do exist, "closing the loop" between theory and experiment is still a challenge. For example, stability of the material can be predicted, but the ability to synthesize it is not known.

- Teaming between theorists, computer scientists, and experimental researchers is complicated by the use of different "languages" and understanding, requiring constant advancement and encouragement of joint projects.

- There is great potential to advance the MGI as researchers trained in both experimental and computational science begin to enter the workforce.

3. The MGI led to progress in data (computational, experimental)-driven electronic and photonic materials research, including of solid and soft materials.

   However, the need for modeling and experiment at the interface of chemistry and materials science has been less addressed, for example, the study of the regime of transition of "molecular-like" materials with discrete optical transitions to large quantum dots; solid-organic interfaces that require specifically developed empirical potential; and condensed phases in quantum calculations of solid materials.

Materials and Chemical Processes for Energy

Session Chairs:
Randy Snurr (Northwestern University) and Inga Ulusoy (Michigan State University)

The breakout session was attended by about 25 individuals from different backgrounds. There were five speakers in the session:

- **Eric Toberer** "Computationally Driven Targeting of Advanced Thermoelectric Materials"
- **Koblar Jackson** "FLOSIC - Efficient Density Functional Calculations without Self-Interaction"
- **Amin Salehi-Khojin** "Operation of Lithium-oxygen Batteries with Long Cycle Life in a Realistic Air Atmosphere"
- **Priya Vashishta** "Materials Genome Innovation for Computational Software (MAGICS)"
- **Hai-Ping Chen** "Exploring Multi-functional Molecular Electronic Materials"

In the talks, different strategies were presented for modeling and predicting materials properties, and different applications were presented, from new thermoelectric compounds to magnetic materials. Broadly defined, the target fields in this session were related to energy conversion and storage, and gas storage and separations.

Summary of important aspects for the future

In short, the most important issues are:

- Scaling of small groups/data sets to larger centers/data sets
- Scaling relations of developed models to realistic materials, and inclusion of parameters for robustness and future fabrication of materials
- Need for more data and software sharing as well as interconnectivity between databases

In the following panel discussion, several topics and questions were addressed as instructed:

Identify examples in which MGI accelerated the discovery of materials

Several successful collaborations between experimentalists and theoreticians were presented in this session. As an example, Eric Toberer described how, through close collaboration with experimentalists, they were able to develop a model that contained physics based parameters, with which they were able to reproduce known interesting thermoelectric materials without any false negatives and very few false positives. They then used their developed tools to predict new materials that are currently being realized experimentally.

Collaboration between experiment and theory

It was found that these collaborations work very well within small groups and with well-defined objectives. The challenge now lies in scaling these successful types of interactions to larger groups (bigger centers) and more complex questions (larger data sets). It was discussed that it takes time to develop trust and construct the foundation for a collaboration between experimentalists and theoreticians. The question as how to shorten this initial time interval was brought up. Also, depending on the field of study, the need for more data to generate reliable models was brought up.

Machine learning

It was discussed to what extent machine learning seems to work for the kinds of applications targeted here. The challenge in finding "good" descriptors was discussed, and the need for physics-based models or scientific intuition. The group also discussed whether machine learning was possible using only experimental data (for example, from high-throughput experiments) or whether theoretical or modeling results were essentially required to generate enough data for machine learning. Different participants had different opinions on this question. A few shortcomings in current capabilities were mentioned, such as the missing scaling relations to real physical systems (no defects, interfaces, isotopes present in the models). Also, the lack of descriptors for processing conditions, robustness, etc. for the future fabrication of the material was brought up.

Making data and software accessible

The need to connect software and databases to facilitate development on multiple scales was discussed. A need for common standards, as well as avoiding "reinventing the wheel" are important points that should be addressed. Also, failed experiments need to be made available to the community. The present databases need to be connected.

Education and next generation workforce

The need for better training in machine-based learning models was brought up. A goal in the training of graduate students is an in-depth training in a particular area plus the ability to collaborate across boundaries.

Where does the field stand with respect to key challenges?

In terms of leading a culture shift in materials research for an integrated team approach, there were many successful examples in the session. Integrating experiment and computation works very well on the small scale; how that translates to larger teams is sometimes a challenge. There are quite a few examples of making digital data accessible, but more efforts have to be put in this direction. As to creating a world-class materials workforce, with the integration of graduate students in the research and encouragement to a team approach in conducting research, that seems very well in progress.

Data-driven Research

Session Chairs:
James Rondinelli (Northwestern University), Dane Morgan (University of Wisconsin)

Speakers: Shyue Ping Ong (University of California-San Diego) *Harnessing the Materials Project for Data-driven Materials Design*; Elsa Olivetti (MIT) *Data Mining for Predictive Synthesis*; Debra Audus (NIST) *Enabling Polymer Informatics through Database Creation*; Matt Miller (Cornell, CHESS) *Extracting Real Time Material Evolution Information as a Synchrotron using Machine Learning Methods*; Benji Maruyama (AFRL) *Autonomous Research of Carbon Nanotube Processing*; Efthimios Kaxiras (Harvard) *Machine Learning for Materials: What We Can Learn from Machines*

Summary: The Implementing Data-Driven Materials Research session provided an impressive set of presentations showing striking successes of the MGI, active cutting edge research areas, and suggestions for the road ahead. The role for machine learning (ML) was one of the newer areas discussed in this session as it clearly emerged as a central pillar of the next phase of the MGI. In its most distilled form, machine learning is any approach that achieves artificial intelligence through systems that can learn from experience to find patterns in a set of data. In other words, ML involves the computer learning to recognize patterns (by supervised or unsupervised methods), rather than programming the computer with specific rules. In materials research, the goal is to have the computer help the researcher work usefully with data, and to do so either more quickly or more effectively, complementing more traditional approaches.

Prof. Ong illustrated what can now be accomplished with available data and more general computational infrastructure that has emerged from the MGI to date, demonstrating multiple examples of materials discovery through high-throughput ab initio computation coupled with data and tools from the Materials Project, including tight integration with experiment to realize the predictions. His work also highlighted the impact of highly curated and accessible data (e.g., with good APIs) and well-designed software (the pymatgen package now has over 1000 developers).

Multiple examples of the present and potential impact of ML were also illustrated by the other speakers. Dr. Audus and Prof. Olivetti both demonstrated the opportunities for text mining with natural language processing, with examples of extracting thermodynamic data for polymers and synthesis methods. These types of text processing approaches are clearly in their early stages in materials science, but the success of these two studies demonstrates their potential. Prof. Miller demonstrated how ML could be integrated with the large data sets emerging from synchrotron facilities to extract valuable information, showing an example of identifying the intermittent processes involved in plastic deformation of magnesium. Prof. Kaxiras demonstrated an additional application of ML, developing neural network potentials for Si and Li-Si and extracting a new measure of local “softness” that characterizes sites of plastic deformation in terms of local structure in amorphous systems. Finally, Dr. Maruyama illustrated the power of integrating ML with automated rapid experiments to develop fully autonomous experiments. Dr. Maruyama described the Autonomous Research System (ARES) platform and demonstrated its use for controlling the growth rates of carbon nanotubes. He identified this as the first autonomous materials development system and proposed how it could be used as an extensible platform to enable many types of experiments.

The speakers themselves, as well as members of the discussion, provided a number of suggestions for challenges and next steps in data-related components of the MGI. These were wide ranging scientific, strategic, and tactical opportunities for researchers both active in data-driven materials research and those active in related scientific domains (computer science, statistics, visualization). Here we itemize a selection of some of the key ideas.

- *Data Generation.* Many materials science and engineering research projects have sparse or small data sets. In soft materials, there is a particular lack of data and generating new data in a uniform manner is pressing. In addition, many experiments and simulations often result in data (and metadata) that is typically not shared, e.g., forces in molecular dynamics simulations that might support potential fitting, and this should be shared more as it supports research transparency and can reduce redundancy in efforts.
- *Data Availability and Sharing.* There is still a major need to increase basic data sharing and access, stressing FAIR (Findable, Accessible, Interoperable, Reusable) principles. All large-scale MGI database efforts should have APIs (application programming interfaces), which make it possible for users to effortlessly query servers and databases. The APIs should be designed as part of present and future materials innovation ecosystems. Similarly, large scale coding efforts should come with documentation, tutorials and example codes/notebooks as they provide paths for training a future workforce where the boundaries between experimentalists and theorists/simulators is blurred. These aspects should be required in data management plans and assessed along with scientific impact when data dissemination forms a core part of a research project. On the other hand, for projects that do not focus on data and tools, we might reduce the focus on data management so as reduce administrative burden. Supplemental funding opportunities could facilitate smaller research teams to disseminate their data through centers with large-scale databases.
- *Software.* We need to keep developing tools and infrastructure to make it easier for bench scientists to share data and codes. For example, making it easier to share effectively tools and data for broader use without extensive curation for the end-user.
- *Machine Learning.* Although the excitement about ML is clear, we must avoid excessive hype and sort out the true opportunities present in ML and more generally Artificial Intelligence (AI) technologies: What data is needed to realize these opportunities? As one example, multiple people pointed out that materials challenges often do not have a “big data” problem but a “small data” problem. This suggested a need to focus not just on “big data” tools but ones that could realize the value held in limited, incomplete, and noisy data.
- *Incentives*. We need to keep developing incentives for researchers to submit data to public resources concurrent with manuscript submissions. For example, direct requirements for sharing data from journals is still very underdeveloped and could greatly enhance data sharing. Although data extraction by text mining is emerging as a powerful tool that requires the cooperation of publishers with their large paper databases, there is still a need to encourage more users to share their data. This practice can eliminate the need to engage publishers directly and those efforts to digitize data can be focused elsewhere. An outcome of a distributed data approach is that data ownership shifts from the researcher to the community, and agencies and institutions should recognize and reward these community efforts.
- *Embracing Small Data Problems.* In cases where data is available, ML algorithms may fail because of sparseness in the representation. Here methods to create higher

dimensional data sets from collected data are of interest. Small data also provides new scientific opportunities to engage researchers in computer science and statistics, who focus on developing ML methods that work on small data problems.

- *Synthesis Guidance:* The MGI has been so successful in accelerating the prediction of promising new materials that the bottleneck for materials development is shifting toward the stage of materials synthesis. Increased efforts to develop data and tools to accelerate synthesis – addressing how to make a predicted material – would be valuable.

Abstracts

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Chemoresponsive Liquid Crystals Based on Metal Ion-Ligand Coordination

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Keywords: *liquid crystals, chemoresponsiveness, anchoring transitions, chemical sensors*

Project Scope

This project tightly couples advances in electronic structure calculations, techniques for synthesis of organic mesogens, and advanced characterization methods to accelerate the design of chemically responsive liquid crystals (LCs) capable of detection of a wide range of targeted small molecule analytes. While previous studies have succeeded in demonstrating the concept of chemoresponsive LCs for a narrow class of chemical targets,[1] guided by advances in first-principles calculations, this project employs novel synthesis techniques to tailor LCs to respond to a wide range of species (e.g., ClO_2, Cl_2, NO_2, NH_3, HCHO, CO). Experimental validation closes cycles of prediction, synthesis and characterization (Figure 1).

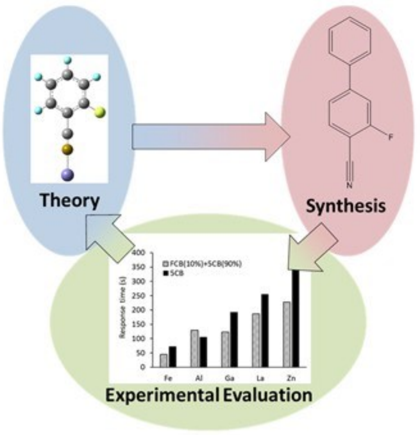

Figure 1. Cycle of calculations, synthesis, and advanced characterization that successfully identified "FCB" as an improved chemoresponsive LC.

Relevance to MGI

This DMREF project is organized around *Generations* of electronic structure calculations, where each generation is designed to improve prediction of key properties of chemoresponsive LCs. For each *generation* of calculations, synthesis and characterization are integrated with computation in tight *cycles* to (i) provide feedback for improvement of the theoretical models and (ii) evaluate and validate the most promising candidate LCs. Our efforts have demonstrated how cycles of computation and experiment can lead to both improved computational models and new materials. Specifically, a successful feedback loop in our *Generation 1*-level effort yielded a simple computational model for design of chemoresponsive LCs based on thermochemical binding energies. In this advance, feedback from experiments was instrumental in refining the model (a so-called *reduced charge model* was developed), which was subsequently used to predict new chemoresponsive LCs with improved sensitivity and selectivity to targeted chemical compounds. Building from this success, we successfully developed a series of more sophisticated *Generation 2*-

level models that included explicit solvent molecules. These predictions revealed that solvent used in experiments can be optimized to enhance responsiveness of the LCs. Experiments validated these predictions. *Generation 3*-level models, which included counter ions, were then developed, revealing that counter ions provide an additional key parameter for optimizing chemoresponsive LCs. *Generation 3*-level calculations have been highly successful in identifying new designs of chemoresponsive LCs (see below).

Technical Progress

While initial calculations used *Generation* 1 calculations (see above), we now largely use *Generation 3* calculations to guide LC designs. The predictive capability of the *Generation 3* computational methods is evidenced

by an exciting series of results related to computationally-driven designs of LCs, which we have subsequently validated via experimental synthesis and physical property characterization. Most importantly, through cycles of synthesis, computation and characterization, our team has designed chemoresponsive LCs that we had not imagined at the start of the project. We summarize select advances below:

Chemoresponsive LCs with improved selectivity [4]. Guided by *Generation* 3 computations, we synthesized 4-(4-pentyl-phenyl)-pyridine and 5-(4-pentyl-phenyl)-pyrimidine and quantified LC responses to dimethylmethylphosphonate (DMMP), a surrogate of nerve gas agents, and water. Consistent with the computations, we found experimentally that pyrimidine-containing LCs undergo a surface-driven orientational transition in response to DMMP without interference from water. Overall, this work identified a promising new class of chemoresponsive LCs based on pyrimidine that are tolerant to water at conditions reported previously to trigger LCs. The result is technologically important because water is a ubiquitous and a particularly challenging chemical interferent in chemical sensing strategies.

Design of high performance chemoresponsive LCs [6]. We achieved a breakthrough in the computational design of chemoresponsive LCs by identifying LCs that exhibit responsiveness based on the interaction of nitrile groups with metal cation-decorated solid surfaces, yet, in contrast to all previously reported nitrile-containing LCs, adopt a planar orientation at a free surface to air. This combination of properties enables the design of chemoresponsive LCs that exhibit faster responses and greater sensitivity to targeted analytes than previous LCs.

Chemoresponsive LCs that respond to new chemical targets [7]. We used *Generation 3* calculations to design surfaces and mesogens that permit detection of analytes not previously detected using LCs. We illustrate the progress by describing *Generation 3* designs (patented) of LCs for Cl_2 gas detection. Computational chemistry methods identified Mn^{2+} cations as surface binding sites that undergo redox-triggered changes in strength of binding to nitrogen-based LCs upon exposure to Cl_2 gas. To evaluate these computational predictions, we prepared nitrile- and pyridine-containing LCs on surfaces decorated with Mn^{2+} binding sites. Following exposure to Cl_2 in the presence of ambient humidity, we confirmed formation of Mn^{4+} (in the form of MnO_2 crystals) and measured an accompanying response of LCs. The LCs were shown to possess the necessary sensitivity and response dynamics needed for monitoring human exposure to Cl_2 gas, and were selective to Cl_2 over other oxidizing agents such as air or NO_2 and other chemical targets (e.g., organophosphonates).

Chemoresponsive LCs based on hydrogen-bonded dimers. Whereas the designs of chemoresponsive LC described above use chemically functionalized surfaces, we have also explored alternative LC designs based on bulk LC phase transitions. Specifically, over the past year, we designed chemoresponsive LCs based on disruption of H-bonded pairs of molecules (using amines). Specifically, guided by computations, we have used cyclohexylcarboxylic acid and benzoic acid derivatives as H-bonded dimers to form LCs. Exposure of these LCs to amines triggers LC-to-isotropic phase transitions.

Future Plans

We have recently discovered that noble metal surfaces (e.g., Au) and noble metal surfaces prepared by under- potential deposition are promising candidates for anchoring chemoresponsive LCs. The nature of these surfaces requires development of new computational models, which will be a focus over the coming months. In addition, a focus over the coming months will be to leverage *Generation 3* calculations to design LCs that respond to important chemical targets. These targets are motived by the potential use of chemoresponsive LCs in sensors that are either
(i) passive and sufficiently light weight that they can be worn to enable personal monitoring of chemical environments, or (ii) sufficiently cheap to form the basis of nodes of massive networks that provide information about chemical signatures in urban environments.

Broader Impact

All members of this DMREF team have participated in *educational activities* aimed at communicating the impact of the MGI initiative to the broader community. For example, at the 2017 UW-Madison *Engineering Expo*, an event attended by 10,000 people, we described to the public how LCs respond to physical stimuli, and how we are designing LCs on computers to respond to chemicals, thereby describing outcomes of our DMREF research project. The DMREF team also hosted a high school teacher over the summer of 2017. The teacher formulated an activity for high school students that started with liquid crystallinity in biology and ended with designs of synthetic (including chemoresponsive) LCs. In summer of 2017, the DMREF team hosted a Madison high school student and several undergraduates (including three women; two were URMs).

Data Management and Open Access

This project has generated a large volume of raw data (from both calculations and experiments), which motivated the development of a web-based platform for archiving and accessing data. The website is operating, storing important computational data generated by high-throughput screening. The built-in search engine allows searches based on mesogen functionality, target analyte or computational methods. The database is currently fulfilling the need to share available data between research groups in the DMREF team. The website is password-protected, but after patent applications and scientific manuscripts are published, all related information will become publicly available on our website to disseminate widely knowledge generated in this DMREF project.

Advancing Along the Materials Development Continuum

This MGI project has enabled high-throughput computational screening of chemoresponsive LCs and in a short period of time has led to the identification of promising new classes of LCs with high technological potential. The chemoresponsive LCs developed in this project have strong potential for commercialization in a range of fields, including defense, medicine, and general industrial safety applications. Two patents have been filed on discoveries from this project, and close interaction with Platypus Technologies LLCs has led to STTR research funding from DoD aimed at computational design of chemical sensors for drones.

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Polymeric Composites and Foams Based on Two Dimensional Surfactants

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Keywords: Graphene, Composites, Conductive, Self-assembly

Project Scope

We have developed a route to self-assembled two-dimensional materials that takes advantage of graphene and boron nitride's surface affinity to the high-energy interface between two immiscible solvents to cause stacked sheets to exfoliate and spread. This approach thus treats the two-dimensional materials as surfactants. Forming emulsions stabilized by these sheets, and polymerizing the continuous phase, results in composite materials with superior electrical conductivity, porosity, and strength. Our main focus is to elucidate the design principles for these nanostructured, multifunctional, two-dimensional material reinforced composites.

Relevance to MGI

Mixing of chemically and physically different species such as polymer chains, colloidal particles, and solvents is one of the major factors hindering future advances in the development of functional materials. A prominent example of this are graphene based polymeric materials, where graphene's lack of compatibility/solubility is commonly overcome by approaches that compromise its superior electrical, thermal, and mechanical properties and make the composite materials less attractive for future development. This research project centers on the development of a unifying theoretical, computational and experimental framework to describe the behavior of two-dimensional materials at the liquid/liquid interface. The approach is multi-scale, reaching from the atomic to mesoscopic dimensions. Using graphene and boron nitride as examples, the work will reveal general selection principles for solvent pairs and reaction conditions for which the novel concept of using two-dimensional sheets as surfactants can be realized. Understanding the governing physical principles of surface activity of graphene and boron nitride will be applied to the emulsions that serve as precursors for the synthesis of foam-like materials reinforced with two-dimensional materials. The theoretical and computational models, developed with novel experimental and analytical approaches, are aimed at the design of materials with optimized mechanical and electrical properties.

Technical Progress

We use a combination of theory, molecular dynamics simulations, synthesis and analytical techniques to elucidate factors responsible for surface activity and emulsion stabilization of 2D graphene sheets. In particular, we use large scale coarse-grained molecular dynamics simulations to study the affinity of the 2D elastic sheets to the interface between two immiscible solvent as a function of the strength of pairwise interactions and degree of substitution of atoms on the 2D sheets. The established envelop of parameters for the sheets' surface activity is used to model emulsion assembly and emulsion templated polymerization for producing polymeric foams with cells coated by 2D elastic sheets. The mechanical properties of the foams are studied as a function of the crosslinking density, 2D-sheet/monomer affinity, and the sheet's bending rigidity. The results of computer simulations are compared with corresponding experimental studies of the graphene stabilized emulsions and composite graphene/polymer foams.

We have extended our interdisciplinary approach to elucidate factors influencing foam selectivity and dynamics of the swelling process. In particular, we have studied swelling ability of the composite graphene poly(butyl acrylate) foams in 17 different solvents. Analysis of the swelling data shows direct correlation between solubility parameter and degree of the foam swelling. The equilibrium swelling ratio of the foam changes with the degree of crosslinking as expected for swelling of the polymer networks in selective solvents. MD simulations of the composite graphene/polymer foams indicate that the capillary forces first drive the liquid to fill the foam cells, followed by swelling of the surrounding polymer network. This swelling process changes the overlap between graphene sheets coating the foam cell. This rearrangement of sheets manifests itself in a change of the foam's conductivity upon swelling.

Functionalizing an AFM probe with graphene and moving it across the liquid–liquid interface of two immiscible solvents allows the interaction forces of graphene sheets with such interfaces to be quantitatively determined. These results help to explain previous results related to the fractionation of graphene oxide, as well as demonstrating the approach can be used for measurements of graphene and boron nitride. These materials have been shown to provide the surfactant character necessary for material synthesis, but the properties of the recently synthesized materials vary considerably. Our analytical results can address this difference, while computational results are explaining how the different surface forces combine to give rise to the material properties.

The kinetics of exfoliation is also major activity. The basic thermodynamic driving force for the self-assembly and exfoliation of the graphene sheets appears to be in hand, but the mechanism (kinetics) is not so clear. Using a combination of kinetic studies based on imaging, acoustic spectroscopy, and microwave assisted mixing, we have begun to understand the role played by such parameters as temperature and starting graphite flake size. Additionally, the interaction of graphene sheets with free radicals has been investigated, with emphasis placed on the role that edges play relative to the basal plane of the sheets.

Future Plans

During the remaining two years we are planning to focus on a) the electrical properties of the foams and to develop frameworks for application of foams as mechanical energy transducers for flexible energy sources, b) determine and quantify the interfacial forces responsible for the observed spontaneous exfoliation and self-assembly, and c) further develop a kinetic model describing the mechanism of exfoliation. The developed foams are uniquely positioned as elastic materials for triboelectric energy generators.

Broader impact

The reinforced polymeric materials described developed during this study could have the potential to be used as strong and lightweight structural materials, electrodes in capacitors and batteries, substrates for flexible electronics, electrically conductive, high surface area catalyst supports, and super-absorbent materials. Additional societal benefit results from the educational outreach program built on the Chemistry Wizards Program started with funds received from the Camille and Henry Dreyfus Foundation. The program participants conduct hands-on chemistry workshops in Connecticut middle schools with largely underserved populations.

Data Management and Open Access

The data are collected and stored on a private server operated by the principal investigators and maintained by the Institute of Materials Science (IMS) at the University of Connecticut. These include: data from nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR) disc centrifuge, images from microscopy techniques (transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM)) and computer simulation data together with input files. The data are available upon request. Suitable data will be made available to the public on web servers after publication and patent status of the work allow for it. A software tool written by the Schniepp group, currently part of a pending publication, has been issued under the very permissive MIT license. It will be uploaded to the publicly accessible Github page of the Schniepp group as soon as a paper is accepted.

Advancing Along the Materials Development Continuum

Ultimately, our synergistic approach will outline design principles for nanostructured, multifunctional, two-dimensional surfactant-reinforced polymeric composites with tailored properties, enabling material development in a fraction of the time that would be required by a trial and error approach alone.

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Rapid Design of Earth Abundant Inorganic Materials for Future PVs

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Keywords: nanoparticles, thin films, solar cells, band edges, earth abundant

Project Scope

Development of novel semiconductors for photovoltaic applications is currently inefficient due to the lack of coupling between computational work and experiments. Our project uses a combined theoretical and experimental approach to screen families of semiconductor materials, such as Cu_3-V-VI_4 (V = P, As, Sb; VI = S, Se). Density functional theory (DFT) calculations identify potentially attractive materials based on optoelectronic properties, and the most promising compounds are then synthesized and characterized. The aim of this project is to rapidly identify and develop materials for the future generation of solar cells.

Relevance to MGI

The project integrates calculations and experiments through a carefully monitored feedback loop. Novel candidate semiconducting materials composed of earth abundant elements are screened using computational methods, and only those that meet certain benchmarked criteria progress to the synthetic stage. The selected materials are then synthesized via solution-processed routes and fabricated into thin films. The optoelectronic properties (e.g. band gap, absorption coefficient) are measured and compared with results from DFT. These results are then used to enhance the calculation routines to correct any discrepancies. Our approach improves the predictive power of calculations and rapidly identifies potential photovoltaic materials more rapidly than previous approaches. We believe that our model for rapid materials development can be extended to other systems in the future.

Technical Progress

The Cu_3-V-VI_4 system was identified as promising for photovoltaic applications through previous work and calculations during the initial phase of this project.[1,2] To validate the properties of this material family, the team successfully developed nanoparticle (NP) synthesis protocols for each phase in the system. Alloy NPs such as $Cu_3Sb_{1-x}As_xSe_4$ and $Cu_3Sb_{1-x}As_xS_4$ were also synthesized to allow for optoelectronic property tuning.[3,4] The optical band gaps vary from 0.4-2.4 eV, enabling a wide range of semiconductor applications such as thermoelectrics, photovoltaics, and LEDs. The band gaps were underestimated by DFT; the experimental results were used to refine the computational parameters to ensure high accuracy.

Fabrication of efficient single-junction solar cells requires a method to sinter NPs into thin films with micron-sized dense grains. Inspired by the liquid-assisted grain growth mechanism seen in films of Cu_2ZnSnS_4 (CZTS) NP films, we discovered that heating Cu_3AsS_4 NP films in As_2S_5 promotes the growth of films with micron-sized dense grains. With no knowledge of the band edge locations, we fabricated solar cells using the standard architecture for Cu(In,Ga)Se_2 and achieved an encouraging preliminary efficiency of 0.35%.[5] We have also fabricated films of micron-sized grains for other materials in the system; they are currently being evaluated for alternative applications.

To more rapidly determine band edge locations of these novel materials and fabricate better p-n junctions, a combined theoretical and experimental approach was utilized. DFT calculations were employed to determine the valence band edge (VBE) alignment between materials of similar crystal structure, e.g. $Cu_3(P,As)(S,Se)_4$ in the orthorhombic enargite structure. Cyclic voltammetry was used to measure the absolute position of the Cu_3PS_4VBE.

By combining this measurement with the calculated VBE alignments, the absolute position of four semiconducting materials was estimated. Finally, the DFT bandgaps were all underpredicted, so the absolute position of the conduction band was adjusted using experimentally measured values. The final band structure of all four compounds is shown in **Figure 1**. The relative band positions of four materials have been estimated through use of computations and minimal measurements; such a model is readily adaptable to other systems. These results suggest that Cu_3AsS_4 solar cells require non-CdS buffer layers to make a favorable p-n junction and higher efficiency solar cells.

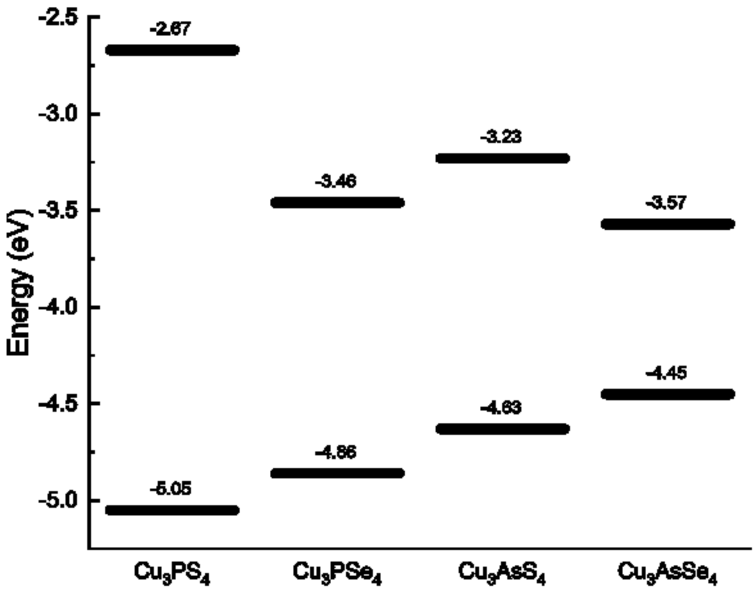

Figure 1. Estimated absolute band positions of compounds in the enargite crystal structure (space group: *Pmn2₁*) derived through a combination of theory and experiment. Relative valence band positions were determined *via* DFT calculations, conduction band positions were determined through band gap measurements, and absolute values were assigned through measurement of the HOMO level on a Cu_3PS_4 thin film using cyclic voltammetry.

Future Plans

The close coupling between theory and experiment will continue throughout the remainder of the project. We plan on extending our screening and synthesis methods to new families of materials, as well as alloy phases of the Cu_3-V-VI_4 system. We expect to discover more materials with promise for solar and other electronic applications through our continuously improving methods. Additionally, we will evaluate the long-term feasibility of materials such as Cu_3AsS_4 via capacitance-based defect analysis techniques. Thermodynamic calculations will be used to correlate the identified defects with specific defect types, which will help tailor the synthesis conditions to tune defect concentrations. To improve device performance, we will also measure fundamental properties such as mobility and carrier concentration, synthesize alternative n-type buffer layers, and explore alternative device architectures through 1D-SCAPS simulations. We will also continue to explore thermoelectric, photovoltaic, and LED applications for our new materials depending on their band gap.

Broader Impact

The broader impact of this project is substantial, as its results reach hundreds of people through workshops, presentations, and hands-on demonstrations. Outreach activities at Purdue University (such as the Duke Energy Academy and NanoDays) are regularly sponsored by the team. Graduate students undergo rigorous interdisciplinary training and serve as mentors for undergraduate students with the aim of developing young researchers for seamless integration into the U.S. STEM workforce. In each activity, the philosophies of the MGI are stressed; we highlight the close collaboration between theory and experiment and illustrate the ever-expanding research into fundamental materials science.

Data Management and Open Access

Datasets for the project, including DFT codes, materials characterization results, and device efficiencies, are available through DataCenterHub, a public platform for research data sharing funded in part by the NSF (Award #1443027). Our project's site is found at https://datacenterhub.org/groups/dmref1534691.

Advancing Along the Materials Development Continuum

The project accelerates materials discovery and development through its coupled theoretical and experimental approach. The computational routines to identify candidate materials are continuously improved via feedback from experimental routines, enabling more accurate results in future calculations. The rapid development of appropriate device architectures is also promoted through our approaches which save significant computational and experimental effort. Future commercialization prospects are high – solution processing is highly scalable, and the materials considered here are earth abundant, alleviating long-term supply concerns. The power conversion efficiencies certainly must improve, though we hypothesize that this will be achieved as soon as a favorable p-n heterojunction is successfully fabricated.

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Hydrogen Materials Advanced Research Consortium (HyMARC)
A DOE Efficiency and Renewable Energy
Energy Materials Network Consortium

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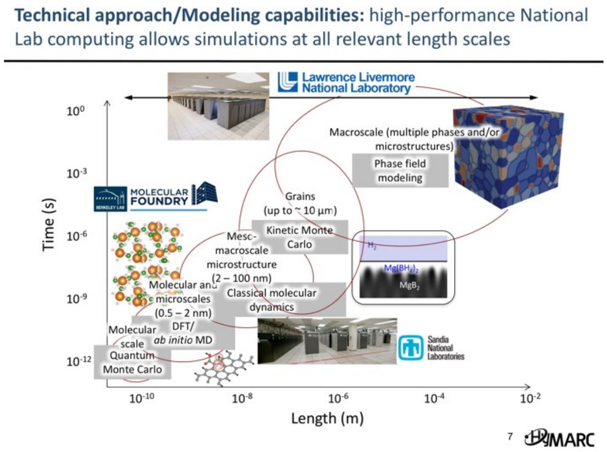
Project Scope

Storage of hydrogen on-board vehicles is one of the critical enabling technologies for creating hydrogen-fueled transportation systems that have potential to provide clean, sustainable transportation, while reducing petroleum use and carbon emissions. Stakeholders developing hydrogen infrastructure (e.g., state governments, automotive OEMs, station providers and industrial gas suppliers) are currently focused on high-pressure storage at 350 bar and 700 bar, in part because no viable solid-phase storage material has emerged. Nevertheless, solid-state materials, including novel sorbents and high-density hydrides, remain of interest because of their unique potential to meet all DOE targets and deliver hydrogen at lower pressures and higher on-board storage densities. A successful solution would significantly reduce costs and ensure the economic viability of a U.S. hydrogen infrastructure.

The goal of HyMARC is to develop foundational understanding of phenomena governing thermodynamics and kinetics of hydrogen release and uptake in all classes of hydrogen storage materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2020 hydrogen storage targets. The HyMARC team is comprised of researchers at five DOE National Laboratories: Sandia National Laboratories, Livermore, CA (SNL; lead laboratory); Lawrence Livermore National Laboratory (LLNL); Lawrence Berkeley National Laboratory (LBNL); National Renewable Energy Laboratory (NREL); and Pacific Northwest National Laboratory (PNNL). Research is also conducted at the Center for Neutron Research at the National Institutes of Standards and Technology (NIST), the Stanford Synchrotron Research Laboratory, and the Spallation Neutron Source at Oak Ridge National Laboratory.



Technical approach/Modeling capabilities: high-performance National Lab computing allows simulations at all relevant length scales

Figure 1. Length and time scales relevant to hydrogen storage material properties and corresponding modeling tools employed by HyMARC to address these. Supercomputing facilities at all three consortium laboratories are being employed to develop a suite of modeling tools spanning the atomic/molecular to macroscale/multiphase materials.

Relevance to MGI

HyMARC seeks to address critical gaps in the science of hydrogen storage by leveraging recent advances in predictive multiscale modeling, high-resolution in situ characterization, and novel material synthesis techniques. Combined with materials informatics, this strategy embodies the approach highlighted within the Materials Genome Initiative (MGI) Strategic Plan for accelerated materials development. By focusing on the underlying thermodynamic and kinetic limitations of storage materials, HyMARC will generate foundational understanding that will accelerate the development of all types of advanced storage materials, including sorbents, metal hydrides, and liquid carriers.

Technical progress

Since its initiation in Sept. 2015, the HyMARC team has developed a suite of computational modeling tools spanning all relevant length and time scales. This model development is performed in concert with measurements using state-of-the-art characterization tools, such as Ambient-Pressure X-Ray Photoelectron Spectroscopy at ALS, neutron scattering and inelastic scattering measurements at NIST, and Low-Energy Ion Scattering measurements at SNL. Some highlights from the past twelve months are:

- An ultrahigh-pressure reactor (up to 1,000 bar H_2 and 400ºC) was brought online that is available for use by seedling projects and other collaborators to generate data at pressures relevant to high-pressure hydrogen storage and to the regeneration of metal hydrides.
- Thermodynamic data previously unavailable for borohydride intermediates were obtained by density functional theory modeling.
- Models were developed that predict the effects on storage material behavior of particle morphology, mechanical strain, internal interfaces, and non-equilibrium mass transport in complex microstructures produced when hydride storage materials decompose.
- Grand Canonical Monte Carlo simulations were shown to accurately predict the uptake of hydrogen at pressures up to 100 bar.
- The role of transition-metal dopants, such as titanium halides, in accelerating hydrogen release from complex metal hydrides, was probed using an integrated synthesis, characterization, and modeling effort. The results are transforming our understanding of materials and challenging concepts thought to be well established.

Future Plans

HyMARC will soon launch its data science and management effort, intended to consolidate extensive data already available from various sources, as well as results from its own efforts. Data hub development will occur in coordination with the DOE program for the Energy Materials Networks to ensure uniformity of data handling with other EMN. In addition, we plan to integrate the various computational models to enable accelerated materials design involving a range of properties, phenomena, and length scales, which is the “grand challenge” goal of HyMARC.

Selected publications

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DMREF: Organic Semiconductors by Computationally Accelerated Refinement (OSCAR).

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Website: *In progress*

Keywords: Organic semiconductors, crystal structure prediction, crystal engineering, polymorphism, structure-function relationships.

Project Scope

The performance of organic materials in electronic or photonic applications is entirely dependent on the molecular solid-state arrangement. Thus, *any* computational approach to discover new materials *must* include the capability to predict crystal structures. For this work, we focus on a class of high-performance organic semiconductors with a substantial (> 300) number of known structures. We are constructing a database of functionalization-to-structure parameters to generate a highly parameterized model to predict crystal packing in this class of materials. From the models created here, researchers will be able to optimize functionalization of their core molecules to maximize performance.

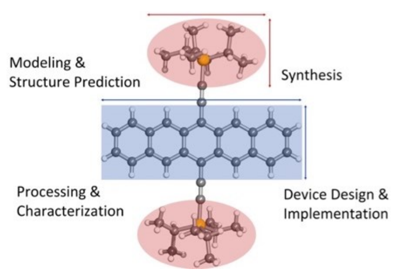

Figure 1. Designing new organic semiconductors through the iterative loop of structure prediction – synthesis – processing & film characterization – device design and performance assessment.

Relevance to MGI

Our team of long-time collaborators works in a tight cycle with several related iterative feedback loops. We began with the construction of a structural database to parameterize our computational model (see data management section for details). Concurrently, we use computational approaches to understand the factors that influence crystal packing in current-generation materials. Details from these calculations by Risko have recommended synthetic targets to Anthony, leading to new high-performance semiconductors. Loo is analyzing thin films of these new materials to determine the impact of process conditions on film structure. This data is immediately fed back to the Risko group to inform development of the computational models. The Jurchescu group is probing transport properties based on ideal crystalline materials, which allows Risko to enhance capability in predicting charge mobility for prospective targets. Device information is fed back to the computational model to predict the next generation of structures to probe by synthesis and thin film / device characterization. The results from these studies verify, or suggest modifications to, the computational model.

Technical Progress

We achieved significant advances in several aspects of this project over the first year of this project, focusing on computational / experimental studies of structure, polymorphism, and disorder in organic semiconductors. We highlight by progress in four related areas: (1) We developed a substantially improved theoretical understanding of the forces impacting the crystal packing of silylethyne-based organic semiconductors. DFT calculations highlighted the subtle interplay of noncovalent intermolecular interactions among the molecular constituents as they drive crystal packing for derivatives that are very similar structurally, and this knowledge will be critical to our advancement of crystal structure prediction as this project proceeds. (2) Computational screening of potential crystal packing motifs has identified new polymorphs of some established semiconductors. We established correlations between the kinetic stability of packing polymorphs with the presence of short intermolecular contacts within molecular unit cells. These short contacts manifest as kinetic barriers for nucleating thermodynamically isoenergetic polymorphs. Applying this framework in addition to computational screening led to isolation and structural characterization of predicted polymorphs. Changing process conditions for thin-film formation led to the generation of thin-film forms appropriate for transistor studies, showing quite reasonable (1 cm^2/Vs) hole mobility. (3) We developed new core molecules to apply the silylethyne functionalization approach to a much broader array of organic chromophores. For initial materials, a joint computational and experimental effort has explored the issue of disorder in organic crystals, and the impact of fluorination on reducing this disorder. Derivatives with different degrees of fluorination were synthesized and evaluated in field-effect transistors. The non-fluorinated (disordered) derivatives yielded the worst mobility (~0.2 cm^2/Vs), although significantly enhanced stability compared to other common semiconductors was noted. Transistors based on di-fluorinated trimers, where disorder was substantially reduced, yield charge carrier mobilities as high as 12.5 cm^2/Vs with remarkably low subthreshold swings, excellent on/off current ratios, and high stability. Trap density of states analysis provided information on the impact of processing on the trap density landscape, which correlates with device performance. (4) Beyond impact on bulk crystal packing, we discovered that subtle changes to the substituents on solution-processable pentacenes dramatically alter its polymorphic landscape. Replacing the Si atom with Ge in TIPS-pentacene, for example, results in substantially more diverse packing polymorphs, which in turn alter the mobility of transistors, with the brickwork packing motif yielding decent mobilities (~10^0 cm^2/Vs) and the slipped stack packing motif yielding poor mobilities ($10^{-3} cm^2/Vs$).

Future Plans

Plans for year 2 include completion of our structural database and initial release to the public. Our current understanding of solid-state interactions is proceeding as expected to predictive use in semiconductor design. We will continue exhaustive analysis of thin films of crystalline semiconductors to expand our understanding of structural motifs that inhibit polymorphic transformations. We will employ our discoveries of intermolecular interactions to refine crystal packing for the new aromatic cores developed as part of this project, as a means to validate our approach. Detailed transport studies of crystalline samples will provide feedback regarding the success of computational predictions.

Broader impact (Only required for NSF projects)

We have uncovered important structural and energetic origins of polymorphism in silylethyne functionalized chromophores, with direct impact on many applications in the organic electronics community. We developed a new class of benzodithiophene trimers whose electronic performance suggests excellent utility for broader organic electronics applications. We have reached out to groups with complimentary expertise to assess the impact of structural factors in material performance, such as the Johnson (NREL) and Scholes (Princeton) groups to understand singlet fission efficiency, and materials developed here have been provided to the Fraboni group (U. Bologna), where the new pentacene polymorph we described above yielded efficient radiation detectors. Hacker (NIST) is evaluating the electronic structure of our crystals using UPS and XPS. Our project aims have been promoted in presentations at 30 scientific meetings. Three undergraduate researchers, two from under-represented groups, have performed research on this project, and several high school students or groups have participated in or been educated in the concepts of this effort. DMREF has supported the interdisciplinary training of 4 graduate researchers, with frequent interaction between experimental and computational participants. Anthony and Risko have incorporated our DMREF concept into their courses in a new undergraduate certificate in materials chemistry. In collaboration with Natalie Stingelin, (Georgia Tech), Risko co-delivered the Telluride Town Talk in July 2017 to an audience of more than 150, discussing how two different approaches to organic semiconductors – theoretical chemistry and polymer science – come together to aid in the design of new materials.

DMREF: Accelerating the Development Of Phase Transforming Heterogenous Materials: Application To High Temperature Shape Memory Alloys (CMMI-1534534)

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Keywords: High Temperature Shape Memory Alloys, Bayesian Model Calibration, Optimal Experimental Design, Precipitate-engineering.

Project Scope

High Temperature Shape Memory Alloys (HTSMAs) exhibit large recoverable shape changes at high stresses and temperatures as a result of reversible phase transformations. Recently, it has been discovered that nanoprecipitation in NiTiHf HTSMAs leads to highly efficient and stable actuation behavior [1]. NiTiHf HTSMAs performance is highly sensitive to precipitate structure, which can be controlled through heat treatments and alloying. The project's **goal** is to develop a materials design framework capable of addressing the following question: given a set of desired performance requirements, establish the likely feasible set of processing + chemistry combinations with a minimal number of experimental iterations.

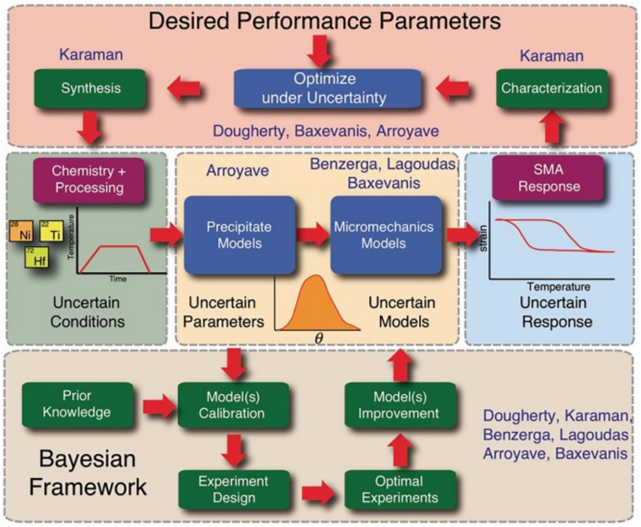

Figure 1: Proposed approach

Relevance to MGI

The framework shown in **Figure. 1** considers that chemistry and processing determine the microstructure of the shape memory alloys (SMAs) and its response and assumes that physical models responsible for the chemistry-processing-microstructure-performance linkage describe the physics relevant to the problem. To this end it uses Bayesian approaches to describe the probability of all the considered models to capture the real response of the material based on the available experimental data.

At the core of the framework a precipitation model is used to predict the precipitate population distribution as a function of initial composition and heat treatment schedule along with a computational SMA micromechanical model that predicts the response of HTSMAs for the given microstructure. The framework uses Bayesian calibration to update the (stochastic) model parameters based on prior knowledge and preliminary data. These updated parameters are used along with the models to design optimal experiments [2], which are then used to refine the models. Finally the framework is used to carry out an efficient search of the SMA materials with desired properties while minimizing the required number of computational (and/or physical) experiments.

Technical Progress

The technical progress of the project can be summarized, in the following complementary tasks:

Bayesian Experimental Design: A Bayesian Experimental Design framework for the multi-objective materials design has been developed (Lagoudas, Arroyave, Dougherty, Karaman). The capabilities of the framework has been demonstrated on the design of precipitation strengthened NiTi SMAs with a set of desired properties where the developed scheme has been used to carry out an efficient search of the SMA materials with desired properties while minimizing the required number of computational experiments. In another front the Efficient Global Optimization (EGO) and Knowledge Gradient (KG) methods has been further developed to operate under a constrained experimental design problem with a truncated Gaussian process model (Dougherty). Furthermore, we theoretically demonstrated that KG and EGO procedures are actually implementations of Mean Objective Cost of Uncertainty (MOCU)-based experiment design under their modeling assumptions (Dougherty).

Micromechanical Model Development: An SMA micromechanical model, based on the finite element method (FEM), for the prediction of thermo-mechanical response of the precipitation hardened NiTiHf SMAs has been developed (Lagoudas, Baxevanis). Furthermore spectral based micromechanical models has been developed to capture the response of SMAs (Benzerga). During the preliminary correlations the spectral methods presented a reduction in the computational cost higher than 2 orders of magnitude with respect to the conventional FEM.

Uncertainty quantification: A Bayesian probabilistic calibration have been performed for an SMA phenomenological model (Arroyave). In this regard, a design of experiment has been applied before calibration to solve the curse of dimensionality through the identification of the most sensitive model parameters. Subsequently, a Metropolis-Hastings algorithm has been applied to find the plausible optimal values and uncertainties of the sensitive parameters given all the available experimental data. Finally, the values and uncertainties of the estimated parameters have been propagated to the model output. In a similar uncertainty quantification problem, a model has been developed to quantify the uncertainty of the measured Ni, Ti, Hf composition values of NiTiHf HTSMAs samples. The model is based on a regression problem with constraints indicating the uncertainty around data.

Composition Effects on Martensitic Transformation: The compositional dependence of transformation temperatures in the Ni-Ti-Hf SMA system has been studied (Karaman). Experiments has been conducted where the nickel and hafnium compositions has been varied from 49.8% to 51.2% and from 0% to 30% (at.%), respectively. The results indicated that the transformation characteristics are highly sensitive to nickel content for all respective hafnium contents. The nature of martensitic transformation is further studied in the light of crystallographic compatibility, strain-glass behavior, transformation arrest, and H-phase precipitation. We also studied, the phase equilibrium in Ni-Ti-Hf system at different temperatures using diffusion multiple experiments.

Thermodynamic Assessment of the NiTiHf System: Binary thermodynamic models for Ni-Ti, Ni-Hf and Hf-Ti were identified (Arroyave) and validated. A preliminary ternary model was created by combining data from the three binaries comprising information for binary phases only. Using experimental data (solutionized data and diffusion triples) generated (Karaman), in conjunction with already available experimental data, the ternary phase diagram is being assessed. Formation energies and finite temperature thermodynamics of binary phases in the Ni-Ti, Ni-Hf and Ti-Hf binary systems have been calculated.

Future Plans

In the remaining of the project, the following tasks are being contemplated:

- Karaman's group continues to generate data on the transformation behavior of precipitation hardened and solutionized Ni-Ti-Hf SMAs over a wide composition range. The samples will be characterized through SEM and DSC to augment knowledge about process-structure connections.
- Lagouda's group will further develop the newly derived NiTiHf micromechanical models. The models will be enhanced and validated by taking into consideration the experimental results reported by Karaman's group.
- Benzerga's group will utilize spectral based micromechanical models to model the response of NiTiHf SMAs using considerably larger RVEs in comparison to the ones used in the finite element method in a higly efficient computational manner.
- Lagoudas and Benzerga's group will begin the incorporation of transformation induced plasticity within shape memory thermodynamically-consistent micromechanical model developed by Lagoudas [3].
- Diffusion multiple experiments will also be carried out by the Karaman group which will be used to fine tune the ternary Ni-Ti-Hf phase diagram developed by Arroyave's group.
- The collaborators are working on implementing a Bayesian Experimental Design framework that uses models that are closing the chemistry/processing-microstructure-performance-chemistry/processing loop to design materials with optimal properties. The framework will be demonstrated first on the well-studied NiTi material system to offer a baseline and then will be extended on the prediction of the response of the NiTiHf system.

Broader impact

The challenges to HTSMAs development are common to a wider range of materials, including the recently discovered Fe-based SMAs, Co-based SMAs, and precipitation hardened β-Ti alloys and the proposed framework has wider applicability beyond HTSMAs. The immediate technological impact of the present award is the accelerated development of high-temperature solid-state actuators for the aerospace and automotive industries and the support of the manufacturing renaissance in the US. Six PhD students, two MS students and one postdoctoral scholar and two undergraduate students are being (partially) supported by the project. **Nineteen** publications have resulted from this work and ten [4-13] are listed here.

Data Management and Open Access

The materials informatics infrastructure will be based on the NIST Materials Data Curation System (MDCS), currently under development by NIST with significant contributions by the PI's group. The MDCS provides the means for capturing, managing, sharing and transforming materials data into a structured format (based on XML) amenable to transformation to other formats. The data is saved in the MongoDB non-relational (NoSQL) database system. Prototype repositories with data for HTSMAs and relevant computational frameworks are developed by the PIs and co-PIs in collaboration with NIST's MDCS group [14].

Advancing Along the Materials Development Continuum

Current efforts towards identification of optimal chemistry+processing combinations in HTSMAs are mostly based on semi-empirical approaches that combine experiments with incomplete models that are unable to bridge scales efficiently. Finally, no systematic, model-assisted, exploration of the composition-processing-microstructure-property space has been carried out. **We expect the proposed framework, as the results of the published work indicate, to significantly accelerate the discovery and development cycle for this important class of functional materials.**

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Integrating theory, computation and experiment to robustly design complex protein-based nanomaterials

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Keywords: protein design, protein assembly, protein nanomaterials, self-assembly, symmetry

Project Scope

The overarching goal of this project is to advance new strategies for designing protein molecules that self- or co-assemble into geometrically specific materials with sizes in the mid-nanometer range. The project elements include a theoretical foundation for how this can be achieved, computational and experimental tools for producing the amino acid sequences of novel proteins with the desired assembly properties, and experimental validation that the novel proteins assemble into the intended architectures.

Relevance to MGI

This project encompasses all the steps from theory and design to production and experimental validation. The theory side includes enumeration of all possible symmetric material architectures that can be achieved by combining two simpler protein symmetries. The computational component includes the development of new software for designing protein interfaces under those specifications. The production component includes the expression and purification of numerous candidate amino acid sequences, as well as experimental method development to enable step-wise assembly of the designed materials on a solid substrate. The validation component includes various experimental techniques, including electron microscopy, small angle x-ray scattering, and X-ray crystallography, to demonstrate the atomic level precision of the designed materials. Many successful cases have been carried from design to validation during the course of this project, including protein homo- and hetero-oligomers, dihedral protein complexes, tetrahedral, octahedral, and icosahedral protein nanocages, two-dimensional layers, and three-dimensional, crystal-like materials.

Technical Progress

- Taking advantage of the improved design methods we reported in Fallas et al. (2016), we have produced numerous heterooligomeric building blocks for making higher-order materials with multiple uniquely addressable subunits. To improve the success rate for design, we have implemented a powerful hydrogen bond network search algorithm in the Rosetta computer program (Boyken et al. Science 2016). The resulting materials are being validated by a combination of SEC-MALS, small-angle X-ray scattering (SAXS) and native mass spectrometry. Four heterotrimeric building blocks have already been successfully characterized. This new generation of materials will allow genetic control of the asymmetric placement of functional groups in three dimensions with atomic-level accuracy.
- In one particular approach to assembly diversification we are developing a design pipeline to convert homomeric assembly components into heteromeric components, thereby creating lower symmetry arrangements that obey higher pseudo-symmetry. We have been successful in creating and characterizing a first generation pseudo-symmetric trimer. These new building blocks will enable increased functional diversity and new opportunities for materials design.
- We have produced several *de novo* repeat protein building blocks (Fallas et al., 2016) that self-assemble into well-ordered helical fibers. Six such materials have been validated by cryoEM. These fibers offer properties of tunability, dynamic assembly, assembly inside *E. coli* cells, and growth from designed anchors. These

could find uses as scaffolds for solving protein structures by cryoEM, increasing valency in binding, making protein-based conductive wires, and tools for detecting and amplifying molecular signals.

- We have designed helix bundles that can trap or 'cage' a bioactive peptide, and then expose that peptide motif upon binding to a competing activating peptide. *In vitro* we have caged the Bim peptide and the split-GFP strand 11 peptide. *In vivo* we have demonstrated caging of a protein degradation signal. We have tuned these de novo switches to exhibit free energy landscapes that fit our engineering goals. These proteins are being developed for use in bioorthogonal signaling networks in synthetic biology, and will ultimately be generalized for constructing protein logic gates in solution or on a cell surface.
- We are making our symmetry-based design methods accessible to others by publishing formal design rules for all possible materials that can be produced within our framework (Yeates, *et al.* Curr Opin Struct Biol, 2016; Yeates, Annu Rev Biophys 2017) We have published papers enumerating design rules for two and three-dimensional materials (i.e. layers and crystals), which includes constructions of 33 different types of 2-D materials and 70 different types of 3-D crystalline materials. Several protein components for testing the design of 3-D materials have been produced in in the laboratory already.
- The symmetry-based construction rules have been reduced to a set of minimal free (rigid body) parameters to simplify implementing the methods in Rosetta and other protein design programs.

Future Plans

Our primary objectives for the future are to: 1) develop new computational methods for designing protein nanomaterials of increasing sophistication and complexity, and 2) develop new computational methods to encode the ability to perform logic in the amino acid sequences of the designed materials. We are working on these computational methods now and expect to generate a number of prototype materials during the next year of the project. These new methods, and the materials they produce, will enable a next generation of protein-based nanomaterials that give the designer/engineer more control over the placement of functional elements and the triggering of a functional response based on designer-defined inputs.

Broader impact

This project continues to provide highly interdisciplinary training for numerous young scientists at the two supported universities. Students and postdoctoral researchers participating in the project are learning how symmetry principles apply to molecular structure, how computer programming can be used to design new functionalities into proteins, and how biophysical and structural methods are applied to large macromolecular complexes. This project has also enabled several students and postdoctoral fellows to participate in conferences where they have had the opportunity to meet and learn from researchers in related disciplines.

Data Management and Open Access

The computer code in this project is being developed within the Rosetta program suite, which is publically available and licensed freely to non-commercial groups. The structural results, i.e. the atomic coordinates of the crystallographically determined structures, are being deposited in the PDB.

Advancing Along the Materials Development Continuum

In addition to enabling the accurate design of materials of increasing size and complexity, our continued method development is also increasing the rate at which we are able to create and characterize new designs, and dozens of new protein nanomaterials have been generated. In anticipation of the broad potential utility of our materials and methods, we have also filed several patent applications related to materials developed during the project. One family of IP has led to the formation of a biotech spinout company using the designed protein nanomaterials as a platform for developing next-generation vaccines. The company has raised >$1M in seed financing and is currently discussing strategic partnerships with several major Pharma companies.

Publications

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Design of active ink for 3D printing: integrating modeling and experiments

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Keywords: additive manufacturing, active particles, self-assembly, focusing, Lattice-Boltzmann method

Project Scope

Active materials consume energy from the environment and constitute a novel class of materials with emergent properties. We proposed a new concept of material for 3D printing termed ‘‘active ink": a suspension of functionalized self-propelled rod-like particles extruded through a nozzle. We used bi-metallic nanorods propelled by decomposition of H_2O_2. Active ink enables controlled distributions of nanorods within a printing voxel leading to composite materials with novel properties not possible for passive particles. Apart from advancing new additive manufacturing concept, the work leads to novel mathematical models and efficient high-performance computational algorithms.

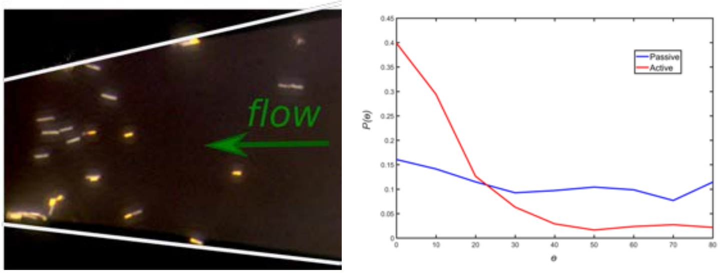

Figure. Illustration of active focusing of self-propelled particles. Left panel: reflection microscopy of 2 μm gold-platinum rods flowing through the nozzle. Right panel: comparison of orientation distribution *P(8)* for active and passive rods. Active rods align predominantly along the nozzle middle line.

Relevance to MGI

This project follows the MGI Strategic Plan in discovery and 3D-printing-based-design of new composite materials by integrating research thrusts from experiment and modeling. We are using a spectrum of multi-scale computational approaches ranging from discrete particle and Monte Carlo simulations to Lattice Boltzmann method to predict extrusion of active ink through microfluidic nozzles. Our computational discrete particle modeling predicted optimal nozzle geometry and flow conditions. It dramatically cut the time needed for exploration of the experimental conditions. Our experiments faithfully confirm theoretical predictions and greatly benefited from the computational insights. We developed a high-performance Lattice-Boltzmann method to treat steric and hydrodynamic particle interactions near the channel wall. Computational design predicted that the experimentally observed migration of particles against the flow can be suppressed by artificial wall bumps. It led to a discovery of novel channel shapes and flow conditions not expected in the beginning of the project. We anticipate that in addition to discovery of optimal shapes and flow conditions, the research will provide the “active ink library” tool for creation of materials with pre-defined structure and controllable function, which will be disseminated in an open access manner for further use in materials science and industry.

Technical Progress

We have developed novel mathematical models and carried out experiments with suspensions of active bimetallic nanorods to understand the non-trivial change in distributions of these rods in trapezoid nozzles, commonly used in 3D printers. Such non-trivial distributions will potentially result in materials with novel properties because, unlike passive particles, active ink particle distribution within a printed voxel can be well controlled. An important feature of active particle trajectories is rheotaxis – tendency to re-orient itself against the flow and swim upstream. Our models and accompanied experiments suggest new nozzle geometries that will reduce rheotaxis and boundary accumulation typically exhibited by active particles, and thus significantly enhance the performance of 3D printers. Specifically, our recent findings are as follows:

Experimental Setup. We synthesized bimetallic gold-platinum nanorods via electrochemical deposition techniques, involving alumina membranes. Microfluidic channels with nozzles were fabricated using a PDMS kit by soft lithography. Solutions containing microswimmers were injected into the channels and the system connected to syringe pumps filled with aqueous H_2O_2. The introduction of hydrogen peroxide activates the self-propelled particles. The nanorods were observed using an inverted microscope and videos were recorded for analysis.

Rheotaxis of bi-metallic rods. We observed in experiments and simulations rheotaxis in confined spaces for autonomous, chemically-powered swimmers [2]. In an assumed Poiseuille flow inside a microfluidic channel, the upstream migration of micromotors occurs predominately in high-shear regimes near a surface. Further investigation demonstrated that rheotaxis can be inhibited or enhanced based upon several factors: background flow, particle velocity, number of nearest surfaces, geometry of the particle, and the number of nearest rheotaxing neighbors. Unique to this study, we observed collective behavior and many particle dynamics of rheotaxing nanorods.

Focusing of active particles. In [1], we considered active particles swimming in a convergent fluid flow in a trapezoid nozzle with no-slip walls. Mathematical modeling is used to analyze trajectories of these active particles inside the nozzle. By extensive Monte Carlo and discrete particle simulations, it was shown that trajectories are strongly affected by the background fluid flow and geometry of the nozzle which lead to wall accumulation and rheotaxis. We describe the non-trivial focusing of active rods depending on physical and geometrical parameters. We also developed in [4] a kinetic approach, based on the Fokker-Planck equation, which captures the focusing of active particle distribution.

Concentration and alignment of active particles. The theoretical predictions allowed a dramatic reduction in the exploration time for the optimal flow conditions and nozzle geometries. We were able to observe in the experiments with bi-metallic gold-platinum nanorods powered by decomposition of H_2O_2 strong alignment of active particles near the nozzle outlet. The experiments also suggested new strategies to counteract rheotaxis. The controlled particle distribution inside a printing voxel will lead to composite materials with novel properties not possible for passive particles.

Five publications [1-5] have resulted from research supported through this award.

Future Plans

Control of the distributions of active particles within a voxel will facilitate 3D printing with tunable properties: elastic moduli, conductivity (thermal and electrical), anisotropy, etc. We will focus on the following directions in the future work:

1. *Optimization of nozzle geometry*. Optimize geometry of a nozzle to enhance extrusion of bi-metallic nanorods and control rheotaxis. For the latter, we will focus on nozzle walls geometries containing so called “anti-rheotaxis”

bumps. The purpose of introductions of these bumps is re-injections of active particles accumulated at walls into the bulk flow.

2. *Reversible Networks by Electric Field*. We have discovered that active rods form complex structures in response to electric field. These complexes "explode" when the field is removed. We plan to analyze both experimentally and theoretically how electric field stimuli may enhance the flow of bi-metallic particles in active ink.
3. *Self-pumping nozzles*. We will incorporate catalytic pumps to fabricate a self-pumping nozzle.
4. *Complex shape active particles*. Thanks to advances in 3D printing, we will print micron-size nanomotors by the means of two-photon photolithography available at PSU. The particles, such are nano-propellers, toroids, etc., will exhibit novel flow properties. Their shape will be optimized via computational design. The 3D nanoprinting will allow control of the particle shape with unprecedented precision. It may lead to the design of active ink with such desirable properties, as chirality and anisotropy.

Broader impact (Only required for NSF projects)

The ability to tune material properties by incorporation of self-propelled particles that harvest energy from the ambient fluid is expected to lead to a myriad of applications, including faster 3D printing and tailored responsive composites. The results obtained and anticipated in the course of this project will be employed in the development of novel experimental, computational, and analytical techniques.

Results of this research have already been presented on various conferences including APS meeting (March 2018, Los Angeles). This project provides highly interdisciplinary training and education for two graduate students (including one female and one Hispanic) and a postdoc at Penn State and a postdoc at U. of Pittsburgh.

Data Management and Open Access

Paper [1] is published in an open access peer-reviewed journal. Data from both experimental and computational work, after publication, is planned to be shared via ScolarSphere at Penn State. All preprint articles arising from the proposed research are posted on the public preprint server http://arxiv.org.

Advancing Along the Materials Development Continuum

The synergy between all the four groups involved in the project will accelerate discovery and development of composite materials which are 3D printed with the use of the active ink. This is and will continue to be done by (*i*) identification of main principles of how the active component alters the ink flow through the printer's nozzle, (*ii*) analysis of the printed material properties as a function of the active particle distribution, (*iii*) creation of predictive computational tools ("active ink library"), and (*iv*) the detailed description of setup, for either experimental or industrial purposes, allowing for a successful application of the active ink.

Publications

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Computational Design of Next-generation Nanoscale DNA-based Materials

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Keywords: DNA nanostructures, programmable biomaterials, computational design, structures prediction.

Project Scope

This research project aims to develop a generalized computational framework for the rational design of structured DNA-based materials of nearly arbitrary nanoscale geometric composition. Computational models of DNA-based self-assembly and structure are being validated experimentally in a highly iterative and integrative manner. Structured DNA nanoparticles and single-stranded DNA tiles are being used to realize complex structured and porous 3-dimenional materials in infinite, extended lattices or finite, discrete nanoscale clusters. Utilization of purely synthetic, single-stranded tile oligos facilitates the realization of up to gigadalton-scale DNA-based materials with unique nanoscale addressability using sequence specification amenable to downstream functionalization with metallic nanoparticles, enzymes, or other functional moieties.

Relevance to MGI

The Bathe lab is developing a top-down computational design procedure for scaffolded DNA origami nanostructures based on DX-edge motifs to produce nearly any arbitrary shaped 2D geometry with high yield (**Figure 1a**) [1], which are validated experimentally in the Yan and Yin labs. They also have developed a computational framework for DNA-based materials design and synthesis [2] that includes bottom-up prediction of 1D/2D/3D nanometer-scale structure and self-assembly properties. Experimental metrics predicted computationally include nanometer-scale structural features of DNA-based materials as well as the folding temperature of multi-strand DNA assemblies in specific buffer conditions. Semi-empirical sequence design algorithms that optimize folding yield for given target multi-stranded and single-stranded origami structures are additionally being developed.

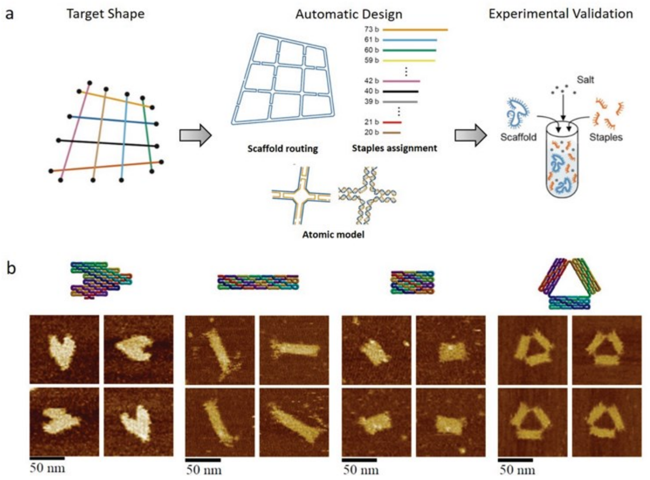

Figure 1. (a) Top-down automatic design procedure for DNA origami nanostructures based on DX-edge motifs [1]. (b) Schematics and corresponding AFM images of single-stranded DNA origami objects based on PX motifs [3].

Technical Progress

We recently initiate the project by developing a top-down computational design procedure for scaffolded DNA origami nanostructures based on DX-edge motifs to produce nearly any arbitrary shaped 2D geometry. This automatic design process enables non-experts to precisely create customized nanoscale wireframe patterns with high yield, which are validated experimentally in the Yan labs. In related work, the Yan lab and Yin lab has collaborated to demonstrate a set of novel strategies to design and construct nucleic acid nanostructures folded from a single-stranded DNA or RNA chain. This new design procedure obviates the need of hundreds of synthetic staple oligonucleotides that are conventionally used to fold scaffolded DNA origami objects [3]. A wide variety of ssDNA and ssRNA structures have been constructed including close-packed lattice-based ssDNA/ssRNA origamis, surface-based wireframe ssDNA/ssRNA origamis, and ssDNA/ssRNA knotted assemblies. Multi-kilo base ssDNA/ssRNA have been synthesized and the formation of such structures were characterized by atomic force microscopy (AFM) imaging. The replicability of those signle-stranded origamis have been also demonstrated both in vitro and in vivo.

Future Plans

The principal aim of this work is to empower our ability to rationally design structured DNA-based materials of nearly arbitrary nanoscale geometric composition, as well as their emergent functional properties that depend critically on their structure. Future plans include the development of computational models to aid in the sequence design of single-stranded DNA origami objects based on PX motifs motivated by experimental work from the Yin and Yan labs (**Figure 1b**) [3], as well as multi-stranded DNA origami objects, including the ability to predict and optimize folding temperature and cooperativity in diverse buffer conditions to maximize yield and fidelity of synthesized materials.

Broader impact

Dissemination of our computational tools to the broader scientific community is realized using the online server http://cando-dna-origmi.org, which enables in silico guidance in the design of de novo nanoscale materials for diverse target applications in materials science and nanotechnology. Training undergraduate and graduate students in integrated experimental-computational approaches to materials structure and property prediction in the PI's laboratories aids in educating the next generation workforce in nanoscale materials science and nanotechnology.

Data Management and Open Access

Our computational developments in 3D structure prediction of DNA origami objects are available online at the CanDo server. We are additionally posting computational scripts there related to material property calculations including atomic structure generation, DNA sequence design, thermodynamic property prediction, and optical properties of hybrid DNA-based materials. We are working with open source software developers to integrate results of our work into computational platforms for broader use beyond the preceding online resource.

Advancing Along the Materials Development Continuum

Our in silico prediction of the nanometer-scale structure of self-assembled DNA origami objects provides immediate feedback to experimentalists and materials designers that would otherwise require significant financial cost, time, as well as personnel resources for synthesis and characterization. Moreover, experimental characterization of nanometer-scale DNA origami structure and emergent functional properties are significantly limited technically by a number of factors. Our single-stranded nucleic acid design framework offers the ability to program custom nano-geometries that can be replicated, amplified, and evoluted to generate selected features and structural related functions. Patents and provisional patents have been filed by the Yin lab on the single-stranded DNA origami synthesis approaches. Additional funding is being pursued by each of our groups in diverse areas related to the research in this project. Each of our groups is additionally exploring various commercialization and entrepreneurial opportunities.

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DMREF: Biologically Inspired Optimized Materials And Technologies Transformed by Evolutionary Rules (BIOMATTER)

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Keywords: bio-inspired materials, mechanical properties, optical properties, chemical properties and reconfigurable properties, multifunctional materials, material design rules

Project Scope: This project targets the conception of generally applicable material design rules that will extend capabilities of state-of-the-art materials far beyond those available today. Gaining a thorough understanding of the fundamental materials design concepts employed by Nature's finest "multi-tasking artists" in combination with the development of novel analytical and computational materials evolution tools will provide insight into synergies and trade-offs in multifunctional materials and result in revolutionary biomimetic material platforms. This research is aimed at systematically identifying foundational design rules that will guide academic and industrial efforts to create the next generation of innovative materials.

Relevance to MGI: BIOMATTER is creating a synergistic platform of expertise in mathematics, modeling, materials synthesis, and characterization through an umbrella collaboration that focuses and coalesces research in the field of multi-functional, programmable materials. Specifically, our project focuses on four connected collaborative research efforts:
(A) Inspiration from Biological Materials. This effort exploits current knowledge about material solutions in terrestrial and aquatic organisms that show superior performance across multiple property classes.
(B) Mathematics, Physics and Evolutionary Optimization. Since many biomaterials exhibits a clear separation of scales, we derive low-order coupled models to characterize the phase space of possible material solutions with a desired set of properties. We then explore our design space using optimization algorithms that mimic biological evolution via computational analogs of random mutation and natural selection.
(C) Computational Models and Algorithms. Computational modeling is used in addition to mathematical and theoretical assessments or where analytical solutions and reduced order models are not possible due to the geometric and physical complexity of the problem.
(D) Experimental Evaluation of Design Rules and Processes. Once a set of design criteria is established, we scrutinize the quality of our design rules by experimental realization and testing of specific material solutions.

Technical Progress

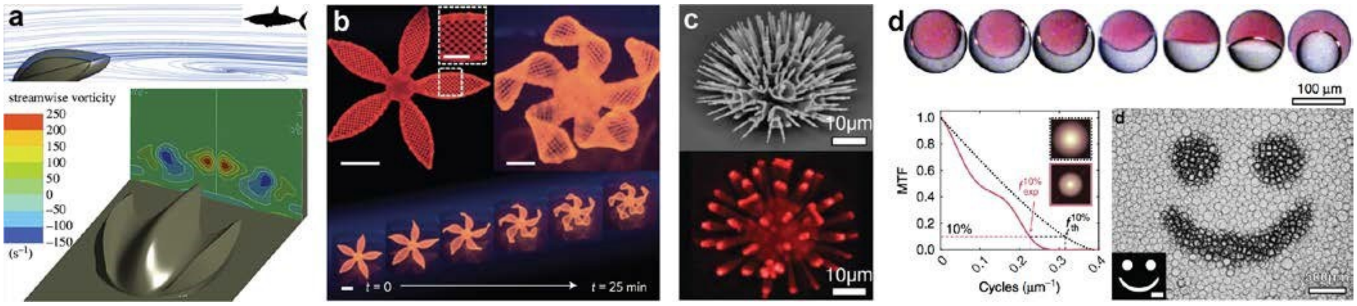
Since the initiation of our program in autumn of 2015, we have started a number of collaborative projects involving several PIs. Existing achievements include:

Bio-Inspired Designs for Passive Lift Enhancement and Drag Reduction: Through parametric modelling to query a wide range of different designs, we discovered a set of shark denticle-inspired surface structures that achieve simultaneous drag reduction and lift generation on an aerofoil, resulting in lift-to-drag ratio improvements comparable to the best-reported for traditional low-profile vortex generators and even outperforming these existing designs at low angles of attack with improvements of up to 323% [1].

Biomimetic 4D printing: Inspired by botanical systems, we printed composite hydrogel architectures that are encoded with localized, anisotropic swelling behavior controlled by the alignment of cellulose fibrils along prescribed four-dimensional printing pathways. When combined with a minimal theoretical framework that allows us to solve the inverse problem of designing the alignment patterns for prescribed target shapes, we can programmably fabricate plant-inspired architectures that change shape on immersion in water, yielding complex three-dimensional morphologies [2].

Controlled Growth and Form of Precipitating Microsculptures: In nature, biological systems use non-conventional self-assembly strategies to produce multifunctional materials with complex morphologies and tunable mechanical or optical properties. A promising inorganic model system for synthesizing scalable and intricate solid geometries by virtue of a "life-like" self-assembly pathway is the chemical coprecipitation of silica with carbonate salts in an alkaline solution. However, a theoretical understanding of the carbonate-silica coprecipitates has been missing owing primarily to the inherent separation of the characteristic length scales of the system, which determines the growth and form. Recently, we made use of this scale separation to develop a geometrical theory of carbonate-silica coprecipitation that not only explains the observed range of intricate shapes, but also predicts the self-assembly of previously unexplored morphologies that we have confirmed experimentally [3].

Reconfigurable, dynamically tunable bio-inspired compound micro-lenses: To realize micro-scale, reconfigurable, optical components with responsiveness to a wide variety of stimuli and adjustable optical properties, we employ multi-phase emulsion droplets. These droplets are fabricated from immiscible hydrocarbon and fluorocarbon liquids that change their morphology depending on changes in interfacial tension. The micro-droplet morphology emulates the features found in retina cell nuclei of nocturnal mammals that help to minimize tissue-light scattering and enhance light collection. Controlling the droplet morphology allows us to use them as responsive micro-lenses that display variable focal lengths. The droplet lenses can be reconfigured to focus or scatter light and form real or virtual images [4].



Bioinspired functional material designs. a) Lift enhancement and drag reduction using shark skin-inspired materials. The fluid flow fields arising in the vicinity of shark denticles (size ~ 200μm) are modeled using computational fluid dynamics. Our modeling efforts provide evidence that the correct placement of the denticles enhances lift and reduces drag. b) 4D printing of reconfigurable bilayer structures. Simple flowers composed of bilayers of cellulose fibers in a hydrogel matrix with controlled bilayer orientations printed after identification of promising geometries using a mathematical model of the mechanics of anisotropic plates and shells to create responsive micro-scale materials. The time lapse sequence at the bottom shows the flowers during swelling of the hydrogel. Scale bars 5mm, inset 2.5mm. c) Precipitation of complex microstructures. A micro-coral that guides light in its individual branches resulting from the carefully controlled growth process. d) Reconfigurable bi-phase emulsion micro-droplets as tunable lenses. The droplet's internal configuration can change in response to variations in chemical environment, temperature, or light exposure. They show good lensing characteristics, as quantified in the displayed modulation transfer function (MTF), and can be used to reversibly produce microscale patterns.

Future Plans

We will continue to study the causalities between hierarchical material architectures, composition and morphogenesis and the emerging properties in a set of exemplary biological systems by analytical and computational analysis of the multi-faceted material parameter interactions underlying true multifunctionality. This will enable us to identify a generalized set of rules for guiding the design and fabrication of multifunctional 21st century materials. Based on this set of design rules, we will fabricate material prototypes using state-of-the-art additive manufacturing, self-assembly and micro-fabrication strategies. A detailed characterization of the prototypes' performance and comparison to the parent biological system(s) will help us evaluate the validity and prediction capabilities of our design rules and refine them in an iterative process.

Broader impact

The five PIs are committed to promote science and engineering to a broad audience. Their work has been recently showcased in a number of exhibitions (Permanent collection NEMO Science Museum, Amsterdam - Part of catalogue of the “Anthropocene" exhibition at the Deutsches Museum Munich - Exhibition “Creating Nano Flowers” as part of “Nature Made” exhibition with François Bernard at Maison et Objet in Paris - Exhibition as part of the exhibit entitled “It’s a Nano World” at the The Children's Museum in West Hartford, CT – NanoDays at the Museum of Science, Boston, MA). Materials produced within this initiative are also used in educational programs at the MIT museum. We have recently contributed with a program centered on “Biological material design and optics” to science education at the elementary school level at the Tufts Eliot-Pearson Children’s School. We also helped organize the Cambridge 8th Grade Science and Engineering Showcase where 400 8th graders from Cambridge Public Schools presented their research to their peers, teachers, and facilitators. The 8th graders attended lab/facility tours at Harvard and science demos by Harvard students and postdocs. Additionally, we helped organizing the Boston Photonics Centennial Conference at Harvard University where keynote speakers and invited speakers, and other participant presented their work on optics and photonics, including bio-inspired photonics and optical materials design

Data Management and Open Access

All analyzed experimental data (such as digital photographs, microscope images, video, spectroscopic data and 3D models) collected as part of this project have been made available in peer-reviewed journal publications and disseminated at topical conferences. The corresponding raw data, which is not necessarily published, is available upon request. Finally, code modules implemented as part of this project are made available in a Github repository titled “DMREF-Biomatter”, to be used and expanded upon by the community.

Advancing Along the Materials Development Continuum

The DMREF BIOMATTER program exemplifies that a detailed understanding of biological functional can provide useful inspiration for synthetic material design. This is especially beneficial in multifunctional materials development; here, biological solutions reveal synergies and trade-offs thereby pin-pointing advanced starting points in large, difficult-to-screen parameter spaces. Our program emphasizes the promise of integrated bio-inspired materials design by relying on advanced modeling and experimentation to identify the working principles and advantages of biological material solutions, their translation into synthetic material analogues, and subsequent rational functionality optimization to satisfy specific application requirements. Our work stresses the importance of thinking beyond the conventionally applied material systems in many engineering fields, as exemplified for instance in our use of fluids for designing tunable lenses. This will greatly enrich the materials library of in optical engineering and other technological disciplines, thereby enabling the design of advanced devices from multifunctional rationally designed materials using tailored fabrication approaches such as our 4D printing technology or the controlled growth of precipitating micro-structures.

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DMREF: Collaborative Research: Multiscale alloy design of HCP alloys via twin mesh engineering.

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Website: In preparation
Keywords: hexagonal close packed, twins, alloys, strength, toughness

Project Scope

Our recent results have inspired the exciting potential of "twin mesh engineering" to overcome the long-standing problem of simultaneous strengthening and toughening in HCP metals. Twin meshes are defined as two or more intersecting arrays of twins within a grain. The goal of our research program is to formulate a scientific framework to design twin meshes based on the effects of solutes starting with first principles. We posit that alloying can be used to tune twin formation and propagation by affecting slip. One important outcome will be a multiscale twin mesh module (TMM) that incorporates processing/twin mesh/-performance information.

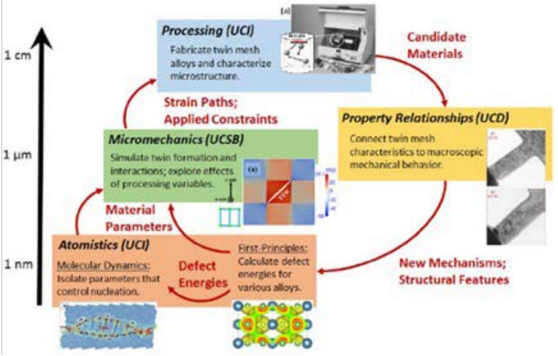

Figure. A schematic representation of the iterative feedback loop used to build the twin mesh module (TMM). As trips around the loops are made, more complex microstructural features, such as grain boundaries or texture, or variations in processing route will be explored. A colored box groups task areas while the vertical axis describes the variety of length scales that are covered.

Relevance to MGI

In this renewal program, we formulate the critical question: *Can alloying be used to make the "right" twin mesh; that is, one that leads to* high strength/high toughness (HSHT)*?* Obtaining the answer poses interesting challenges as the space for twin meshing is vast and the slip-twin inter-relationships highly scale dependent. These include alloying element and concentration, processing pathways and conditions, twin-mesh characteristics (number of intersecting arrays, volume fraction), and starting microstructures (texture, grain size, grain boundaries). To address these challenges, we propose to build a multiscale TMM as a predictive vehicle to strategically guide selection of alloying elements to achieve high-strength/high toughness (HSHT) highly twin-meshed HCP alloys via first principles (See Figure). The purpose of the TMM is to probe the binary alloy parameter space efficiently and effectively by linking inputs/outputs from first principles calculations to micromechanics to polycrystalline plasticity and eventually to large-scale forming simulations.

Technical Progress

In our prior NSF DMREF program, we proposed an original approach to solve the long-standing problem of strengthening and toughening in HCP metals via the novel concept of "twin mesh engineering". We aimed to demonstrate that twin meshes, defined as two or more intersecting arrays of twins within a grain, can be engineered to achieve unprecedented combinations of strength and toughness in HCP metals. For pure HCP metals (Mg), we showed that *slip dislocations can form twins*, and, that one mechanism for forming a twin embryo involves the reaction of two gliding dislocations. Furthermore, by uniquely isolating and testing different twin morphologies grown in-situ, we demonstrated that, when compared to the cases of no twins or to a regular array of twins, a 3D twin mesh is a much more powerful strengthener. With the discovery of new profoundly strong roles of slip on twin formation, we are motivated to redirect research towards strategies that would control the activation barriers for dislocations and understanding how they would affect twin mesh formation.

Future Plans

A primary objective of this DMREF is to advance the fundamental understanding of how alloying affects the interactions of slip and twinning from the atomic to polycrystal scales, and to use this knowledge to develop a 3D twin-meshed microstructure for high strength and high formability. To this end, we plan to develop a twin mesh module (TMM), an iterative framework that loops through the following four components (see Figure): (1) Atomistic modeling of alloying effects, (2) Twin-twin and twin-slip micromechanics, (3) Processing of materials with 3D twin mesh microstructures, and (4) Strength and strain-to-failure property measurements. Each task will be a collaborative effort involving participation of all DMREF members. From a scientific standpoint, these components follow the natural progression of twinning across the scales. Task 1 entails the atomic to nanoscale mechanisms involved in slip to twin embryo formation. Task 2 focuses on the submicron to micron subcrystal mechanisms involved in twin propagation and thickening. Task 3 includes the micrometer to millimeter scale relevant to multiple, twin-mesh formation. For instance, we aim to determine initial texture/processing pathway combinations that would form profuse 3D twin meshes. Task 4 involves the "macro-scale", as characterized by stress and strain gradients with a wavelength of a few centimeters associated with the non-homogeneous conditions of mechanical strength, ductility, and formability tests. For TMM to be reliable, the connections between these scales should be based on fundamental knowledge. To this end, we plan to include co-dependently designed experiments and modeling, specifically in-situ, multi-beam diagnostics, combined with rigorous, mechanistic based calculations, with both spanning the atomic to polycrystal length scales. We plan for several loop cycles to be performed over the duration of the program, with each loop involving reductions in alloy space, new alloy compositions, or new energetic parameters.

Broader impact

Our prior DMREF program was very successful in educating and training both undergraduate and graduate student participants, not only in the details of the technical aspects of the program, but also in the powerful MGI strategy of integrating experimental and computational methods. Students working primarily as experimentalists have collaborated directly with others with expertise in computation, and vice versa. The result has been very rewarding, not just in the professional development of the student, but in the resulting accomplishments of the program. In the renewal, we will build on this success by continuing to have teams of students interacting routinely so that computational activities inform experimental design and experimental results inform computational design, thereby facilitating the iterative feedback loop shown in the Figure. We will also introduce these integration strategies, as well as the technical discoveries, into the materials science courses offered at the three UC campuses. Students will continue to be encouraged to present their research at national and international meetings, and to utilize extensive on-campus resources for graduate student professional development. As mentioned above, the twin mesh hub (TMH) website and portal will also promote education and workforce training.

Data Management and Open Access

The team proposes to apply the MGI paradigm of integrating computation with experimentation to accelerate materials discovery and development, specifically to establish the guiding principles that would identify which alloy(s) generate the "right" twin mesh. To this end, we will build a twin mesh hub (TMH) that serves as a vehicle for transferring information across approaches and length scales. For scientific purposes its role is two-fold, to understand how alloying effects permeate across the continuum and how changing parameters in one space (e.g., processing space or alloying space) affect another. Technically, TMH provides a way to collectively document the data, software used, experimental techniques, input/output files, interrelationships between theory/computation/experiment, and to quantitatively describe how alloying effects pervade across the scales. TMH will serve as a centralized hub for the team to access files, and as an open-access tool for industry and other investigators to utilize findings from our research.

Advancing Along the Materials Development Continuum

High strength/high toughness structural alloys have great potential for commercialization in applications needing lightweight materials with improved performance (aerospace, ground transportation, military, nuclear energy, space). Our TMM aims to guide the design of alloys, which, unlike the pure metals studied in the prior DMREF, are used more often in industrial applications. Once the fundamental alloy-enabled physical mechanisms that accentuate the desirable twin meshes are understood, quantified and implemented into the TMM, this module will have generic application to many other materials with low-symmetry crystal structures that deform by twinning. The TMM will strive to eventually guide synthesis pathways using forming techniques that are more consistent with industry practices. Materials will ultimately be made in sheet and rod form, which are suitable geometries for testing mechanical behavior and are consistent with those used to build structures.

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Designing Microstructure for Engineering Toughness

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Keywords: MGI, fracture, toughness, microstructure, optimization

Project Scope

The project explores the use of digital methods of material synthesis including 3D printing and ink-jet printing to synthesize structural materials with exceptional mechanical properties. Specifically, the proposed project seeks to develop a fundamental understanding of the relation between material microstructure and fracture toughness and to use this understanding to design microstructures for desired toughness subject to the constraints of stiffness, strength and synthesis. It exploits emerging methods of digital and additive manufacturing to synthesize materials with the designed microstructure, and use microstructure and mechanical characterization to validate the designs.

Relevance to MGI

This project, schematically depicted in the figure at right, has developed a theoretical framework that is used to design and optimize microstructure for the desired effective toughness through extensive computation. The designs are then synthesized using digital methods, and characterized by mechanical testing and microscopy. The results are used to improve the theoretical framework. The entire project team works collaboratively with multiple overlapping tasks involving PIs and graduate students working in groups. Theory and computation have identified unprecedented opportunity to design materials with very high toughness, with asymmetric toughness, etc. and these have been achieved experimentally. Further, the experimental results have enabled improvements in the theoretical and computational framework. We have provided training to our students in this iterative process, and made our code widely available.

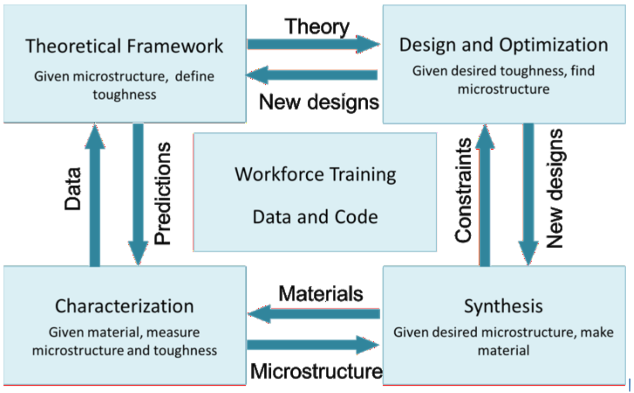

Figure. The iterative loop used to develop microstructure for desired fracture toughness, and activities to promote broader impact.

A specific example of the success of this iterative framework is the design of particulate microstructures. Theoretical considerations followed by parametric optimization led to a design of a particulate microstructure where the toughness can be enhanced while substantially maintaining elastic modulus. The synthesis and testing revealed that this was indeed the case; however, the enhancement in toughness turned out to be even larger than the prediction of the theory. This in turn led to a clearer understanding of the boundary condition used to develop the theory.

Technical Progress

We have demonstrated that it is indeed possible to design and synthesize heterogeneous media that have higher fracture toughness than either of its constituents without a significant loss of stiffness. We have also designed and demonstrated a `fracture diode' where the crack propagates in one direction, but is pinned in the opposite direction.

We have made significant advances in understanding of the effective toughness of heterogeneous materials: We have obtained a predictive understanding (computational prediction validated by experiment) of stress fluctuation and crack renucleation at interfaces as toughening mechanisms. We have developed a process for optimizing the combination of toughness and stiffness in particulate composites. We are developing a new topology optimization approach to optimize microstructure for toughness; this is nontrivial since crack propagation is a history dependent process determined by critical points. We have demonstrated this in a model setting and are working on the general setting. We are developing a phase field approach to study fracture in heterogeneous elastic/plastic materials. The project has also led to advances in materials characterization: We have developed a new experimental protocol using the `surfing boundary condition' to measure the effective toughness of heterogeneous materials. We have also developed a new approach to measuring strain using the grid method. Finally, we are developing a novel approach to 3D printing ceramics with complex microgeometries using preceramic polymers.

Future Plans

In the final year of our project, we expect to demonstrate enhanced toughness of 3D-printed ceramics.

Broader impact (Only required for NSF projects)

This project has contributed to the training of six graduate students (two completed doctoral thesis and four in progress), one graduate intern, five summer undergraduate researchers. Further, three graduate students involved in the project taught an after-hours course in a local high school on mechanical properties and testing. Principal investigators have given plenary lectures in professional meetings. Finally, we have initiated collaborations with industry. All data is shared among project participants and archived on local servers. The fracture code is available publicly

Data Management and Open Access

All data is shared among project participants and archived on local servers. The fracture code is available at http://bitbucket.org/bourdin/mef90-sieve

Advancing Along the Materials Development Continuum

We collaborate with HRL Laboratories on 3D printing of pre-ceramic polymers.

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Towards more robust models for nanostructure

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Keywords: Nanostructure problem, Distance Geometry problem, Inverse Problem, Robustness.

Project Scope

Goal: Obtain quantitatively accurate structural models for nanomaterials by solving the nanostructure inverse problem (NIP)

Roadblocks:

1. The NIP is difficult to solve
2. When it can be solved it is often ill-posed resulting in a multiplicity of structural solutions
3. It is difficult to reliably assign uncertainties to model parameter estimates

Approaches:

1. Put the mathematical underpinnings of the NIP on a firmer basis
2. Find new approaches for solving the NIP
3. Find better ways to assess the robustness of the results
4. Develop computational infrastructure for robust NIP solutions and make it available to the community

Materials systems:

1. Oxide, carbide and nitride nanosystems. polymers, nano-structured materials in general.

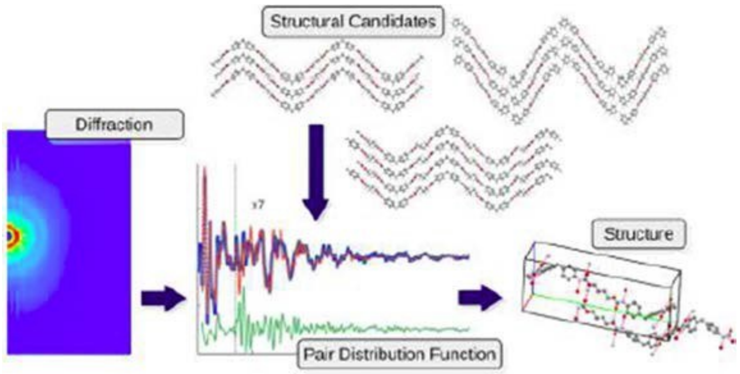


Figure. *The Nanostructure inverse problem*. The forward problem is, “given an arrangement of atoms for a nanostructure, what is the x- ray diffraction pattern?” The inverse problem that we are trying to solve is “Given a measured diffraction pattern, what is the arrangement of atoms that gave rise to it?” Answering this question robustly is critical to nanoscience and nanotechnology, but in general this is an ill-posed and generally intractable inverse problem

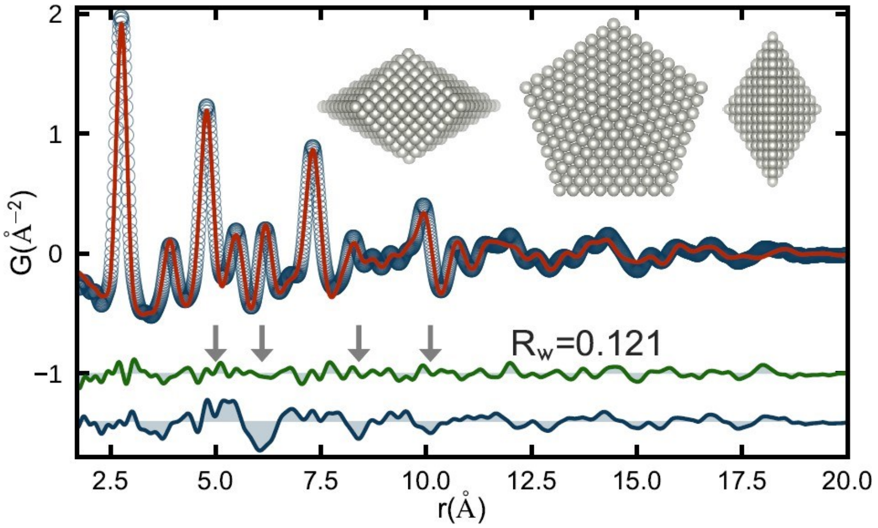
Relevance to MGI

Knowledge of structure is the keystone of the materials discovery process because structure determines properties. The quantitative robustness of nanostructure models then has a critical impact on the speed that new materials can be transitioned to technology and is a key bottleneck to the MGI goal of accelerating materials adoption. Improving and assessing the robustness of nanostructure models requires a tight coupling of applied mathematics, statistics and computation with experiment. Data analytics approaches are key because of the ill-posed nature of the problem. Tight coupling to experiment is critical because key approximations made in the statistical models (such as the independent and identically distributed (IID) nature of underlying errors) are often very poorly met in practice and so improved statistical methods are required. Our collaboration process not only involves frequent meetings but is based on the successful community coding model with activities shared through GitLab, an open-source equivalent to GitHub where members of the team can view and contribute to activities across the project.

Technical Progress

Mathematical underpinnings: By expressing the nanostructure inverse problem in terms of the graph theoretical Unassigned Distance Geometry Problem (UDGB), we have placed it on a more rigorous mathematical footing that will allow for a more systematic study of the NIP. We have developed correspondence retrieval methods which allow regression problems to be solved in which there are multiple signals of interest to be recovered that arrive as an unordered multiset. We plan to map this onto the UDGP to handle the assignment part of the problem.

NIP structure solution: We have shown that stochastic algorithms for cluster buildup tend not to find the ordered structure solutions favored by nature. We have therefore adopted a completely different approach to structure solution based on algorithmically building plausible ordered nanoparticle core clusters and testing these against measured PDFs systematically. This works well for metallic nanoparticles but we want to extend them. We have shown that using clustering we can increase the efficiency of selecting structural candidates. We have also shown that machine learning can predict with good efficiency the crystallographic space-group of a measured pair distribution function, something that has previously not been accomplished and will make cluster model selection much more efficient.



Solving the NIP by selecting structural candidates from databases of candidates. In this case the PDF was from a small Pd metallic nanoparticle and it turned out to be best fit by a Marks decahedron 4 nm across. Machine learning is being applied to speed up this process by clustering measured PDFs which allows us to select the class of core-cluster to attempt first from the database.

Robustness of solutions: We have explored the degeneracy of nanostructure solutions that can be found that are consistent with the PDF data. This has been tested on real data from CdSe clusters that were synthesized by Jon Owen at Columbia. We find that some structural information is very robust, but other structural parameters such as nanoparticle shape are not and result in multiple structure solutions that are as good as, or better than, the presumed correct solution and a multiplicity of plausible solutions. We are working on solutions to this problem.

Computational infrastructure: We have been building a software framework for running diffraction experiments at the XPD synchrotron beamline, with an end-goal of quasi-real-time streaming data analysis so that we can store analyzed nanostructure data to databases and make them available for the modeling developments we describe above. The current working release of the xpdAcq software is v0.7.1 (http://xpdacq.github.io/). This is now widely used by the materials community who do experiments at XPD. The real-time analysis software pipeline, xpdAn is at release v0.2.2, which is built on a new streaming data pipeline infrastructure called SHED (v0.2.1) that we also developed under this grant.

Future Plans

In the final phase of the project we will take the mathematical developments, and software infrastructural developments, and integrate them to produce useful tools for the community to study scientifically and technologically relevant NIPs. We will also apply them to materials systems under study in the group.

Broader impact (Only required for NSF projects)

The software infrastructure will be, and is being, used by researchers from a wide range of different communities as it is installed and running at the XPD beamline at the NSLS-II synchrotron at Brookhaven National Laboratory. We also make our modeling software available to a wide community of researchers ranging from chemistry, pharmaceuticals and materials to conservation of cultural relics. The code is disseminated with high quality documentation and is robust, tested open source software. We make heavy use of GitHub for encouraging community involvement in the code development.

Data Management and Open Access

Our data analysis software framework saves intermediate and final results in databases. These can be exported, or published, to have a DOI, though this infrastructure is not quite finished yet. The codes developed as part of this project are available at the following URLS:

https://github.com/xpdAcq/xpdAcq
https://github.com/xpdAcq/xpdAn
https://github.com/xpdAcq/SHED

Advancing Along the Materials Development Continuum

The goal of this project is not to commercialize the tools but to make them available to researchers in academia and industry to use in their materials discovery/development workflow. However, continued maintenance of the codes is a challenge and some kind of freemium model for making them available to industrial users may be explored.

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HybriD^3: Discovery, Design, Dissemination of Organic-Inorganic Hybrid Semiconductor Materials for Optoelectronic Applications

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Co-Principal Investigator: Kenan Gundogdu, Department of Physics, North Carolina State University, kgundog@ncsu.edu.
Co-Principal Investigator: Franky So, Department of Materials Science and Engineering, North Carolina State University, fso@ncsu.edu.
Website: https://hybrid3.duke.edu.
Keywords: Organic-inorganic hybrids, layered perovskites, carrier levels, optoelectronic materials

Project Scope

The HybriD^3 project aims to accelerate the discovery, design, and dissemination of new organic-inorganic (O-I) hybrid semiconductors, particularly layered O-I perovskites, combining six teams located in North Carolina's research triangle area. Layered O-I perovskites encompass a vast space of potential compounds, juxtaposing (i) molecular components with tunable properties and (ii) amenable inorganic complements. Fig. 1a shows an early example, bis(aminoethyl)-quaterthiophene lead bromide (AE4TbBr4) [1]. The project focuses on optoelectronic properties, aiming to improve upon efficiency and production cost profiles afforded by current semiconductor alternatives. A capstone deliverable will be a freely accessible O-I hybrid database (perovskites and related).

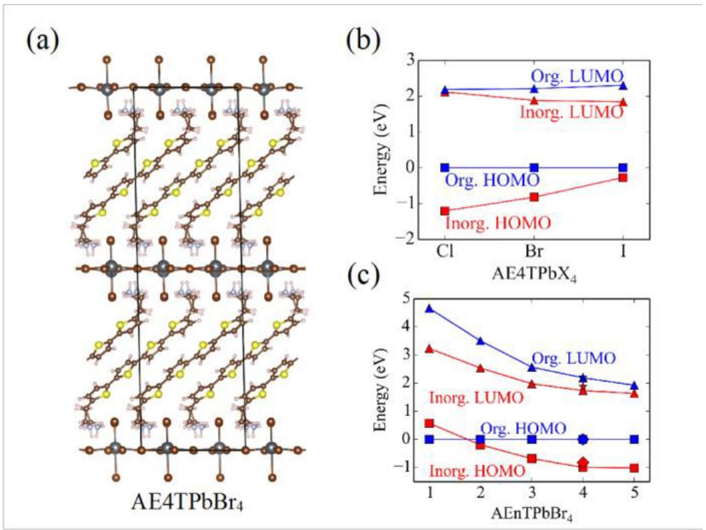

Figure 1. (a) Structure of AE4TPbBr4. (b) Frontier energy levels of the organic and inorganic components, varying the halogens X = Cl, Br, I. (c) Frontier energy levels, varying the number of thiophene rings n = 1, 2, 3, 4, 5. At n=4, star and diamond symbols indicate the impact of different molecular conformations. The highest occupied level on the organic component is chosen as the reference energy (zero).

Relevance to MGI

O-I hybrids are currently experiencing a dramatic resurgence in interest as materials for photovoltaics. Much of this activity is focused on the narrow group of 3D perovskites with size-restricted organic functionality. Layered perovskites lift the size restriction and thus allow, in principle, the full flexibility of organic chemistry to refine a materials space of tunable semiconductors (see Figs. 1b, c for examples of computationally predicted tuning of carrier energy levels in oligothiophene based lead halides). The large unit cells associated with non-trivial organic components create a challenge for either computation or experiment: Computationally, expensive and high-level methods are needed to predict electronic and optical excitations faithfully. Experimentally, devising new synthesis protocols for a given material is time-consuming. HybriD^3 addresses this challenge in a synergistic feedback loop between computational (Blum, Kanai) and experimental (Mitzi, You, Gundogdu, So) groups, utilizing computation to pinpoint likely promising candidate materials, while employing experimental synthesis to zoom in on specific candidates, validate, and provide feedback suggesting new or refined materials for further computational screening. The results of this accelerated discovery effort are disseminated in an open database, designed to reflect the specific materials characteristics of organic-inorganic hybrids, and are further validated in prototype devices for light-emission.

Technical Progress

In the initial stage of the project (since October 2017), the team focused on laying the groundwork for computational and experimental discovery. Computationally (Blum/Kanai), first-principles exploration of the electronic properties of a broad range of O-I hybrids was begun, comprising initially lead halides combined with oligothiophenes (example in Fig. 1a-c), acene-based functionalities, and other known electronically or optically active aromatic functionalities. As a second thrust, the technical infrastructure for the proposed freely accessible O-I hybrid database was created in close contact with international collaborator Dr. Matti Ropo (now University of Turku, Finland), building on his experience with the "*aminoaciddb*" database of small-molecule conformations (Ref. [2]). The initial database interface is now working at https://materials.hybrid3.duke.edu, focusing on example data including experimental and computationally predicted atomic positions, photoluminescence, and electronic band structures. For the computational predictions, van der Waals corrected semilocal density functional theory (DFT) is employed to predict the atomic structure of large O-I hybrid unit cells (more than 400 atoms in Fig. 1a). The demanding level of hybrid DFT including spin-orbit coupling is employed to yield qualitatively reliable predictions of band edges and band alignments (Figs. 1b, c), leveraging a linear-scaling all-electron implementation [3] capable of handling such large systems. Results from this initial screening are informing initial organic synthesis efforts (You group), focused on a series of oligothiophene (n=1-4) based ammonium salts (iodide, bromide, chloride) for the growth of 2D perovskites. Efforts in materials synthesis (Mitzi group) are focused on creating particularly the n=2 and n=3 materials included in Fig. 1c, providing valuable calibration points for the initial theory effort, as well as enabling advanced materials characterization of properties not yet amenable to accurate computational predictions - photoluminescence as well as optical and THz spectroscopy (Gundogdu group). In the So group, initial efforts focused on producing 2D-3D organometallic halide perovskite films with high photoluminescence quantum yield (PLQY) and good morphology, by using a non-polar solvent washing technique during spin coating. The PLQY and the film morphology are largely affected by the selection of non-polar solvents (chlorobenzene, toluene and chloroform) and annealing conditions.

Future Plans

We will extend our hybrid DFT based computational exploration of layered O-I hybrid candidates to a broader range of materials, both expanding the range of inorganic components and identifying different promising organics. Together with the nascent data base, this will create an increasingly large catalogue for the HybriD^3 team and for the wider community to select specific target compounds for a deeper exploration. A key (often underestimated) aspect of computationally predicting new materials is to accurately predict their structure. While the experimental component of HybriD^3 provides some measure of fallback for the validation of our specific predictions, we will focus on devising a broader, more accurate structure prediction methodology tailored for O-I hybrids. Furthermore, we will extend the computational studies to cover neutral excitations (including, but not limited to excitons), developing new model Hamiltonian methodologies for their prediction as well as connecting to high-level quantum Monte Carlo calculations for validation (Blum / Kanai groups). Synthesis efforts in the You group will continue to focus on making particularly interesting molecular components identified in the computational "first pass", particularly to (a) modify the structure of such oligothiophene to achieve different band gap and energy levels (aided by computational efforts) and (b) initiate the synthesis of acenes with ammonium salts. Correspondingly, the Mitzi group will focus on devising synthetic routes both for thin film deposition and for single crystal growth of new O-I compounds containing these organic components, followed by time-resolved spectroscopic characterization in the Gundogdu group. Finally, in the So group, highly efficient perovskite LEDs are expected to be fabricated based on the high quality 2D-3D perovskite films. Studies on the correlations among processing, optoelectronic properties and device performance will be conducted comprehensively through characterizations including photothermal deflection spectroscopy, transient absorption, transient PL and thermal admittance spectroscopy.

Broader impact (Only required for NSF projects)

The HybriD^3 project will provide an interdisciplinary training platform in key materials technologies including next-generation high-performance materials computation, advanced synthesis/characterization of novel materials, electronic/optical characterization of novel devices. We will also offer four-day training workshops with both hands-on and lecture components on "Electronic structure based simulation of nanostructured functional materials", and "Synthesis, characterization and device prototyping of organic-inorganic hybrids", respectively. These workshops will be open not only to the HybriD^3 groups, but also to computational and experimental undergraduate/graduate students in materials science, chemistry and physics at Duke, UNC, and NCSU, from Durham's North Carolina Central University and other interested N.C. and U.S. institutions. In addition to these workshops, all PIs teach undergraduate/graduate courses in materials science, chemistry and physics and will incorporate novel insights from HybriD^3 in those classes.

Data Management and Open Access

The computational and experimental data will be collected in the freely accessible database (https://materials.hybrid3.duke.edu). The realization of this database follows the pragmatic format of the "*aminoaciddb*" database recently published by Ropo, Baldauf, Blum [2]. This format serves a page per assessed system, visualizing the structures using the jmol plugin and providing access to further data by dedicated links. The database operates on standard open-source infrastructure including the Apache2 server and the Django framework to create the actual webpages. A MariaDB database is used to store information of each system (e.g., the nature of the organic/inorganic components), but actual data such as atomic structure and electronic properties will be stored as text files in a database directory hierarchy, which can be accessed directly on the server. The project website (https://hybrid3.duke.edu) contains information about the project team, publications, future workshops, etc.

Advancing Along the Materials Development Continuum

While our project is still in its initial phase, we are actively working on the foundation for broader dissemination and acceleration of O-I materials discovery. We plan to offer collected data to larger, general open materials data bases such as aflow, the Materials Project, or NOMAD. Furthermore, HybriD^3 will collaborate with industry leader Springer Materials to also incorporate the HybriD^3 data into their product for long-term sustainability. Industry outreach will also be pursued in the Research Triangle, which has demonstrated strength both for start-ups and existing leading companies in areas including optoelectronics.

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Computation Of Undiscovered Piezoelectrics and Linked Experiments for Design

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Website: https://materialsmine.mines.edu (computed materials database)
Keywords: piezoelectric, combinatorial reactive sputtering, nitride, heterostructural alloys, advisory board

Project Scope

Combinatorial reactive sputtering and high throughput characterization and measurement capabilities screen both compositional and processing spaces guided by computation with a focus on nitride piezoelectrics of potential interest for applications such as the FBAR filters crucial to modern wireless communication. Engagement of 20 companies from 7 countries and 3 continents in an industrial advisory board (IAB) maintains relevance and accelerates adoption of newly-discovered materials and alloys. Success is measured both in improved scientific understanding and the deployment by industry partners of technologies based on new and/or improved materials.

Relevance to MGI

Focusing specifically on piezoelectric thin films for microelectromechanical systems (MEMS) prioritizes a subset of materials properties (permittivity, elastic stiffness, piezoelectric tensors and electromechanical coupling) and enables an iterative feedback loop that is a tight coil along the vector of progress to deployment. AlN dominates the piezoMEMS field today despite modest piezoelectric properties because 1) it is fab-friendly, both in terms of chemistry and fabrication, and 2) its high mechanical stiffness, low electrical and mechanical losses, and low permittivity allow for efficient operation in high frequency resonators. Thus, a search to replace AlN must start with these parameters in mind. Our efforts focus on nitrides in part because they are underexplored relative to oxides and because of the potential for alloying and/or integration with existing AlN devices and infrastructure.

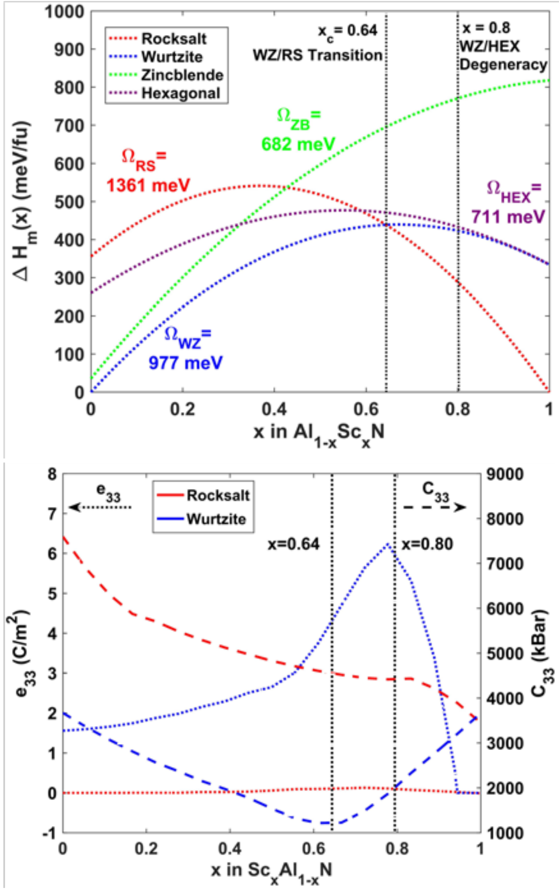

Figure 1. Energetic proximity (top) to a hexagonal polymorph drives an increase in piezoelectric stress coefficient (e_{33}) that is decoupled from the elastic softening that accompanies the wurtzite/rocksalt structural transition in $Al_{1-x}Sc_xN$.

Mixing enthalpy calculations identify candidate compositions expected to exhibit structural frustration known to enhanced piezoelectric response in oxides, then alloy calculations determine electromechanical properties. Combinatorial sputtering rapidly fabricates alloy samples across the compositional ranges of interest and high throughput measurements validate the calculations. IAB companies are able to provide input and receive early access to discoveries, leading already to DMREF-developed materials in the product pipeline of multiple partners.

Technical Progress

Efforts to date can be divided into two categories: AlN-based alloys and previously-unexplored compounds. In both cases, computation and experiment have proceeded hand-in-hand, and each has a flagship success story.

The $(Al_{1-x}Sc_x)N$ system has received a great deal of attention prior to and during this project because Sc additions greatly enhance piezoelectric strain coefficients in such alloys. We extended this work with a more thorough understanding of the origins of the enhancement (Fig. 1) and showed that similar mechanisms could be leveraged using Cr or Y instead of Sc (see publications 4 and 5). A much more insightful advance came guided by both materials insight and computation; two of the greatest limitations to broader deployment of $(Al_{1-x}Sc_x)N$ are 1) the enormous energy cost of alloying ScN into AlN (fortunately sputtered films are far from equilibrium, but this drive to segregate leads to many of the fabrication difficulties for the system) and 2) the fact that the enhanced electromechanical strain in $(Al_{1-x}Sc_x)N$ is driven in roughly equal parts by an increase in the intrinsic piezoelectric stress coefficient and a decrease in the elastic modulus with increasing x. Thus, ScN additions increase strain at the expense of the stiffness that is desirable for many resonator applications. One of our students hypothesized based on crystal chemistry arguments—and subsequently confirmed with calculations—that adding both BN and ScN to AlN could mitigate both of these issues (Fig. 2). We are still finalizing the work on the (Al,Sc,B)N system, but preliminary results showing that adding both BN and ScN can maintain much of the enhanced strain of ScN modifications without sacrificing stiffness (and in some cases, even slightly increasing stiffness) were so promising that (at least) three IAB members currently have (Al,Sc,B)N products in development.

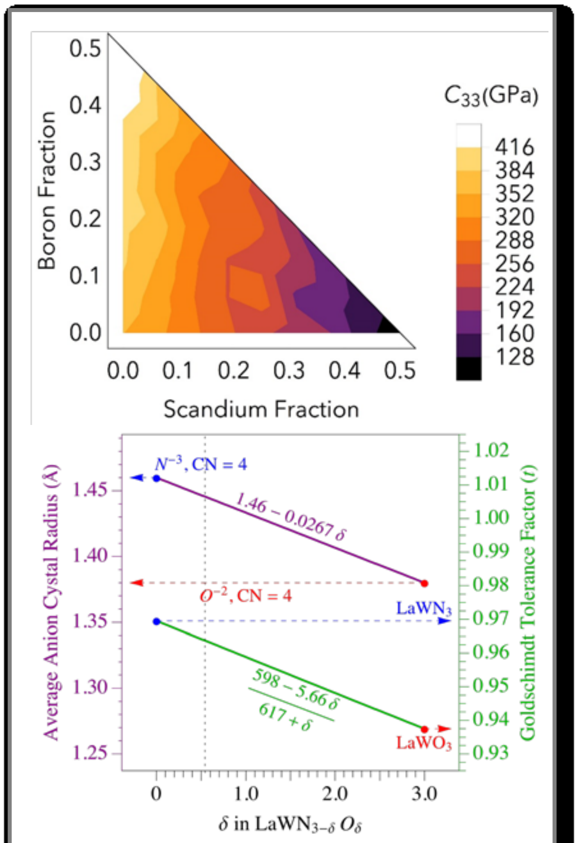

Figure 2. (top) BN additions to $(Al_{1-x}Sc_x)N$ do not degrade the enhanced strain so crucial to this system while maintaining the stiffness of AlN. (bottom) $LaW(N_{3-8}O_8)$ enables exploration of perovskite crystal chemistry—a playground for functional oxides—in nitrides.

We have also made significant progress with other materials systems. In particular, perovskite $LaWN_3$ and $LaW(O,N)_{3+8}$ are of interest both academically and industrially because of the possibility of leveraging many of the same crystal chemical techniques (such as tolerance factor, Fig 2) used in high-performance oxide piezoelectrics for decades as well as the opportunity to explore anion combinatorial systems. PI Stevanovic has also led efforts to identify materials with strong van der Waals character to their bonding in certain planes as a method of engineering greater electromechanical strain.

Future Plans

Efforts will continue in ternary and quaternary alloys with AlN as well as exploring more non-wurtzite structured nitrides. Development of combinatorial anion fabrication capabilities is in progress. Armed with data from the first two years of the project, we are currently working hard to integrate our broad and (relatively) shallow computational datasets with the significantly more sparse and heterogeneous, but occasionally very deep, experimental datasets. Such efforts are targeting 1) making such combined data available using the NIST/NREL Materials Data Curation System (MDCS) and 2) the use of active subspace approaches in order to deploy traditional Gaussian process models as well as machine learning techniques to guide both analysis and future directions.

Broader impact (Only required for NSF projects)

The graduate students and post-docs on this project have worked together very closely such that they self-identify as computational vs. experimental far less than their advisors do. Interactions with the IAB members have ranged from simple conversations during IAB meetings to in-person visits, shared samples/datasets, and employment opportunities offered to students; being able to apply the MGI philosophy all the way from discovery to the early stages of deployment within a single graduate career has been invaluable to the students, PIs and IAB members. An undergraduate course on computational techniques in materials science was also developed by PI Stevonovic, and integration of computational tools across the undergraduate curriculum were part of the overall curriculum revision (effective fall 2018) driven by PIs Brennecka and Packard. Results are being disseminated via publications and openly-available databases as described elsewhere.

Data Management and Open Access

Calculated data and associated code, parameters, etc. are available at http://materialsmine.mines.edu. We are working closely with NIST and NREL to integrate our experimental data as well as the existing High Throughput Experimental Materials (HTEM) Database (http://htem.nrel.gov) with calculated data according to the NIST/NREL MCDS. Samples have been shared with IAB members and are available to anyone in the community upon inquiry (obviously more useful once the combined datasets launch).

Advancing Along the Materials Development Continuum

Our IAB consists of representatives from 20 companies spanning 7 countries and 3 continents. There is no cost for membership, we simply ask that representatives participate in the (roughly) quarterly web-based meetings to provide input and feedback. By design, all of the work associated with this project is (eventually) publicly available and we maintain a focus on fundamental science. Our IAB includes suppliers, equipment manufacturers, OEMs, and end users, with companies ranging from startups with <10 employees to massive multi-national corporations, providing a valuable diversity of priorities, questions, and viewpoints. It has been not only a sounding board, but also a valuable resource for collaborative measurements and analysis. Most important, two materials discovered/developed during our project are currently under advanced stages of development by IAB members and should be deployed soon.

Publications

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Development of Fundamental Design Rules for Material-Liquid-Nanoparticulate Interfaces that Optimize Control of Friction, Adhesion and Wear.

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Website: https://nanodesign.wordpress.ncsu.edu/
Keywords: Friction, nanoparticles, adhesion, wear, multi-physics

Project Scope

A Quartz crystal microbalance (QCM) and complementary macroscale experiments are being used to characterize the tribological response of a series of nanoparticulate-substrate-solvent (NSS) systems, with the goal of using statistical analysis to identify intrinsic properties of the system components that correlate with performance. Molecular computation is used to better understand the chemistry and physics underlying the experimental results and statistical correlations. The goal is to provide a framework for creating designer lubricant systems that may ultimately replace traditional petroleum-based lubricants, hence helping to mitigate the environmental impact associated with the latter.

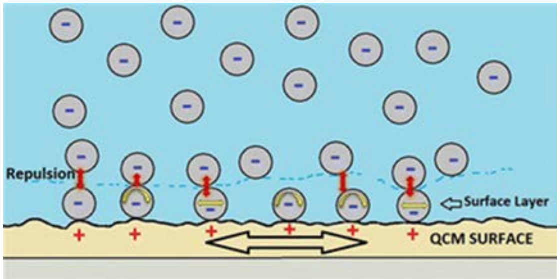

Figure. Illustration of nanoparticles on a QCM substrate, and the different mechanisms that can influence friction and wear.

Relevance to MGI

This project connects experimental measurements of tribological performance with the intrinsic properties of the NSS components through a statistical analysis in an attempt to uncover correlations between these intrinsic properties (their "genes") and performance that can be extended to new operating conditions. The most recent work, for example, focused in the search for materials genes for a relatively limited system – one type of nanoparticle, TiO2, and five substrates, Al, Au, Cr, Ni, silica and 304 stainless steel – but one that was strategically chosen to prove the MGI concept for nano-particle lubrication.

Technical Progress

We devised a QCM for viscous liquids at temperatures of up to 300°C to study nanoparticles in oil at relevant temperatures. We reported on the system response for iron and gold coated QCM crystals to two common lubricant base oils, polyalphaolefin and halocarbon. The results were consistent with predictions that incorporate electrode nanoscale surface roughness into their analysis.

The nano-tribological properties of gold surfaces immersed in aqueous suspensions of negatively charged SiO$_2$ nanoparticles were examined by QCM and Atomic Force Microscopy methods. The SiO$_2$ nanoparticles reduced resistance to shear motion at the QCM's solid-liquid interface. The effect was concentration dependent, with ca. 1.5 wt% yielding the maximum reduction in shear. An electro-kinetic mechanism was proposed where loosely bound nanoparticles roll and/or slide on the surface, while upper layers of nanoparticles slip over the surface layer because of the repulsive electrostatic forces between the individual particles.

To better understand the relation between charge and adhesion from our experiments we created two atomic models of octahedral nanodiamonds that mimicked the negatively (COO- surface groups) and positively (NH3+ surface groups) charged structures. The simulations revealed a molecular water layer containing Na+ counter ions between a nanodiamond with COO- functional groups and the gold that is not present for NH4+ surface groups. The lack of cancelation of electrostatic interactions due to counter ions and the water layer leads to an electrostatic force of adhesion for the positive particle that is nearly three times larger than that of the negative particle. This work demonstrated how functionalization and electrostatics can work together to determine adhesion.

We focused on a search for materials genes for a relatively limited system – one type of nanoparticle, TiO_2, and five substrates, Al, Au, Cr, Ni, silica and 304 stainless steel – but one that was strategically chosen to prove the MGI concept for nano-particle lubrication. TiO_2 is an effective nanoparticle additive for a variety of systems. Our choice of substrates encompasses a range of physical, electrical and chemical properties, and possible genes were chosen to reflect these properties. "Bulk" and "surface" candidate performance factors were selected from parameters provided from the response of a QCM to addition of nanoparticles to the surrounding fluid. Statistical analysis identified several unanticipated correlations among the genes that have complicated the process of identifying a definitive set of properties that lead to QCM performance. Performance also appears to depend strongly on the substrate bonding type, with data outliers for ceramics with respect to metal substrates. Improvements in the statistical analysis, an expanded database of substrates, and better theory is being pursued to prove the MGI hypothesis for this application.

Future Plans

Extend our studies to include the effects of applied electric and magnetic fields on the tribological properties of nanoparticles. Use ball-bearing on QCM experiments to better connect nanometer-scale to macroscopic response. Shift focus from TiO_2 to Fe_2O_3 and silica nanoparticles to extend our understanding the effect of size, surface charge and magnetic properties on tribological response, and extend our studies of nanoparticle dynamics to thermal chemistry and film formation. Extend our modeling studies to include the effects of surface functionalization on the rolling-sliding response of nanoparticles at interfaces. Develop Gaussian Process non-parametric regression models and the Expected Improvement criterion to better statistically model the response surface.

Broader impact (Only required for NSF projects)

We are educating eight graduate, four undergraduate, one high school student, two senior researchers and the four PI's in four academic departments on the power and limitations of advanced statistical analysis applied to problems in materials science, chemistry and physics. Through weekly group meetings and small-group interactions our team members are also being educated in the nuances of molecular modeling, statistics, synthesis and experimental design. Our outreach included NanoDays where 400+ elementary, middle and high school students visited our laboratories and spoke to graduate students, saw equipment, and played a simple tribo-electric coke-can race to engage hands-on with the fundamentals of physics. As a portion credit for a 300-level Environmental Science course, a group of undergraduate students visited and learned about our DMREF collaboration. We are also working with a high school student intern to refine the instructions and materials for a granular-packing-friction outreach experiment. The intent is to ensure experiment quality and clarity for primary and secondary school students.

Data Management and Open Access

New atomic modeling code for incorporating induced charges in metal substrates have been developed for distribution with the community LAMMPS modeling code, and will be available from our website. Raw data for the QCM experiments will soon be made available through our website as a searchable database.

Advancing Along the Materials Development Continuum

One of our goals has been a web-based interface that the tribology community can use to predict performance for a set of lubrications components, with the concept of developing lubricant systems for specific applications and conditions. We are working on the data needed to populate such a tool. No other industrial outreach or commercial activities have been proposed or are planned.

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A Data-Centric Approach for Accelerating the Design of Future Nanostructured Polymer and Composite Systems

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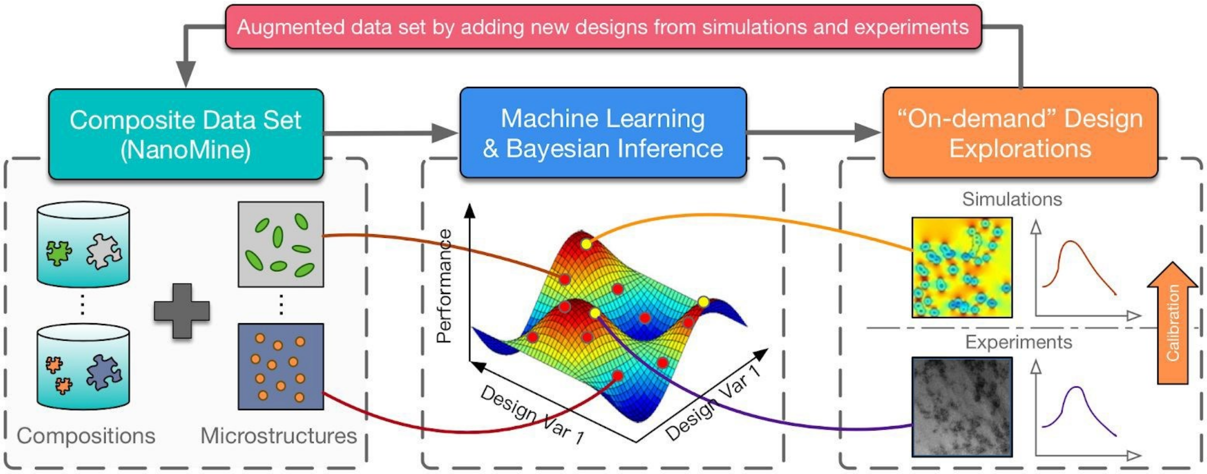
Website: http://nanomine.northwestern.edu:8000
Keywords: nanostructured polymers, polymer nanocomposites, dielectric breakdown, machine-learned scale bridging, material design by Bayesian inference

Project Scope

The objective of this interdisciplinary DMREF research program is to formulate a novel, data-centric approach to accelerate development of next-generation nanostructured polymers with unprecedented and predictable combinations of properties. We are developing (1) multiscale modeling strategies that bridges length scales by using machine learning approaches and data analytics, (2) robust interphase models built using curated and custom generated experimental data, and (3) materials design tools validated through test cases. Our approach integrates broadly curated data and analytics with physics based computational modeling and rigorous design strategies, with an initial focus on designing polymer nanocomposites for dielectric and mechanical properties.



Curated experiment and simulation data (composition, surface chemistries, processing conditions, structural features) from literature serve as initial data set

Machine Learning and Bayesian inference suggest new designs to explore for meeting property targets

Explore new designs using both simulations and experiments with calibrated model

Fig. 1. A closed-loop data-driven design approach for nanostructured polymeric materials. Bayesian inference on existing data suggests new designs explored using targeted experiments and multiscale simulations, which then feed back into NanoMine, an MGI data resource for nanocomposite materials.

Relevance to MGI

This program complements and significantly expands our work on creating a nanocomposite data resource (NanoMine) by developing new methods, models and algorithms to address challenges in data-driven material design. First, the challenge of understanding polymer physical properties in the vicinity of surfaces will be addressed using targeted experiments and curated data to develop robust interphase models. Second, the challenge of integrating from composition and interface properties to continuum property prediction will be addressed by applying heuristic methods such as quantitative structure-property relationships (QSPR) that use scale-dependent descriptors and machine learning tools to bridge the length and time scales between physics-based approaches such as density functional theory calculations, molecular dynamics simulations, and continuum response models. Finally, the challenge of assembling and integrating past data with advanced analysis tools and new physical experiments is addressed by developing a Bayesian optimization approach, where an effective mixed-variable Spatial Random Process modeling technique will be employed to guide adaptive data collection. The result will be an integrated design approach that employs multiscale models and is validated through careful quantification of microstructure, processing, and local and bulk properties within specific case studies.

Technical Progress

For microstructure characterization and reconstruction, we have developed a descriptor-based approach that offers physically meaningful and reduced dimensionality of design representation to facilitate processing-structure-property mappings and materials design. Using the nanodielectric polymer system as a testbed, we developed finite element models of dielectric breakdown and relaxation processes in polymer nanocomposites. In parallel with data-driven approaches to parametrizing these models, we have also initiated first-principles and molecular dynamics simulations to evaluate carrier trap depths, dielectric response and viscoelastic response for dielectric breakdown and mechanical property simulations. We generated and used data sets for three polymer systems and particles with three surface modifications under a variety of controlled processing conditions to create processing-structure-property mappings in predictive modeling. In addition, we developed a combined FEA and adaptive optimization approach for interphase property calibration. State-of-the-art computational design methods like design of experiments, metamodeling, and multicriteria optimization, are used to manage the computational complexity and expedite microstructure design optimization. To further reduce the problem dimension, we developed a parametric design approach based on the spectral density function and the Gaussian random field (GRF) representation for microstructural design. A case study for nanodielectrics in capacitor design is introduced to demonstrate the integration of the processing-structure and structure-property relationships to develop optimized materials for achieving multiple desired properties. Finally, a Bayesian optimization based design approach has been proposed to integrate physical dataset with “on-demand” simulations and experiments.

Future Plans

We will continue to collect targeted data on dielectric and mechanical properties of the nanocomposite interphase, and create case studies to validate models of local interphase behavior. We will also develop comprehensive and precise interphase FE models by taking advantages of AFM and EFM data and develop a data-mining framework to transform the local measurement and simulation data into mathematical descriptors (e.g., shift factors) of interphase behavior. We will continue to develop detailed physical models that complement the data-driven approaches, including large-scale DFT calculations to evaluate local density of states and trap-depth distributions for dielectric breakdown models, and atomistic as well as coarse-grained MD simulations to assess frequency-dependent dielectric and viscoelastic properties. The mixed-variable Bayesian optimization based framework, which we have developed for mathematical problems, will be demonstrated to adaptively optimize the microstructure and composition of nanodielectrics through real design case studies.

Broader impact

The results of this research could have significant economic impact on society through innovations in new nanostructured polymers that impact dielectric materials across a wide range of industries including energy, consumer electronics, and manufacturing. The data, tools and models will be integrated and shared through NanoMine, a data resource, and our outreach is primarily focused on building the coordination of the Nanocomposites community through NanoMine. In addition, we will interact closely with the nanocomposites community through graduate students in other groups and a focused workshop to create a *virtual organization* of integrated designers and researchers to test and improve the models. Finally, significant educational components will reach undergraduate and graduate communities via interdisciplinary cluster programs at our institutions, undergraduate research opportunities, web based instructional modules and workshops.

Data Management and Open Access

All digital data, models and web-based tools developed as a part of this program are made publicly available without charge immediately after publication through NanoMine (http://nanomine.northwestern.edu:8000). Data from this project is also integrated into NIST-based centralized resources and registries via ChiMAD (http://chimad.northwestern.edu), as appropriate. Preserved data include imaging results, physical property data (processed and raw), input and output files from simulations. Metadata standards are still evolving for the material systems considered and will be implemented into the NanoMine schema and ontology, as it continues to develop. We will work with interested industrial partners to address concerns of using public data in NanoMine and its tools integrated with proprietary data.

Advancing Along the Materials Development Continuum

The polymer nanocomposite material data collected in this project are being integrated into NanoMine, an open polymer nanocomposite data resource that is being developed under the support of the NSF CDMR and DIBBS program. Trough NanoMine, we are working to develop interest in the nanocomposite materials community to adopt our data-driven materials design methodology and tools, which is a key focus of the MGI initiative. The developed microstructure characterization and reconstruction techniques, including both the descriptor-based and spectral density function based approaches, have been applied to the tire material design and interphase modeling of viscoelastic properties, in a separate project supported by Goodyear Tire Company.

Publications

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Materials engineering of columnar and living liquid crystals via experimental characterization, mathematical modeling and simulations

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Website: None
Keywords: Chromonic liquid crystals, shape optimization, clustering, liquid crystal flow, living liquid crystals.

Project Scope This research focuses in the study of lyotropic chromonic liquid crystals (LCLC) aggregates as well as their composites with swimming bacteria. The hierarchical structure of LCLCs, in which individual molecules self-assemble into supramolecular aggregates bound by weak non-covalent bonds gives rise to complex macroscale structures. Furthermore, LCLCs are nontoxic and can be easily interfaced with swimming bacteria, enabling studies of the out-of-equilibrium behavior of ordered soft matter. Recent progress on the alignment, viscoelasticity and biological compatibility of the LCLCs, allows the team to perform 'closed loop' experimental characterization and theoretical description.

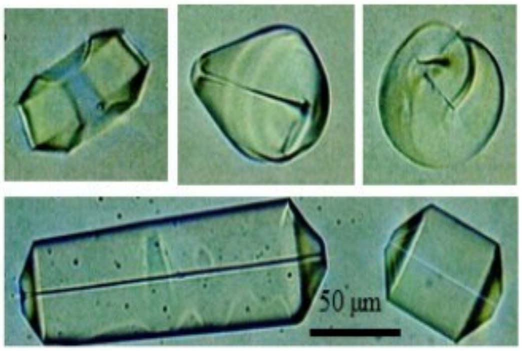

Figure. Chromonic DSCG columnar nuclei surrounded by the isotropic phase with faceted shapes determined by bulk elasticity and anisotropic surface tension.

Relevance to MGI

This project follows the rich collaborative tradition that has resulted in important accomplishments in liquid crystal science. These include the synthesis of a super-strong polymer Kevlar, creation of the industry of liquid crystal displays, drug delivery, electrolytes, nano-templated materials and colloidal systems. Mathematical modeling and analysis have often played significant roles towards such endeavors. The goals of this research group are motivated by challenges at the interface between soft matter and biology as well as to the exploration of LC living systems. Whereas the former may contribute to a better understanding of packing and control in biological matter, the latter may lead to exciting new nano-transport technologies.

Examples of the MGI dynamics that have emerged from the research include: (1) the developed models of chromonic aggregates have suggested ranges of concentration of coarsening agents (polymers such as PEG) for laboratory experiments, that allow matching shape optimization parameters with actual experimental ingredients. (2) Another very different and surprising twist has been the realization that a great deal of the analyses of the Leslie- Ericksen equations of liquid crystal flow do not suitably reflect the physics. This has led to modifications of the current approximating approaches with new analytic and numerical discretization outcomes.

Technical Progress The research carried out so far involves three main themes: (1) Hexagonal chromonic liquid crystal aggregates, (2) Analysis of approximation methods of the Leslie-Ericksen equations of liquid crystal

flow,(3) Nematic, chromonic solitons under an applied alternating electric field, (4) Experimental work on living liquid crystals.
Chromonic liquid crystals (water friendly) consist of plank like molecules, with significantly different electric properties on the sides and top and bottom faces, that under an appropriate range of concentration, tend to form columns that align along the corresponding cylinder axes. At even higher concentrations, the columns for aggregates of six elements, resulting in the *columnar or hexagonal phase,* that has the properties of a two-dimensional solid crystal on planes perpendicular to the column directions, while behaving like a crystal along the columnar direction. Bending of columns and shear deformation of cross sections are the main modes of deformation. The simpler mathematical model does not account for elasticity of cross sections but it involves the bending energy of the Oseen-Frank theory coupled with a discretely-symmetric surface energy. This results on a free boundary problem whose solution results in faceted toruses (and topologically equivalent shapes), with hexagonal meridian cross sections. The shape predictions have shown a remarkable agreement with the images resulting from experiments. This work is expected to be published in the next two months.

The mathematical aspects of the Leslie-Ericksen equations developed in the decade of the sixties still pose a formidable challenge to analysis and numerical simulations, with well-posedness remaining an open problem [1], [2], [3]. Methods developed to approximate such equations rely on relaxing the unit director constraint of the liquid crystal director (average direction of molecular alignment) by imposing a penalties on the energy. Whereas such an approach has shown remarkable success in studies of equilibrium of many physical systems (including superconductivity), an appropriate modification of the rate of dissipation function is also required. For this, rheological studies that followed the synthesis of the Kevlar fiber play an essential role.

Electric field induced collective reorientation of nematic molecules placed between two flat parallel electrodes is of importance for both fundamental science and practical applications. We find electrically driven three-dimensional particle-like solitons representing self-trapped waves of oscillating molecular orientation. The solitons propagate with a very high speed perpendicularly to both the electric field and the initial alignment direction. The solitons preserve spatially-confined shapes while moving over distances hundreds of times larger than their size and survive collisions. During collisions, the solitons show repulsions and attractions, depending on the impact parameter. The solitons are topologically equivalent to the uniform state and have no static analogs, thus exhibiting a particle-wave duality. We anticipate the observations to be a starting point for a broad range of studies since the system allows for a precise control over a broad range of parameters that determine the shape, propagation speed, and interactions of the solitons [5].

In a recent APS meeting, T. Turiv presented some of the ongoing work on *Swimming Bacteria Guided by Modulated Nematic Director.* Micro-swimmers of biological and artificial nature exhibit remarkable collective behavior. This work deals with the collective motion of motile Bacillus subtilis dispersed in a water-based lyotropic chromonic NLC with spatially varying director. The director field represents an alternating one-dimensional system of splay and bend stripes imposed through surface photoalignment. The bacteria exhibit threshold-less unidirectional collective motion along the splay bands. If a bacterium enters the patterned field with a “wrong” direction of swimming, the patterned director realigns it by 180° and the bacterium continue to swim along the same direction as other bacteria. The demonstrated unidirectional linear motion of bacteria can be used for micro-cargo transport [4].

Future Plans

The forthcoming work will mostly focus on the study of bacteria swing in a chromonic, nematic liquid crystal. Special attention will be devoted, first, to geometrically simple flow such as shearing, in order to determine patterns of swimmers, in particular, those produced by groups of bacteria swimming along opposite directions. This part of the project will require a main effort in modeling the ‘mixed system’. An initial approach will consist in setting up a two-component liquid crystal model that ‘phase-separate’ bacteria according to their swimming direction. The prominence and ubiquity of defects will call for the second approach, based on imaging and statistical methods. We will now regard the system as a field of defects, with the goal of developing a discrete, effective model for its dynamics.

Broader impact (Only required for NSF projects)

The research itself is expected to result in a broad impact on various branches of science as LCLCs represent an excellent model of self-assembled soft matter controlled by the balance of elasticity and anisotropic surface energy. Description of the shapes of chromonic nuclei will generalize the Wulff construction, contribute to further development of shape optimization methods, and thus help in understanding of biologically relevant systems such as DNA packings in confinement. Understanding the dynamic behavior of LLCs will help to develop new approaches to control the dynamic behavior of swimming bacteria, namely, their concentration distribution in space, shape of their trajectories and polarity of swimming. Bacteria are used primarily in biotechnological production of useful chemicals. The proposed research will outline the potential of using the swimming ability of bacteria in constructing microscale dynamical systems for mixing, targeted delivery of microscopic cargos. The work has also resulted in relevant results on the analysis and numerical simulation of the Leslie Ericksen equations of liquid crystal flow.

Data Management and Open Access

The PIs have an active presence in domestic and international scientific meetings and workshops. Through the Institute for Mathematics and its Applications (IMA), University of Minnesota, Calderer, in collaboration with the other PIs of the grant have organized two workshops, at the IMA, University of Minnesota:
Liquid Crystals, Soft-matter Packing, and Active Systems: Materials and Biological Applications (January 16-20).
Liquid Crystals, Metamaterials, Transformation Optics, Photonic Crystals, and Solar Cells(February 27-March 2). In addition, there are ongoing research groups working on topics related to the grant, during the period January 15, 2018 through July 31, 2018. The PIs also participated in the scientific meeting, *Variational Models of Soft Matter,* organized by Duvan Henao and M.Carme Calderer, at the *Pontificia Universidad Catolica de Chile,* in Santiago, on the dates of January 10-15, 2017. The research will be published in the scientific literature, and codes developed for chromonic liquid crystals and bacteria will be made available to the community.

Advancing Along the Materials Development Continuum

Research in packing of hexagonal chromonic liquid crystals may help understand the analogous problems in biology, in particular, those related to viral encapsidation. In fact, the shapes found in chromonic liquid crystals are very close to those in confined DNA, with a gap of several orders of magnitude. Chromonic systems have the potential to be developed into future technologies for drug delivery devices. Bacteria and liquid crystal systems may develop into new prototypes of transport devices at the micron scale.

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DMREF/Collaborative Research: Controlling Hierarchical Nanostructures in Conjugated Polymers

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Keywords: polymer, electron microscopy, image analysis

Project Scope

The grand challenge of this project is to develop a framework for predicting nanostructure formation within functional polymer thin films using computational methods developed and optimized using feedback from experimental systems. The **Ganapathysubramian**, **Chabinyc**, and **Hawker** groups aim to define synthetic targets and structural information necessary to develop robust computational models that will allow coating processes to direct polymer assembly. New conjugated materials have been synthesized and methodologies for quantitative analysis of structural information at the nanoscale have been developed (Figure 1).

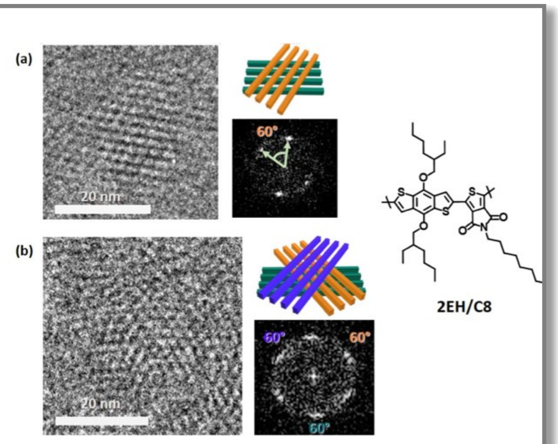

Figure 1. Ordered semiconducting polymers have complex domain boundaries showing quasi-epitaxial overlaps (**a, b**) that influence charge transport. High resolution electron microscopy can reveal such domain boundaries, but requires high throughput statistical analysis to provide quantification of their structure

Relevance to MGI

Our research team has complementary expertise in computation (**Ganapathysubramanian**), physical characterization (**Chabinyc**), and synthesis (**Hawker**). We will accelerate the ability to discover new printable semiconductors by synthesizing model polymers to provide benchmarking data for development of codes that can predict conditions for the formation of controlled morphologies. These codes, in turn, will be used to predict the behavior of new materials reducing the design space. Our research effort will develop open source codes for modeling processing effects on morphology and provide open access structural datasets, such as high resolution maps of nanostructures in semiconducting polymers, for the materials research community.

Technical Progress

New building blocks for semiconducting polymers. Materials with tailored backbone structures can help to validate the predictions of processing and structural models. **Hawker** has designed a macrocyclic benzodithiophene based monomer utilizing a novel direct and scalable macrocyclization synthesis procedure (Figure 2). This macrocyclic BDT derivative restricts π-stacking when incorporated into the conjugated backbones of donor-acceptor polymers. Using this building block, we have examined how aggregation of conjguated polymers in solution impacts their physical properties. In comparison with traditional systems, the cyclic BDT building block has been found to enhance photoluminescence and direct the solid-state morphology in solution-cast films by impacting the texturing of the π-face of the backbone and modifying the local order.

Grain boundaries in semiconducting polymers. **Chabinyc, Hawker,** and **Ganapathysubramanian** have studied how the morphology of a semiconducting polymer, PBDTTPD, can be controlled by the structure of sidechains substituted on the conjugated backbone. Using three different derivatives of PBDTTPD we have elucidated the interplay between solution aggregation, crystallization and long-range morphology. Our results show that minor variations in side-chain structure drive both texture and ordering of boundaries between ordered domains. We find epitaxial domain crossings in thin films of PBDTTPD observed by high resolution transmission electron microscopy (HR-TEM) that corroborate a geometrical relationship defined by the dimensions of the backbone and separation of chains induced by the sidechains (Figure 1). The formation of ordered domain boundaries is related to aggregation in solution, as more concentrated films lead to a denser cross-hatched morphology. The same effect is not observed in the polymers that break the geometric rule for the quasi-expitaxial ordering where crystallites in films are formed with an edge-on orientation. A publication on this work is nearly finalized.

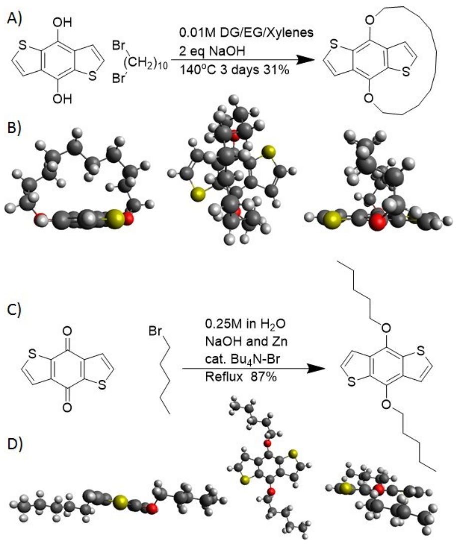

Figure 2: A) Synthesis of cyclic BDT using phase separation conditions. B) Three separate views of the X-ray structure of cyclic BDT showing one π-face blocked. C) Synthesis of acyclic BDT using standard conditions. D) Three separate views of the X-ray structure of acyclic BDT showing both π-faces open.

Graph based TEM analysis software: A quantitative characterization of the microstructure is critical for understanding device performance. While several microscopy based imaging techniques -- including Transmission Electron Microscopy (TEM) -- are currently available to visualize the microstructure, analyzing the resulting data has remained predominantly manual. This makes extracting microstructural information from microscopic images subjective, slow and error-prone. We introduce a mathematical framework and associated software, GRATE, that integrates concepts from graph theory, image analysis and hierarchical (quad-tree) image decomposition to automatically extract a suite of microstructural features from TEM image data. Both local traits like lattice spacing, orientation and size measures as well as global traits like number and size distribution of crystallites are efficiently extracted. The software is modular, extensible and is packaged into a simple graphical user interface that can reduce time of adoption by polymer researchers. We illustrate the framework using both synthetic and actual TEM data. Both the framework and software are intended to help the researchers to objectively analyze HRTEM images and thus reduce the time from discovery to production of materials.

Computationally identifying optimal processing conditions Because processing conditions heavily influence the microstructure, identifying optimal fabrication conditions is a crucial step towards the development of high-performance devices. Current state-of-the-art approaches remain predominantly trial-and-error, which are time and resource intensive. In recent work, **Ganapathysubramanian** group integrated a morphology evolution framework (based on a phase-field model) with a heuristic optimization scheme to systematically identify promising processing conditions. Working with a simple model system, we showed how annealing time and substrate patterning can be simultaneously tuned to achieve a variety of tailored microstructures. We found that the appropriate choice of cost functional is critical to achieving meaningful results, which emphasizes the need for a tight collaboration between experimental and computational experts (which this DMREF proposal enables). The methodology presented provides a scalable and extensible approach towards the rational design of tailored microstructures with enhanced functionalities. This is work that has been accepted for publication in *Computational Material Science,* and another paper I under review in *Materials Discovery*.

Future Plans

We now have the tools in-place to enable an iterative design loop for new semiconducting polymers. The GRATE code now produces reliable interpretation of HR-TEM images to provide quantitative information about the in-plane charge transport pathways in thin films. We will now develop charge transport simulations using a hopping model and efficient graph-based analysis to predict bottlenecks for transport based on the structure of experimentally determined grain boundaries. Because of our ability to predict the likelihood of such boundaries using geometric design of polymer backbones and the casting conditions, such as concentration, we will use these results to design new polymers with our novel building blocks to test the predictions from the integrated theory.

Broader impact (Only required for NSF projects)

The project has provided critical training in multidisciplinary research to several graduate student researchers, two of whom have now graduated and have careers in industry. **Chabinyc** continues to act as an organizing for the local science night for a K-6 school that draws ~200 students and their families. **Hawker** mentored a undergraduate student during the summer on synthetic work related to the project. Graduate student and post-doctoral researchers (McDearmon, Page, O'Hara) have led student activities explaining basic concepts on topics such as hydrophobiticty, magnetism, etc. via the UCSB MRL "It's a Materials World" that visits local schools with a high URM population – 1000+ students. **Ganapathysubramanian** mentored undergraduate honors student on using ideas from machine learning and graphics to enable fast quantification of microstructures

Data Management and Open Access

The **Ganapathysubramanian** group has a bitbucket page where all the software being developed is curated and stored. The GRATE code is available (and will also be posted on the group website) at www.bitbucket.org/baskargroup/grate.

Advancing Along the Materials Development Continuum

The ability to carry out high throughput analysis of the morphology of polymers can reduce the time required to study structure-property relationships as a function of processing conditions.

Publications

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2. "An optimization approach to identify processing pathways for achieving tailored thin film morphologies", S Pfeifer, O Wodo, B Ganapathysubramanian, *Computational Materials Science* 143, 486-496, 2018

3. "GRATE: A framework and software for GRaph based Analysis of Transmission Electron Microscopy images of polymer films", Pokuri, B., O'Hara, K., Chabinyc, M, Ganapathysubramanian, B. *ACM Transations in Mathematical Software, Submitted.*

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6. "Process optimization for microstructure-dependent properties in thin film organic electronics", S Pfeifer, B Pokuri, B Ganapathysubramanian, *Materials Discovery*, *submitted*

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7."Donor-fullerene dyads for energy cascade organic solar cells" Cowart, J. S., Liman, C., Garnica, A., Page, Z. A., Lim, E., Zope, R. R., Baruah, T., Hawker, C. J. & Chabinyc, M. L. *Inorganica Chimica Acta* **468,** 192–202 (2017).

8."Removal of Residual Diiodooctane Improves Photostability of High-Performance Organic Solar Cell Polymers" Tremolet de Villers, B. J., O'Hara, K. A., Ostrowski, D. P., Biddle, P. H., Shaheen, S. E., Chabinyc, M. L., Olson, D. C. & Kopidakis, N. *Chemistry of Materials* **28,** 876–884 (2016).

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Computational Design, Rapid Processing, and Characterization of Multiclass Materials in Ti-B-X Platform

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Keywords: Multiclass materials, titanium, titanium boride, composite, cermet, ceramic, phase diagram

Project Scope

This project is engaged in iterative alloy design, processing, and characterization to gather the processing/property data for specific material systems based on ternary Ti-B-X (X=Fe/Mo/Nb) titanium system compositions. Using computational calculations, knowledge of the phase stability, alloying approach, solute partitioning of elements between the metal and boride phases, as well as the electronic structure and properties of ternary borides, a rich fundamental base of material data is being created for Ti-B-X system to simultaneously benefit the material designs in three material classes: metal-matrix composites, cermets and ceramics (Figure 1). The conceptual basis for material design has originated from PI's earlier works[1],[2],[3] in titanium material systems.

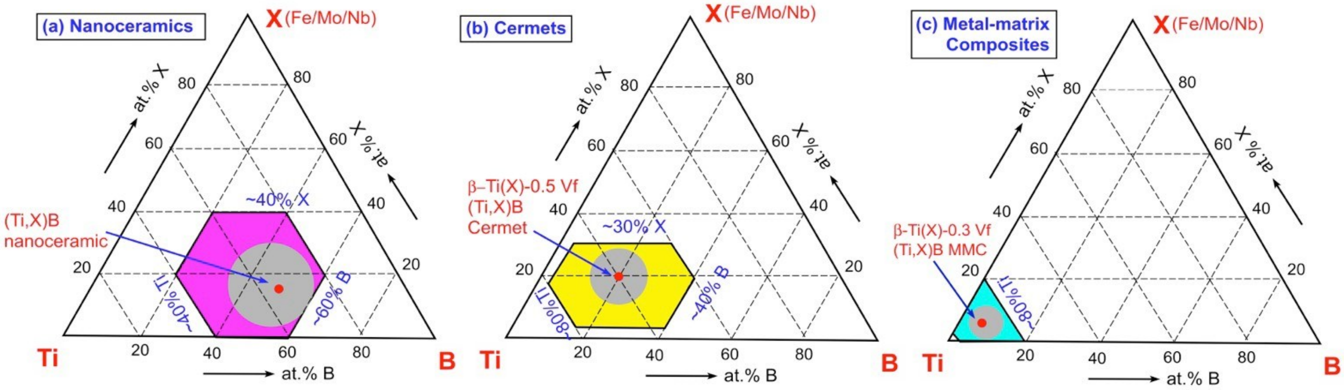

Figure 1. Compositional domains in the Ti-B-X system relevant to material designs in three material classes

Relevance to MGI

The project team is engaged in computational design, electric-field-activated synthesis, and application-specific characterization of three material classes (ceramic, cermet and metal-matrix composite (MMC)) that are designed on the basis of Ti-B-X (X=Fe/Mo) system as a platform. The proposal focuses on core research themes (composition design, phase transformations) which simultaneously benefit these distinct material classes, leading to much greater impact on technological advances and on industry, in contrast to traditional design approaches focusing on a single material class or composition. The team iterates material designs, performs rapid synthesis of designed compositions, and evaluates the key properties and benchmarks against competing structural materials.

Technical Progress

This project has successfully completed design, processing, and evaluation of about two-thirds of material concepts that was set out as the goal original the proposal. Extensive progress has been being made on several fronts: (i) several compositions have been designed for the Ti-B-Fe/Mo material classes, by CALPHAD approach, through extensive compilation of thermodynamic data and phase diagram constructions; (ii) rapid processing approaches utilizing powders, in electric-filed induced sintering, has been established successfully; (iii) several promising TiB-based ceramics and cermets have been produced and tested. These tasks have enabled the practical realization of multiclass materials in Ti-B-X system (Figure 2) as was set out in the original proposal.

Specifically, the present project has compiled extensive thermodynamic data, which constitutes the genomic basis for our work on Ti-B-X systems. This has enabled material design of the ternary and/or quaternary systems focused in this work, for which complete thermodynamic descriptions were not previously available. Our current database was used to evaluate the phase diagram data of Ti-B-Fe, Ti-B-Mo, Ti-B-Nb, Ti-B-V and Ti-B-W systems, for the purpose of rigorous validation of our CALPHAD approach. Examples are shown in Figure 3.

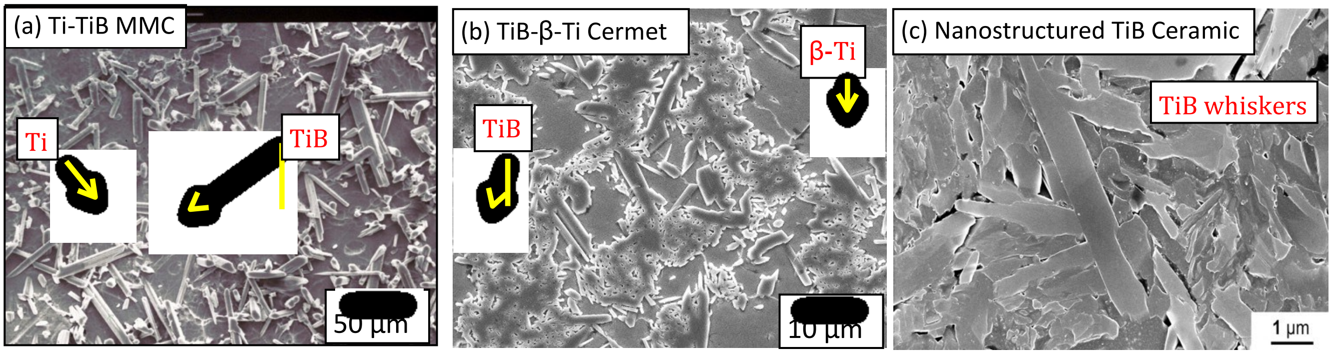

Figure 2. Material designs: (a) Ti-TiB MMC with TiB whiskers (~24% TiB), (b) TiB-β-Ti cermet (~60% TiB) containing ductile β-Ti metal phase, (c) TiB nano-ceramic with TiB ceramic (~84% TiB; 15% β-Ti phase)

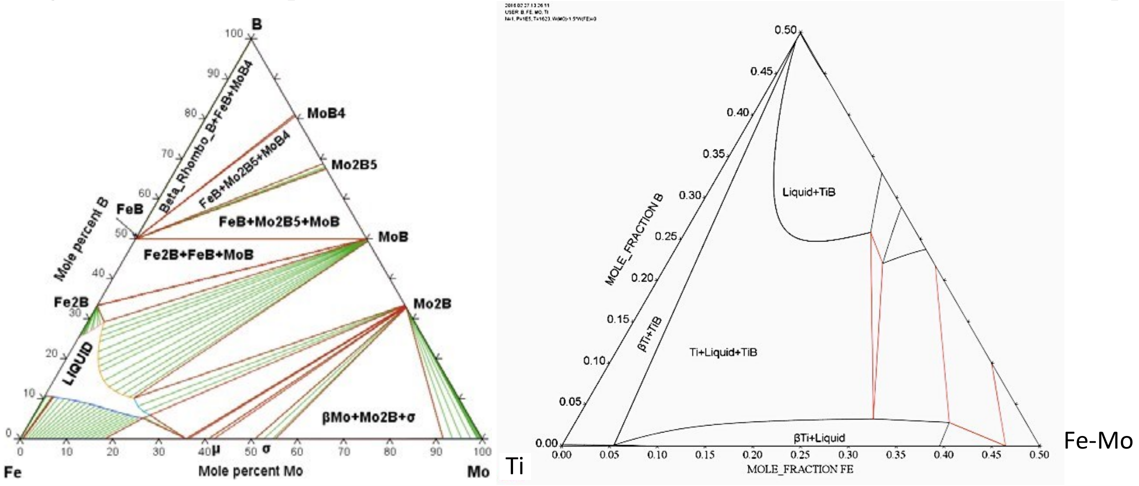

Figure 3. (a) Phase fields in Fe-Mo-B ternary diagram and (b) TiB-Fe-Mo pseudo ternary diagram 1300 C, determined by CALPHAD approach, for the determination of suitable materials processing windows.

Future Plans

In the remaining period of this project, we will complete the alloy design of TiB-based MMCs by additional CALPHAD calculations. Refinements to β-phase alloy design and CALPHAD calculations will be made to develop commercial compositions, which will be designed with, further-enhanced fracture toughness. Additionally, the research will further explore the potential of a new titanium tetraboride that has been first synthesized here.

Broader impact (NSF Projects)

A. Advancing New Materials Design Data and Technology: The project advances computational ternary phase diagram calculations of titanium-based systems as a fundamental approach to design new materials. First, in TiB ceramics, this has helped achieve high hardness and toughness, in the TiB nano-ceramic with a high volume fraction (~ 0.98)) of boride phase, by the alloy design of beta phase that is stabilized by Fe/Mo for enhanced fracture toughness. Secondly this directly impacts the design of Ti-TiB metal matrix composites, where the ductility of the matrix β-Ti phase is automatically enhanced to compete with high strength steels. The material designs of TiB-β-Ti cermets with intermediate proportions of β-Ti matrix and (Ti,Mo)B hard phase fit naturally between the extremes represented by ceramics and MMCs. This represents a holistic design approach.

B. Advancing Education Opportunities: The funding has supported one post-doctoral researcher, several graduate students at UofU and at UIUC. At the UofU, Co-PI Sanders trained several students in laboratory experimentation, instrumentation, and mechanical testing and provided industry-oriented training. PI Sanders has also trained the students to run the electric-field-activated sintering (EFAS) unit. At UIUC, PI Trinkle has been engaged in training and developing high school science teachers to expand science education in the city, and to develop valuable connections for identifying talented minority students to recruit to UIUC.

C. Advancing Commercialization Opportunities: The commercialization objectives have been (i) the development of prototypes for industrial-scale testing of the designed ceramics and cermets and (ii) gathering additional test data on industry-specific properties such as wear/ballistic resistance. The GOALI industry members in the Industry Advisory Panel have advised on the key steps for successful commercialization. The PIs will continue to push the commercialization objectives as set out originally in the proposal.

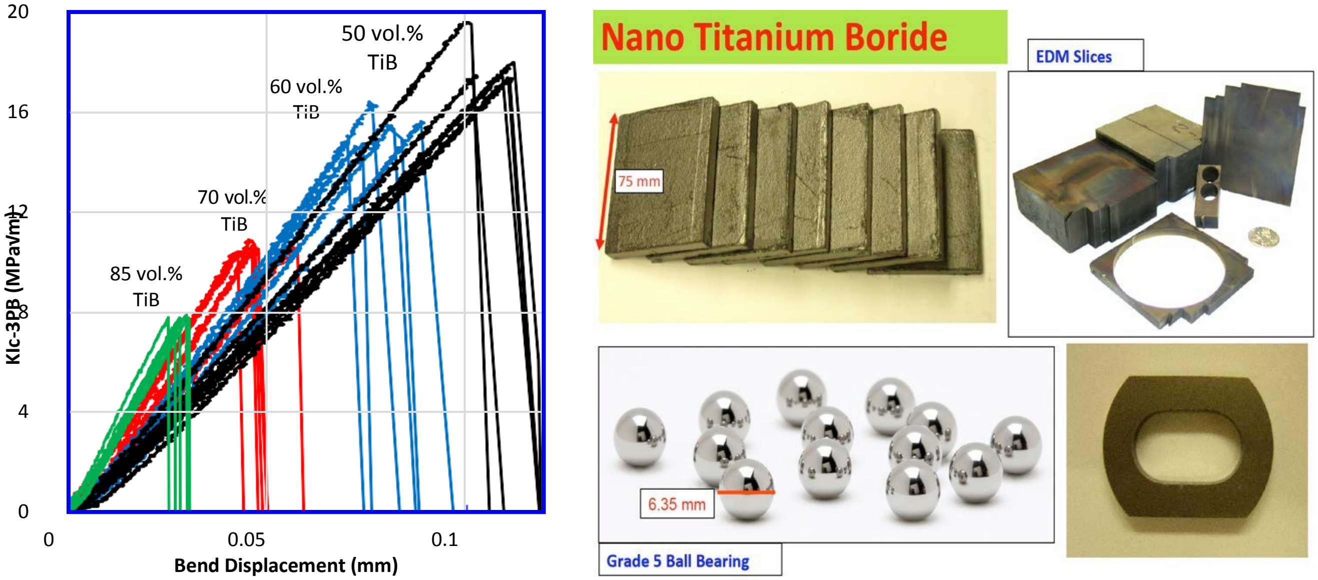

Figure 4. (a) Fracture toughness of TiB ceramic/cermet as affected by beta phase and (b) application development

The TiB ceramic with 15 vol.% of β-Ti phase has been found to have a very high flexural strength (~870 MPa) and high fracture toughness (7.7 MPa√m). With increasing amount of beta phase, toughness levels reaching ~20 MPa√m (for 50% TiB cermet with 50% beta phase; Figure 4(a)) have been achieved. These are quite an exciting set of results. The hardness/strength/toughness levels are on par with or exceed certain engineering ceramics and cermets. In particular, the TiB nano-ceramic is an attractive material for application in dies, ball bearings, nozzles, armor, and biomedical implants. The cermets are promising for cutting tool and hard facing applications. Figure 4(b) shows some prototypes or large sized blocks that have been made in pursuit of applications.

Data Management and Open Access

All computational data will be made available through the NIST MatDL project, where datasets are given unique digital object identifiers. The thermodynamic data on ternary titanium systems, which have been developed for the present project, are presently hosted in the computers used by the PI's research group at the University of Utah. They are also open to other students/faculty in the university. We are looking for nation-wide hosting.

Publications

1. S. Rou, K. S. Ravi Chandran, "First principles calculations of elastic constants of Ti_3B_4 and experimental validation by nano-indentation," J. Am. Ceram. Soc., in Press, March 2018.
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6. H. Kim, D. R. Trinkle, "Mechanical properties and phase stability of monoborides using density functional theory calculations." Physical Review Materials 1 (2017) 013601.
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[3] S. Madtha and K.S. Ravi Chandran, J. Am. Ceram. Soc., Vol. 95, 2012, pp. 117-125

Exploring Multi-functional Molecular Electronic Materials

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Website: none
Keywords: SMM, cluster, electron-transport, multifunction, ligands.

Project Scope

We search for and design novel nano-structured, multifunctional molecular electronic materials aimed at tailoring and controlling their electronic and magnetic properties through a combination of size-selection, chemical modification, interactions with environment, and external fields. In this NSF-funded project, we explore 1) the magnetic switching function of polynuclear manganese-oxo clusters that is inspired by a new concept of molecular magneto-capacitance recently introduced by our theory team, 2) the electro-resistance characteristics of other nanoscale and molecular systems, and 3) emerging phenomena when systems scale from nano-scale to meso-scale.

Relevance to MGI

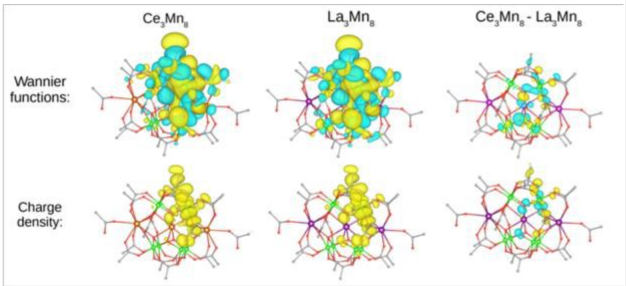

Figure. (Top panel) Plot of Wannier orbital onto Mn-d_{z^2} subspace for Ce_3Mn_8 (left) and La_3Mn_8 (middle) with isovalues, and difference between them (right). The difference is mainly from Ce *f*-orbitals that provide an unexpected pathway for Mn-Mn exchange coupling. Bottom panel: the corresponding charge density and charge density difference.

We combine first-principles quantum level theory and meso-scale models for electron correlation and transport with experiments on targeted cluster and molecular systems to advance the state of art of functional electronic materials. The project is designed to be a seamless combination of high-level quantum mechanical calculation coupled with meso-scale theoretical modeling, fabrication/synthesis, transport characterization, STM measurements, and cyclic voltammetry that enables measurement of quantized charging process of an ensemble of ions in solution. A three-pronged team involving leading experts in computation and modeling, fabrication and synthesis, and transport/STM/voltammetry characterization, are in place to fulfill these goals. The "genome" of the materials in this study is the properties of molecule/cluster, ligands, and supporting substrates. The overarching goal is to search through as many combinations of these properties as possible in order to find the best multifunctional molecular system.

Technical Progress

The perovskite manganites $AMnO_3$ and their doped analogues $A_{1-x}B_xMnO_3$ (A and B = main group and lanthanide (Ln) metals) are a fascinating family of magnetic oxides exhibiting a rich variety of properties. They are thus under intense investigation along multiple fronts, one of which is how their structural and physical properties are modified at the nanoscale. The molecular compound $[Ce_3Mn_8O_8(O_2CPh)_{18}(HO_2CPh)_2]$ ($Ce^{III}_2Ce^{IV}Mn^{III}_8$; hereafter Ce_3Mn_8) bears a striking structural resemblance to the repeating unit seen in the perovskite manganites. By combining magnetic measurements and first-principles calculations, we have established that Ce_3Mn_8 exhibits both the combination of pairwise Mn^{III}_2 ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions and the resultant spin vector alignments that are found within the 3-D *C*-type AFM perovskites. Our calculations reveal not only the expected nearest-neighbor Mn^{III}_2 exchange couplings via superexchange pathways through bridging ligands but also an unusual, direct Mn^{III}-Ce^{IV}-Mn^{III} metal-to-metal channel involving the Ce^{IV} *f*-orbitals (Figure). Although this molecule has zero net moment at its AFM ground state, our calculations show that it has a strongly spin-dependent charging energy. Our theoretical analysis shows that this can be used to build an adiabatic spin pump, without requiring a magnetic field or tunable spin-orbit coupling, when the molecule is connected to two unpolarized electrodes with oscillating chemical potentials. Onsite Coulomb repulsion between electrons of opposite spin causes a spin-dependent suppression of the current, leading to a pumped spin current. Consequently, the Berry-phase-like geometric current is highly spin-polarized. We explore the space of driving parameters to demonstrate the generation of either a fully polarized or a pure spin current. Negative differential conductance is also predicted. These possibilities highlight the advantage of molecular antiferromagnets over FM molecules and quantum dots in generating and manipulating low-power spin currents.

The unusual role of the Ce *f*-orbitals leads us to investigate whether Ce plays a similar role in other magnetic molecules. We studied several $[Mn]_nCe_m$ clusters, including Mn_3Ce_2 and Mn_5Ce_3 with three different ligands, where the magnetic interaction between Mn ions vary between FM and AFM. Energies of all spin configurations for each molecule are calculated and fitted to a quantum Heisenberg model, from which the exchange parameters between all Mn pairs are extracted. These values are compared to those extracted from experimental susceptibility curves with good agreement. Pathways of magnetic interaction identified using the Wannier function method again show a critical role played by the Ce *f*-orbitals in the competition between FM and AFM coupling.

Magnetic properties of a nitrate-containing Mn_{12} derivative (Mn_{12}-nitrate), which is the first example of Mn_{12} based three-dimensional networks, were also investigated experimentally and by first-principles calculations. Nitrate ligand substitutions lead to enhanced magnetic anisotropy of Mn_{12}-nitrate with respect to unsubstituted Mn_{12}-acetate compound, which is manifested by the enhanced energy barrier of magnetization reversal. Nitrate ligands form hydrogen bonds with water ligands of neighboring Mn_{12}-nitrate molecules. Inter-molecular hydrogen bonds are not only responsible for a diamond-type three-dimensional crystal structure, but also for antiferromagnetic inter-molecular magnetic couplings, which cause exchange-biased hysteresis loops. Inter-molecular magnetic coupling was estimated to be $J/k_B = 0.002$ Kelvin, in agreement with DFT calculation.

Future Plans

We will explore functionality of nano-clusters and single molecule nano-magnets to manipulate the self-capacitance of the nano-particles and to reduce the magnetic field needed for a low-spin state to a high-spin state transition. We will investigate ligand effects (e.g by carboxylate substitution) on magnetic states of Mn_3-Mn_{12} and isomer structures of oxide clusters M_mO_m (M=Zn, Zr, Hf, Si, Mn, Co, Ni, etc, and m, n =3,4,5…). We will also investigate effects due to metal substitution (e.g. $Mn_{12-x}M'_n$, M′=Fe, Co, Cr, La, Ca, n = integer). From calculated results, we shall choose ones that have high magnetocapacitance and low switching field to be experimentally synthesized in solution followed by voltammetry and transport studies to confirm calculation. We will also expand our search to include magnetic molecules that show promise of multiferroic functionality via spin-state transitions, e.g., $[Mn^{III}(pyrol)_3(tren)]$, also known as Mn(taa). Our objectives and approaches are:

(1) Using first-principles calculation, we will investigate effects of support surfaces on which SMM and clusters can be deposited. Our preliminary results show that monolayer *h*-BN strongly affects the magnitude of charging energy and thus capacitance. We will also design various embedding environments to modulate and enhance the desired effect. Collective behavior when these SMM and clusters form films and/or crystalline solids will also be modeled. Promising candidates will be chosen for experimental scrutiny. Feedbacks will be used to guide theoretical calculations.

(2) Using first-principles calculation, we will investigate electric field induced changes in magnetic state and conformation. Results will be tested and verified in experiments using bias voltage, gate voltage and electron injection. Experimental results will be interpreted through transport models built on first-principles parameters.

(3) For search of multiferroic magnetic molecules with spin state transitions, we will develop an automated approach for constructing a Landau-type free energy for multiple phases from experimental phase diagrams with given number of order parameters. The approach combines random search with local optimization to minimize the difference between the model the targeted phase diagram. This will be applied to the magnetic field-temperature phase diagram of Mn(taa) crystals and other potential multiferroic magnetic molecular materials.

Broader impact (Only required for NSF projects)

Results from the studies will be of great importance to the development of future electronic applications. Expected outcomes also have the potential to impact other important areas such as catalysis and energy storage. The project will provide multi-disciplinary training to graduate students and postdocs that address the modern challenges of a career in science. An important component is full immersion in the interdisciplinary culture of a national lab (ORNL), and the international collaboration. The PI and co-PI's will also be actively involved along a broad front in activities involving education, outreach and workshop organization.

Data Management and Open Access

Our general principle is open access and sharing. The practical policy is often constrained by the manpower needed to maintain a web site. We will construct two web-based interfaces: one is already in place that distributes computer codes in compliance with the gnu general public license; the other will be set up to allow others to access our data files (coordinates, images, etc.) in compliance with copyright laws if they are published. We will use a public data center such as the *Cambridge Crystallographic Data Centre*. New computer codes are shared after resultant papers are accepted for publication. There may be a delay depending on how long it takes to make the code user friendly: 2-6 months for general users, 1-2 months for collaborators. Our policy for posting data is after formal publication. We will insure that such practices are compliant with policies of national security, funding agencies, and journals.

Advancing Along the Materials Development Continuum

Our proposed program has three tightly connected components: Computation/modeling; fabrication/synthesis; and spectroscopy/transport, with first-principles calculation driving and directing experiment. Theoretical modeling will connect experimental observables with microscopic processes. The coordination between experiment and theory is a critical component for accelerating materials discovery.

Hurdles to be overcome for bridging fundamental research and industrialization are *time* and to a lesser degree, the funding model. Research is and should be in many cases decades ahead of manufacturing and commercialization, which depend on cost and social parameters. Nevertheless, in the past, the PI has filed a patent jointly with an experimentalist whose research projects are funded by venture capitals.

Publications

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High Throughput Exploration of Sequence Space of Peptide Polymers that Exhibit Aqueous Demixing Phase Behavior

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Keywords: Recombinant polymers, phase behavior, stimulus responsive, LCST, UCST

Project Scope

Stimulus responsiveness is a striking feature of proteins in nature, whereby responses to chemical and physical stimuli lead to sharp conformational or phase transitions. Unlike proteins, current bioinspired designs of repetitive polypeptides have focused on a tiny fraction of the vast conceivable expanse of sequence space. The overall **goal** of this project is to develop generalized materials design rules, by combining experiments, fast and accurate physics-based computer simulations, and data science to accelerate the discovery and development of a potentially huge class of thermally responsive polypeptide materials by a systematic exploration of sequence space. Success will be measured by the identification of new sequence motifs that differ significantly from extant sequence that when polymerized show a range of LCST and UCST phase behaviors.

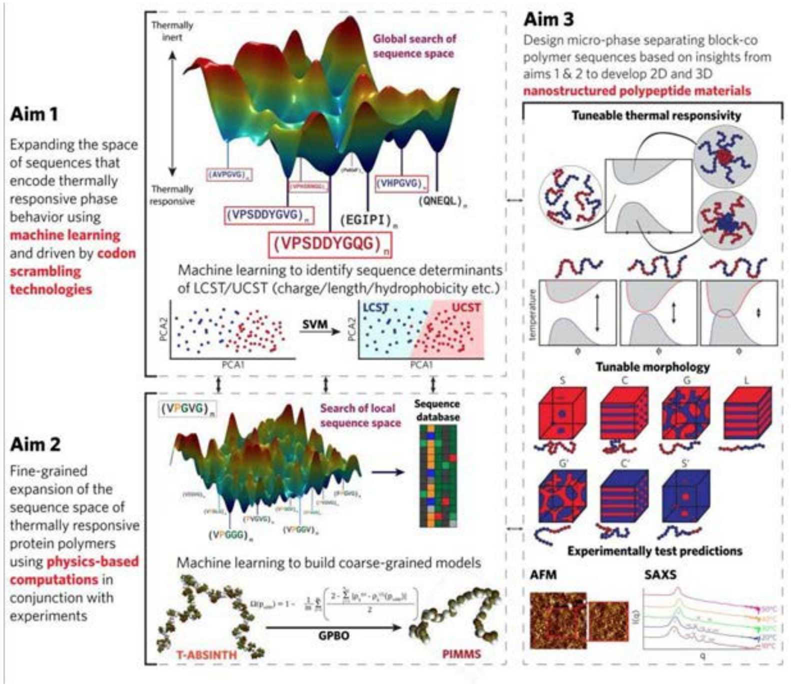

Figure. Schematic showing the Specific Aims (SAs) and their connections. In **SA 1,** we will use discovered sequence heuristics and combine these with machine learning methods and high-throughput experimental synthesis and characterization methods to expand the landscape of sequences that encode UCST (red) versus LCST (blue) behaviors. In **SA2**, we will zoom into specific islands in sequence space and use physics-based multiscale simulations that combine atomistic simulations (T-ABSINTH) and machine learning aided sequence-specific coarse-grained simulations (PIMMS) to uncover the relationships between sequence-encoded information and thermally responsive phase behavior. In **SA3**, we will build on preliminary observations showing the designability of block copolypeptides (BCPs) that mix LCST encoding blocks with UCST ones to expand the combinatorial space of BCPs and help us realize sequences with bespoke material properties and structures.

Relevance to MGI

This research project addresses the MGI goal to control material properties through design, by developing a multiscale approach that integrates machine learning with atomistic and coarse-grained molecular simulations of aqueous —LCST and UCST— phase behavior of peptide polymers and high-throughput synthesis and experimental characterization. The proposed methodology spans multiple length scales as it couples predictive, sequence-specific molecular-level simulations on one end to the large-scale self-assembly and microphase separation behavior of block copolypeptides. The approach we have chosen integrates modeling, analysis, and computational simulations, and is validated and refined through experiments, thus fulfilling a key objective set forth by the MGI.

Technical Progress

First, a set of candidate LCST and UCST peptide polymers were identified from "soft" heuristics [1] that relate the sequence of peptide polymers to phase behavior. In tandem, two approaches were developed to synthesize large (~10^3 gene), repetitive gene libraries— codon scrambling [2], and a complementary method based on rolling circle amplification— that enable generation of a library of polypeptides. Using these sequence heuristics as a guide, we synthesized a library that encodes genes for the repetitive amino acid motif $[PGXXXX]_n$, where n = 24-28 and X is any amino acid. The library has two important attributes: (i) its size is necessary to cull a large majority of insoluble or low-expressing sequences, and (ii) its diversity allows for an unprecedentedly broad coverage of the amino acid sequence-space to feed our predictive models. To rapidly identify soluble protein expression in *E. coli*, we have implemented the Colony Filtration (CoFi) blot method, which has allowed us to identify ~30 unique soluble proteins out of 478 unique candidates. The library-transformed candidates were identified with next generation sequencing (NGS) and the soluble genes were identified with Sanger sequencing of screened *E. coli* colonies. The soluble proteins have been expressed by *E. coli* in a 24-well format and are currently being evaluated for aqueous phase behavior.

To expand the sequence diversity of polypeptides that exhibit phase behavior, we have also identified unstructured polypeptides having no discernible repeat sequence that also exhibit LCST phase behavior. Nonrepetitive sequences comprise an as of yet unexplored sequence space, as the increased sequence complexity offers a higher diversity of synthetic sequences, allowing us to better understand stimuli-responsive behavior. To this end, we designed an algorithm that promotes well-distributed, structure-breaking residues, Pro and Gly, while maintaining amino acid fractions of their repetitive counterpart sequence of the form: $[PGGXXX]_{40}$, where X is any amino acid. We have currently identified 8 new sequences with verified LCST behavior.

The design and deployment of machine learning based methodologies and high-throughput physics-based computations methods awaits the availability of the first round of data, which will become available shortly. The physics-based approach was structured around the use of high-throughput single-chain, atomistic simulations to design sequences with bespoke coil-to-globule transitions. We have adapted a previously developed genetic algorithm to be interoperable with a second generation ABSINTH implicit solvation model that includes temperature-dependent free energy of solvation, which will be required for us to obtain sequences that show LCST behavior. We have completed the calibration phase of the second generation ABSINTH model.

In parallel, we have started to explore and harness the properties of genetically engineered, intrinsically disordered, stimulus-responsive block-co-polypeptides for their self-assembly into highly-ordered, microphase separated supramolecular structures. We have used small angle X-ray scattering and atomic force microscopy to study these polypeptides, and have identified several key factors (including relative block length, temperature and concentrations) to drive the ordered structures with highly regular characteristic features including hexagonal cylinders and lamellae.

Future Plans

At the synthesis level of the materials generation pipeline, we have established protocols consisting of high-throughput repetitive gene synthesis, and protein production/screening. Our next immediate step is to purify proteins via multiplexed histidine-tagged protein purification systems. This would enable us to verify the thermal behavior of these proteins via standard optical techniques such as turbidimetry. Upon discovery of our first set of novel temperature-sensitive polypeptides from this protocol, we would continue to iterate this pipeline to provide a feed of sequence data for our computational pipeline.

The computational pipeline serves to relate sequence-encoded information to thermally responsive behavior with a combination of multiscale, physics-based modeling and data-driven classification. The next objective in developing the machine learning and computational simulations pipeline is to test the accuracy of the T-ABSINTH paradigm for large-scale comparative simulations of temperature dependent coil-to-globule transitions. Once we have a concrete sense of the extent of accuracy, the next step will involve a combination of our Monte Carlo simulation engine with the GADIS, Genetic algorithm approach to veer off the ELP manifold and design novel sequences that will span a range of target lower critical solution temperatures. This will kick-start the iterative process of going between computation and experiment to test the validity of the central hypothesis and to refine the procedure by which novel sequences are designed.

At the structural end of the pipeline, we plan to: (i) expand our repertoire of micellar nanostructures formed at low solution concentration to highly ordered structures such as hexagonal cylinders and lamellae at high concentrations; (ii) understand the key variables driving microphase separation in these materials such as relative molecular weights, concentration, temperature, and the polymer-polymer and polymer-solvent interaction parameters; and (iii) translate or replicate these ordered nanostructures in form of surface-supported thin films.

Broader Impact

The proposed research will have a direct impact on the evolution of the fields of intrinsically disordered proteins, of bioinspired materials, and of biointerface science. Furthermore, through an integrated and innovative approach, we will train a world-class materials science and engineering workforce for careers in academia or industry by creating customized *Individual Development Plans* for all trainees and by fostering their *Professional Development and Training*. We will do the latter by: (i) supporting our trainees to participate in Gordon research conferences in Bioinspired Materials and Biointerface Science, the two premier avenues for dissemination of this research, and (ii) by fostering cross-disciplinary training by research stays in each other's laboratories or that of our international collaborator (Gradzielski, TU-Berlin) to foster team integration and cross-disciplinary learning and training. The PIs will also organize a mini-summer school each year in which the trainees and the PIs get together in person to learn and discuss the latest, relevant developments in stimulus-responsive polypeptide synthesis, characterization, and simulation. This venue will also serve as an annual, in person meeting of the teams from Duke and Washington University. The first mini-school is planned for late summer 2018. The unique, integrated training offered by this investigator team and project, will create the next generation of interdisciplinary materials scientists, equally adept across diverse disciplines, ranging from synthetic biology and big data science to molecular simulations and materials design.

Data Management and Open Access

In addition to tool development, an important objective of the proposed activities is the establishment of databases that keep connected data and metadata together and searchable. Specific to this proposal, the codon scrambler software is already available through a Duke-supported, publically accessible web portal. All gene constructs generated in this work will be made available for use in research through Addgene. In addition, we will publish our findings in peer-reviewed journals and present our work in seminars and at scientific conferences. Through this sharing plan, we intend to allow others to build on our research in a manner that maximizes data access and transparency.

Advancing Along the Materials Development Continuum

This project is accelerating the discovery of new "soft matter" by combining —fir the first time—cutting edge synthetic biology with machine learning and physics based simulations to generate new polypeptide sequences with defined materials function. Although aqueous phase behavior is the material property chosen fotr this project, this approach, once validited, can be applied more broadly to the discover of other classes of soft matter. Several patent applications have been filed on the new polypeptides discovered thus far, and their use as a "fusion" tag for the purification of recombinant proteins has been licensed to a start-up company, Isolere Bio.

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JARVIS: Understanding Fundamental Material Interactions and Properties with Classical Physics, Quantum Physics and Machine Learning

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Keywords: classical force-field, density functional theory, low dimensional materials, machine learning, descriptors.

Project Scope

The goal of JARVIS is to computationally screen and characterize materials for specific applications. The properties of interest include energetics, structural, mechanical, optoelectronic, dynamical and transport properties. The repository consists of three-, two-, one- and zero-dimensional materials. We use classical force-field, density functional theory and machine learning for calculations. We also use experiments to guide computation and vice-versa. We have identified thousands of novel low dimensional materials and characterized them through millions of calculations. We built new public repositories and distributed the scripts publicly. We measure impact through the number of web-visits, papers citations and downloads and github forks.

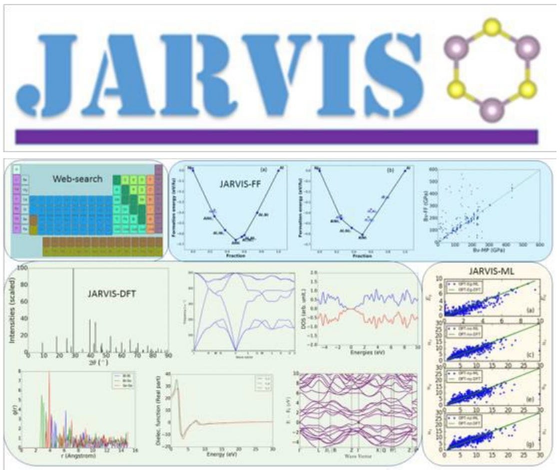

Figure. JARVIS-FF, JARVIS-DFT and JARVIS-ML webpages

Relevance to MGI

JARVIS (Joint Automated Repository for Various Integrated Simulations) provides useful tools to computationally screen materials, which is a very important aspect of MGI. We use sophisticated computational techniques that can help improve computational results in an efficient way (such as use of OptB88vdW, TB-mBJ potentials, high throughput computation of large scale properties through classical force-field calculations). We use experiments such as X-ray diffraction for two-dimensional materials (such as $MoTe_2$), transmission electron spectroscopy (to identify Wulff plots and catalytic sites) , Raman spectroscopy (such determining Raman and infrared modes), ellipsometry (such as determine the experimental dielectric function) and compare directly to our computational results for benchmark, validation and further screening of materials. We have identified thousands of novel low-dimensional materials which would take years otherwise to identify through experiments. Another important aspect of our project is the public dissemination of available data. We built public websites and set-up MongoDB database for RESTful API, enabling users to avail data without doing thousands of calculations themselves. All the scripts used in this work are distributed through github. We collaborate with various universities and organizations such as Stanford University, George mason university, Penn state university, university of Florida, university of Chicago, Northwestern university, Google, Citrine to help inculcate their research.

Technical Progress

In JARVIS-FF, we have characterized more than 3000 materials through more than 25000 classical force-field calculations for defect and surface energies, which are difficult to obtain using other atomistic approaches such as density functional theory. The JARVIS-DFT consists of more than 25,000 materials with more than 100,000 property calculations. We have generated big dataset for properties such as heat of formation, conventional and improved DFT bandgaps, dielectric function, exfoliation energies, elastic properties, phonon properties, electronic properties and transport properties such as effective carrier mass, Seebeck coefficient. We use this data to train machine learning models based on combined descriptors of chemical and structural descriptors to computationally pre-screen materials. All these repositories (JARVIS-FF, JARVIS-DFT and JARVIS-ML) are highly integrated and act as complimentary to each other. We obtain all the available interatomic potentials/classical force-fields and corresponding to a FF we obtain all the DFT relaxed structures and carry out classical force-field calculations on them enabling a one-to-one comparison of FF and DFT data. This helps a user to pre-select a FF before calculations. We used uncertainty predictions in density functional theory lattice constants to identify novel low dimensional materials and compared with data-mining approaches. While other main DFT databases mainly consist of bulk properties we generate data for single, multi-layer materials also. We provide datasets such as exfoliation energies, frequency dependent dielectric functions, META-GGA bandgaps which are not available in any other database. We have highest number of elastic property database in the world. We investigate how does optoelectronic, mechanical and other properties change as we go in higher/lower dimensions. We identified quite a few novel negative Poisson's ratio materials. Work-function of single layer materials can be used for band-alignment applications, which is critical in semiconductor device applications. Some of our experimental collaborators are trying to synthesize computationally predicted single-layer 2D materials based on the exfoliation energy data and compositional complexity. All of this progress happened in one and half year of timeline and the project is still expanding. JARVIS was awarded by NIST-MML accolade award in 2017. JARVIS was integrated with other well-known projects such as LAMMPS, materials-project, nanohub, materials data facility. We obtained a lot of positive response from users for using the data and the scripts.

Future Plans

In JARVIS-DFT, in addition to 3D and 2D materials we are generating data for 1D and 0D systems. We are generating data for multi-layer materials also. In JARVIS-FF we are adding sophisticated FFs such as SNAP, COMB, ReaxFF and carrying out calculations for phonon related properties which are otherwise difficult to obtain though DFT. We are improving the JARVIS-ML methodology to predict both single output (such as bandgap, , modula of elasticity, heat of formation) and multi-output properties (such as density if states and dielectric function) . We are also integrating JARVIS-ML with genetic algorithm to help identify if the DFT stable structure is same as in ML predictions to help analyze limitations of ML models. We are collaborating with various national labs, universities and companies so that they can use our data and we can get their feedback to improve our database and infrastructure framework.

Data Management and Open Access

The data is publicly available through our websites https://jarvis.nist.gov/ , https://www.ctcms.nist.gov/~knc6/periodic.html, https://www.ctcms.nist.gov/~knc6/JVASP.html and https://www.ctcms.nist.gov/jarvisml/ . We provide the source code for JARVIS at https://github.com/usnistgov/jarvis . We also provide our database as JSON files (https://github.com/usnistgov/jarvis/blob/master/jarvis/db/static/explore_db.py) and provide data through Figshare repositories. Our JARVIS-API is targeted towards REST-API based obtaining all the data. Most of our published papers are open access to enhance worldwide easy readability.

Advancing Along the Materials Development Continuum

Using MGI approaches we identified novel low-dimensional materials which are otherwise very difficult to carry out though experiments. Our DFT, FF and ML predictions can help narrow down the materials of interest for detailed experimental investigation. We also collaborate with various universities and organizations such as Stanford University, George mason university, Penn state university, university of Florida, university of Chicago, Northwestern university, Google, Citrine to help inculcate their research.

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DMREF: Collaborative Research: Helical Protein Assemblies by Design.

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Co-Principal Investigator: Gevorg Grigoryan, Departments of Computer Science and Biological Sciences, Dartmouth College, gevorg.grigoryan@dartmouth.edu.
Co-Principal Investigator: Edward Egelman, Department of Biochemistry & Molecular Genetics, University of Virginia, egelman@virginia.edu.
Website: None.

Keywords: Self-assembly, protein, peptide, nanotube, designability.

Project Scope

A novel framework is being developed for the targeted design of synthetic protein assemblies at atomic-level accuracy and their experimental characterization. The main objectiuve is to target **helical assemblies**—i.e., solenoid-like structures composed of elementary structural units (protomer) repeated with a screw-axis symmetry. The idea behind our design approach is to seek the most **designable** assemblies given a pre-specified protomer structure. Potein structure search algorithms have been developed that can estimate the natural designability of a given structural motif based on its abundance in the Protein Data Bank (PDB).

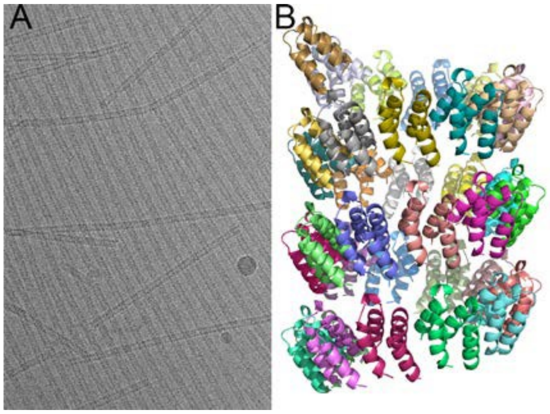

Figure 1. A. Cryo-EM image of HEAT peptide filament assemblies. **B.** Helical reconstruction of HEAT peptide assemblies. The asymmetric unit corresponds to a dimer in which a Trp-Trp interaction is postulated between protomers in the dimeric asymmetric unit.

Relevance to MGI

This project employs the concept of protein designability as a mechanism to promote and control association between folded protein motifs with an aim to create protein-based materials of defined structure and function. Designability in the context of protein engineering refers to robustness of a protein fold in sequence space. A proxy for designability is the frequency of occurrence of a structural motif within the Protein Data Bank (PDB). This approach will be employed to search for designable interfaces between protomers within the protein structural databank. The ultimate objective of the proposed research is to define sequences based on simple secondary or tertiary structural elements that are competent for self-assembly into nano-scale materials with extended helical symmetry. Computational methods will be employed to interrogate the protein structural databank to identify designable interfaces within robust structural motifs. Suitable candidate sequences will be computationally optimized and synthesized. Proven biophysical methods will be employed initially to identify sequences with promising self-assembly behavior. State-of-the-art high-resolution structural analyses will be performed on these assemblies using Iterative Helical Real-Space Reconstruction (IHRSR) from cryo-EM images. These analyses will inform future rounds of computational modeling and design, thus establishing a dynamic feedback loop between theory, synthesis, and advanced methods of structural analysis.

Technical Progress

Our approach uses TERMs—tertiary motifs that capture fundamental sequence/structure relationships: each is a “snippet” of structure that captures the secondary, tertiary, and quaternary environment around a single residue. Prior research shows that TERMs characterize structural designability. The use of different geometries in nature varies dramatically, such that natural abundance is related to designability (e.g., abundant motifs must be designable). The Grigoryan lab has catalogued all naturally abundant TERMs and has identified the basic computational approach that will enable creation of helical assemblies from abundant TERMs that can be computationally optimized.

Initial efforts focused on a TERM derived from an alpha helix-loop-beta strand motif in which a series of three peptides was designed. We have demonstrated that these peptides form fibrillar assemblies that match many of the features in the original computational design. All three peptides form high aspect-ratio fibrils from aqueous solution in which the lateral dimensions and conformation approximately match the computational design. STEM mass/length measurements was consistent with the model for two of the peptides while for the third peptide the measured M/L was significantly less than the model. TEM images of the latter assemblies display a morphology that suggests that the tubes do not fully close, which confirms the STEM mass/length measureemnts. Even for the two "well-behaved" peptide specimens, regions are observed in which the tubes are locally unwound into ribbons. SAXS measurements on the closed tubes indicated that the cross-section of the tubes was deformed relative to the computational model.

More recent computational designs focused on exploring the structural landscape of helix-loop-helix TERMs, which appear, based on computational analyses, to be a more structural robust platform for the design of helical assemblies. Spencer Hughes, a student in the Conticello lab, worked in conjunction with members of the Grigoryan lab to design peptides from TERMs based on helical hairpin motifs. Matching of lateral and axial interactions was explicitly considered during the computational design. Six different peptide sequences wewre identified for further investigation. Many of these peptides assembled into filamentous structures with dimensions that matched the computational designs. However, the need to bury significant surface area led to peptides with a high degree of hydrophobicity and limited solubility in aqueous solution. Often, the assemblies could not be easily dispersed in aqueous solution and aggregated extensively in a manner that made them unsuitable for subsequent structural analysis. While two of the peptides were further optimized for solubility using TERM-based design, the resultant assemblies still displayed extensive lateral association that limited further structural analysis.

A novel TERM based strategy was developed in conjunction with the Grigoryan lab in order to provide better control of lateral and axial interactions without loss of solubility. This approach was based on a domain-swapping strategy in which interacting peptide motifs would be directly linked together across the axial interface, which would strengthen the interaction. Several peptides were designed based on linked dimeric coiled-coil and HEAT repeat motifs. These peptides were synthesized and preliminary structural characterization was performed using CD and TEM. In either case, the conformation and dimensions of the assemblies were consistent with the computational design. Several promising candidates have been identified in either case for further analysis. One of the HEAT motif assemblies spontaneously crystallized spontaneously. X-ray crsytallography was employed to determine the structure of the assembly. The structural data indicated that one of the designed interfaces was maintained, however the other interface rearranged such to form a sheet-like structure that was reminiscent of an unwound nanotube. However, a structurally related sequence forms relatively ordered filaments, in which the corresponding power spectrum indicates a degree of helical order.

As yet, due to the challenges associated with obtaining highly ordered helical specimens from the designed peptides, we have been unable to solve the structures of computationally designed assemblies to near-atomic level resolution using cryo-electron microscopy. However, we have solved the structures of two related helical hairpin peptides using cryo-EM helical reconstruction to medium level resolution (circa 5 Å resolution). These helical hairpin sequences were derived from the consensus sequences of two tandem repeat proteins, HEAT and LRV, that were related to TERMs used as a starting point for computational design. In addition to being novel assemblies, these two structural analyses enabled us to refine methods for screening *de novo* designed peptide assemblies as potential candidates for cryo-EM structural determination.

Future Plans

The computational methods developed in the Grigoryan lab appear robust for the relatively rapid generation of peptide sequences that can form helical assemblies. However, thus far, few peptide sequences form structures that conform to the computational model. Although the designed peptides often self-assemble into filamentous structures, the resulting structures do not display the degree of order that was observed in the computational model. In addition, solubility and lack of colloidal stability continue to be a significant challenge. These problems are also observed in the reconstitution of biologically derived filamentous assemblies *in vitro*. This challenge suggests a need for a rapid method to screen solution conditions to identify ones that promote the formation of well-ordered assemblies. Ideally, this process would be applicable in a high throughput approach. Differential scanning fluorimetry has been employed to identify conditions that promote the formation of stable protein complexes for cryo-EM and X-ray diffraction analyses. The advantage of this technique is that it employs readily accessible equipment, i.e., quantitative PCR thermal cycler, and can be performed using conventional microtiter plate analyses for high throughput, parallel analyses. This method will be investigated along with high throughput SAXS analysis to better optimize solution conditions that promote self-assembly.

Broader impact (Only required for NSF projects)

Graduate students and postdocs have been provided the opportunity to work in collaborators labs or in the labs of participating institutions to develop new skills. The project has also supported the participation of students from under-srepresented groups as well as a high school teacher that serves that community. Outreach activities to the general public have involved the development of events for the Atlanta Science Festival.

Data Management and Open Access

The Grigoryan lab has developed a novel, holistic computational protein design method that relies solely on TERM-based information to select sequences towards a given template. A publication describing the details of this framework, called dTERMen (for design with TERM energies), is being prepared, with code to be made freely available for non-profit purposes. Excitingly, other labs have begun to employ dTERMen for their work. Dang *et al*., *PNAS*, **114**(41), 2017 represents the first example (of which we are aware) of an outside lab using TERM-based computational protein design (without our involvement in the project). The Keating lab (MIT, Biology) has now designed several peptide-based inhibitors using dTERMen. Further, we are currently collaborating with the Baker lab (University of Washington) to design a series of novel protein structures. Code, databases, and results related to TERM-based design and analysis has been (and will continue to be) made available through grigoryanlab.org/terms.

Advancing Along the Materials Development Continuum

Structurally ordered helical assemblies may be considered as one-dimensional supramolecular polymers, which have been an active research area within organic soft materials. However, few design principles have been elucidated thus far. Peptide- and protein-based materials represent useful substrates for the construction of these types of materials as well as the development of general design principles due to the large amount of structural data within the Protein Data Bank that can be employed to assist in the design. Thus far, we have been able develop computer programs that employ designability criteria to rapidly generate structural prototypes of peptide assemblies *in silico*. The challenge to implementation of this approach has focused on identification of designs that correspond to well-behaved assemblies, that is, in the sense that the corresponding peptides form higher order assemblies that meet the design criteria and can be dispersed readily in solution. While progress has been established in terms of computational design and experimental analysis, the loop has yet to be closed with regard to the connection of the two practices and will be the focus of future studies.

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Photocatalysts by Design: Computational Screening of Reconstructed Perovskite Semiconductor Electrodes for Efficient Solar-to-Fuel Conversion

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Keywords: hydrogen fuel; water splitting; photocatalysts; electrochemical interfaces; Schottky barrier heights.

Project Scope

The production of renewable fuels by splitting water into hydrogen and oxygen under solar illumination has the potential to revolutionize the generation of electric power for the transportation and residential sectors. The goal of this project is to accelerate the design of photoelectrodes for the production of hydrogen fuels by developing and applying computational capabilities that extend the scope of conventional quantum-mechanical simulations to predict solar-to-fuel conversion at reconstructed photocatalytic electrodes. An integrated experimental and computational cycle is followed to validate the theoretical approach; specifically, the Schottky barrier height is being used here as an aggregate of the performance parameters that collectively determine photocatalytic activity.

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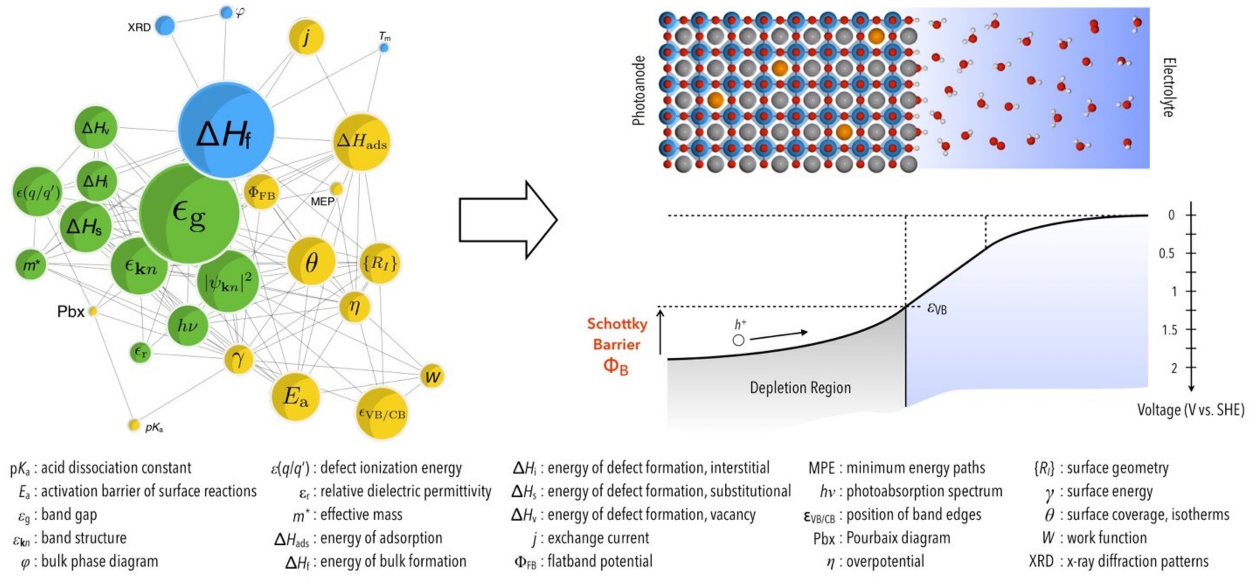

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Figure 1. A systematic survey of the computational literature reveals a wide range of accessible performance factors, which can be categorized into thermodynamic (blue), photovoltaic (green), and electrocatalytic (yellow) parameters (left). Yet, none of these factors account for the coupling between the photoelectric and electrochemical processes that underlie photocatalysis. The key concept of our screening protocol is centered around calculating and measuring the Schottky barrier √$_{\text{B}}$, as the figure of merit that meaningfully aggregates these diverse performance factors.

Relevance to MGI

Upon surveying the literature in search of relevant performance indicators, we found that none of the ~25 metrics that are routinely calculated to assess photocatalytic activity reflects the strong coupling between photovoltaic and electrocatalytic processes at the origin solar-to-fuel conversion (Figure 1). The tools developed in this project aim to bridge this gap. Our new quantum–continuum model extends the scope of the quantum simulations for studying the depletion region over length scales of up to 1,000 nm, which is otherwise computationally inaccessible with an exclusively quantum-mechanical approach. Through an integrated experiment–theory loop, we aim to validate the quantum–continuum method on a range of oxide materials, and then test robust design criteria enabling large-scale computational searches for new classes of photocatalysts. Our integrated experimental and theory effort leverages the expertise of Abruña in photoelectrochemical experimentation, Dabo in quantum–continuum modeling, Fennie in the computational design of advanced oxide materials, Gopalan in the photophysics of complex oxides, and Schaak in materials discovery and nanoscale synthesis to accelerate the development of new photocatalysts.

Technical Progress

The first six months of the project have been focused on (1) validating the accuracy of the newly proposed quantum–continuum approach in predicting the electrical response and chemical stability of reconstructed photoelectrodes and (2) establishing the experimental protocols to probe the overall charge–voltage response of the photocatalytic surfaces (Mott–Schottky voltammetry), to measure their local photocatalytic activity (scanning electrochemical microscopy), and to determine the photocatalytic products (gas chromatography). As an example of a prototypical photocatalyst, we performed a computational study of $SrTiO_3$ in an effort to elucidate its voltage-dependent reconstruction in aqueous environments and the impact of such reconstruction on the position of the band edges and on the heights of the Schottky barriers. Following this validation, a series of previously identified promising photocatalytic candidates, exhibiting favorable band alignments with respect to water reduction and oxidation, have been synthesized or acquired by our team (namely, $AgInO_2$, $AgGaO_3$, Ca_2PbO_4, Cu_2PbO_2, $NaBiO_3$) and their band gaps have been determined by means of diffuse reflectance spectroscopy. Photo-electrochemical measurements and quantum–continuum calculations are currently being performed for these samples to further validate and refine our experimental and computational capabilities. Additionally, our team is currently confirming unexpected observations indicating a possible photocatalytic activity for $Ca_3Ru_2O_7$ polar materials.

Future Plans

The current focus is on finding a suitable tradeoff between computational cost and chemical accuracy in predicting band alignment (valence and conduction edges) and band bending (Schottky barrier heights). Simultaneously, we are narrowing down the list of possible photocatalytic materials based on simplified initial estimates of band gaps, bulk formability, band edges, elemental abundance and toxicity, and synthesizability (Figure 2), leading to the identification ~250 candidates at this stage of the project. Our next

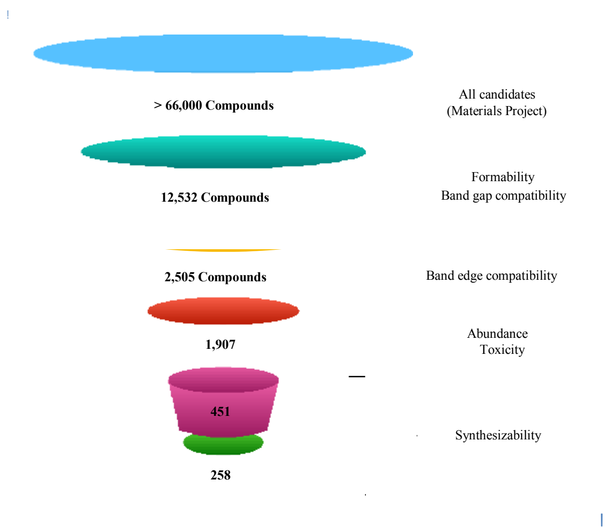

Figure 2. Initial screening of candidate photocatalytic materials has been carried out using criteria of formability, band-gap and band-edge compatibility, abundance and synthesizability. The resulting 258 candidates are now being categorized into structural families for further computational screening and experimental validation, focusing on the voltage-dependent stability and Schottky barrier heights of their low-index terminations as performance metrics.

task is to divide the candidate materials into structural families and to then examine representative candidates from each of these families to prioritize subsequent computational screening.

Broader Impacts

To replace the transportation fuels of today, tens of millions of barrels of renewable fuels need to be produced every day. It is possible to synthesize fuels by converting biomass into biofuels but there is debate over the use of agricultural resources to produce fuels instead of food. This provides a strong motivation to develop solar-to-fuel conversion via artificial photosynthesis, the direct catalytic transformation of water and carbon dioxide into hydrocarbon fuels or splitting of water into hydrogen and oxygen without exploiting biomass. Interdisciplinary training of students is at the core of our program. Two undergraduate students are working on this research for course credit and for thesis project. The graduate and undergraduate students involved in computational modeling will be given opportunities to participate in experiments of critical relevance to the validation of their models. Students participating in the experimental part of the project will attend computational training schools. A new edition of the QUANTUM-ESPRESSO workshop is being organized at the Pennsylvania State University.

Data Management and Open Access

The computational tools developed in this project will be freely available online for download; these tools will be hosted on the web-based repository service *Github* for distributed revision control and source code management. The Materials Project database (www.materialsproject.org) is being used for our initial materials screening. We will exploit the high-throughput computational platform AiiDA (www.aiida.net) with its data-management capabilities to schedule and execute computer calculations and to store the resulting data and metadata. A workflow for the automated generation and geometric optimization of surface structures in aqueous environments has been created and is being further developed.

Designing and synthesizing nano-metallic materials with superior properties

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Keywords: composite, metal, plasticity, microstructure, nano

Project Scope

Flow localization is a major obstacle to the technological use of nanometallic materials (NMMs). We hypothesize that flow localization in NMMs may be suppressed by tailoring microstructure morphology, accelerating the transition of these materials from the lab to applications. This project uses an iterative design-synthesize-test cycle to systematically improve understanding of flow localization in NMMs with complex, interpenetrating "bicontinuous" morphologies. This project advances methods of NMM synthesis, microstructure quantification, and testing for flow localization. The success of this project is measured by our ability to identify the microstructure characteristics that control flow localization and to use such insights to design and synthesize new NMMs with greater plastic flow uniformity.

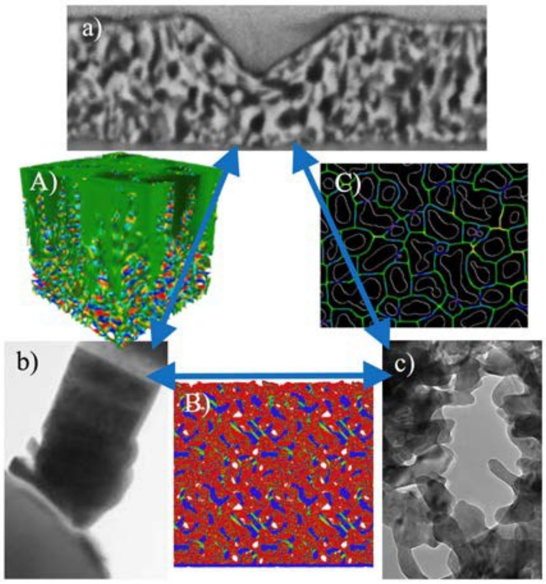

Figure. This project integrates experiments [a) indentation of dealloyed NMMs, b) pillar compression of physical vapor-deposited NMMs, c) in situ TEM straining of nanoporous gold] with computations [A) phase field, B) atomistic simulations, C) digital image analysis] to understand and avert flow localization.

Relevance to MGI

Flow localization arises from the interplay of material architecture (morphology, microstructural length scale), defects (dislocations, interfaces, surfaces, impurities), and loading conditions. Thus, designing materials resistant to flow localization is much more complex than targeting a single property that might be cleanly linked to electronic structure through first principles calculations. To address this challenge, we formulate our design strategy as an iterative design-synthesize-test process that integrates experiments and modeling. They key to its success is close coordination between researchers at the collaborating institutions. For example, a joint effort by TAMU and VT led to the development of the AQUAMI code as well as its application to the discovery of microstructure/processing relations in NPG. This effort extracted new insights from already published data without the need for any new experiments or simulations, markedly accelerating research on this unique material. Another example comes from the integration of NMM synthesis *via* vapor co-deposition at UMich with phase field models of microstructure self-organization at TAMU. These investigations revealed a structure/processing “phase” diagram to guide the design of co-deposited NMMs with tailored properties, including resistance to flow localization.

Technical Progress

The key technical achievements of this project are:

- Demonstration of microstructure self-organization in physical vapor co-deposited composites of phase separating metals. Three distinct morphologies of interpenetrating phases were identified and their formation was explained through phase field modeling. These results guide the future synthesis of co-deposited composites with designer microstructures.
- Development of solid metal dealloying as a high throughput method for synthesis of thin film nanocomposites with controllable connectivity of the constituent phases.
- Identification of three key factors contributing to the suppression of flow localization in bicontinuous nanocomposites: a) incoherent interfaces, b) isotropically interconnected microstructure morphology, and c) non-percolating, non-codeforming phases.
- Observation of plastic flow localization in individual ligaments of nanoporous gold during *in situ* TEM imagining of crack propagation in this material.
- Quantification of load partitioning in atomistic simulations of plastic deformation in two-phase NMMs and of onset of hardening upon pore collapse in nanoporous gold.
- Development and dissemination of the AQUAMI code for quantitative analysis of complex microstructures.
- Application of AQUAMI to the characterization of microstructure/processing relations in nanoporous gold.

Future Plans

Since this project is in its final year, our priorities are to a) complete the ongoing (and final) design-synthesize-test cycle for NMM development and b) prepare manuscripts on all work done to date and submit them for publication in peer-reviewed technical journals.

Broader impact (Only required for NSF projects)

Our project has engaged in vigorous mentoring and outreach activities to prepare the future workforce for success in a MGI-driven materials development landscape. It supports four PhD students, one Masters Student (female, recently graduated), and two postdoctoral researchers (one of which recently transitioned into a tenure-track faculty position at Arizona State University). At Texas A&M University (TAMU), this project supported the founding of the Trajectories to Graduate School (TTGS) program, which advises, encourages, and mentors underrepresented minority students on their transition into top-ranked graduate programs. At Virginia Tech (VT), this project supported a summer camp for girls from area high schools interested in pursuing a degree in STEM fields. At the University of Michigan (UMich), this project supported a RET program for Michigan high school teachers, delivering modules related to materials design for use in classroom instruction.

Data Management and Open Access

This project requires quantitative analysis of microstructure in NMMs with complex internal morphologies. To that end, we have developed a new, user-friendly code named “AQUAMI” (short for “Automatic QUantitative Analysis of Microscopy Images”). This code uses advanced computed vision algorithms to distinguish individual phases with a microstructure and to determine their shapes, dimensions, and orientations. AQUAMI has been escribed in detail in a recent peer-reviewed publication [Stuckner *et al.*, 2017]. It has also been uploaded to NSF’s NanoHub repository, where it may be freely downloaded by the broader materials community. A new study that uses AQUAMI to extract new insights about microstructure/processing relations in nanoporous gold (NPG) is currently under review [McCue *et al.*, 2018].

Advancing Along the Materials Development Continuum

This project moves NMMs along the materials development continuum from stage 1 (discovery) to stage 2 (development) and, in some cases, 3 (property optimization). The key activities enabling these transitions are the coordinated, iterative, cross-institutional collaborations integrating experimental and modeling investigations of NMMs. These collaborations are evidenced by joint publications by members from different institutions participating in this DMREF project.

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μMAG: Micromagnetic Modeling Activity Group

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Keywords: micromagnetics, standard problems, public code

Project Scope

The Micromagnetic Modeling Activity Group (μMAG) is the worldwide collection of researchers interested in the development, validation and use of micromagnetic modeling software. It pursues two broad activities, the publication of standard problems and the release of a micromagnetic solver and associated utilities as public code.

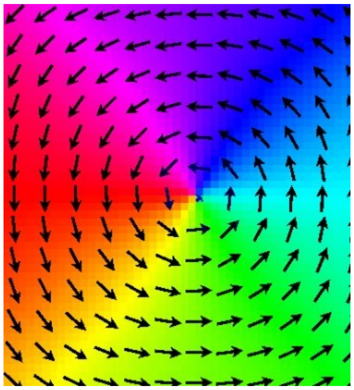

Figure: μMAG Standard Problem 5 examines the movement of a vortex in response to a spin polarized

Relevance to MGI

MGI seeks to use computational approaches to reduce the time and cost of developing new materials. Fundamental to this strategy is the need for confidence in the results of our computations. μMAG has a record of success in improving the reliability and accountability of micromagnetic modeling software via its program of standard problems, and its production of the OOMMF solver as public code with an extensible architecture. These needs and efforts continue while we seek to continually adapt to the changing background in computing technology.

Technical Progress

OOMMF software has been available for download in source code form, and as binaries for the Windows platform. It is now also available for installation-free use online through the nanoHUB service [1] of Purdue University. This permits use of the tools by people less comfortable with maintaining software installations on their own systems, opening μMAG benefits to a broader audience. OOMMF software adaptation to multicore, high memory bandwith systems first made calculations of a billion-spin system feasible. This in turn has enabled empirical examination of the error effects of some discretization and algorithmic choices. A newly developed technique for computing the demagnetization field based on a hybrid fine/coarse representation of magnetization[2,3] is showing good promise as a way to trade off a controlled amount of additional error for significant gains in simulation speed. In pursuit of these code improvements, the source code management of OOMMF was converted from CVS to git. The new system better supports multiple branches of concurrent development, so that more ambitious code improvement efforts can be taken without undue risk to the interface stability required by users of the extension architecture. The latest standard problem addresses the proper computation of spin momentum transfer, a physical phenomenon important to the technologies of sensors and MRAM elements.

Future Plans

Two ideas for standard problems are under consideration, one to examine the simulation of spin wave dispersion in a magnonic waveguide, and one to examine the sensitivity to different criteria for deciding when a computation state is considered a stable magnetization configuration. Public code work continues on computation techniques that compute more efficiently without uncontrolled introduction of errors. Software development always includes the maintenace of keeping programs well matched to the capabilities of modern hardware and software foundations. Earlier work produced a port of the OOMMF software to GPU hardware[4]. Revisions to OOMMF may permit that work to be brought under an appropriate revision of the extension architecture, extending its utility and lifetime. While OOMMF has always been open in the sense of source code availability, we have not opened tracking of the development process itself. After migrating our source code management to git, we are poised to add that layer of openness via use of a system like github. This approach is increasingly popular in the software development world, and we are considering it.

Broader Impact

The OOMMF software collection has unmistakeable impact in the science and engineering of technologies founded on magnetic properties of materials at the nanoscale. It has been cited in more than 2500 peer-reviewed journal articles[5], and in more than 20 awarded U.S. patents. In 2017, it was downloaded by more than 9000 users from the NIST servers. OOMMF distributes a collection of 14 extension modules developed by non-NIST programmers, demonstrating the effectiveness of the extensible architecture. A number of utility programs supporting effective use of OOMMF have also been created by non-NIST developers, including notably the JOOMMF project[6] that integrates the OOMMF solver with the Jupyter notebook[7] system, and the MAGE tool[8] for generation of OOMMF input files.

Data Management and Open Access

The volume of data required to specify standard problems and publish contributed solutions of them is modest. Likewise, the distribution of public code releases is not overly demanding in resources, nor a challenge to search or navigate. Publication on web sites has been adequate to the needs of the project. See our Future Plans for possible changes here.

Advancing Along the Materials Development Continuum

The focus of µMAG is on the testing and improvement of software, which in turn is used to explore parameter spaces of material attributes. While this plays an important role in determining material needs for technology applications, its contribution to materials development itself is indirect.

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Computationally-driven design of advanced block polymer nanomaterials

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Website: http://pscf.cems.umn.edu
Keywords: block polymers, soft materials, self-consistent field theory, complex phases, inverse design

Project Scope

The project is developing the computational methods required to design block polymers with interesting and new structural properties and testing the predictions of these tools experimentally. The key tool is self-consistent field theory (SCFT) for block polymers, a rigorous mean-field treatment providing both free energies and morphologies of block polymer melts. The initial applications focused on discovering new sphere-forming phases in the tetrablock terpolymer poly(styrene)-*b*-poly(isoprene)-*b*-poly(styrene)-*b*-poly(ethylene oxide) (SIS'O) and enticing opportunities in related sphere-forming phases of diblock and triblock polymers. The renewal application focuses on bottle-brush polymers and ABCA-type tetrablock terpolymers, with an emphasis on optically active materials.

Relevance to MGI

The heart of this project are new tools based on SCFT. We have developed and released an open-source SCFT code, packaged as an OS-X executable with solved examples, for broad use by the community. This tool can be used for the "forward" problem, where the block polymer chemistry is given and one wants to determine the equilibrium morphology. We also are developing wrappers around SCFT that solve the "inverse" problem, where the target morphology is known and one wants to determine a polymer formulation that will produce this morphology. Both problems are tremendously difficult – for tetrablock terpolymers, the phase space for a single-component melt is already 9 dimensional, and size of the phase space explodes as the number of blocks increases [1]. In tandem with the latter activities, we are developing synthesis methods to access challenging new regions of the chemical space, such as ABCA-type polymers, and characterizing these materials using a suite of methods, in particularly TEM, SAXS and dynamic mechanical spectroscopy. The net outcome of this project is not only the computational tools required to guide us through the high-dimensional design space, but the experimental tools that allow us to realize the most tantalizing predictions from our models.

Technical Progress

We have made progress on a large number of different fronts, ranging from (i) the development of new tools for solving the inverse problem using genetic algorithms and particle swarm optimization to (ii) technical advances in SCFT enabling the study of complex phases to (iii) discovery of novel sphere-forming phases in a range of block polymer systems to (iv) modular synthetic methods enabling the facile synthesis of various ABC, ABAC and ABCA architectures. The most comprehensive body of work, involving extensive collaboration between theory and experiment *and* between the teams at UMN and UCSB, involves the discovery of a "cornucopia" of sphere-forming phases in SIS'O. As illustrated in the figure, this research began with computational studies at UMN that identified the most promising region for exploration, in particular noting that the asymmetry between the terminal styrene block (S) and the internal styrene block (S') was a key feature. These polymers were synthesized and characterized at UMN, revealing a large number of sphere-forming phases beyond the typical body-centered cubic

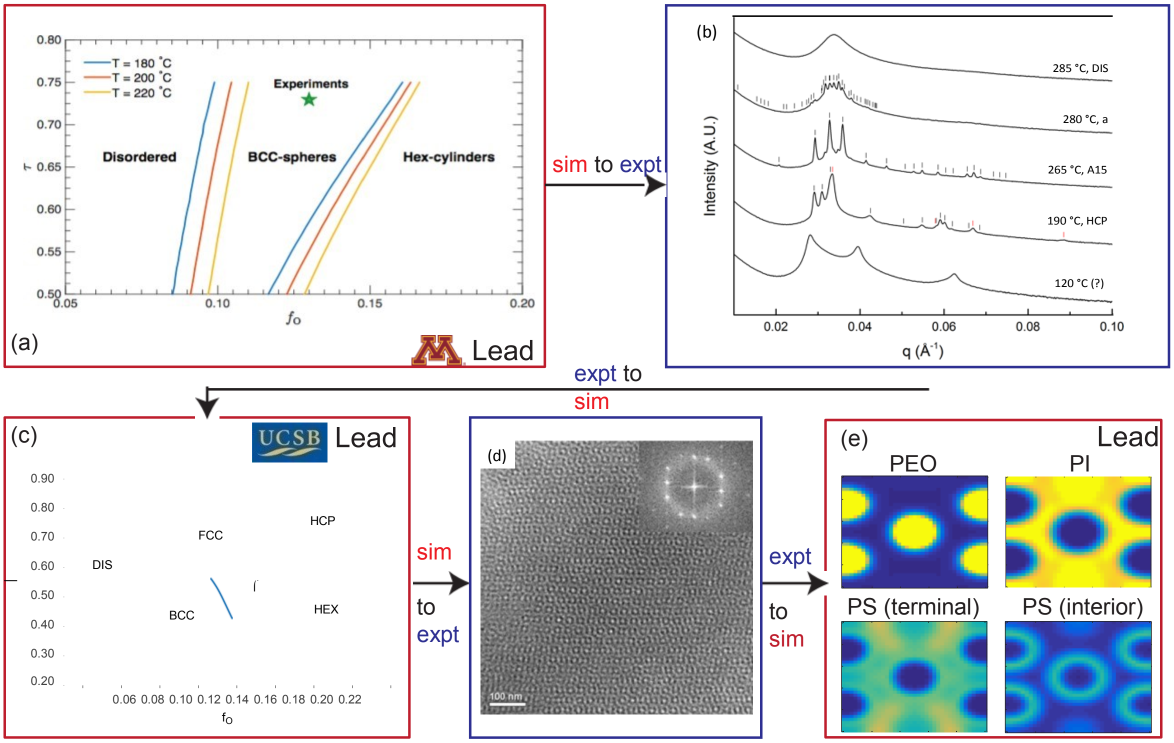

Figure. MGI approach to materials discovery in tetrablock terpolymers. (a) SCFT calculations (UMN, lead) suggest a region of SIS'O phase space favoring particle-forming phases. PS asymmetry given by $\tau = N_S/(N_S+N_{S'})$ and f_O is the volume fraction of the O-block. (b) Experiments yield a cornucopia of such phases in the expect region as a function of temperature (χ parameters). Synchrotron SAXS patterns at selected temperatures during slow heating ramp (1 °C/min) of SIS'O with $\tau = 0.68$. The tetrablock was freeze-dried from benzene and received no thermal treatment prior to the experiment. An unknown phase with possible rhombohedral symmetry (based on TEM experiments) is seen at 120 °C. (c) Further SCFT calculations (UCSB, lead) corresponding to the experimental composition suggest that a σ-phase should be stable. (d) TEM image and FFT (inset) confirm the A15 phase in a SIS'O with $\tau = 0.70$. (e) Further analysis by SCFT (UMN, lead) yields the detailed structure of the A15 phase.

phase. Most notable was the discovery of an A15 phase, which had not been seen before in block polymers. This experimental discovery lead to further SCFT work, led by UCSB, that suggested that the σ-phase, not A15, should be the equilibrium structure. However, the free energy difference between these two phases is very small. Motivated by the calculations, the UMN team refined the parameters appearing in the SCFT calculation and indeed found a region of the phase space where A15 is stable due to segregation of the matrix. The morphological insights gained by SCFT complement the experimental characterization by TEM.

Future Plans

The renewal of this project is focused on a key design problem in SCFT and a challenging materials target. All SCFT calculations rely on accurate estimates for the Flory-Huggins parameter χ_{ij} characterizing the non-ideal mixing of block *i* and block *j*. We are engaged in a systematic study of this problem, and plan to leverage the inverse design tools developed previously to improve the χ-parameters appearing in our calculations. We then plan to use the improved data in the design of novel bottle-brush polymer materials with interesting optical properties.

Broader impact (Only required for NSF projects)

The methodological improvements, both in the application of SCFT and the analysis of the output, will have a broad impact on the community. In particular, adding them to our Broadly Accessible SCFT platform further lowers the burden for new users to implement SCFT in their own work. In this respect, we were delighted to see a key experimentalist in the field (Rick Register, Princeton University) show how his group used our platform to provide a theoretical basis for the experimental results. Theoreticians also continue to show interest in using the platform. For example, Greg Grason (UMass-Amherst) presented results that not only used our software, but also used our post-processing codes to produce the figures. The mixture of simulations, experiments, and the software development allows for substantial professional development for the postdocs and grad students as they learn about the different areas of the project through formal and informal interactions with other members of the team. The project has also involved the participation of an undergraduate student Naveen Pillai, a female graduate student Carol Tsai, and a female postdoc Madelyn Radlauer.

Data Management and Open Access

The open-source SCFT software is available on http://pscf.cems.umn.edu, along with a philosophical motivation for our MGI project and a selection of solved examples. The latest version of the source code for advanced users is maintained on Github by our colleague, David Morse. We have also published a perspectives article “Broadly Accessible SCFT” in *Macromolecules*, which has reached a broad audience of potential users.

Advancing Along the Materials Development Continuum

The MGI-inspired computational and experimental tools arising from this project are being leveraged to pursue applications by industry consortia at UCSB and UMN, including the Complex Fluids Design Consortium at UCSB and the Industrial Partnership for Research in Interfacial & Materials Engineering (IPRIME) at UMN.

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DMREF: Collaborative Research: Materials design of correlated metals as novel transparent conductors

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Website: none.
Keywords: correlated electron systems, density functional theory, dynamical mean field theory, thin film growth, bulk synthesis.

Project Scope

The major goal of this project is to utilize a combined experimental and theoretical approach to predict and synthesize new materials candidates for the application as transparent conductors. While the common design strategy is to take a wide band gap semiconductor, in this project the search is based on a fundamentally different design paradigm. Here a material exhibiting strong electron correlation effects is chosen that has a high carrier concentration despite a large carrier effective mass, and an energetically isolated conduction band. The scope is to utilize first principles predictions in conjunction with experiments to find robust descriptors to accelerate materials composition search to identify potential candidate materials. New materials will be compared to the existing champion material ITO using the well-established figure of metric for transparent electrode.

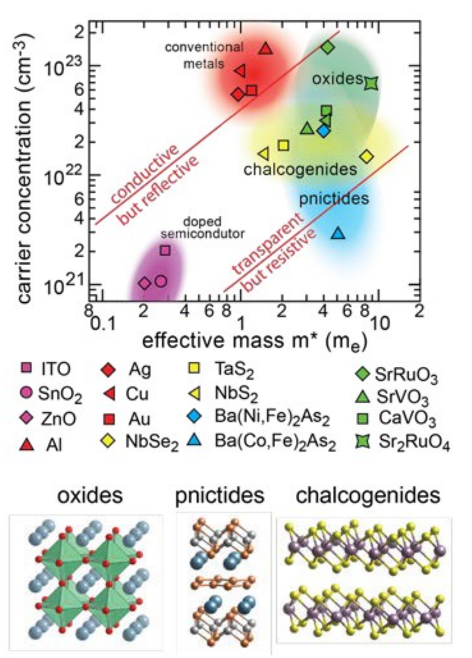

Fig. 1. Searching the large materials design space of transition metal oxides, pnictides and to identify promising material candidates for the application as transparent conductors.

Relevance to MGI

An integrated theory and experimental approach is employed to identify material design descriptors that are relevant to the figure of merit for a transparent conductor. The goal is to establish simple links between atomic scale features and the chemistry of compounds and the mesoscopic properties relevant for transparent conductors, namely carrier concentration, effective mass, scattering time, and optical absorption. Using these descriptors, families of materials, namely transition metal pnictides, chalcogenides and oxides, will be mined from existing materials databases. Synthesis of these materials will be performed in close collaboration with theoretical efforts. While DFT and DMFT helps prioritizing the synthesis efforts, analysis of the experimental results will inform about the robustness and relevance of the descriptors chosen and their effectiveness to identify suitable candidate materials. This way design principles will be refined for use in further searches at the database and DFT levels. Applying the integrated theory and experimental approach, new chemistries have been identified within the first period of this project that perform even better. The applicability of the concept of transparent conductor has been expanded to application areas demonstrating the cross-fertilizing character of the highly complementing theory and experimental approach.

Technical Progress

We have searched the materials design space of ‘bulk’ transition metal dichalcogenides to identify materials with promising band structure and optical properties. A few composition have been down-selected and it is currently being investigated how the number of layers will affect the electrical and optical properties. From the transition metal oxide family, two new chemical compositions are being identified by DFT/DMFT that have a superior performance compared to ITO. Progress has been made to synthesize these new oxide material by sputtering. Optical and transport properties have confirmed the first principle predictions.

A careful study to determine the work function of $SrVO_3$ by forming Schottky contacts with Nb-doped $SrTiO_3$ has found a large value of 5.15 eV for $SrVO_3$, in excellent agreement with first principles calculation of band alignments in oxide heterostructures. This is a significant result, because it suggests that ohmic contacts can be formed with p-type semiconductors, making correlated metals a suitable choice as replacement for p-type transparent conductors. It further identifies another parameter that has to the added to the set of important descriptors, namely the work function of the correlated metal. This descriptor is the key guiding principle to identify transparent conductors that will form a small contact resistance with p-type semiconductors.

We have further identified aliovalent substitution of the transition metal oxides to be an efficient strategy to improve the performance of transparent conductor. While it is not clear yet at this point from a fundamental point of view why the electrical conductivity and the optical transparency improves, early insights from first principle predictions suggest not only a Fermi level repositioning, but also a sizeable redistribution of the density of states near the Fermi level, allowing to shift the interband absorption edge towards the UV spectrum as well reshaping the interband transition peak. Both affects enhance the figure of merit for transparent conductors, and casting these trends into proper descriptors are currently being investigated in detail.

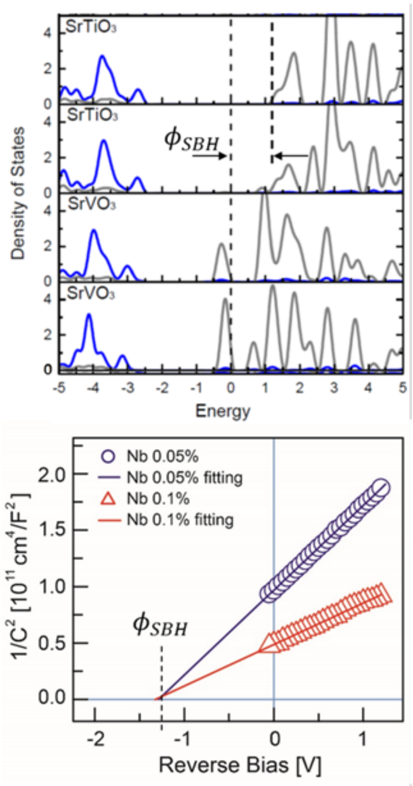

Fig. 2. Predicting the work function of correlated metal using first principles studies of band alignments in oxide heterostructures and in conjunction with Schottky barrier height measuremetns on semiconductor-metal-junctions.

Future Plans

Future directions are geared towards completing the current technical progress. Specifically the synthesis of the newly predicted oxide transparent conductors by sputtering is a high priority. While some of the compounds are less competitive in direct comparison with standard ITO or $SrVO_3$ for the application as transparent conductor in the visible, they outperform existing p-type transparent conductors by orders of magnitude. The prediction of work function from first principles is not straight forward. We plan to spearhead an effort to close this gap by developing a strategy how to extract work function of metals from DFT. Specific heterostructures are being experimentally investigated to confirm the predictive methodology. The team has started to compile existing literature data and the new data obtained during the first period to provide a comprehensive survey and analysis of transparent conductors.

The change in optical and electrical properties observed for $CaVO_3$ with time can be attributed to electronically active defects such as oxygen vacancies. Controlling the cation to anion ratio in these compounds is an alternative design strategy to enhance the performance. In future we plan to evaluate the effectiveness of this strategy through a combination of experimental investigation and first-principles calculations of the effect of doping and selected defects on optical absorption. Since correlation strength is a critical descriptor but hard to measure experimentally, in particular in case of thin films, we have identified a possible pathway towards extracting the correlation strength from low temperature magnetotransport for ultraclean correlated metals in the limit of high magnetic fields. We plan to finalize this work and compare it to theoretical results obtained from first principle methods.

Broader impact (Only required for NSF projects)

The multi-prong approach employed requires a very close and vivid collaboration among the research groups with complementing expertise. Graduate students are actively involved in this process by giving updates and participating in the regular discussion during the teleconferences. This trains the future generation of scientists and engineers to think holistically about the challenge at hand and allows them to improve their communication skills talking to collaborators with a different skill set and expert knowledge. This interdisciplinary research employs modern communication and data sharing infrastructure to ensure team members can access and interpret all data. Outreach efforts are being planned for late summer 2018 to visit middle/high school students in the class room and at summer camps in the greater Los Angeles area to enthuse young scholars by providing them five different hands-on-activities. The goal is to involve them in different scientific exercises that have either a strong theoretical, synthesis, or characterization component, but are complementary. The goal is to discuss with the group how these individual, diverse scientific experience can be combined to achieve an even greater insight into a topic of interest and use this as an example what the idea behind the materials genome initiative is.

Data Management and Open Access

Experimental and theoretical end results are shared within the research group using a cloud. No experimental or computation metadata are being shared among the group and with the public at this point, but data and samples are being made available upon request. We have identified a gap of optical data base that expands beyond existing band structure databases to facilitate data-enabled science for optoelectronic, photonic and plasmonic applications and would like to append such a database to existing infrastructure.

Advancing Along the Materials Development Continuum

Give the many materials design parameters of transition metal chalcogenides, pnictides and oxides, ranging from crystal structure/symmetry, composition/chemistry, and layering scheme spans a large materials configuration space that requires theory guided approach to accelerate discoveries and keep expenses to a minimum. Experimentally verifying all these composition, even if high throughput synthesis techniques are being employed. While a new transparent conductor material, which can be made thinner and is made from more abundant and environmentally benign elements, targets the main disadvantage of In-based transparent conductors a real market entry point has thus far not been identified. Currently, addressing the risk to deposit these materials in a more economic scalable technology, such as sputtering, is key to demonstrate the potential to scale up the materials synthesis? Entrepreneurial activities, such as I-corps or SBIR are planned, but at the current stage considered a premature step.

Publications

1. M. Brahlek, A. Sen Gupta, J. Lapano, J. Roth, H.-T. Zhang, L. Zhang, R. Haislmaier, and R. Engel-Herbert, *Frontiers in the growth of complex oxide thin films: Past, present and future of hybrid MBE*, Adv. Funct. Mater. **28**, 1702772 (2018).

2. J. Roth, E. Arriaga, M. Brahlek, J. Lapano, and R. Engel-Herbert, *Temperature-dependent growth window of* $CaTiO_3$ *films grown by hybrid molecular beam epitaxy*, J. Vac. Sci. Technol. A **36**, 020601 (2018).

DMREF: Antiperovskite interfaces for materials design

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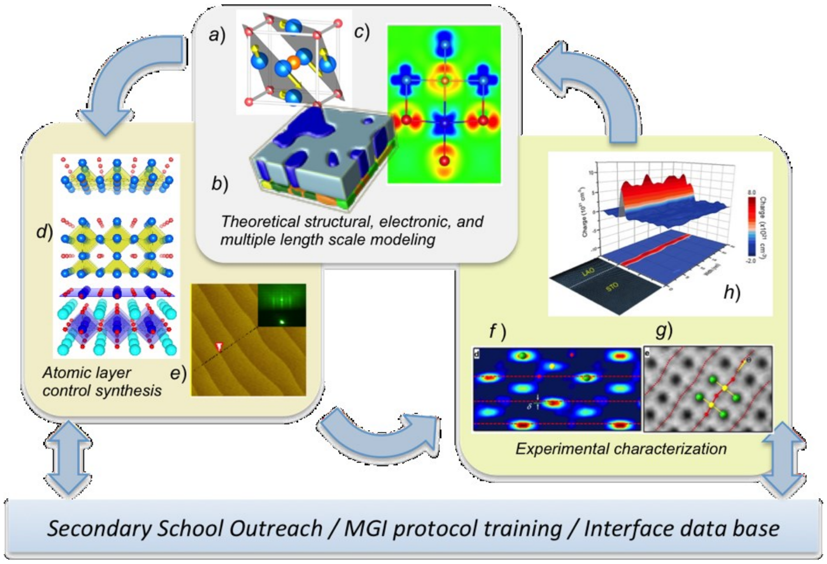
Keywords: perovskite, antiperovskite, interface, magnetism, epitaxial

Project Scope Our objective is to develop new materials systems based on interfaces between antiperovskites and perovskites, artificially layered antiperovskite superlattices, and new epitaxially stabilized antiperovskite materials, for electronic sensing and processing applications.

We develop underlying design principles for these material systems by using advanced first-principles methods to design novel interfacial electronic and spin materials. Understanding this wide array of structures will put in place valuable information about the crystal chemistry of atomic scale antiperovskites and heterostructures, incuding interface atomic structure and bonding, nterfacial spin order and multiferroicity.



Counterclockwise from top: Theoretical Modeling, showing *a*) frustrated spin structure of $GaNMn_3$, *b*) ferroelectric domain structure of a $(SrTiO_3)_4/(BaTiO_3)_8$ superlattice, *c*) antiperovskite interface bonding calculation; Interface Synthesis, showing *d*) layer by layer growth *e*) AFM/RHEED pattern of epitaxial growth; Characterization, showing *f*) Synchrotron reconstruction of polar metal *g*) TEM analysis of bond angles in polar metal *h*) in line holography of interfacial charge.

Relevance to MGI Success in this program requires models of the physical interactions whose predictions should be experimentally validated, and methods to connect models over multiple length scales. Iterative experimental feedback, including atomic-layer control synthesis, and atomic-scale structural and electronic characterization, will guide essential refinements to our theoretical approaches. An example of this is our investigation of the interface structure between antiperovskite Mn_3GaN and perovskite LSAT (see technical progress section below). Theoretical predictions were refined with experimental input. In particular, atomic positions from high-resolution TEM supplied feedback to the theoretical calculations, which then determined that the growth sequence stabilized an unexpected interface structure that provides design flexibility at the perovskite / antiperoskite interface. Another example is our modification of the electronic properties of the antiperovskite Dirac semimetal Cu_3PdN (see technical progress section below). Feedback from theoretical doping calculations enabled positioning of the Fermi level, a common issue in Dirac semimetals, by nitrogen annealing.

These exemplify the computational and modeling aspects of the project combining with the synthesis, growth, and characterization to enhance the project outcomes.

Technical Progress We have made significant progress on synthesis of thin-film epitaxial antiperovskite materials and heterostructures, and in the characterization and understanding of their physical characteristics.

Using a combination of ab-initio interface calculations, and state-of-the art synthesis and atomic-scale structural and chemical analysis, we have achieved one of the pillars of our program, the successful interfacing of antiperovskite and perovskite structures and understanding of the bonding mechanism. This unique class of heterointerface based on nitride antiperovskite and oxide perovskite materials promises a new direction for materials design, opening a vastly unexplored avenue interfacing oxide perovskites with materials having dissimilar crystallochemical properties. We find that stabilizing such heterostructures with the structural and chemical quality required to promote the desired physical phenomena, and understanding the origin of this stabilization, required a combined effort of experimental synthesis, characterization, and ab-initio theory, primarily due to the constituting materials have large geometrical and chemical strain, such as is the case with perovskite/antiperovskite interfaces. We synthesized atomically sharp interfaces between nitride antiperovskite Mn_3GaN and oxide perovskite $(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$ (LSAT) as a prototype example of antiperovskite-perovskite interface. Using a combination of atomic-resolution scanning transmission electron microscopy (STEM) and spectroscopic techniques, we determined the atomic-scale structure and composition at the interface. The epitaxial growth between Mn_3GaN and LSAT is mediated by interfacial monolayer that acts as a bridge between the two “anti-structures”. We anticipate our results to be the starting point for the development of functional antiperovskite-perovskite heterostructures.

We have synthesized and characterized the nitride antiperovskite Cu_3PdN, proposed as a new three-dimensional Dirac semimetal. The experimental realization of Cu_3PdN and the consequent study of its electronic properties have been previously hindered by the difficulty of synthesizing this material. We report fabrication and both structural and transport characterization of epitaxial Cu_3PdN thin films grown on (001)-oriented $SrTiO_3$ substrates by reactive magnetron sputtering and post-annealed in NH_3 atmosphere. The structural properties of the films, investigated by x-ray diffraction and scanning transmission electron microscopy, establish single phase Cu_3PdN exhibiting cube-on-cube epitaxy $(001)[100]Cu_3PdN||(001)[100]SrTiO_3$. Electrical transport measurements of as-grown samples show metallic conduction with a small temperature coefficient of the resistivity of $1.5x10^{-4}$ /K and a positive Hall coefficient. Post-annealing in NH_3 results in the reduction of the electrical resistivity accompanied by the Hall coefficient sign reversal. Using a combination of chemical composition analyses and ab-initio band structure calculations, we determined the interplay between nitrogen stoichiometry and magneto-transport in the framework of the electronic band structure of Cu_3PdN. Our successful growth of antiperovskite Cu_3PdN thin films initiates investigation of its physical properties and their dependence on dimensionality, strain, and doping.

Future Plans We will expand our efforts to a broader class of antiperovskite materials, and to the manipulation of interfaces to generate new electronic and magnetic functionalities. These include novel magnetic structures at carbide antiperovskite interfaces, and induced polar and ferroelectric properties in antiperovskite heterostructures. An essential component of this work is the theoretical modeling of structural and ferroic order.

The antiperovskite carbides provide a broad class of materials with great potential for heterostructure applications. Our first efforts will be in Mn_3GaC, a material which in bulk shows collinear spin order. Heterostructures with the non-collinear Mn_3GaN promise novel interfacial spin structures qualitatively different from those at perovskite heterointerfaces. The larger number of magnetic ions in the antiperovkite unit cell compared to perovskites promise richer magnetic interactions, and the anion electronic characteristics of the antiperovskite magnetic ion compared to the cation perovskite magnetic ion leads to different electronic interactions. The lattice match of these two antiperovskites promise atomically abrupt interfaces. We will investigate the structure, electronics, and magnetism of these interfaces, guided by theoretical calculations.

Our geometric design of a perovskite polar metal (T.H. Kim et al, Nature **533**, 68 (2016)) uncovered design principles that control polar distortions. But basic design principles have not yet been discovered for antiperovskites. Understanding the propagation of structural distortions in an antiperovskite superlattice, and the change in phonon properties related to these distortions will feed into theoretical investigations proposing antiperovskite heterostructure layer arrangements and orientations susceptible to polar distortions. The structural and electronic characterization will play a central role in validating the theoretical predictions of interfacial structure and bonding.

Superlattices of antiperovskite and ferroelectric perovskite can be used to induce polar distortions in the antiperovskite layers and determine their propagation characteristics. $XNMn_3$ (X=Ag or In) and $BaTiO_3$ layers present a good lattice match, as do $ZnNMn_3$ and $PbTiO_3$. We will also explore new design principles with two nonpolar antiperovskites coupling different symmetries to generate improper ferroelectricity, with different stacking sequences controlling the polarization direction.

Broader impact Graduate and undergraduate student education is an integral part of this proposal. Our goal is broad experience for all students, not only in research, but also in the feedback process central to the MGI program. Our primary program is an annual research workshop for participants, collaborators, and potential collaborators. This immersive workshop provides the essential glue for the program, providing summary and brainstorming activities. It is an invaluable opportunity for junior participants, involving them in the collaboration/planning process, and also purposefully including them in the theory/experiment/characterization feedback that makes MGI successful. Students are co-advised by the team faculty. Beginning research students collaborate with laboratories of the UW-Madison PIs and collaborating National Laboratories.

Data Management and Open Access We have established a thermodynamic database of various perovksite materials using parameters collected either from experimental measurements or from first-principles-based calculations, and are extending this to antiperovskites. With the database, we have performed high-throughput phase-field simulations to generate a repository of ferroic domain structures and evaluated corresponding physical properties. We have also proposed several descriptive metrics and computer vision tools to quantify and visualize the microstructures, which can further facilitate the machine learning of structure-property relationship and enable microstructure-sensitive materials design. We will apply our data-driven approach to construct a thermodynamic database of antiperovskites informed by DFT calculations, with advanced antiperovskite/persovskite heterostructures and interfaces.

Advancing Along the Materials Development Continuum Antiperovskite materials have a broad range of ferroic properties, but specifically different from perovskites due to their inverted ionic arrangement that lead to their unique properties. This unique class of heterointerface based on antiperovskite and oxide perovskite materials promises a new direction for materials design, particularly in heterointerfaces, where they open a vastly unexplored avenue interfacing materials with dissimilar crystallochemical properties. We are only beginning to explore the antiperovskite materials suitable for epitaxial growth, and their interfaces with both antiperovskite and perovskite materials. This has great potential to be a commercially relevant technology for a range of electronic sensing and processing applications. A key component will be the development of antiperovkiste materials characteristics, parameters, and heterostructure design principles.

Publications

1. C. X. Quintela, et al *Epitaxial thin films of Dirac semimetal antiperovskite* Cu_3PdN. APL Mat. **5**,096103. (2017).
2. D. Lee et al, *Isostructural metal-insulator transition* under review at Science (2018)
3. D. Lee et al, *Sharpened* VO_2 *phase transition via controlled release of epitaxial strain,* Nano Lett. **17** 5614 (2017)
4. J.-M. Hu et al, *Phase-Field Based Multiscale Modeling of Heterogeneous Solid Electrolytes* ACS Appl Mat & Int.. **9**, 33341 (2017).
5. H. Lee et al, *Direct observation of a two-dimensional hole gas at oxide interfaces*, Nat. Mat. **17**, 231 (2018)
6. T.J. Anderson et al, *Interfacial B-site atomic configuration in polar (111) and non-polar (001)* $SrIrO_3/SrTiO_3$ *heterostructures*, APL Materials. 5 096110 (2017)

Engineering Stable Glass Films Using Molecular Design and Surface-Mediated Equilibration

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Website: 'none'.
Keywords: Stable glasses, molecular glasses, Mobile surface layer, Stable glass thin films, Suzuki cross-coupling

Project Scope

The goal of this project is to design molecular glasses with tailored structural motifs and intermolecular interactions that can produce stable glasses with specific characteristics upon physical vapor deposition (PVD) onto various substrates. It has been shown that enhanced surface mobility can allow rapid equilibration of molecules when the substrate is held below the glass transition temperature (T_g). We combine synthesis, high-throughput characterization methods, and molecular level insight provided by molecular dynamics simulations to design stable glasses with specific characteristics such as structural anisotropy or microstructures.

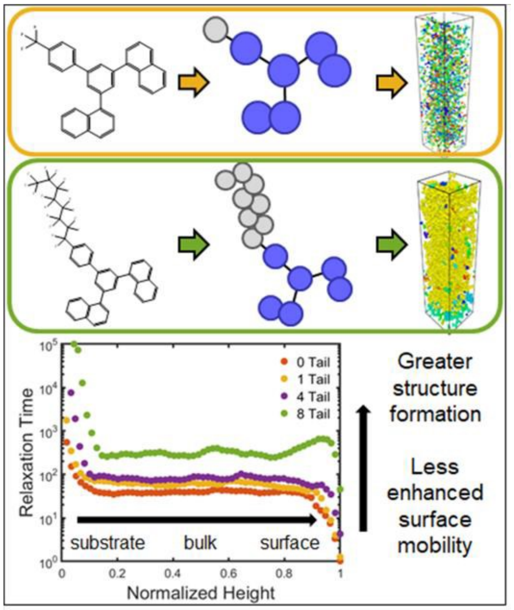

Figure. Coarse grained models of organic glass formers containing fluorocarbon tails of increasing length, corresponding to an increased tendency to separate and form microstructures. Simulated PVD is used to systematically study how these interactions and the resulting microphase separated domains influence ability to form stable glasses. This model suggests that increasing molecule tail length results in decreased thermodynamic and kinetic stability in PVD films. The relaxation time near the surface of ordinary glass films of these molecules remains bulk-like, and the surface diffusion is markedly reduced due to a trapping mechanism where the tails are unable to move between local phase separated

Relevance to MGI

The overarching goal of this project is to encode functional properties of stable glasses (SGs) in their molecular structure. To achieve this goal, it is important to predict the effect of changes in specific molecular motifs on the properties of SGs. Molecular dynamics simulations are an integrated part of the design and prediction process. Figure 1 shows an example, where a series of molecules with increasing fluorocarbon tail lengths were designed to induce microstructure during PVD. Simulations indicated that there is an interplay between structure formation and enhanced surface mobility, which is an important aspect of SG formation. We found that by increasing fluorocarbon tail length, the system would indeed form microstructures, but segregation and cluster formation hinders the mobility and thus stability. A balance between the two processes can be obtained by reducing the bulkiness of the molecule and the chain lengths. We have now synthesized a series of these molecules to test this prediction.

We have synthesized 20+ molecules and have made stable glasses of many of them. Insights provided by simulations, as the example above shows, are crucial in informing the structures of interest and changes needed to improve the outcomes.

Technical Progress

1. Origins of birefringence in stable glasses: Birefringence in PVD glasses often implies molecular alignment like liquid crystals. The molecules either tend to align along the substrate at cold temperatures, or normal to the substrate closer to T_g. As such, it remains unclear whether these glasses share the same energy landscape as liquid-quenched or aged glasses, which is an important fundamental question.

To address, the **Walsh** group designed has designed new molecules, such as (9-(3,5-di(naphthalen-1-yl)phenyl)anthracene) that retains a spherical shape due to their hindered rotation. **Fakhraai**'s lab then explored birefringence in these glasses and in collaboration with Profs. James Kikkawa and Joseph Sobutnik (Penn) showed that while the molecules remain perfectly isotropic, the PVD films are still optically birefringent, with the value of birefringence correlating with increased density. This is an important finding that shows 1- birefringence does not always imply molecular orientation, and 2- dense packing of isotropically oriented molecules can be achieved upon PVD, likely sharing the same energy landscape as aged glasses.

We are currently studying analogs of this molecule that have the same molecular weight, but with more rotational freedoms in their substituents. Our preliminary theoretical and experimental studies imply that these molecules may form better packings, due to increased intra-molecular entropy, but may also show molecular orientation upon PVD. **Riggleman** and **Fakhraai** are exploring the effect of molecular alignment or lack thereof, on surface diffusion and mobility.

2. Design of Novel Glassformers: Walsh and **Fakhraai** have designed a series of 20+ molecular glassformers that form SGs. Key variations in structure such as intra-molecular entropy and inter-molecular interactions have been explored to determine their effect on the surface mobility and stability. It is found that aspect-ratio can be an important factor in enhancing mechanical properties (Collaboration with Kevin Turner, Penn) while not significantly affecting stability. Intra-molecular degrees of freedom play an important role in enabling more pathways towards equilibration, likely contributing to enhanced stability.

3. Trisarylbenzene Glassformers with Fluorinated Tails: Trisarylbenzes with fluorinated tails could provide useful applications. Similarly, structured polymer bilayers have been used to separate charge between donor and acceptor components in photovoltaics. Surface-Mediated Equilibrium (SME) during PVD offers a powerful method to create these bilayers without structure disruption by allowing each surface layer to optimize its local configuration. Three compounds with various tail lengths and levels of fluorination have were synthesized by Georgia Huang, an undergraduate student at **Walsh** group. **Fakhraai** group is currently exploring their glass- and stable glass- forming properties.

Riggleman's simulations showed that phase-separated microstructures can form during simulated PVD of coarse-grained surfactant-like molecules with various fluorocarbon tail lengths (Figure 1). We have found that SG of C-1 molecule do not form any significant phase-separated structures and remains disordered, while the C-8 molecule develops some local structure. However, the formation of structure appears to prohibit stability. This is a significant finding that implies strong correlation between structural moieties and their ability to produce stable glasses, representing a knob that can be tuned. **Fakhraai** has experimentally verified some of these predictions.

Future Plans

1- Bulk stable glasses: A fundamental question that arises from the studies above is whether birefringence (either due to molecular ordering, or anisotropic packing) is necessary for stable glass formation, or it is just a bi-product of the directional deposition of molecules. To that end, the **Riggleman** group has been exploring whether it is possible to create a bulk stable glass without resorting to the simulated vapor deposition procedure. They adopted a modification of the temperature-accelerated molecular dynamics (TAMD) algorithm, which is an enhanced sampling technique commonly used in biological simulations to force a system to escape from low energy states. We anticipate that this algorithm will enable us to create bulk stable glasses that do not require simulated vapor deposition, which will provide deep insights into the nature of stable glasses.

2- High-throughput experiments: We have recently finished the design of a new ultra-high vacuum chamber that will allow us to perform in-situ and high-throughput experiments on PVD glasses with a wide range of deposition temperatures. We plan to ramp up our studies of structure-function relationships and start our exploration of the effect of film thickness on properties of PVD glasses.

3- Publicly available experimental and simulation meta-data: We plan on launching a new website to make our molecular structure and properties as well as simulation meta-data available.

Broader impact (Only required for NSF projects)

We have employed a diverse group of students and trainees for this project. The students/trainees work together to tackle diverse range of problems. The starting material for the Suzuki cross-coupling reaction used in this research, 1-bromo-3-chloro-5-iodobenzene, is synthesized every semester by undergraduate students in the Chem 245 lab (undergraduate organic lab) taught by Walsh. The material is collected at the end of each semester and used for further synthesis, which is performed by undergraduate students in Walsh lab. Undergraduate and graduate students collaborate on all aspects of the project from designing and synthesizing the compounds, to characterization and modeling and simulation. All students work with at least two PIs on the project. The group meets weekly on Fridays to discuss progress and challenges.

We are planning on making the structure and glassforming abilities of all the synthesized compounds publicly available through a collaboration with NIST. This will help other researchers to use these compounds for other applications. Our compounds have a broad and accessible range of T_gs (273-373K), which is remarkable for non-polymeric glasses.

Data Management and Open Access

While we are just beginning to write our first publications primarily supported by this award, data will be made publicly available as it is published in either text-readable or open-access data formats. Furthermore, any simulation and analysis codes written for the purposes of this project will be made available on the website for this project that will be launched soon. As an example of this practice in the context of other work, **Riggleman** has a section on his website for simulation codes (rrgroup.seas.upenn.edu/code/). These sections will be expanded as we begin publishing work primarily supported by the MGI program. To make our molecular and glass characterization more broadly available, we have held preliminary discussions with scientists (Dr. Debra Audus) at the National Institute for Standards and Technology to provide them with our structure and property characterization of the glasses we have prepared.

Advancing Along the Materials Development Continuum

Molecules with chemical structure similar to those employed in our studies are commonly used as the active layers in organic light emitting diodes (OLEDs). The chemical and processing routes explored in our studies could uncover a novel class of more efficient materials for OLED devices. Through a separate collaboration between **Riggleman** and ExxonMobil, we are discussing areas of mutual interest for collaboration, though these discussions are still in early stages.

Publications

1- Cubuk, E. D., *et al.* "Structure-property relationships from universal signatures of plasticity in disordered solids.", *Science,* **358,** 1033-1037 (2017).
2- 2- Liu, Tianyi, *et al.* "Birefringent Stable Glass with Predominantly Isotropic Molecular Orientation." *Physical review letters* **119,** 095502 (2017).

DMREF: Collaborative Research: Design and synthesis of novel materials for spin caloritronic devices

Lead Investigator: Gregory A. Fiete, Department of Physics, University of Texas at Austin, fiete@physics.utexas.edu
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Website: None.
Keywords: caloritronic, magnon, spin-orbit, thermal, correlated

Project Scope

The project combines theory, characterization, and materials synthesis efforts to better understand spin caloritronic phenomena and devices. The effort is built on three key and interlocking elements: (1) A theoretical understanding of the physics associated with spin caloritronic phenomena, including computational and theoretical tools for screening and designing new materials for spin caloritronic devices. (2) Measurement of spin caloritonic properties of a broad variety of single crystals of magnetic and antiferromagnetic insulators (ferrimagnetic rare earth iron garnets, double perovskites, spinels, antiferromagnetic layered materials produced by high-pressure synthesis). (3) The fabrication of spin caloritronic thin films devices exploiting materials with superior properties.

Relevance to MGI

An iterative feedback loop is formed among the co-PIs. Fiete will develop a microscopic theory for understanding the physics associated with spin caloritronic phenomena, as well as computational tools for screening and designing new materials for fabrication of spin caloritronic devices. The simulation work will include the materials for generating spin current, the metallic materials used to convert spin current into electric potential with a high efficiency, and the interface design. The project will capitalize on the extensive experience and expertise of Zhou in growing a broad range of bulk single crystals with peculiar magnetic properties like uniaxial, easy-plane, anisotropy and biskyrmion textures. Earth abundant elements are prioritized in the computational screening and design for the spin caloritronic devices. Some of the most challenging problems lie in the material synthesis, especially with Earth abundant elements, which will be addressed with high-pressure synthesis. The procedures, the fabrication, and measurement techniques for spintronic devices developed in Chien's laboratory will be used to study the performance of spin caloritronic devices made from these new materials. The experimental results will be compared with the computational model and provide new inputs to further refine the model, forming the feedback loop.

Technical Progress

(GAF) In collaboration with a PhD student working on the project, model Hamiltonians for an AFM system (with non-collinear spin texture) are being developed and solved to extend existing theories focused on systems with a net magnetic moment (ferri and ferro magnets). The insights gained from this work will guide computationally focused material-specific studies.

(CLC) Proper choices of materials and methods are essential for exploring pure spin current phenomena and devices. By studying spin injection we show that ferromagnetic insulators (e.g., YIG) are good choices, while ferromagnetic metals (e.g., permalloy = Py, Co) are not. Material selection is important to distinguish pure spin current effects measured via the inverse spin Hall effect from parasitic effects (e.g., rectification, anomalous Nernst) in Spin pumping (SP) and longitudinal spin Seebeck effect (LSSE) experiments.

(JSZ) In order to identify and synthesize materials for caloritronic devices that are superior to the most popular combination of YIG and Pt, the ferromagnetic insulators $La_{1-x}Sr_xMnO_3$ (LSMO) and $LaMn_{1-x}Ga_xO_3$—with a magnetic moment intensity triple that of YIG—have been grown with the floating zone method. In addition, perovskite $SrIrO_3$ (SIO) [been predicted to have an ISHE much larger than Pt] has been synthesized under high pressure. The LSMO/SIO device is being fabricated by pulsed laser deposition and will be sent to CLC at JHU for testing.

Future Plans

(GAF) In the short-term model Hamiltonians will continue to be the focus of theoretical study to uncover general design principles based on energetic and symmetry arguments. Later, a transition to more computationally and materials-specific calculations will be made.

(CLC) Crystals and samples are being grown at both UT and JHU for spin caloritronic measurements. The so-called inverse Rashba-Edelstein effect in Bi and Bi/Ag bilayers and all-insulator magnonic devices will be studied.

(JSZ) Under the hypothesis that a metal showing a high ISHE would also have a high thermoelectric powder S, a new metal oxide $SrPbO_3$ will be synthesized and fully characterized. The preliminary data show S~ 100 μV/K, which is significantly higher than a S~ 9 μV/K of Pt.

Broader Impact

(GAF) A graduate student is being trained in theory and interaction with experimental and synthesis groups. The student also participated in a UT outreach program, joint with JSZ.

(CLC) Undergraduate physics majors are scheduled for a summer outreach program to interest them in pursuing graduate studies in the area of the physics of materials.

(JSZ). A demonstration of crystal growth with an image furnace in a public event of Explore UT has been given. Students involved in the project explained to visitors the entire process from how the functional materials can be designed with a quantum mechanical calculation to the real time demo of crystal growth.

Data Management and Open Access

Publications will include information on how to access the experimental and theoretical data from the project.

Advancing Along the Materials Developments Continuum

Spin caloritronic devices are candidates for electrical components that turn heat into usable energy. Our integrate effort targets a system that can be useful for establishing practical limits on how efficiently this can be achieved.

Publications

W. Lin and C. L. Chien, "Evidences of pure spin current", submitted to Nature Materials.

DMREF: Multiscale Theory for Designing Hierarchical Organic Materials formed by Self-assembly

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Website: https://www.chem.indiana.edu/mmdl/
Keywords: molecular design • organic materials • nanostructures • 3D self-assembly • multiscale modeling

Project Scope

Our objective is to understand how intermolecular interactions drive the hierarchical assembly of molecular building blocks into patterned and functional organic materials. We focus on the ordering of flat organic molecules onto graphite and in solution to produce supramolecular packing structures that are of interest for organic photovoltaics and optical materials. Force field and multiscale simulations will be developed for design. We hypothesize that co-facial and ionic contacts between synthesized molecules direct patterned assembly in 2D and in 3D. We expect to show ordering of functional molecules into materials with light capture and emission properties.

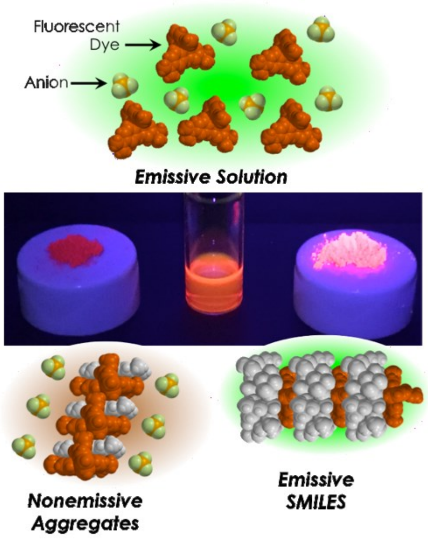

Figure. (left) Emission from fluorescent dyes in solid state (powder shown) is normally quenched. But the bright emission seen in solution (middle) can be rescued (right) by hierarchical organization into small-molecule ionic lattices (SMILES).

Relevance to MGI

This project addresses the challenges of MGI by using an integrated approach within the Molecular Materials Design Laboratory (MMDL) at IU to design molecules and their packing structures by close collaboration between experts in molecular and supramolecular modeling, molecular synthesis, and real-space surface and film characterization. These solutions emerge from weekly meetings involving PI, Co-PIs, postdocs, and graduate student researchers involved in theory, synthesis, and characterization. The weekly meetings are augmented by annual full-day strategic planning workshops. Within each sub-field, significant advances are being made in sequence-specific molecule synthesis, use of co-solutes to control self-assembly, new modes of multiscaling, and computations of □-□ stacking between molecules larger than benzene. Working together, a multiscale approach is intrinsic to the design of long-range and hierarchical ordering of organic materials in 2D and in 3D. Consideration of new modes of hierarchical ordering led to the discovery of a whole new class of optical materials called small-molecule ionic lattices (SMILES) that circumvent a 150-year old problem of aggregation-induced quenching. This discovery exemplifies the MGI goal of accelerating materials discovery by building the fundamental knowledge base needed for designing and making molecular materials with specific, desired functions.

Technical Progress

Controlling the hierarchical self-assembly of organic molecules into highly organized 2D architectures is key to achieving bottom-up fabrication of functional organic films. We have designed molecular platforms to leverage the feedback look of synthesis – surface characterization – modeling. This feedback loop is at the heart of the MMDL. We used it to gain new insight into molecular level aspects of the self-assembly occurring in highly organized 2D architectures. Molecular dynamic (MD) simulations provided spatial and temporal information on self-assembly of alkoxybenzonitriles at the octanoic acid/graphite interface. The self-assembly was benchmarked with scanning tunneling microscopy experiments. Simulations successfully predicted the molecular packing.

Non-covalent interactions play crucial roles in materials science. Special attention has focused on ππ interactions due to their importance in hierarchical structures with electronic applications. However, accurate determination of binding energies between large π-surfaces is challenging. We uncovered substantial discrepancies between calculated energies (dispersion-corrected density functional methods) and those derived from experiment. Theory overestimates the energy substantially. We are carrying out systematic studies on a test set of large π-systems to develop an efficient protocol for the determination of accurate interaction energies.

We have developed multiscale methods that allow retention of the atomic level details by taking the course-grained picture back to an atomistic one. We showed how the multiscale approach involving large time steps allows simulations of plasmons in materials not possible with traditional methods. We are using density profiles in place of the many-particle MD picture to enhance the simulation speed while retaining atomistic details.

We have also made advances in the synthesis that will enable understanding and control. We developed high-yielding, stepwise synthesis pathways to the macrocycles we are studying. This is significant by allowing us to alter the intermolecular code that guides assembly, and to add electronic and optical character to materials.

The SMILES discovery highlights scientific progress on controlling the hierarchical organization of molecules in materials. The discovery of a totally new class of fluorescent materials was made in collaboration with Bo W. Laursen (Denmark). The discovery provides the first practical and reliable solution to a 150-year old problem called aggregation-induced quenching that renders optical materials made from the hierarchical packing of dyes unpredictable and poorly understood. This perplexing problem was overcome by the creation of SMILES. These materials are composed of a cationic dye and anion complex. The ionic lattice formed in the solid state is believed to both spatially and electronically isolate the cationic dyes from each other. By simply mixing the dyes with the macrocycles, both the color and the bright emission intensity seen in solution can be directly translated into solids of all varieties. For this reason, this new material has the potential to positively impact applications where fluorescence is critical, such as in lighting, safety materials, and luminescent solar concentrators.

Future Plans

The future plans for the project are to develop and extend the discoveries made in hierarchical materials. These include combining multiscale simulations with experimental variations in self-assembly, all characterized with SAXS, to develop fundamental understanding of hierarchical structures and design custom functionality in multi-component molecular films for organic photovoltaics and organic semiconductors. We also expect to greatly extend the discovery made in fluorescent materials composed of small-molecule ionic lattices (SMILES). The extremely high densities of □-based fluorophores make the SMILES materials of interest for labeling, display technology, and solar energy, among other potential applications. Despite their promise, much remains unknown experimentally and theoretically about the molecular-level details of how the organization (such as □□ stacking of large aromatics) and long-range coupling of fluorescent molecules in solid-state materials produce high-intensity emission and new emissive states. SMILES materials offer the first real chance to address these questions by enabling strategies to be developed for the first time to deliberately re-introduce and ultimately tune-up coupling the dyes in a rational manner. These materials will therefore enable the Molecular Materials Design Lab to address untested assumptions about mechanisms of energy transfer in the excited state of organic materials.

Broader impacts

To impact communities with the MGI philosophy outside our team, over 37 presentations have been given around the country and the world. 800 people were impacted. PI Flood and CoPI Tait co-chaired a four day symposium on “Hierarchical Self-assembly of Organic Monolayers, Bilayers, and Films,” at the ACS Meeting, San Francisco (2017) that included 54 oral presentations, graduate students, undergraduates, and visitors from eleven foreign countries. Outreach activities are ongoing at local children's science center WonderLab in Bloomington, impacting 200 members of the public so far. One graduate student is undertaking a graduate education research analysis of the collaborative structure of our project. 12 pre-service teachers discussed the observation and inference aspect of the nature of science. She shared our collaborative strategies in a graduate class to address nature of science and to bridge between authentic scientific research and scientific inquiry in the classroom.

Data Management and Open Access

Digital data and program outputs are being made publicly accessible and useful to the community by providing it in the primary literature. The digital software program to carry out multiscale simulations (DMS) will be released as part of Nanohub. The project has provided the community with access to its outputs in the form of newly derived force field parameters. They will be made available to the CHARMM user community. We are now making plans for combining experiment and computation data into a searchable materials data infrastructure for SMILES materials. A sustainable and scalable database is envisioned. Initially, the database will be populated with data from SMILES materials collected by our team and others. In the future, it can be made open for contributions from other types of fluorescent materials composed of molecular building blocks.

Advancing Along the Materials Development Continuum

The project helped accelerate the discovery of a new optical material, the fluorescent SMILES. The MGI approach provided a mandate to screen various methods for preparing new materials. The prospects for commercialization of SMILES are good. Hurdles for commercial viability relate to customer discovery, hence participation in I-Corps. One patent application has been filed on macrocycles and one provisional patent has been filed on SMILES. However, further development of fundamental design rules is needed to accelerate emergence of a totally new level of understanding and mastery of optical materials composed of organic molecules.

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Polymer Property Predictor and Database

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Keywords: polymers, databases, machine learning, information extraction pipeline

Project Scope

Polymer informatics has the potential to revolutionize material discovery; however, to maximize the utility of informatics, large, accessible datasets are required. Our ultimate goal is to harness the power of computers and reduce the human effort needed to develop such datasets by developing generalized pipelines for polymer property extraction from the literature. In the process, we are also making our datasets freely available online.

Relevance to MGI

In order to fulfill and surpass the MGI goal of materials discovery in half the time with half the resources, experimental data is needed to ensure reproducibility of experiments, validate new physics-based models, and train artificial intelligence. However, the current painstaking paradigm of manually extracting data from the literature is time-consuming, expensive and ultimately limited. Here, we focus on collecting this trapped scientific data, specifically, experimentally measured polymer properties by harnessing the power of machine learning and automation. As this project is at the intersection of machine learning and polymer science, the team is also made up of computer scientists with expertise in machine learning and chemical/molecular engineers with expertise in polymer science in order to maximize productivity. Thus far, we have developed two pipelines for information extraction from the literature, which have resulted in a database of Flory-Huggins chi parameters and glass transition temperatures along with the data provenance. Many aspects of our work are generalizable, and we expect that the tools developed will assist with further collection of experimental polymer data and that the resulting freely available polymer data will fuel not only informatics, but also research in general.

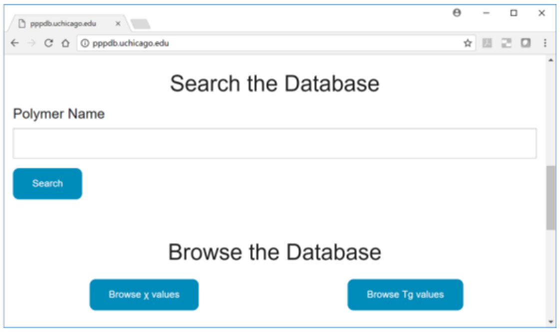

Figure. A screenshot of the database available at http://pppdb.uchicago.edu.

Technical Progress

Our initial efforts involved a simple pipeline starting with html versions of articles from the journal *Macromolecules*. The relevant meta-data was automatically extracted and then the polymer names and properties were extracted using crowdsourcing. From these efforts, we found that a significant amount of human time was spent viewing articles that did not contain the property of interest, the Flory-Huggins chi parameter. To see if we could reduce this time, we used supervised machine learning to identify the most promising articles, achieving both precision and recall around 90% for the case of polymer-polymer Flory-Huggins interaction parameters. Following up on this initial work, we sought to further decrease the need for human input. Turning to a new property, the glass transition temperature, we built a more sophisticated information extraction pipeline. This pipeline relies on a modified version of the natural language processing software, ChemDataExtractor,[1] which identifies chemical entities and after our modification, finds glass transition temperatures using a rule-based approach. Building on this effort, we developed software to identify which chemical entities were polymers and set up multiple modules to deal with cases where the output from ChemDataExtractor was not a polymer-property pair. Specifically, these other cases, which in total account for almost 80% of the output, deal with compound-property pairs, solitary properties without a chemical entity, and label-property pairs (e.g., polymer1A). Using this pipeline, thus far we have identified roughly 250 polymer-property pairs and expect to be able to easily capture at least 100 more.

Future Plans

Based on the results of the two developed pipelines, we found that one of the largest bottlenecks was the identification of polymer names and linking those names to structure, synonyms and acroymns. Thus, we have plans to develop a small, manually curated, annotated polymer name dataset including synonyms and acronyms and then use this dataset to improve computer recognition of polymers via machine learning. This will address issues such as the identification of polymer classes, labels, extraneous prefixes and suffixes, etc. Additionally, improved polymer recognition would add to the usefulness of the resulting database by improving searchability and is relevant to our ultimate goal of generalized polymer property extraction pipelines for use in informatics and research.

Data Management and Open Access

All of the datasets are freely available at http://pppdb.uchicago.edu. To further improve the accessibility of this data, it is also available at the Materials Data Facility (https://materialsdatafacility.org/). Additionally, work is in progress to develop an automated pipeline to transfer the data to Citrine Informatics, which hosts one of the largest materials databases. Finally, modifications to the ChemDataExtractor[1] to find the glass transition temperature were incorporated within their codebase and are available at http://chemdataextractor.org/.

Advancing Along the Materials Development Continuum

Although there are several polymer databases available, most of them suffer from either a lack of digitization, small sizes, or prohibitions on downloading all of the data. However, for applications such as polymer informatics, which has the potential to discover, develop, and deploy new materials twice as fast at a fraction of the cost, FAIR (Findable, Accessible, Interoperable, Re-useable) data is needed. Ultimately FAIR data in the quantities needed for informatics is not possible without either the development of pipelines such as ours or significant funding to develop databases with human curators. Thus, the results of our efforts are meant to follow these FAIR data principles allowing researchers and engineers from across the globe in academia, government and industry to apply informatics to fulfill the objective of MGI.

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Programmable Chemomechanical Materials

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Website: none.

Keywords: chemomechanics, reaction-diffusion networks, soft robotics, chemical oscillators.

Project Scope

The research is divided into two thrusts; dynamics of reaction-diffusion networks and chemomechanics of gels. The objectives are to engineer reaction-diffusion networks that generate prescribed spatio-temporal chemical patterns, which drive chemo-responsive gels to change volume and generate force. We utilize the Belousov-Zhabotinsky (BZ) chemical reaction, confined in reactors on the 100 micron scale, fabricated in the elastomer PDMS using microfluidic techniques. The force generating chemomechanical elements are PNIPAM gels to which the BZ catalyst is covalently bonded to the backbone.

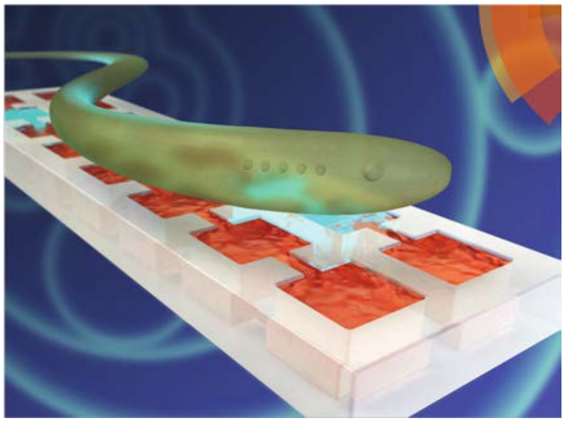

Figure 1. *Lab on a Chip* cover illustration of a microfluidic reaction-diffusion network designed to produce a spatiotemporal pattern equivalent to an eel's neural network that controls swimming.
T. Litschel, M. M. Norton, V. Tserunyan and S. Fraden, *Lab on a Chip* **18**, 714, (2018).

Relevance to MGI

To achieve the MGI goals we placed theorists and experimentalists, and engineers, neuroscientists, chemists and physicists in the same labs and offices. This led to rapid exchange of results between the disciplines and has pushed the bioinspired science further than had all parties worked independently. One consequence of deeply intertwining theory and experiment is that the papers are longer and more difficult to complete, but are more meaningful and impactful than separately published results. Highlights include fabricating artificial nervous tissue based on design principles found living organisms and modeling the artificial tissue using a combination of non-linear dynamics, network and neuroscience theories. Our work on this subject was selected for the cover of Lab on a Chip and as a "HOT" article, a designation reserved for papers receiving particularly high scores during peer review. Implementing the MGI strategy has transformed the career trajectory of the students. One theory graduate student, Ian Hunter, has grown from being solely a theorist into designing and performing experiments and is on track to becoming an exceptionally well rounded scientist.

Technical Progress

Highlights of the reaction-diffusion (RD) networks thrust, are, first, the production of the first fully synthetic reaction-diffusion network that has functionality similar to the neural network that controls the swimming of the lamprey. To accomplish this, we have fabricated a reaction-diffusion network in which inhibitory and excitatory coupling were concurrently utilized in a PDMS microfluidic chip to create a biomimetic neural tissue. The network comprises two linear activator-coupled arrays with transverse inhibitor coupling. Low-levels of light-inhibition were applied to the array to control the direction of wave propagation. A second highlight is the study of star, or acyclic, RD networks, which are important as all networks are comprised of either cyclic or acyclic sub-graphs. We combined experimental measurements with theoretical modeling of star network dynamics at 3 different levels ranging from finite element, which provides an accurate description of the networks at the cost of conceptual understanding to phase models which simplify and idealize behavior, but deliver conceptual understanding. A rich phase behavior was uncovered as a function of the number of arms of the star and the degree of coupling strength. In one limit, we were able to reduce high dimensional dynamics to one dynamical variable, which allowed full qualitative and quantitative understanding of the network behavior. A third highlight is development of an experimental and theoretical model of a chemical network to develop optimal methods for non-linear control. This system consists of 3 oscillators arranged on a ring and possesses two attractors, clockwise and counter-clockwise waves. These are known as splay states because each oscillator fires with the greatest possible phase difference between neighbors. Reaction-diffusion networks with multiple dynamical attractors have the potential for creating control circuits for soft-robotics with multiple "gaits" using a single network, or can be used for storing information. Using a phase-model, we examine the dynamical attractors of the system as a function of light-gradients that, to leading order, change the frequency of each drop. This theory behind this process is shown in Fig. 2A-B. The phase-portrait of the unperturbed system is shown in Fig. 2A and possesses two attractors with basins of attraction that are equal in size. As the light gradient is increased, the basins change in relative area and the attractors move slightly. At a critical light gradient, the system undergoes a bifurcation that eliminates one of the splay states, Fig. 2B. This provides an open-loop control strategy that is being tested experimentally. An optimal control light perturbation that minimizes the control effort is also being investigated. For this project, theory leads experiment (an image of the PDMS array is shown in Fig. 2C); experimental results will be used to critique the hypothesis shown in Fig. 2 and make improvement.

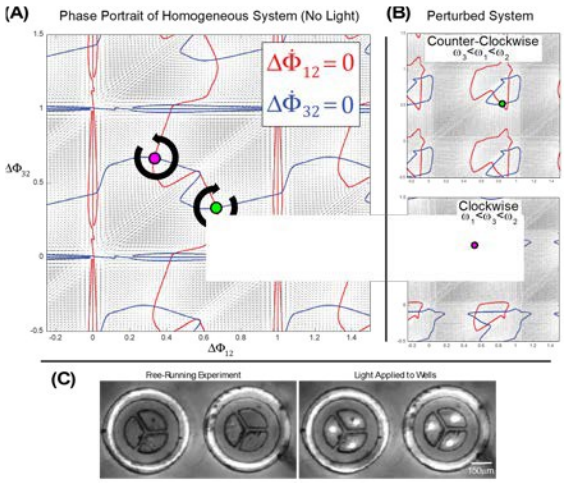

Figure 2. (A) Phase model prediction of the phase-portrait of the 3-ring network. Red and blue lines are nullclines, gray arrows are the local system velocity. The two attractors of interest are labeled as green (clockwise wave) and magenta (counter-clockwise wave) circles. (B) When light is applied, the natural angular frequencies of the nodes decreases. (C) Stills from preliminary experiments showing the free-running and light-perturbed systems; in both cases light is applied to a ring-well around the system to maintain a constant chemical boundary condition.

Future Plans

We made significant progress in both the theoretical understanding and fabrication of reaction-diffusion networks and the prospects for rapid progress in the near future are high. Our pioneering research will have an impact in the emerging field of systems chemistry, which in analogy to systems biology, is concerned with networks of chemical reactions. Up to now, systems chemistry has focused on the reaction networks themselves. Our work is one of the first to focus on the spatial extent of chemical networks and we have made substantive progress in developing a general framework to engineer a wide range of spatiotemporal patterns in chemical networks. The remaining challenges are to develop optimal control strategies. One problem at the forefront of research on non-linear networks is to establish the minimal size of a subset of a network that can be used to control an entire network. The solution of this problem is known for linear networks, but no solution exists for non-linear networks. Our work will shed light on this important problem in control of non-linear networks.

The development of chemomechanical actuators remains a great challenge. There is an absence of understanding of the underlying physicochemical basis of chemoresponsive gels. The experimental systems suffer from lack of reproducibility, there is a bewildering range of unexplained behaviors, and there is a lack of clarity on which non-equilibrium effects are transient and which are steady-state. Faced with this undesirable state of the field, our approach has been to take a step back backward. Currently active gels are synthesized in one-pot methods. The virtue is simplicity, but the gels suffer from large and uncontrolled variability. We are currently investigating 2-step methods in which uniform gels are synthesized and subsequently functionalized, enabling systematic optimization and characterization gels as a function of a number of important physicochemical properties, such as the polymer, gel rigidity, gel uniformity and catalyst concentration.

Broader impact (Only required for NSF projects)

Several of the undergraduate researchers are minoring in art. This led to a collaboration with two Brandeis sculptors to create an art piece inspired by our DMREF research that was presented in an annual university art fair that was designed to communicate our research goals and methods to a general audience.

Data Management and Open Access

Any software used for modeling chemomechanics, analyzing NMR or x-ray scattering data developed in the course of this research will be freely distributed and available for download on the groups' websites when they are reliably bug free. The codes and algorithms used will be provided without any restriction or under the terms of the GNU Public License version 3.

Advancing Along the Materials Development Continuum

The goal of this project is to establish the engineering and design principles for materials with the functionality of neural tissue and muscle using model experimental systems. The gels and chemical reactions we use are intended to provide proof of concept of autonomous chemical based soft robots, but the forces generated, response speed, displacement amplitude and chemical safety of the chemomechanical gels need to be improved for applications.

Publications

N. Zhou, X. Cao, X. Du, H. Wang, M. Wang, S. Liu, K. Nguyen, K. Schmidt-Rohr, Q. Xu, G. Liang, B. Xu, *Hyper-Crosslinkers Lead to Temperature- and pH-Responsive Polymeric Nanogels with Unusual Volume Change*. Angew. Chem. Int. Ed. **56**, 2623 (2017).

T. Litschel, M. M. Norton, V. Tserunyan and S. Fraden, *Engineering reaction–diffusion networks with properties of neural tissue*, Lab on a Chip **18**, 714, (2018).

Inorganometallic Catalyst Design Center

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Keywords: metal organic frameworks; catalysis; active site; electronic structure

Project Scope

The Inorganometallic Catalyst Design Center (ICDC) devotes itself to the computationally guided discovery of new classes of energy-science-relevant catalytic materials and of their underlying structure-function relationships critical to advancing further catalyst discovery. ICDC pursues hypothesis-driven experimental and computational and theoretical research in the area of heterogeneous chemical catalysis. We focus on chemistry at the forefront of the shale-gas revolution, especially: (a) catalytic transformations of C1–C4 alkanes into feedstocks and (b) catalytic liquefaction of geographically stranded gas. In addition to the discovery of new classes of catalytic materials, ICDC work elucidates the structure-function relationships that define their performance.

Relevance to MGI

We develop novel quantum chemical, molecular mechanical, and combined quantum mechanical and molecular mechanical approaches to explore the structures, stabilities, activities, and selectivities of realized and as-yet-unrealized catalytic materials, where the latter are proposed as targets for synthesis by the experimental teams in the Center. Moreover, we use the results of the quantum mechanical calculations to develop microkinetic models.

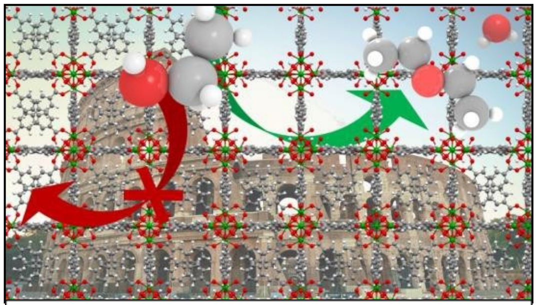

Figure 1. Using the precisely engineered, reactive structure of a metal-organic framework, ethanol can be induced to dehydrate to diethyl ether (following the green arrow pathway) but not ethylene (the blocked, red-arrow pathway.

Technical Progress

As described in roughly 100 peer-reviewed papers published since the inception of ICDC less than 4 years ago, we have theoretically, computationally, and experimentally explored— from a fundamental catalysis science perspective— a diverse collection of energy-relevant transformations, all catalyzed by tailored materials in the extremely rich field of MOFs.

Future Plans

We plan to continue studying catalysis at metal organic frameworks using a synergistic approach that involves theory, computation, synthesis of novel materials, characterization and catalytic testing.

Publications

ICDC publications are available at www.chem.umn.edu/ICDC

Interoperability of advanced sampling and electronic structure codes and data reproducibility

Giulia Galli (UoC&ANL), Juan De Pablo (UoC&ANL), Marco Govoni (ANL), Francois Gygi (UCD), Jonathan Whitmer (ND), Maria Chan (ANL), Paul Fenter (ANL), Nicola Ferrier (ANL), Sharon Glotzer (U.Michigan), Mercouri Kanatzidis (NU), Monica Olvera de la Cruz (NU). Paul Nealey (UoC&ANL), D.Talapin (UoC&ANL).

In this talk we will present the activity of the Midwest Integrated Center for Computational Materials (MICCoM: http://miccom-center.org/), with focus on recent results on code interoperability and data reproducibility. MICCoM develops and disseminates open source software, validation procedures and data to predict and design functional materials for energy conversion processes. The Center's vision is built on the premise that the discovery and design of innovative materials requires the ability to predict transport and dynamical properties of complex systems across multiple length scales. The distinctive objectives of the center are therefore to: (i) develop **interoperable codes** for simulation of materials at multiple length and time scales; (ii) focus on **heterogeneous materials**, inclusive of defects, interfaces and building blocks assembled out of equilibrium; (iii) focus on **spectroscopic and transport properties**.

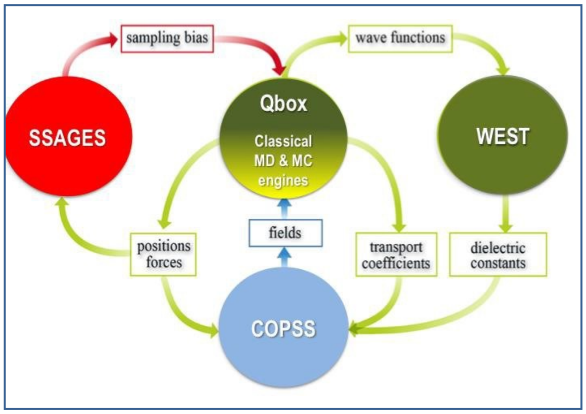

Figure 1: Illustration of interoperability of the codes developed by MICCoM (Qbox, WEST, SSAGES and COPSS), and of classical MD and MC engines used within the center. Arrows indicate data shared between the codes.

Software -- The four interoperable codes developed by MICCoM (WEST, Qbox, SSAGES and COPSS) are summarized in Fig.1. **WEST** performs large-scale many-body perturbation theory calculations providing electronic and optical spectroscopic characterization of complex materials. Recent additions include the calculation of electron-phonon interaction in large systems and the solution of the Bethe-Salpeter equation in finite field. **Qbox** is a first principles molecular dynamics (MD) code using Density Functional Theory (DFT) and hybrid-DFT. In addition to the simulation of thermodynamic and structural properties of materials, Qbox allows for the calculations of vibrational spectra, ionic conductivity and, since recently, heat transport coefficients [1]. While public versions of Qbox and WEST existed before the center was established, **SSAGES** and **COPSS** were born with MICCoM. SSAGES provides a comprehensive suite of advanced methods for phase space sampling organized into a unified framework that can be used as a wrapper for quantum and classical MD and Monte Carlo (MC) engines. We recently coupled SSAGES [2] and Qbox coupled in a seamless manner [3]. **COPSS** provides a suite of sophisticated techniques to couple continuum and particle-based simulations for neutral, charged, and polarizable particles interacting in a dielectric and hydrodynamic continuum.

MICCoM is organized into four code teams – WEST, Qbox, SSAGES and COPSS, with team leaders responsible for software development and the corresponding verification and validation tasks. There are presently four tasks defined according to their materials focus: **Semiconductor Nanoparticles** (SNP), **Thermoelectric materials** (THM), **Liquid crystals** (LC), and **Solid/Water interfaces** (SH2O). All four tasks address heterogeneous systems with complex interfaces and/or building blocks, and include calculations of spectroscopic and/or transport properties. The objective of these tasks is not only to provide the community with validated models, but also with tutorials and detailed documentation c [illegible] s.

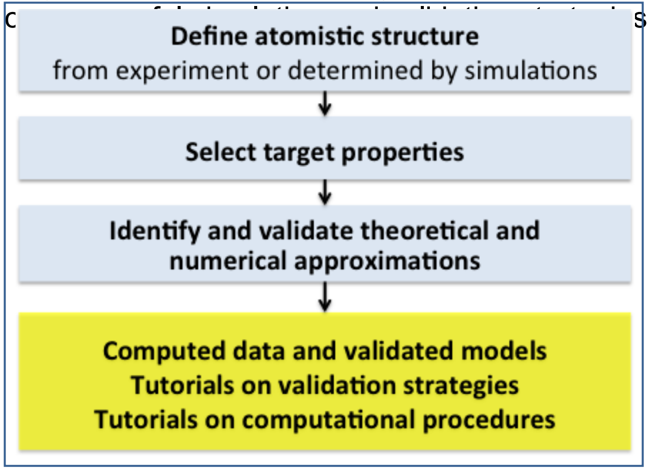

Figure 2: Validation strategy and expected outputs.

Validation – Establishing robust validation procedures is a major goal of the Center (see Fig.2). Procedures have been identified for interfacial properties of specific embedded and isolated semiconductor nanoparticles, and for elastic properties of inhomogeneous liquid crystals that exhibit topological defects [4]; these validation procedures continue to be refined and augmented with data for additional systems as they become available. Computation and measurement of thermal transport coefficients for doped semiconductors are in progress, with additional work required to define robust and general validation procedures. The same is true for X-ray reflectivity profiles of aqueous solutions interfaced with oxides.
In addition, collections of computed data for simple molecular properties (e.g. ionization potentials and electron affinities) have been made available online [5]. A corresponding effort is ongoing for band gaps of solids within an international US-European collaboration.

Data – We defined and implemented a new data dissemination strategy that consists of: (i) Creation of collections of spectroscopic data and first-principles MD trajectories. (ii) Dissemination of data on a per-publication basis using jupyter notebooks made publicly accessible via a three-step framework. The software just released online (Qresp http://qresp.org/) consists of GUI for data curation, metadata collection, and a GUI for data exploration. Notebooks may be used to fully reproduce and track the provenance of all data in each paper. The use of searchable notebooks will be applied center-wide. (iii) Development of a framework (Signac) designed to aid in the integration of various specialized data spaces, tools and workflows.

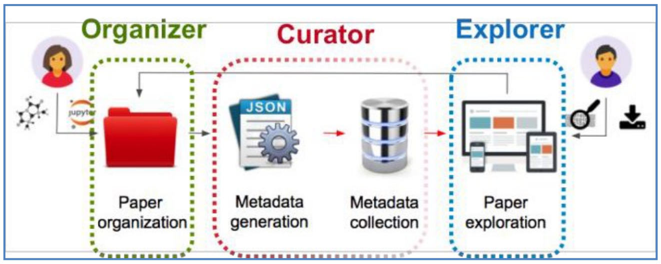

Figure 3: MICCoM digital data infrastructure.

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Shear driven formation of nano-diamonds at 0.6 GPa and 300 K

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Website: none.
Keywords: diamond; shear strain; sub-gigapascal transformations

Project Scope

Our goal is to advance multiscale theory, modeling, and experiment to enable revolutionary new approaches to find nanostructured superhard but ductile BCN materials that we synthesize using high pressure, shear, and temperature. We combine theory and atomistic simulations to search for new compositions of nanostructured superhard but ductile phases, then we use continuum simulations to predict the pressure, shear, and temperature conditions to synthesize the predicted optimum system, then we utilize our unique rotational diamond anvil cell (RDAC) to apply large plastic shear deformation at high pressure to dramatically reduce the pressure and temperature required for phase transformations (PT).

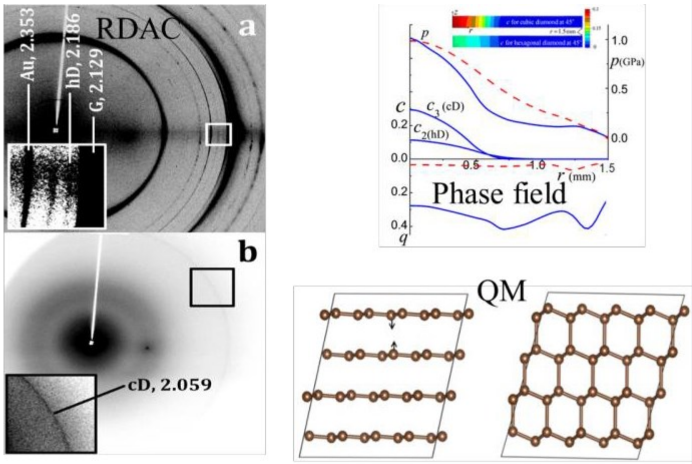

Fig 1. Coupling experiments, atomic modeling and phase field modeling demonstrate that appllying large plastic shear on graphite in rotational diamond anvils can form hexagonal and nanocrystalline cubic diamond at extremely low pressures of 0.4 and 0.7 GPa.

Relevance to MGI

We are developing rigorous methodologies to integrate 1st principles based multiscale modeling with RDAC characterization optimize coupling of modeling and theory to find optimal experimental procedures to control formation of desired new phases pressure.

We use a RDAC to superpose unlimited plastic shear at pressures up to 100 GPa which we show to produce diamond at 1% of the pressure usually required, opening a new powerful technology for producing new materials under modest pressure temperature conditions, guided by simulations.

Our demonstration of Synchrotron X-ray diffraction and fluorescence of the ruby particles provides in situ measurements of phase evolution and pressure fields.

We are developing methods for first-principles based atomistic reactive dynamics simulations (millions of atoms for microseconds) based on quantum mechanics (100s atoms for picoseconds) and applied here to superhard ductile BCN ceramics will be very useful for many other MGI projects requiring QM accuracy for predictions and simulations of large scale structures and mechanical properties on complex materials with realistic distributions of defects.

For the nanoscale, the phase field approach (PFA) describes interaction of plasticity (dislocations and twinning) with various PTs is developed and calibrated using ReaxF2 atomistic simulations.

Technical Progress

The transformation pathways of carbon at high pressures are of broad interest for synthesis of novel materials and for revealing the Earth's geological history. We have applied large plastic shear on graphite in rotational diamond anvils to form hexagonal and nanocrystalline cubic diamond at extremely low pressures of 0.4 and 0.7 GPa, which are 50 and 100 times lower than the pressures required for hydrostatic compression and well below the phase equilibrium. Large shearing accompanied with pressure elevation to 3 GPa also leads to formation of a new orthorhombic diamond phase. Our results demonstrate new mechanisms and new means for plastic shear-controlled material synthesis at drastically reduced pressures, enabling new technologies for material synthesis.

Future Plans

To iteratively couple modeling at each scale and experiments to improve models and identify material parameters (superhard phases of carbon and icosahedron based materials), to optimize experimental searches for new loading paths, phases, and nanostructures; to find ways to reduce transformation pressure and to retain the high pressure phases at ambient pressure.

Broader impact (Only required for NSF projects)

The methods being developed for large scale atomistic simulations (millions of atoms for milliseconds) and for multiple time scale continuum simulations of phase transformation provide new insights on realistic materials to c couple directly with the experimental synthesis and characterization of Nanoparticles andlarge composites. Coupling this with RDAC experiments will accelerate MGI developments of new and improved materials for energy, environment, water, sustainability. More specifically superhard but ductile materials being developed have numerous applications as components of composite for cutting, polishing, and drilling tools for various industries (including the oil industry).

Data Management and Open Access

We are making available our parameters for the reactive force fields (ReaxFF) used in large-scale molecular dynamics (MD) simulations.to simulate shear transformations from graphite to diamond and for inducing shear failure in polycrystalline B4C and related system

Advancing Along the Materials Development Continuum

Our method coupled the RDAC experiments, modeling and simulations that will accelerate MGI developments of new and improved materials for energy, environment, water, sustainability. Our approach can be applied to develop and synthesize high pressure materials much faster than traditional methods.

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DMREF: Design Rules for Flexible Conductors: Predicting Chain Conformations, Entanglements, and Liquid Crystalline Phases of Conjugated Polymers

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Keywords: Mechanical properties, charge mobility, organic electronics, rheology, chain properties.

Project Scope

This project will predict and measure fundamental properties of conjugated polymers that are warranted for any theory linking the molecular structure with macroscopic properties. We will develop and validate three computational tools:

1. Persistence lengths from numerical integrations of torsional potentials
2. Nematic coupling parameter from the combination of MD and SCFT under applied tension
3. Entanglement length as a function of the packing length for flexible and semiflexible chains

The combination of theory, simulation and experiment will lead to the development and validation of the aforementioned tools, and in addition, to the refinement of design concepts for conjugated polymers.

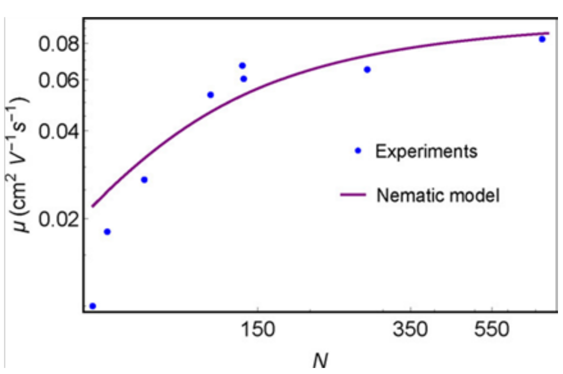

Figure. Charge mobility μ versus number of repeat units N for a conjugated polymer. Dots represent experimental data from the literature. Solid line represents model developed within this project to describe charge transport in nematic conjugated polymers. From *ACS Central Science*, in press, DOI: 10.1021/acscentsci.8b00011.

Relevance to MGI

Recent work by the PIs suggests a computationally inexpensive approach to predict the persistence length of conjugated polymers. The work of this program is validating this approach, with experimental measurements on synthesized polymers using neutron scattering in the melt or light scattering in dilute solution. Furthermore, the combination of simulations and experiments generates values of the persistence length for various conjugated polymers that are of interest to the community. The PIs are also leveraging their development of a new approach combining MD simulations and SCFT to predict the nematic coupling parameter and the nematic-to-isotropic transition temperature. Predictions of the phase behavior of various conjugated polymers that vary in stiffness are compared with results from rheology, light microscopy and depolarized light scattering. In addition, the work tests scaling relationships for the entanglement length versus packing length, to predict the entanglement length of any conjugated polymer from the molecular structure, and test these predictions with rheological measurements. The combination of theory, simulation and experiment provides an opportunity to refine design concepts for conjugated polymers.

Technical Progress

The project has made progress in a variety of thrusts. As described below, we have developed a new approach for predicting interaction parameters, developed a new theory for predicting charge mobilities as a function of molecular weight for conjugated polymers, measured basic properties of conjugated polymers such as glass transition temperatures and entanglement lengths, and examined the role of side chains on chain motion. Crucial to these efforts are the integration of synthesis, characterization and theory.

We have developed a new approach based on thermodynamic integration to predict the Flory-Huggins interaction parameter from molecular dynamics (MD) simulations (*Physical Review Letters*, 2017, 119 (1), 017801). This adds another dimension to our growing computational toolbox, which includes tools to predict the persistence length (*Macromolecules*, 2014, 47, 6453) and nematic coupling parameter (*Macromolecules*, 2015, 48, 1454). Current efforts are focused on applying our predictions of the Flory-Huggins parameter to model conjugated polymer systems that can be studied experimentally.

We have addressed the origin of the dependence of charge mobilities on molecular weight, which to date has been under debate. Starting from the observation that nematic order, in the bulk or at interfaces, is ubiquitous for semiflexible conjugated polymers and that the effect of liquid crystalline order on charge transport remains unclear, we have explored the consequence of nematic order on charge transport. Using an analytical model, we demonstrate that nematic order leads to an enhancement in charge mobilities when compared to isotropic chains. Furthermore, we predict a quadratic dependence of the charge mobility on molecular weight of the chains. Analysis of the probability of forming hairpin defects also shows how the persistence length affects charge transport in conjugated polymers. We speculate that the prevalence of nematic order in conjugated polymers explains the reported increase in charge mobilities with molecular weight (see Figure and *ACS Central Science*, in press, DOI: 10.1021/acscentsci.8b00011).

A significant portion of our activities also include measurements of fundamental properties of conjugated polymers. Although we did not originally appreciate the degree of confusion regarding the glass transition temperature (T_g) of conjugated polymers, we have demonstrated that rheology is a powerful tool for measuring T_g (*Macromolecules,* 2017**,** 50 (13), 5146). We have also used rheology to measure the entanglement length for various conjugated polymers, including for PFTBT, poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PCDTBT), regioregular P3HT, and regiorandom P3HT. These are the first measurements of entanglement molecular weights of any conjugated polymer. Measurements of the persistence length of polymers, and liquid crystalline clearing transition temperatures are also on-going.

We have also demonstrated the integration of theory and experiment in addressing the role of side chains on chain motion of conjugated polymers. Furthermore, we predict that thermal fluctuations have significant impact on apparent coherence lengths from X-ray scattering experiments and charge mobilities extracted from thin-film transistors. Altogether, these efforts have made significant contributions to our understanding of how the chemical structure affects macroscopic properties of conjugated polymers.

Future Plans

Future work will leverage the computational tools developed through this project to predict properties of various conjugated polymers, compare predictions to experiments, and provide opportunities to refine theory. For example, we propose an explanation for the growth habit of semiflexible polymers that depends on stiffness of the chains. An important class of polymers is stiff because the deflection angle between adjacent monomers is small, such that even under free rotation of dihedral angles the chain tangents are correlated for a considerable distance along the chain. For this class of polymers, we assume that density varies smoothly between crystals and amorphous regions, such that stiff chains impose constraints on how chains can pack at the crystal-amorphous interface. As an example, we have calculated the crystal dimensions for P3HT. On-going efforts will compare these calculations with those of stiffer polymers, such as PFTBT, and compare both predictions to TEM measurements of crystal dimensions. Other efforts include comparing predicted nematic to isotropic transition temperatures to measurements using rheology, comparing predicted persistence lengths with measurements using light scattering, and comparing measurements of the entanglement length using rheology with theoretical predictions.

Broader impact

We have leveraged the integration of computational and experimental activities within this proposal to design projects suitable for students transferring from smaller campuses to the central University Park campus at Penn State and for remote mentoring activities. Our initial Polymer Materials Design Scholars Program (PolyMDSP) includes two students, one that transitioned from a small non-PhD campus to the central campus at Penn State, and a second that spent a summer working on experimental research at Penn State and is now performing computational research activities remotely from Philadelphia.

Furthermore, we have started assessment of the impact of our activities. In the summer of 2017, five students participating in research associated with this project as undergraduate researchers were surveyed and interviewed, once at the beginning of the summer and once at the end of the summer. To target the educational objectives for the project, students were asked about leadership, teamwork, research, and their science and engineering self-efficacy. Overall, at the end of the summer, students discussed a much more in depth definition with respect to research with more examples of what research could be. At the end of the summer, all of the interviewed participants expressed that they were "highly interested" in going to graduate school and felt that it was a more achievable expectation than they initially thought. They also felt they had a better understanding of what graduate school was.

Data Management and Open Access

Motivated by the existing confusion of basic properties of conjugated polymers, the PIs have developed a simple website to report the glass transition temperatures of conjugated polymers prior to publication (https://sites.google.com/site/gomezgroupatpsu/home/tg-of-polymers). We also currently working with Penn State's Scholar Sphere to develop a publicly available database of measured T_g's and densities that is searchable. In addition, our publication on developing a theory to describe charge transport in conjugated polymers is open access (*ACS Central Science*, in press, DOI: 10.1021/acscentsci.8b00011) and therefore available to the public without charge.

Advancing Along the Materials Development Continuum

Measurements of the glass transition temperature, and the database of these values, will support commercialization efforts of conjugated polymers given the importance of this parameter for processing strategies. Furthermore, we expect that the computational tools that have been developed, which now include predictions of the persistence length, nematic-to-isotropic transition temperature, Flory-Huggins interaction parameter χ, and charge mobilities of conjugated polymers, will accelerate the development of conductive polymers for industrial applications.

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Design of Multifunctional Catalytic Interfaces from First Principles

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Keywords: Heterogeneous catalysis, Density Functional Theory, Metal-oxide interfaces, Water-gas shift reaction

Project Scope

This project seeks to develop design rules and multifunctional catalysts for reactions occurring at metal/oxide interfaces. We combine periodic Density Functional Theory (DFT) calculations, advanced synthesis techniques, rigorous measurements of reaction kinetics, and high resolution TEM characterization to understand the atomic-level structures of metal/oxide interfaces and to predict trends in the reactivity of these interfaces for model reactions such as water-gas shift. The identification of robust correlations between activation barriers, binding energies, and structural/electronic features of the catalysts, as have been previously described for metallic catalysts, will permit development of reactivity predictions and, ultimately, genome-based catalyst screening.

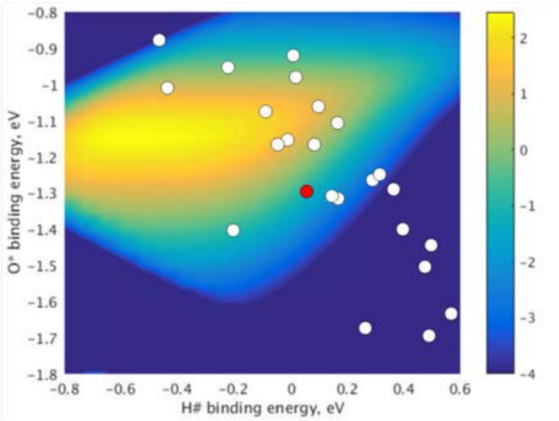

Figure 1. Computational analysis of descriptors and trends for water-gas shift on Au nanoparticles supported on doped MgO substrates. Contours denote rates predicted from theoretical scaling relationships, while open circles correspond to particular dopants.

Relevance to MGI

This effort focuses on development of a comprehensive, first principles-based modeling paradigm for multifunctional catalytic interfaces, including both supported catalytic metal nanoparticles and thin film oxides on metallic substrates. These materials have the potential to overcome fundamental bottlenecks associated with simpler catalytic structures. Through a tight coupling of theory and experiment, including DFT calculations, microkinetic rate theories, incipient wetness and colloidal synthesis strategies, HRTEM, STEM, EDS, and XPS characterization, and rigorous measurements of reaction rates and kinetics, we have developed detailed descriptions of these metal/oxide interfaces and have generalized the models to identify fundamental descriptors suitable for computational screening of catalytic materials. These descriptors have been identified using theoretically-focused strategies, including DFT-based development of scaling relationships, linear free energy relationships, and catalyst structural properties, and combination of these relationships with kinetic rate theories which are carefully calibrated against experiments. In addition, we have coupled theoretically-calculated descriptors with experimentally-measured rates to accelerate identification of reactivity trends for both oxide-supported metal nanoparticles and inverse catalysts with oxide films on metal substrates. These efforts are facilitated by continuing development of computational and experimental tools and databases to accelerate determination of supported nanoparticle structures, microkinetic rate predictions, calculated descriptor values, and experimental kinetic data.

Technical Progress

Our studies have focused primarily on the Water-Gas Shift (WGS) reaction, a model chemistry involving conversion of CO and H_2O to CO_2 and H_2 that also plays a central role in catalytic processes from reforming to biomass conversion. Below, we summarize two stories from recent work that illustrate the integration of theory, synthesis, characterization, and kinetics in this DMREF program, as well as the development of predictive capabilities for catalyst design.

An important focus of our effort has been on analysis of reactivity that occurs at the interface between metal nanoparticles and oxide substrates. Such supported metal nanoparticles are ubiquitous in heterogeneous catalysis, but analysis of reactivity trends to facilitate catalyst design is almost non-existent on such systems. We have considered Au nanoparticles (which are excellent WGS catalysts) supported on simple MgO substrates as model systems, and we investigated use of oxide dopants to tune catalytic properties without causing large disruptions to the structures of the oxide and the metal nanoparticle. We have demonstrated that scaling relationships between adsorbate binding energies (previously found to exist on simple metal and oxide surfaces) also exist for adsorbates at the interface between Au and doped MgO substrates. This is, to our knowledge, the first demonstration of scaling relationships at any metal/oxide interface, and this result has further led to development of a theoretical volcano plot of log(rate) of WGS, with the binding energies of O* and H* as descriptors (Figure 1). *The existence of volcano plots for catalysis at Au/doped oxide interfaces holds forth promise for design of metal/oxide catalysts. Tantalizingly, the fact that the scaling relationships appear to be more tunable than corresponding relationships on simple catalysts also implies that there is more opportunity to alter volcano plots, thus providing more flexibility for catalyst optimization.*

In further work, we have extended our studies of doped oxides to probe the properties of Au nanoparticles on diverse oxide substrates with many fundamentally different structures. We have greatly accelerated the identification of descriptor-rate relationships for these systems, which are structurally much more complicated that the model Au/MgO system, by seamlessly combining experimental rate measurements with computational descriptor analysis. From our analysis on the doped Au/MgO system, we found that when dissociated H_2O at the Au/MgO interface is involved in the rate limiting step, the rate correlates with the binding energy of H—OH*# such that stronger binding of this intermediate gives higher rates. Extending this insight to other oxide supports, we calculated the dissociative binding energy of water on seven different Au/oxide systems. We found that there is a strong linear relationship between dissociative adsorption energies of water and measured WGS reaction rates. *This suggests that dissociative binding energy of water can serve as a descriptor for support effects in WGS on supported Au systems, and higher rates are obtained for catalysts that bind this intermediate more strongly. This analysis, which is considerably faster than the pure theoretical correlations described above, is an exciting step towards predictive design of catalysis at metal/oxide interfaces.*

Future Plans

The identification of descriptors for the water-gas shift reaction at the interface between metal nanoparticles and oxide substrates and between oxide films and metal substrates (the latter results are not described in this report) provides a strong basis for catalyst screening efforts that explicitly target design of multifunctional nanocatalysts. Future efforts require expanding the existing database of such descriptors for different types of metal nanoparticles and for different classes of (doped) oxide substrates. Such efforts are underway, and through careful synthesis and characterization of promising candidates that emerge from this analysis, identification of multifunctional catalysts with enhanced properties for WGS and related reactions could be expected.

Broader impact (Only required for NSF projects)

The project is developing design principles for water-gas shift catalysts and is, in a more general sense, leading to a systematization of computational and experimental methods to identify improved multifunctional catalysts for a variety of industrially-relevant reaction chemistries. In the course of the project, multiple graduate students are being trained in state-of-the-art computational, theoretical, characterization (TEM), and kinetic techniques. Throughout the projects, the PIs have sought to make sustained and significant investments in the scientific and intellectual development of a targeted number of disadvantaged high school students at a very early stage in their academic careers, with a view to significantly increasing the probability of their choosing to attend a university (and to pursue STEM studies while there). In summers of 2015-7, the PIs have hosted multiple economically disadvantaged or underrepresented high school summer interns. Additional community-level outreach, in the form of visits to local high schools and engagement with the local community, is taking place at the co-PIs institution (JHU), while Purdue PIs facilitate and participate in day-long, catalysis-themed workshops for academically outstanding high school students in central Indiana every summer. The students are exposed to state-of-the-art catalyst theory and participated in hands-on experiments for fuel cell operation and TEM operation.

Data Management and Open Access

This project generates both electronic and print data which integrate experimental studies and molecular simulations. The print data largely consist of procedures, notes, and observations recorded in laboratory notebooks, as is quite normal in the course of experimental research. The electronic data include simulation codes and results, as well as data generated from analytical and spectroscopic instruments, and, together with associated computational tools, are being prepared for online databases.

Advancing Along the Materials Development Continuum

The team is currently investigating collaborative opportunities with industry to further explore our catalyst design methodologies.

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Building a High-Throughput Experimental Materials Collaboratory (HTE-MC)

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Website: https://mgi.nist.gov/htemc
Keywords: Integration, Data Sharing, High-Throughput Experiment, Standards

Project Scope

The High-Throughput Experimental Materials Collaboratory (HTE-MC) seeks to leverage (and expand) existing high-throughput experimental investments to enable broad access to HTE methods, tools, and data. NIST and NREL are taking a leading role building and integrating infrastructure, as well as convening stakeholders. If successful, this project will improve the findability, accessibility, interoperability, reusability (i.e., FAIR data principles) of HTE data on a scale comparable to well-known computational resources, such as Materials Project, OQMD, and Aflowlib.

Relevance to MGI

The HTE-MC seeks to:

- Lead a culture shift in materials research by applying concepts of the "collaborative" or "sharing" economy to experimental synthesis and characterization resources
- Integrate experimental synthesis and characterization tools with AI-enabled materials data infrastructure
- Improve the findability, accessibility, interoperability, and reusability of HTE data

Technical Progress

We have worked with our partners at NREL to develop modular data models (as XML schemas) to support interoperability of data and metadata. For example, we have developed interchange formats for common experimental characterization techniques, and for the combinatorial library. A record conforming to the library schema will enumerate all digital artifacts (i.e., data) associated with the library.

We have launched a registry and repository to enable the adoption of FAIR data principles within the HTE community. This instance is intended to be a node in a federation of registries and repositories.

We have conducted a HTE-MC workshop to socialize the idea and clarify the technical and organization model.

We have conducted a broader hackathon around integration of services within the materials data infrastructure.

Future Plans

We plan to focus on populating the HTE registry and repository and integrate it with other services. We plan to host hackathons within the HTE community to focus on adoption of the materials data infrastructure.

Broader impact (Only required for NSF projects)

Data Management and Open Access

The primary objective of this project is addressing data management, open access, and FAIR data principles.

Advancing Along the Materials Development Continuum

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Challenges in the Digital Materials Enterprise: Structural Materials Examples

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The digital materials enterprise can be thought of as the suite of experimental and computational tools, along with their associated infrastructure, necessary to capture the form and function of a 'real-world' material in the digital environment of a computer (or set of computers). Given the goal of representing the essence of a material digitally, the term 'avatar' or more specifically 'materials avatar' captures the intent of the digital materials enterprise. In generating a materials avatar, its creator must consider five foundational questions: 1) what experimental tools exist to capture and 'digitize' the aspect(s) of form and/or function of interest, 2) what digital processing is required to structure/reduce the raw digital data and what algorithms exist, 3) what quantitative metrics effectively 'compress' the digital data to a useable form while retaining salient detail, 4) what methods/tools exist to computationally instantiate or 'decompress' the quantitative metrics into digital renderings of the material, and finally 5) what simulation environments exist to accept the digital renderings and allow them to function in the 'digital world'. These questions are often difficult to answer themselves and the workflow between them presents even more barriers. This talk aims to introduce these concepts, discuss the challenges and provide some current examples of this general construct within the structural materials community.

DMREF: Doping and Defects in Diamond for Electronics

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Keywords: Diamond, Doping, Defects, Electronics

Project Scope

Diamond's electronic properties are superior compared to currently used wide bandgap semiconductor materials. To realize the potential of diamond for electronic diodes and transistors it is crucial that the electric field breakdown strength be large and that desired p-type and n-type doping profiles be achieved. The goal of this project is to advance the scientific and engineering knowledge needed to form desired doping profiles for diamond electronic devices and to reduce the defects in diamond such that the full high voltage potential of diamond devices is achieved.

Relevance to MGI

Research is being conducted to better provide theoretical analysis and predictive simulations for understanding doping profiles in diamond (and electronic activation of dopants) resulting from epitaxial growth and ion implantation. After consistency with experimental data is achieved through feedback and iteration of theory, simulation and experiments, the resulting knowledge base will be used to create mainstream simulation products for the broader diamond materials and devices community. Namely, we aim to develop the necessary physical models so that diamond doping profiles can predicted by process simulations using, e.g., Transport of Ions in Matter (TRIM/SRIM) and Stanford University Process Modeling (SUPREM). In addition, the doping studies will provide critical details for developing materials inputs for mainstream device simulation tools. Another key to understanding the details of doped diamond is the modeling of the electronic structure of point defects using Density Functional Theory (DFT) to predict the configurations of vacancies, interstitial defects, on-site chemical doping, and doping by complexes. In this research task, the point defect electronic structures and formation energies will be simulated. These calculations will work directly with the experimental tasks on annealing and basic transport properties.

Technical Progress

The synthesis/processing activities of the first portion of this project have primarily focused on homoepitaxial growth of diamond with high quality and low defects. For electronic devices doping of p-type diamond with boron is done from low levels of 10^{15} cm^{-3} up to high doping levels of 10^{20} cm^{-3}. A particular focus is on the dislocation defects as they grow into the epitaxial diamond layer as it is deposited. These dislocation defects are a particular problem with boron doping as the boron tends to

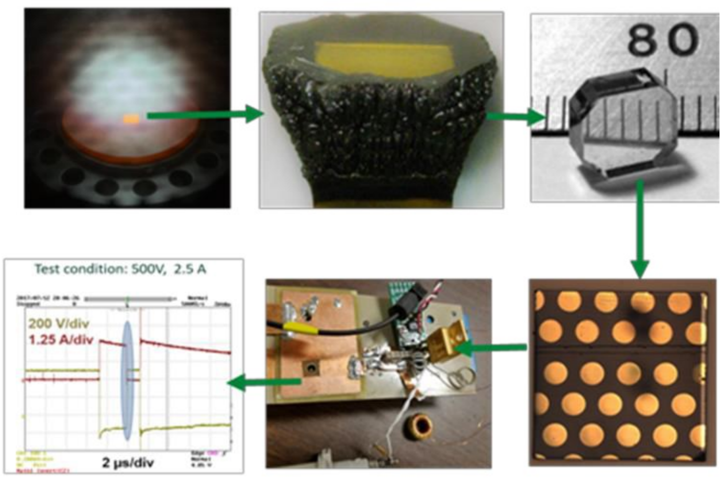

Figure 1. Diamond growth process, grown diamond piece, cut and polished substrate, diamond Schottky diodes, diamond diode in a switching test circuit, and electrical test waveform at 500 V and 2.5 A.

concentrate along this defects and produce a path of higher conductivity leading to reduced breakdown voltage and increased leakage current in devices. A common doping profile for electronic devices that we have been studying is we start with an undoped diamond substrate, then grow a thick p^+ doped layer (10-30 microns thick) and final grow a p^- (lightly doped) layer of 1-20 microns thick. The growth of the p^+ layer increases the dislocation defect density by a large factor. Specifically, if the starting substrate has a dislocation defect density of ~10^3 cm^{-2} the density has been seen to increase up to ~10^6 cm^{-2} in the p^+ epilayer deposition. This is a significant result in that it points to a direction the research investigation needs to take in the future. Getting high voltage, low leakage vertical diodes and transistors will require producing p^- layers with low dislocation defect densities, while still being able to form p^+ regions for ohmic contacts in vertical devices.

The characterization activities have included measuring the electrical properties of the boron doped diamond (carrier concentration versus temperature, Hall mobility, and electrical resistivity), the electrical compensation of the boron doping and the dislocation defect density. We are using the technique of etch pits to indicate the intersection of dislocation defects with the surface of the diamond. Work is also being done to use photoluminescence to understand the incorporation of impurities during diamond homoepitaxial growth on terrace and step regions of the growth.

Activity has also commenced on the computational modeling of diamond doping. Our first studies have been in the direction of predicting the boron doping on diamond as a function of temperature during implantation or the annealing temperature. The approached uses a first principles *ab initio* method as implemented in Quantum Espresso using norm-conserving pseudopotentials within the local- density approximation (LDA) to the density functional theory (DFT). Various Boron doped configurations were modeled in unit cells containing 54 (3 x 3 x 3) super-cell) and 128 (4 x 4 x 4 supercell) atom carbon atoms in diamond structure. One B atom in 54 atom unit cell corresponds to 1.85% doping and 0.7% doping in a 128 atom unit cell. All structures were allowed to relax. These initial simulations gave predicted results for various quantities including Fermi level. More recently the simulation of boron in the vicinity of vacancies has been started to understand annealing process after boron ion implantation into diamond.

Future Plans

A major effort of this project is now focused on ion implantation of boron into diamond for p-type doping. A limitation with the boron doping of diamond via ion implantation is that the activation percentage of the boron has been low. Currently, boron ion implantation is being done into high purity undoped epi-layers on diamond substrates under different temperature conditions. Then the implanted substrates are being characterized and subjected to various high temperature, high pressure and/or non-equilibrium conditions to study the activation of the boron doping.

Broader Impact

A new on-line graduate level course on diamond technology has been developed and it is being offered for the first time this semester (Spring 2018).

Advancing Along the Materials Development Continuum

The diamond material and devices development effort at Michigan State University is being done in collaboration with the Fraunhofer USA Center for Coatings and Diamond Technology. Following on funding has being started with DARPA (DREAM program on high frequency high power transistors), industry on diamond power electronics transistors, and two small businesses with MSU as the subcontractor on two Phase II SBIR contracts (with Plasmability and Kyma Technologies- US Army as prime) on making larger area diamond substrates.

Publications (Three conference papers have been presented and two journal papers in preparation).

Iterative Machine Learning – High Throughput Experimental Platform for the Discovery of Novel Amorphous Alloys

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Keywords: amorphous alloys, high-throughput experimentation, machine learning, closing the loop

Project Scope

We are working to combine machine learning (ML) predictions with high-throughput experimentation to create a 1000x acceleration in the rate of amorphous alloy discovery. To create a highly predictive ML model, we augment the physical attributes contained within the MagPie framework with physiochemical heuristics from several alloy selection models. The predictions are then validated by high-throughput synchrotron diffraction studies on continuous composition spread libraries. The results are fed-forward to refine the ML model and create the predictions of the next system for study.

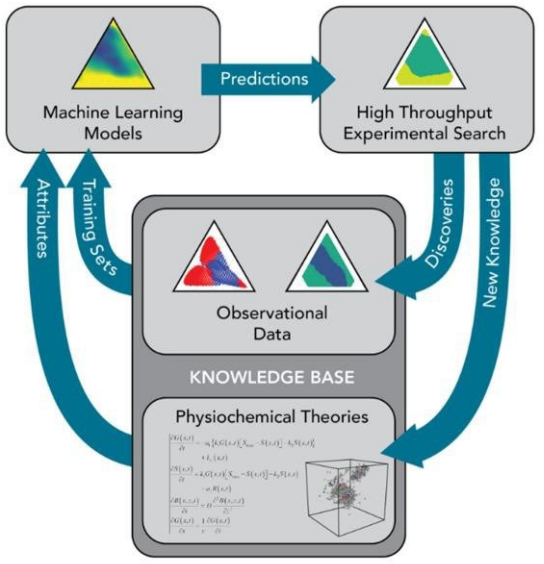

Figure. Schematic depiction of a paradigm for rapid and guided discovery of materials through iterative combination of ML and high-throughput experiments.

Relevance to MGI

Our efforts impact the MGI by:

- Incorporating physiochemical theories into predictive machine learning models
- Increasing the rate of experimental materials realization of the predicted materials by 1000x
- Increasing the amount of open materials data for known amorphous alloys by 6x
- Creating a smooth theoretical-machine learning-experimental pipeline for discovery and exploration of new amorphous alloys
- Discovering new alloys and creating a deeper understanding of their formation

Technical Progress

We are working with several partners around the world to investigate the efficacy of our approach. We first train our ML model (random forest regression) on previously reported data, a set of parameters, composed of elemental properties and physiochemical theories, and synthesis method. The predicted alloy systems are then ranked using a set of criteria including: largest number of glass formers, highest probability of glass formation, proportion of alloys that have not previously been reported, and largest uncertainty in the prediction. In this study, Co-V-Zr was selected for deposition by combinatorial sputtering because it contains a large region of previously unreported amorphous alloys. The experimental observations, made via synchrotron x-ray diffraction, are in qualitative agreement with the predictions but there are discrepancies in the precise compositions predicted. The experimental classifications are used to retrain the ML model and the quantitative agreement between the experiment and model are substantially improved. The retrained model is used to predict two more unexplored amorphous alloy containing systems and an alloy system that should be crystalline. The experimental cycle is rerun and the new predictions validated. The key discover isn't three new alloy systems but of a model that continuously improves performance with each experiment, becoming more predictive and lowering the off-diagonal terms in the confusion matrix.

Future Plans

We are currently exploring the use of this new paradigm in the discovery of high hardness, corrosion resistant, and low resistivity amorphous alloys. The ML model is being expanded to include predictions of material functionality, the predictions are validated via small volume mechanical and electrochemical studies. A second thrust is to identify predicted materials systems that either: (a) violate well-established heuristics for amorphous alloy formation or (b) have the largest impact on the predictions over the set of all predictions.

Broader impact (Only required for NSF projects)

Data Management and Open Access

The data for all the published materials, the code used to make the predictions and plots are all available for free online. The source code used to generate plots and perform the machine learning are available at https://github.com/fang-ren/Unsupervised_data_analysis_CoFeZr and https://github.com/fang-ren/Discover_MG_CoVZr. The experimental data are available at https://materialsdata.nist.gov/handle/11256/945 and https://publish.globus.org/jspui/handle/ITEM/992.

Advancing Along the Materials Development Continuum

A traditional bulk experiment might produce 5 alloys a day, whereas our high-throughput approach can generate 1,000 alloys a day (this is a 200x acceleration). The addition of the ML guidance (with a model precision around ~80%) provides an additional 10x acceleration by focusing on ternaries likely to contain some amorphous alloys for an overall increase in discovery rate of new materials on the order of ~1000x.

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Design and Testing of Nanoalloy Catalysts in 3D Atomic Resolution

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Website: None.
Keywords: Pt alloy nanostructures, oxygen reduction reaction, atomic resolution 3D imaging, force field development

Project Scope

The project involves an integrated approach of synthesis, 3D characterization, and multi-scale simulation of metal alloy nanostructures to improve the catalytic efficiency of the oxygen reduction reaction (ORR) in fuel cells. The focus of the past year has been on the testing of ORR activity of Pt based metallic alloys with transition metals M (M=Fe, Co, Ni, Cu, Cr, Mn, V, Mo). Multi-scale simulations aim at correlation of computer predictions of ligand-directed alloy shape and internal morphology with cutting edge measurements by equally sloped tomography to discover atomic ordering principles, accelerate experimental activity testing approaches, and suggest new catalyst designs. Improved interatomic potentials and theory will support composition and performance design.

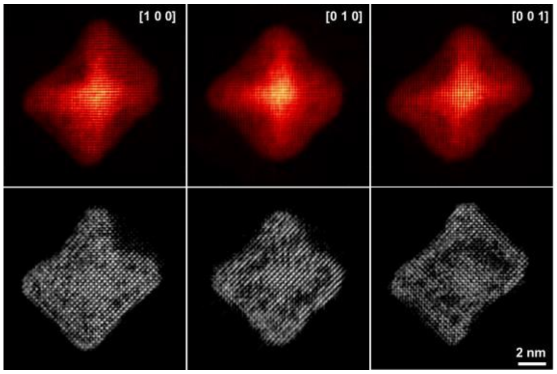

Figure. 3D reconstruction of Pt3Ni-Mo nanoalloy catalysts at atomic resolution. Top, Viewing along the {100} zone axes of the Pt3Ni-Mo nanoparticle from the 3D reconstruction. Bottom, Single central atomic layers along the corresponding directions. Element segregations between Ni and Pt are clearly identified.

Relevance to MGI

The team of three PIs has synthesized new nanocatalysts with designed compositions and shapes (Huang), imaged the positions of all atoms in 3D resolution using the world's most powerful electron microscope (Miao), and carried out performance tests in fuel cells in a close feedback loop with predictions by multi-scale modeling and simulation (Heinz). Fundamental understanding of synthesis controls, atomic-scale order, and associated reactivity of the nanoalloys driven by simulation has generated insights for the rational design of catalyst performance (ORR, hydrogen oxidation). The newly developed Pt catalysts exceed 2017 DoE targets for ORR activity by 30 times. Polarizable models for metals were developed that accurately predict interfacial properties with water, gases, and biomolecular ligands, as well as the effect of external electric fields up to the 100 nm scale. Large-scale multi-dimensional, spatial, spectral, and temporal image data sets have been generated from AET experiments and MD simulations and saved in primary and standardized (e.g., ASCII) format, and are shared on web-based repositories. The development and integration of new synthesis, imaging, and predictive multi-scale simulation tools benefits improvements of related materials as well as the computational user community.

Technical Progress

Jagged Pt nanowire catalysts, as well as the Pt3Ni-Mo nano-octahedral electrocatalysts synthesized by Huang, are of very high ORR activity and surpass the 2017 DoE targets for specific mass activity by 30 times. Doping with transition metals builds further on these findings to boost the activity and durability of PtNi/C octahedral nanoparticles (NPs). Measurements and simulations showed that Mo atoms are preferentially located on the vertex and edge sites of Mo-PtNi/C in the form of oxides which are stable within the wide potential window of the electrochemical cycle. Understanding the role of Pt, Ni, and Mo atoms points out a possible way to stabilize the favorable shape and composition of nano-scale catalysts. Miao and Huang then applied atomic electron tomography (AET) to determine the 3D atomic arrangement of a Pt3Ni-Mo nanoalloy catalyst. The nanocatalyst is composed of a Pt-rich core, a Ni-rich shell and another Pt-rich shell whereby the Ni-rich and Pt-rich regions are segregated and intercalated with each other. The element segregation results in large strain up to 6% in the nanocatalyst, which is expected to greatly influence the oxygen adsorption energy on the catalytic surfaces of the Pt3Ni-Mo nanoparticle and is investigated by DFT and MD simulations by Heinz. Miao and Heinz analyzed the structure of Au-Pd core shell nanoparticles and possible morphologies of the phase boundary consistent with coherent X-ray diffraction imaging. Heinz analyzed chemical bonding in a broad set of alloys based on experimental data and quantum mechanics, which shows that the polar character due to electronegativity differences between metals can be greater than in minerals and is often larger than in polar organic compounds. The inclusion of such polarity (ionic character) of alloys in MD simulations is essential toward quantitative reactivity predictions and engineer nanoalloy catalysts from single-atom level to hundreds of nanometers in higher precision. Miao determined, for the first time, the three-dimensional atomic arrangement of chemical order/disorder in a Pt-Fe materials system with 22 picometer precision. The measured atomic positions and chemical species were used as input to quantum mechanical calculations to correlate crystal defects and chemical order/disorder with material properties at the single-atom level. This work makes significant advances in characterization capabilities and transforms our understanding of material properties and functionality at the individual atomic level. Huang and Heinz also carried out the analysis of the assembly of Pt nanocrystals into 1D chains and 2D sheet structures driven by T7 peptides. The hydrogen-bond stabilized assembly of T7 peptides in solution as well as directional binding onto platinum cubes helps direct the formation of the ordered superstructures. Heinz developed new polarizable models for Au, Pt, and a range of other metals, which are the most accurate to-date for simulations of metal surfaces and interfaces up to the scale of millions of atoms. The models reproduce the adsorption of water and gases, including Henry constants of gas adsorption. They are applied for simulations of gas adsorption and surface reactivity along with ORR measurements by Huang and to determine alloy characteristics with Miao.

Future Plans

We will work towards better mechanistic understanding of ORR elementary steps, surface and strain engineering of the catalysts. We will construct a new volcano plot for a library of alloys using the new models and simulations, in aqueous solution and with one order of magnitude higher precision than previously feasible, and test prediction in the laboratory. We will perform testing of the catalysts in fuel cells and share data via websites and repositories in addition to publications.

Broader impact

Several graduate students, postdocs, and undergraduate students have been trained in the interdisciplinary area of biomimetic synthesis, modeling, and characterization. New research collaborations evolved from interactions between the PIs, external collaborators, team members, and at professional meetings. Major advances in methods were made, such as Pt wires and alloys with multiple times higher mass activity in ORR than reported before. Electron tomography in atomic resolution reveals state-of-the-art critical insights for understanding catalytic properties. New modeling tools for metals and alloys enable a transition from qualitative guidance to specific reactivity predictions by inclusion of polarizability in electric fields, validation of interfacial properties, and interactions with reactants up to 100 million atoms. The combination of tools allows rational understanding and accelerated discovery of catalysts and functional nanomaterials beyond this project, for example, in carbon dioxide reduction, biofuel production, new sensors, electrode materials for batteries, and adaptive biomaterials. Efforts to extend the LAMMPS molecular dynamics code to add reaction features to the accurate and simple potentials interatomic potentials are underway. The project involves participation in the Research Experiences for Teachers program at UCLA, in the High School Summer Research Program at UCLA, regular lectures and demonstrations by PhD students to students and teachers in elementary and middle schools in Boulder, and a minority PhD student.

Data Management and Open Access

All data are shared through publications, online supporting material, and repositories that are accessible through the journal websites. A significantly updated and expanded website of Interface MD for the simulation models is in progress (https://bionanostructures.com/interface-md/). Links to data can also be found on the websites of the PIs. Code and parameters are also shared on NanoHub, GitHub, and the Accelrys/Biovia community site to support the user and developer community.

Advancing Along the Materials Development Continuum

The project has driven the integration of methods that allow rational understanding and tailored designs of ORR catalysts. The next step involves testing in fuel cells towards commercialization. The computational methods and models developed in this project have been utilized by Corning and Procter and Gamble and advance products related bioactive glasses and personal care.

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Programming mesostructured colloidal soft matter through complex quenching and annealing

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Website: none.
Keywords: Thermal processing, colloidal solids, gels, glasses, rheology.

Project Scope

Although thermal processing is a powerful tool to develop materials with exceptional mechanical properties, it has yet to be widely employed to create colloidal solids due to a lack of abilities and understanding for how to initiate and control phase separation in slow, arrested systems. We seek to use tight integration of experiment, theory and simulation to understand how kinetics of diffusion, aggregation and phase separation conspire to select and control morphology in a model thermoresponsive colloidal system. The resulting framework will be used to design thermokinetic routes to colloidal gels that achieve unique structure and exceptional mechanical toughness.

Relevance to MGI

Our approach to developing this new framework combines state-of-the-art experimental and computational abilities for tandem measurements of particle structure and material properties in which experimental discovery and computational prediction can be accelerated to reveal new material morphologies and performance. In particular, the speed of computation will be leveraged to nimbly explore the range of possibilities opened up by thermal processing, and guide the development of hypotheses that can be iteratively tested in experiment, ultimately to guide the design of advanced materials with controlled structure and superior performance.

Technical Progress

We developed an experimentally-derived phase diagram (Figure 1a) for a model system involving colloidal nanodroplets with thermoresponsive polymer linkers (Figure 1b). Mapping a previously measured interaction potential onto an effective square well yields predictions for equilibrium fluid-fluid coexistence boundaries and non-equilibrium arrest transitions including pair percolation and attractive glass transitions. The latter intersects the equilibrium fluid-fluid spinodal, providing a clear route to thermal processing of colloidal solids with arrested spinodal structure of dense and dilute domains, whose length scale can be controlled with the depth of thermal quenching into the spinodal (Figure 1b). We measured the colloid volume fraction in the dense and dilute domains using NMR upon sedimentation of the gel structure after a rapid temperature jump with variable quench depth into the spinodal. In simulations, we find that such gels form dense strands with volume fraction and dynamics matching an attractive glass, highlighting the

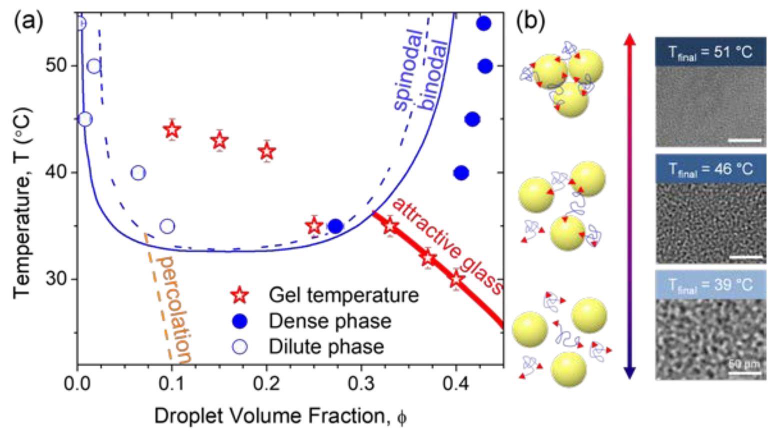

Figure 1. (a) State diagram for the model system of nanodroplets with polymer linkers. Lines indicate predicted boundaries from a square well fluid with temperature-dependent well depth. Points indicate experimental data obtained for incipient (stars) and sedimented (circles) gels. **(b)** Micrographs of gels obtained by quenching to different temperatures produces gels with varying arrested length scales of phase separation.

competition between glass formation and phase instability during gelation. Overall, we find that the volume fraction in the dense strands of arrested gels is greater than that of the equil-ibrium dense phase. Simulations indicate that this "overshoot" in the arrested density of the spinodal structure is due to the nonlinear kinetics associated with coarsening of network strands with dense, glassy interiors.

Future Plans

To more closely couple experiment and simulation, we will match a temperature-dependent interaction potential for the model system using measurements of the second virial coefficient. This will enable the design of "thermokinetic trajectories", i.e. time-dependent temperature programs, by which to measure the influence of quench rate and quench depth on structure evolution in colloidal gels. In experiment, thermokinetic trajectories will be executed in a state-of-the-art rheo-microscope that enables simultaneous rheological measurement and imaging, to be coupled with custom image analysis methods to extract the static and dynamic structure factor. In simulation, computations involving tabulated potentials and time-dependent thermostats will be developed in order to execute trajectories, from which analogous rheological and structural-dynamical measures can be extracted. These measurements will enable quantitative validation of the matched interaction potential through comparisons of the equilibrium phase behavior and attractive glass transition.

Validation of a matched interaction potential will enable deep studies aimed at understanding how thermokinetic trajectory through equilibrium phase space controls the selection of gel morphology as well as temporal evolution of gel structure and linear/nonlinear rheology. Initial studies will focus on relatively "simple" trajectories (e.g. quenching to a fixed temperature at constant rate) through regions of phase instability and arrest. The results will be used to develop and test kinetic theories to describe the various rate processes involved (diffusion, aggregation, spinodal deocmposition), and how they are up- or down-regulated using parameters of the thermokinetic trajectory. These theories provide scaling predictions that elucidate general classes of behavior to predict the arrested morphology, structural features and mechanical properties of thermally processed colloidal solids. Ultimately, these predictions will be used to design new thermokinetic trajectories aimed at producing novel mechanical properties, including enhanced resilience to yielding.

Broader impact

This project has impacted the training of 3 graduate students in the PIs' laboratories in a new paradigm of materials research and design that iteratively combines the leaps in vision available by dynamic simulation with novel experimental approaches. This is achieved through virtual and in-person group meetings, intellectual exchange through detailed tutorials, and physical exchange through short research stays in collaborators' laboratories. In the long term, these novel approaches, and the new intellectual frameworks they produce, will be disseminated to the larger community through a series of publications, as well as the development and presentation of a short course and associated review article on colloidal gels by the PIs.

Data Management and Open Access

Computational codes for image analysis developed are made available to the broader community through PI Helgeson's website (https://engineering.ucsb.edu/~helgeson). Video imaging data of colloidal gel structure will be incorporated into the tutorials for new users to learn the methods and validate workflows.

Advancing Along the Materials Development Continuum

Our research will elucidate new design principles for engineer the thermal processing of colloidal solids with controlled morphology, structure and mechanical properties. This will be developed through new experimental tools and theoretical/computational models that provide precise control of thermal trajectories, and a map to guide their selection through the vast available possibilities. Eventually, these tools could potentially be used to design new processes schemes for materials with novel or exceptional properties, or enable feedback control of thermal processing of colloidal gels and glasses in additive manufacturing processes.

DMREF: Toolkit to Characterize and Design Bi-functional Nanoparticle Catalysts

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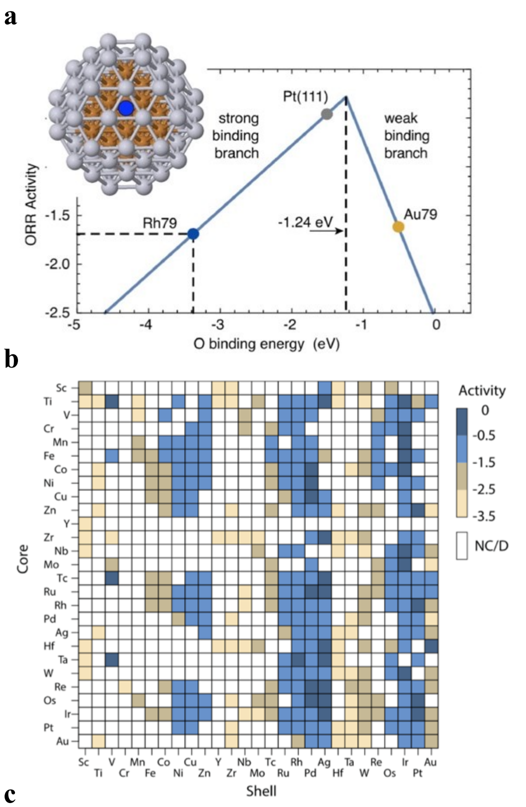
Keywords: catalysts by design, dendrimer encapsulated nanoparticles, CO oxidation

Project Scope

The focus of this project is the development of methods to enable the design and characterization new nanoparticle (NP) catalysts. While our focus is on computational methods, the bulk of the effort is the integration of the computational methods with a synthetic, characterization, and design cycle. As a team, we computational screen for new catalysts, synthesize well-defined NPs, use new computational methods to aid in their characterization, and then evaluate the catalytic performance so we can test and improve upon reactivity descriptors. Once validated, the data-driven design cycle speeds-up the discovery of new catalysts.

Relevance to MGI

In the first step of the design cycle, density functional theory (DFT) calculations are used to screen for NPs that are active for CO oxidation.[1] Our experimental model system, that of dendrimer-encapsulated NPs (DENs) allows for the precise synthesis of mono-, bi-metallic, and oxide NPs, as well as random alloy and core@shell geometries. DENs are sufficiently small, being 1-2 nm and containing up to a few hundred atoms, so that the entire particle can be included in our calculations.[2] Atomic-level characterization of NP size, composition, and structure are confirmed using electron microscopy, X-ray absorption spectroscopy, and electrochemical methods. Each of these methods is combined with DFT-based Monte-Carlo calculations to evaluate candidate structures according to their calculated stability.[3] Finally, the activity of the NPs are measured and compared with the calculated expectations. Discrepancies between experiment and theory are resolved by calculations of reaction mechanisms and the identification of more accurate reactivity descriptors and more detailed experiments to verify the fidelity of the theoretical model. By combining experiments and theory in our design cycle, we are able to determine appropriate reactivity descriptors, reaction mechanisms, and ultimately accelerate materials discovery.



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Core@shell	O binding (eV)
{Ru,Re,Os,Tc}@Ag	−1.15, −1.22, −1.24, −1.29
{Os,Ir}@Pt	−1.18, −1.42
Ru@Pd	−1.43

Figure 1. *(a) Volcano plot for the oxygen reduction reaction (ORR) showing the optimal oxygen binding energy near Pt; (b) Computational screening of all transition metal core@shell nanoparticles; (c) the optimal candidates based upon both activity and stability under ORR conditions.*

Technical Progress

1. Theoretical Determination of Candidate Nanoparticle Catalysts: A computational screening of 79-atom core@shell transition metal nanoparticles for the oxygen reduction reaction (ORR) is shown in **Figure 1**. [4] Our model, shown in **Figure 1a** was screened in terms of the oxygen binding energy to find particles with near-peak activity. The most active candidates are identified as dark blue in **Figure 1b**. After additionally considering the stability of the particles both in neutral and oxidizing environments, the best candidates were identified (see **Figure 1c**). Combined with a similar analysis for the hydrogen evolution reaction (HER), this study provides a variety of bimetallic particles which are predicted to be catalytically active, of which the best will be studied experimentally.

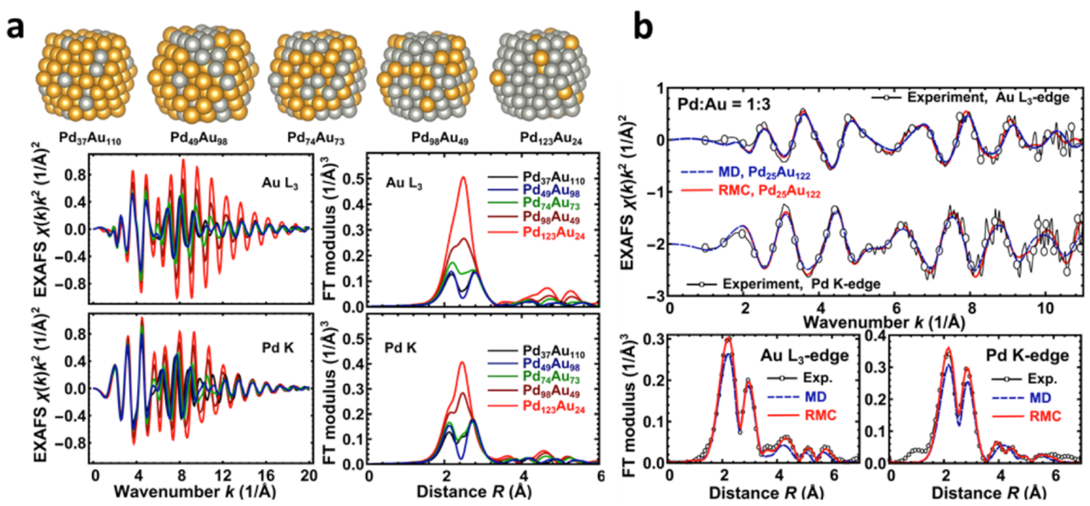

Figure 2. *Calculated EXAFS and Fourier-transformed (FT) EXAFS for MD structure models of PdAu particles with different composition (**a**). Comparison of experimental Pd K-edge and Au L_3-edge EXAFS with theoretical EXAFS for MD structure model that gave the best agreement with experiment (theoretical spectra obtained before and after the model fine-tuning with RMC method are shown in (**b**)).*

2. Characterization of Nanoparticle Structure: Data Analysis Methods: Analysis of local structure around metal atoms via the EXAFS method is a common approach for determination of structure motifs in bimetallic particles. However, to unambiguously determine shape, size and 3D structure of a nanoparticle, analysis of EXAFS contributions from distant coordination shells is required. Conventional approaches to EXAFS data analysis are unable to provide such information for such complex systems as heterometallic particles. We have developed advanced EXAFS data analysis approaches, based on direct modeling of nanoparticle 3D structure via molecular dynamics (MD) [5,6,7] and reverse Monte Carlo (RMC) methods [5,7]. In particular, we have demonstrated that MD-generated time-dependent structure models for PdAu particles with sizes ca. 1–3 nm can be used to calculate configuration- and time-averaged theoretical EXAFS spectra that qualitatively agree with the experimental EXAFS data. Therefore by directly comparing experimental EXAFS with theoretical spectra, obtained for a broad range of different structure models (**Figure 2a**), we could determine the most probable size, shape, composition, and alloying motifs in the investigated particles. Classical MD simulations with empirical Sutton-Chen potential, used in this study, were not in a quantitative agreement with experiment (**Figure 2b**), showing that the bond-length distributions are not accurate due to the empirical potential. Therefore the structure models that gave the best agreement with experimental EXAFS data were further refined via RMC simulations (**Figure 2b**) to get access to the bond length distributions and disorder effects in the investigated materials [5].

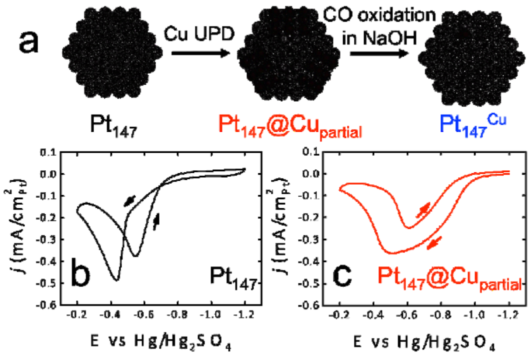

Figure 3. *(a) Synthetic scheme of formation of $Pt_{147}@Cu_{partial}$ and the subsequent conversion to Pt_{147}^{Cu} during continuous CO oxidation in NaOH. (b) and (c) Rotating disk voltammograms for bulk CO oxidation using Pt_{147} and $Pt_{147}@Cu_{partial}$ DENs-modified glassy carbon rotating disk electrode.*

***3.* CO oxidation using Pt DENs activated by Cu underpotential deposition:** In this study, we show that the catalytic activity of Pt DENs for dissolved CO electrooxidation is dramatically improved after activation by Cu underpotential deposition (UPD). Activation is accomplished by adding a partial Cu shell to a 147-atom Pt core, generating $Pt_{147}@Cu_{partial}$ structures having diameters of ~2 nm (**Figure 3a**). [8,9] **Figure 3b** and **c** show rotating disk voltammograms for bulk CO oxidation in CO-saturated 0.1 M NaOH using Pt_{147} and $Pt_{147}@Cu_{partial}$ DENs-modified glassy carbon rotating disk electrode. $Pt_{147}@Cu_{partial}$ DENs exhibit an onset potential of ~300 mV more negative than the naked Pt_{147} DENs. The activity of $Pt_{147}@Cu_{partial}$ DENs is also improved by over an order of magnitude at low overpotentials. [10] Importantly, our electrochemical results indicate that the improved activity is not directly attributable to the Cu shell, but more likely from a small number of active sites on the Pt_{147} DENs surface. The number of active sites on the surface of each nanoparticle is estimated to be < 1 per facet based on adsorbed CO stripping experiments. Density functional theory (DFT) calculations suggest that these special sites are comprised of individual Cu atoms surrounded by Pt on the (100) facets of the DENs (**Figure 3a**). DFT also indicates that these Cu sites are thermodynamically stable, have ~1 eV lower CO binding energy, and ~0.2 eV higher affinity for OH binding than the Pt sites. Accordingly, oxidation of CO adsorbed onto Pt atoms is facilitated by the presence of nearby OH groups located on Cu atoms.

Broader impact

Starting in the Fall of 2015, a new Freshman Research Initiative (FRI) course called *Computational Materials (CM)* was created with the goal of introducing undergraduates at UT Austin to computational chemistry research. This course introduces students to methods for both global and local optimization, giving students the opportunity to implement and benchmark methods. CM also teaches students how to utilize electronic structure software to model materials for catalysis applications. More than 50% of students in FRI are from backgrounds underrepresented in science.

Figure 4. *The 2nd summer cohort of the freshman research initiative stream in computational materials.*

Data Management and Open Access

All products will be made available to the public via the web portal http://theory.cm.utexas.edu/dmref/. The web portal makes the software and data available to the public and it will expose the metadata enabling anyone to intelligently search through the data repository.

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DMREF: Collaborative Research: Design and Discovery of Multimetallic Heterogeneous Catalysts for a Future Biorefining Industry

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Keywords: Biomass, aqueous catalysis, uncertainty quantification.

Project Scope

Our objective is to establish a new, multidisciplinary research approach based on deep integration of computation, data informatics and experimentation for the rapid design and discovery of novel, multimetallic heterogeneous catalysts with exceptional activity, selectivity, and stability in aqueous-phase, biorefining applications. Our central hypothesis is that the discovery and design of such materials requires (1) rapid, in silico screening of catalytic materials in aqueous phases, (2) the ability to synthesize, characterize and evaluate catalysts that have and retain well-defined active sites in aqueous media, and (3) systematic procedures for correlation and reconciliation of computational insights with experimental observations.

Relevance to MGI

A key roadblock in our ability to accelerate catalyst discovery through computations is the lack of knowledge regarding the structure of catalytically active sites in supported metal nanoparticles. Only with a deeper understanding of active sites can descriptors for computational screening studies be identified. The challenges in identifying active sites in working catalysts can be understood by recognizing that traditional preparation methods for supported, multimetallic catalysts yield heterogeneous size and composition distributions in metal clusters. This creates a plethora of active sites of which often only a minority determines the overall performance. Next, computational catalysis has limitations in predicting absolute activities of specific site structures in industrial catalysts due to the limited accuracy of DFT. It is therefore proposed to establish a new approach for correlating computational predictions to experimental observations; identifying active sites; and enabling computations to help accelerate the design and discovery of multimetallic catalysts by (1) increased emphasis in the use of scalable synthetic methods alongside comprehensive characterization to create well-defined, multimetallic catalytic materials and (2) using knowledge about computational and experimental uncertainties in active site identification, to suggest most informative experiments, and to predict optimal catalyst designs through the powerful machinery of probability and information theory.

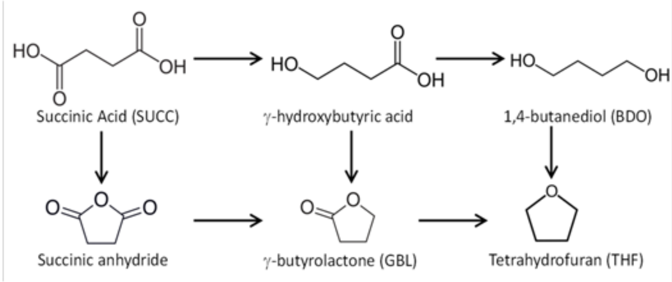

Figure 1. Pathways for the HDO of SUCC to BDO, GBL, and THF.

Technical Progress

As a case study for our integrative approach, we have chosen the hydrodeoxygenation (HDO) of organic acids such as succinic acid (SUCC) in aqueous media over supported multimetallic catalysts

(Fig. 1). This chemistry could allow for the selective production and facile recovery of bio-based 1,4-butanediol (BDO), γ-butyrolactone (GBL) and tetrahydrofuran (THF). To demonstrate rapid progress in our research strategy illustrated in Figure 2, we also studied the HDO of propanoic acid (which is a simplified surrogate molecule of SUCC) over transition metal surfaces for which we possess a computational database based on previous projects. Experimentally, we found in agreement to our calculations that the HDO of carboxylic acids to produce alcohols and aldehydes is kinetically difficult, while secondary reactions (aldehyde decarbonylation, C-C hydrogenolysis, and alcohol hydrogenolysis) are facile. This favors the formation of light alkanes and oxygenate fragments and leads to poor HDO selectivity. Further, primary and secondary products of the carboxylic acid HDO, primarily aldehydes and carbon monoxide, bind strongly to metal surfaces and dramatically impact measured rates even under "differential" reactor operation. Accordingly, a major focus of our work has been establishing strategies for quantifying primary, secondary, and tertiary reaction rates in the presence of strongly binding reaction products. We have thus far developed models that are able to capture both species production rates and product selectivity over a wide range of temperatures and partial pressures. Next, we have applied our Gaussian process (GP) approach to our database of the HDO of propanoic acid over eight transition metal surfaces (Ni(111), Pd(111), Pt(111), Rh(111), Cu(111), Ag(111), Ru(0001), and Re(0001)). For adsorption energies, we observe that there is no statistical significant difference in favor of GP over linear scaling models due to the relatively small number of data (this assumes that optimal descriptors have been identified, otherwise GPs can possess significant advantages). In contrast, for transition state energies, we see a statistical significant difference in favor of GP compared with BEP correlations. Finally, we applied our Bayesian calibration and Bayesian model selection strategy to identifying active sites in the water-gas shift (WGS) reaction of Pt/TiO_2 catalysts. For this chemistry, we already possessed necessary experimental kinetic data, DFT data, and microkinetic models. We conclude that the Pt edge interface site is the active site for the WGS in the catalysts studied experimentally when compared with the terrace and interface corner sites. Also, even in the presence of uncertainty, the CO-promoted redox mechanism at the edge active site is found to be the dominant reaction mechanism.

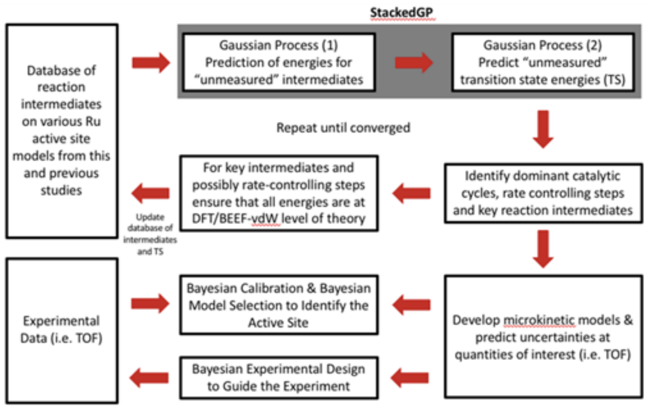

Figure 2. Uncertainty quantification pipeline and interconnectivity of the tasks.

Future Plans

- Complete our computational database for the HDO of SUCC over various transition metal surfaces
- Develop a computational database over Sn modified transition metal surfaces
- Controlled deposition/synthesis of "promoter" metals, such as Sn, onto Pt and Ru clusters via strong electrostatic adsorption. Preliminary catalyst evaluation results already show that Sn addition promotes HDO selectivity to alcohols by suppressing rates of secondary reaction pathways
- Detailed characterization of bimetallic catalysts through synchrotron facilities at Brookhaven National Laboratory
- Finalize development of GP and StackedGP to predict transition state energies
- Finalize development of GPs to predict adsorption and transition state energies for the HDO of SUCC from a database of the HDO of propanoic acid and SUCC
- Add Bayesian experimental design to the UQ framework to guide the experimental process
- Apply the final UQ framework to HDO of SUCC

Broader impact

The methodology employed in the study can potentially guide materials selection and catalyst design for many applications beyond the specific catalysts and reaction demonstrated here. Rigorous standards are set for both the experimental and computational work, that when combined with statistical analysis, provide confidence heretofore lacking in the certainty with which new catalytic materials can be predicted.

Data Management and Open Access

The performed and proposed work requires software development in computational catalysis and uncertainty quantification. All software will be maintained under the Git source code management system hosted on BitBucket (bitbucket.com). All software packages resulting from the proposed work will be released to the community under the GNU GPL or LGPL. Next, the PIs plan to develop a tutorial website explaining the application of the proposed uncertainty quantification methodology to computational catalysis once relevant papers have been published. The website will contain links to code repositories, publications, study cases, archives of computational and experimental data. This website will also serve as a forum for practicing engineers to submit questions and concerns regarding their modeling domains.

Advancing Along the Materials Development Continuum

SUCC has already emerged as a commercially viable bio-commodity that is used in niche applications, and targeted design of catalysts for its upgrading will enhance its potential as an industrial alternative to petroleum-derived maleic anhydride (MA). It is additionally worth noting that the chemistry proposed here captures several challenges that are broadly characteristic of biomass refining. Specifically, it is reductive in nature, it targets the removal of oxygen through the addition of hydrogen, and it is anticipated to occur in acidic aqueous phases. Thus, HDO of SUCC is a compelling model system that can generate activity and stability insights that will be broadly applicable to biomass refining chemistries.

Publications

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Collaborative Research: Design and Synthesis of Novel Magnetic Materials

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Website: https://novomag.physics.iastate.edu/.
Keywords: Magnetic Materials, Heusler Alloys, Genetic Algorithm, Nano Clusters, Non-Equilibrium Synthesis.

Project Scope

The discovery of new magnetic materials is of paramount importance in materials research and technology. The main goal of our collaborative research is to develop new rare-earth-free magnetic materials exhibiting high magnetic anisotropy, high magnetization and high Curie temperature. Experimental work is focused on the fabrication of novel nanostructures and nanoclusters with entirely new magnetic properties as compared to the corresponding bulk materials and Heusler alloys with large spin polarization and promising spin-electronic properties. Theoretical work is centered on recent theoretical advances in quantum modeling algorithms and software, and data-mining and machine learning techniques implemented on high-performance computational platforms.

Relevance to MGI

In this project, combined theoretical and experimental search is explored to design new magnetic intermetallic compounds, which will be Fe-, Co-, or Mn-rich and free of strategically vulnerable rare-earth elements and expensive metals like Pt or Au. Iterative back and forth feedback loops between theory and experiment teams have been utilized in our work with initiatives from either theory or experiment. For example, our recent work on $Fe_{3+x}Co_{3-x}TM_2$ (TM = Ti or Nb) [1–3]. Experiment team proposed possible hard magnetic materials with chemical formula of $Fe_3Co_3TM_2$. Theory team then performed genetic algorithm search with inputs from experiment and solved the crystallography of the materials. With insights from theory work, experiment team was able to substitute Co by Fe to have better, in term of magnetic properties and material cost, hard magnetic compounds of $Fe_{3+x}Co_{3-x}Ti_2$ with $0 \leq x \leq 3$. The inputs from experiment helped us narrowing down the phase space for theory search and thus the theory search was significantly improved in efficiency. On the other hand, insights from theory work on crystallography, substituents and dopants helped us developing better target-specific experimental strategies to improve the materials and hence speeding up the discovery of new materials.

Technical Progress

a. Discovery of Metastable Nitride Magnetic Compounds by complementary computational and experimental methods: Adaptive genetic algorithm (AGA) search performed at the Ames laboratory have discovered several Co_3N compounds with non-cubic structures having density functional theory (DFT) predicted high magnetocrystalline anisotropy, high magnetic moment, and high Curie temperature. The experimentalists at the University of Nebraska was able to synthesize Co_3N with the rhombohedral and $CdMg_3$-type hexagonal structures in the form of nanoclusters. The experiment saturation magnetization (M_s) and anisotropy (K_1) are 1.65 and 0.84 μ_B/Co and 10.1 and 10.4 Mergs/cm^3, for $CdMg_3$-type and rhombohedral Co_3N nanoclusters, respectively.

b. Determination of crystal structure for the newly synthesized Fe_2CoC compound: Experimentalist at the University of Nebraska has successfully synthesized a new Fe_2CoC compound. However, the crystal structure of this compound was initially unknown. Using AGA search, the Ames Laboratory team determined a detailed crystal structure of the compound: orthorhombic and space group: *Pnma*. The experimental results show high Ms ≈ 1.17 or 1.09 $\propto_B$/magnetic atom at 10 or 300 K. Magnetocrystalline anisotropy for the Fe_2CoC compound is also estimated as about 9.6 Mergs/cm^3 at 10 K and about 8.6 Mergs/cm^3 at 300 K using the experimental magnetization curves.

c. Novel Heusler alloys with tailored spin polarization and magnetic moment: In a joint effort between Iowa State and Nebraska, we successfully fabricated novel Mn_2CrGa-based Heusler compounds with small magnetization and high spin polarization, which are promising for spintronic applications. The suitable spin-electronic properties are achieved by substituting Fe or Pt for Cr and optimizing the composition. Mn_2CrGa and $Mn_2Cr_{0.6}Fe_{0.4}Ga$ are indexed to the cubic unit cell of the B2 structure, whereas the $Mn_2Cr_{0.6}Pt_{0.4}Ga$ is indexed to the tetragonal unit cell of the D022 structure. The magnetic moment per formula unit are 0.4, 0.07, 0.02 μ_B/f.u. for these compounds. Point-contact Andreev reflection (PCAR) measurements show appreciable spin polarizations in these samples, 64.2 ± 1.1% for Mn_2CrGa, 60.6 ± 2.5% for $Mn_2Cr_{0.6}Pt_{0.4}Ga$, and 59.8 ± 0.8% for $Mn_2Cr_{0.6}Fe_{0.4}Ga$.

d. Advances in predicting the properties of magnetic clusters: The use of our further developed first-principles code, PARSEC enabled us to examine magnetic Co and Ni clusters with a size range well beyond previous work. We clarified how the total magnetic moment per atom varies as the cluster size increases and obtained the results consistent with experiment. We analyzed the spatial distribution of the local magnetic moment, which explains the non-monotonic enhancement of the total magnetic moments in Co and Ni clusters. We also examined the effect of N-substitution on the magnetic properties of Co clusters. We found that a few atomic percent of N substitution can enhance the net magnetic moment in comparison to that of pure Co cluster, where a N-substitution site plays a key role for the enhancement.

Future Plans

We will continue to focus on the discovery of new magnetic materials with high saturation magnetization (M_s), large magnetocrystalline anisotropy (K_1), high Curie temperature (Tc), high spin polarization, and promising spin-electronic properties by combined theory and experiment explorations. Our focuses are on the following material families:

- Fe- and Co-rich intermetallic compounds such as $Fe_{3+x}Co_{3-x}X_2$, Fe_3CoX (X = Hf, Zr, Bi, Ti, etc.) and non-cubic 1:5 and 1:7 compounds like Co_5X and Fe_7X (X = Hf, Zr).
- $Mn_{4-x}TM_xN$ compounds with TM = Co, Fe and $0 \leq x \leq 4$.
- $Fe_{16-x}Co_xN$ ($0 \leq x \leq 4$) and (Fe,Co)-S compounds.
- Novel magnetic Heusler compounds with focus on investigating disorder effects in ternary and quaternary compounds.

Many metastable structures have been produced by non-equilibrium synthesis methods such as rapid quenching and thin-film/cluster sputtering or deposition. We are going to extend the zero-temperature structure prediction from AGA to a more comprehensive computational approach that can combine the structure and kinetic determination at finite temperatures with materials-informatics/machine-learning to elucidate the relationship between high temperature structures and phase selection pathways. Some advanced computational techniques such as Cluster expansion enabling Monte Carlo simulation, short-range order (SRO) and medium-range order (MRO) in undercool liquid and glass, and structure motif will be used in conjunction with AGA for these tasks.

Broader impact

We have trained next generation materials researchers, educated students and attracted underrepresented groups to science, including 1 senior research associate, 2 junior scientists, 2 postdoctoral fellows and 3 graduate research assistants last year. We established a vigorous program of attracting underrepresented groups, reaffirming our educational components and maintaining contacts to the private sector. The relevant programs include (1) the Alice in Wonderland program at Texas, (2) the Nanocamp and STEM after school program at Nebraska (3) Bright lights program for middle school students at Nebraska. The gender imbalance in STEM disciplines is a pressing concern.

The Alice in Wonderland program targets high school girls, who participate in research in physics and related areas over the summer before they make decisions about colleges. Participants work in real research labs in the Departments of Physics or Chemical Engineering. We participate in this program by supporting two high school students in this program and help mentor their career choices. We actively mentored several high school students within our group. The Nanocamp at Nebraska also targets high school age students in science related projects. We have mentored several undergraduate and high school students and some of their research results were accepted for presentation in the national conference (Annual Conference on Magnetism and Magnetic Materials) or received Poster award (Nebraska's summer research symposium).

Data Management and Open Access

Our developed computational codes (AGA and PARSEC) are made available to the community free of charge, under the GNU General Public License. The AGA code currently can be obtained via contacting our project PIs at Iowa State University. PARSEC code is accessible from http://parsec.ices.utexas.edu/. We have been building a structure database to provide, in tabular form, data on crystallography and thermodynamic and magnetic properties of materials from our work. The structure database is opened to public and can be accessed on our project website: https://novomag.physics.iastate.edu/.

Advancing Along the Materials Development Continuum

Our combined experimental and computational research has identified several materials with good potential for development as permanent-magnet or information-processing materials. The feedbacks and interactions between theory/computation and syntheses are crucial in helping us to narrow down the search phase space and hence speeding up the discoveries of the new high performance and/or low cost materials. The most promising materials discovered in our work are the Fe- and Co-rich compounds: Fe_3Ti and Zr_2Co_{11}, which have anisotropy field induction and saturation polarization values in the range of 7 T and 1 T. Nanocomposites based on these alloys already have been shown to have energy products of about 20 MGOe or 160 kJ/m^3, and further work on developing these materials for application is underway.

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Control Phase Selection in Liquid Solidification for Materials Discovery and Synthesis

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Keywords: structural hierarchy, crystal gene, crystal nucleation, phase diagram

Project Scope

We integrate experimental and computational tools to study structural transformation in undercooled metallic liquids. In particular, we solve high temperature stable or metastable crystal phases involved in the transformation; establish structural hierarchy during crystallization or glass formation in prototypical systems; develop new methods to simulate crystal nucleation under realistic experimental conditions; and determine phase diagrams for uncharted compositional space. Our goal is to understand and control phase selection during solidification by specific compositions or heat process.

Relevance to MGI

Materials synthesis often starts with liquid phases. Depending on the cooling process, the liquid phase may undergo equilibrium phase transitions or can be driven deeply out of equilibrium and form various metastable crystalline phases or glasses. Understanding and controlling the phase selection is thus an important step toward achieving desired structures and functionalities. We combine experimental and computational efforts in a positive feedback loop: Experimental results on liquid structures and thermodynamic parameters provide crucial information for developing a reliable interatomic potential for expedited structure prediction, large-scale molecular-dynamics (MD) simulations, and free energy calculation. Such computational work can solve unknown crystal structures, identify key factors governing phase selection, and expand phase diagrams to previously unknown compositional space, which, in turn, provides useful guidelines for experimental synthesis.

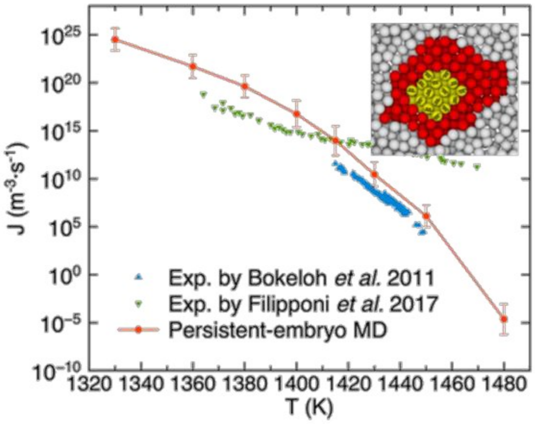

Figure. Application of persistent-embryo method to simulate nucleation of Ni under realistic experimental conditions. The calculated nucleation rate compares favorably with experiments.

Technical Progress

Al alloyed with ~ 10 at.% Sm represents a typical Al-rare earth (RE) system that can sustain deep undercooling and form amorphous solids or nanocrystalline composite materials with much improved mechanical properties compared with pure Al [1]. When as quenched $Al_{90}Sm_{10}$ alloys are gradually heated up, it undergoes a multiple-step devitrification process which involves various unknown metastable phases. Using an efficient genetic algorithm, combining MD, density functional theory, and x-ray diffraction, we determine the atomic structures of these metastable phases in full site-occupancy detail [2–4]. Our analysis shows that these metastable structures share the same dominant motif surrounding Sm atoms as the undercooled liquid. The coincident motif, or "crystal gene", supports the notion that liquid/glass ordering at high undercooling may give rise to topological invariants between the non-crystalline and crystalline states that provide kinetic pathways to metastable phases that are not accessible during near equilibrium processing [5].

Crystal nucleation from liquid is a fundamental phenomenon [6] that plays a central role in materials design and processing [7]. In most cases, it is also a typical rare event inaccessible within the limited timescales of the conventional MD simulation. We developed a "persistent embryo" method to facilitate crystal nucleation in MD simulations by preventing small crystal embryos from melting using external spring forces [8]. We applied this method to the pure Ni case for a moderate undercooling where no nucleation can be observed in the conventional MD simulation and obtained nucleation rate in good agreement with experiments. Moreover, the method is applied to simulate an even more sluggish event: the nucleation of the B2 phase in a strong glass-forming Cu-Zr alloy. The nucleation rate was found to be 8 orders of magnitude smaller than Ni at the same undercooling, which well explains the good glass formability of the alloy. This opens a new avenue to study solidification under realistic experimental conditions via atomistic computer simulation.

Future Plans

Solidification techniques are widely used in materials synthesis. In order to reach the desired structure, it is essential to know the melting curve (liquidus line) as shown on a phase diagram. With such information unavailable for a large part of the compositional space, experiments still heavily rely on a trial-and-error approach to determine the right liquid compositions. We recently developed a self-contained algorithm to evaluate free energy for both solid and liquid phases of an alloy system based on a classical potential [9]. Our experience shows that a reasonable phase diagram can be constructed from these calculations if liquid properties at compositions of interest, such as radial distribution function and melting points of typical solid phases, are explicitly included in the development of the potential. Taking this phase diagram as the starting point, we then use extensive data collected from trail-and-error experiments to refine the theoretical model to better reproduce some known features of the phase diagram (such as specific points on the liquidus line). The refined model is expected to expand its predictive power and can provide useful guidelines for further experiments. This process will be iterated to expedite materials discovery and synthesis.

Acknowledgement

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DMREF: Adaptive Control of Microstructure from the Microscale to the Macroscale (NSF-CMMI-1729336); EAGER/DMREF: In-Situ Thermomechanical Processing and Measurement in the SEM (NSF-CMMI-1647005)

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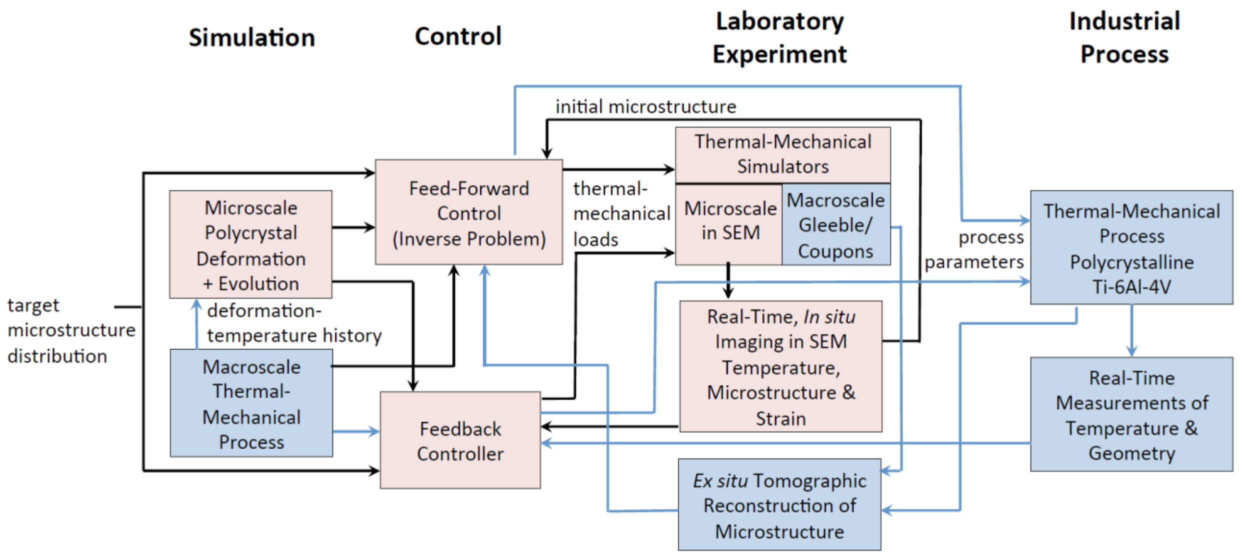
Co-Principal Investigators: Daniel Lewis, MSE Department, RPI, lewisd2@rpi.edu, Antoinette Maniatty, MANE Department, RPI, mania@rpi.edu, John Wen, ISE Department, RPI, wenj@rpi.edu

Website: Internal:http://confluence.cats.rpi.edu/display/DMREF/NSF+DMREF+ACME+Home; external access to be provided soon

Keywords: Control, real time, in-situ, microstructure, thermomechanical processing

Project Scope

New techniques are being developed to examine thermomechanical processing conditions and mechanical measurements in-situ to a scanning electron microscope (SEM), by in-situ heating, stressing, and indentation. This allows real time observation of microstructural evolution during thermomechanical conditions relevant to processing of Ti-6Al-4V alloys. These observations will be coupled to simulations of desired processing trajectories and feedforward and feedback control strategies to allow adaptive control of microstructural evolution. Macroscopic characterization methods will be applied in collaboration with industrial partners to extend findings to manufacturing scales.



Overall project strategy. Real-time observations of microstructure and deformation of Ti-6Al-4V are made in-situ in the scanning electron microscope, with the temperature and strain controlled in real-time (pink boxes, black connectors). This creates an "*adaptive microscale simulator"* for refining and validating the microscale model and control strategy. Blue boxes and connectors illustrate the pathway to extension to macroscale industrial processes. In collaboration with our industrial partners, we will use macroscale process models to define local temperature-deformation trajectories at key locations in Ti-6Al-4V macroscopic parts during manufacturing processes. Those trajectories will then be verified experimentally, using both the *adaptive microscale simulator* and a macroscale thermal-mechanical simulator, which will either be a test coupon or a sample tested in a Gleeble system

Relevance to MGI

The macroscale engineering properties of metals are directly linked to microstructural characteristics generated during thermo-mechanical processing. Controlling the processing conditions to create a desired microstructure and resulting macroscale properties is a priority for materials manufacturers. This project focuses on development and application of the methodology and algorithms necessary to actively control materials processing to achieve a target microstructure. The major contribution will be the synthesis of experimental characterization, process control, and microstructure simulation to predict, monitor and control microstructural evolution during materials processing. Further, methods to scale-up our microscale techniques to macroscale industrial applications are being developed in partnership with multiple industrial collaborators.

Technical Progress

Under the EAGER/DMREF award (081516-073118), a unique apparatus (manufactured by Kammrath and Weiss, Dortmund, Germany) for integrating high temperature, high tensile stress, and mechanical property measurements in-situ to a dual scanning electron and ion beam microscope is being developed, which we call our *adaptive microscale simulator (AMS).* The first phase of installation, enabling stage temperatures up to 1000° C and tensile stresses to over 1 GPa has been implemented. Experiments have been performed over this heater temperature and stress range for both Ti-6Al-4V and steel alloys. Experimental challenges presently being addressed include: (i) Direct measurement of sample elongation using focused ion beam fiducial marks (to obviate issues due to sample motion in its mount during stressing, which affect the integrated optical encoder readings), (ii) Sample vs heater temperature calibrations and thermal shielding. While the heater reaches 1000° C, the temperature of the sample surface is inevitably lower (from an additional thermocouple attached to the imaged sample surface, over two hundred degrees lower than the stage temperature at the highest heater temperatures). To this purpose we are designing heat shields to largely cover the sample in the stage, and to protect the surrounding apparatus (electron and ion lenses, detectors etc., the temperatures of which are all continuously monitored by thermocouples. We note that our target temperatures are ~800° C for recrystallization and 1000° C for the α to β phase transus in Ti-6Al-4V. The integrated nanoindenter for modulus and hardness measurement, and increased stage heating capability to 1200° C are being installed later this month (March 2018).

Under the full DMREF award (090117-083121), initial progress has included. (i) Experimental – application of the AMS to Ti-6Al-4V alloys at heater temperatures up to 1000° C, and sample stresses up to 1 GPa (to the point where substantial sample necking or fracture is observed). SEM imaging has been successfully performed over this range of conditions, and microstructure evolution observed during straining at both room and elevated temperatures, or during annealing alone. In parallel, to identify the most interesting conditions for in-situ observations in the AMS, and for simulation, we are developing a library of "post mortem" images of microstructure (including α lath colony and basket weave structures under different heat treatment conditions) using standard optical metallography methods. (ii) Simulation – Polycrystal finite element deformation model work initiated. A Monte Carlo (MC) grain growth model was calibrated to Ti-6Al-4V above the β transus and recrystallization formulation defined using driving energy from deformation model. Simulations of the β to α phase transformation are being developed using a multi order parameter phase field model. This model will be capable of capturing the competitive growth of different α variants and will be integrated with MC results to integrate phase and grain growth dynamics. (iii) Control – Initial focus is on developing algorithms for controlling phase and microstructural evolution during cooling from above the β transus, integrated with phase field models. We are using an extension of the isothermal Johnson-Mehl-Avrami equation for transient temperature control. The control problem is posed as adjusting the cooling rate and terminal temperature to achieve both desired α-phase percentage and a specified function (in terms of temperature, cooling rate, and α-phase amount) characterizing the microstructure of interest. We have also investigated laser-based heat treatment as in additive manufacturing. The laser speed and power are adjusted based on the temperature feedback to achieve desired cooling rate and melt pool temperature.

Future Plans

For the next year of the full DMREF award, we will focus on the following activities: (i) Experimental: Application of the AMS to detailed measurements and understanding of dynamic and static recrystallization phenomena in Ti-6Al-4V alloys, and depending on attainable temperatures in the AMS, initial experiments of phase evolution as functions of treatment at temperatures above the β transus, and as a function of cooling conditions. These measurements will be coupled closely to phase field and Monte Carlo simulations. (ii) Simulation: Initial Monte Carlo simulations of recrystallization phenomena in Ti-6Al-4V alloys, updated deformation model, and initial phase field models of both grain and phase evolution during thermomechanical processing. Initial comparisons to dynamic experimental data (iii) Control: Control strategies developed for input control of temperature and strain in during thermomechanical stressing of Ti-6Al-4V in the AMS. (iv) Extension to Macroscale: Ongoing consultation with industrial collaborators with input into design of experiment-simulation-control loop; Development of optical tomography techniques at cm^3 scale.

Broader impact (Only required for NSF projects)

This work is designed to provide the framework for new adaptive process control methodologies that can be of significant competitive advantage to the US metals manufacturing industry. Collaborations with major materials, component and systems manufacturing companies (Carpenter Technologies, Ducommun and General Motors) will provide the necessary industrial relevance and expertise. Graduate and undergraduate student researchers involved in this project will be exposed to an interdisciplinary set of engineering methodologies as well as exposure to industrial practice, and a core foundation of common expertise across the project will be developed.

Data Management and Open Access

Our data management/dissemination plan incorporates public access to suitably curated and documented data sets and simulation codes. A key initiative will be to develop schema (ontologies) - in collaboration and consistent with relevant national materials data bases / registries - to store, address and search the format of the processing trajectories data we are developing (i.e. large sequences of experimental and simulated images of evolving microstructure, and associated control sequences). We plan to make available full sets of data processing streams, incorporating all available experimental, simulation and control data. This material will be available both through our wiki site and through appropriate databases/registries, as our project matures.

Advancing Along the Materials Development Continuum

A key goal of this project is to translate knowledge learned in the laboratory environment to macro-scale industrial processes, by extending knowledge derived in the AMS to thermo-mechanical processing of macroscopic samples under conditions that manufacturers employ in the development of their process sequences, such as in a Gleeble system or in test coupons subjected to equivalent processing conditions. A set of industrial partners spanning materials providers, component and systems manufacturers (e.g. Ducommun, Carpenter Technologies, and General Motors provided letters of support for our proposal) will be strongly engaged in the project as it evolves.

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FLOSIC: efficient density functional calculations without self- interaction

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Keywords: Self-interaction, de-localization error, charge transfer, magnetic exchange couplings

Project Narrative

Fundamental development of new theoretical and computational approaches to enable efficient density functional theory calculations that are exactly corrected for the electronic self-interaction error. Our team will develop, test, and validate a user-friendly, open source software package, scalable over the number of electrons, that implements the Fermi-Löwdin-orbital-based self-interaction-correction[1-3] (FLOSIC) to DFT. The code development effort will be integrated with theoretical research investigating the use of FLOSIC with sophisticated semi-local density functionals such as the new “strongly constrained and appropriately normed” SCAN functional for both ground-state and time- dependent applications. Additionally, the FLOSIC code will be tested and validated through research involving heterogeneous, transition-metal-based catalysts and molecular magnets. Work is accomplished on the NERSC computers.

Technical Progress

The initial steps in this new project have been directed at improving the FLOSIC methodology. The performance of the FLOSIC code has been improved by roughly an order of magnitude through enhanced parallelization and algorithmic development. A procedure for computing analytical atomic forces in FLOSIC has recently been implemented and tested. Schemes for improved optimization of the so-called Fermi-orbital descriptors or FODs are under development. A paper was published reporting optimized FLOSIC-LDA calculations for atoms up to Kr.[4] We also completed a study comparing/contrasting the results of FLOSIC calculations with previous implementations of self-interaction-corrections in DFT and contributed to a benchmark study of FLOSIC using the G2 molecule test set.

Future Plans

The overarching goal of the project is to make possible self-interaction-free calculations for molecules and solids at a computational cost comparable to traditional density functional theory. The project has three integrated thrusts – theory, software development and implementation, and method validation. The planned theory research involves investigating the use of sophisticated new semi-local functionals such as the SCAN functional[5] and its successors within FLOSIC. An important effort is understanding where SCAN-like functionals that are designed to satisfy all known constraints on the exact functional need self-interaction corrections and how to implement FLOSIC in order to achieve the corrections in those circumstances but not others where the functionals give accurate results, for example, near equilibrium bond configurations. This will involve exploring alternative expressions for the SIC that can be implemented in the FLOSIC framework. A second theory initiative involves adding SIC to TDDFT calculations by using orbitals from self-consistent FLOSIC calculations to build the required response functions. Use of SIC orbitals is expected to yield improved descriptions of excitations.

The software development effort is aimed at creating an efficient, user-friendly code that implements FLOSIC for both localized and periodic systems, and for atoms across the periodic table. Significant progress has already been made in code parallelization and optimization (see above). Our objective is to produce code that will take full advantage of highly parallel next-generation machines with low memory per processor. Additional algorithmic and development initiatives include improving self-consistency and FOD optimization schemes; implementing FLOSIC in periodic calculations; including f-electrons and relativistic corrections; and allowing for non-collinear magnetism. The development team will work closely with the theory group to implement and explore the use of SCAN and related functionals in the FLOSIC code.

The theory and development work will be validated in a variety of ways, for example, by carrying out benchmark FLOSIC calculations on popular test sets to allow comparison with the performance of other functionals. We have strong interests in two areas, transition metal chemistry and molecular magnetism, where we plan coordinated theory and experiment efforts. In the first case, we will synthesize and characterize new metal organic framework (MOF) systems with open metal sites and investigate the binding of important adsorbates at those sites. The outcomes of this work will be compared to the results of FLOSIC calculations on cluster-based models of the same chemistry. For molecular magnetism, FLOSIC calculations will be done on sets of complexes using transition metals with different degrees of localization, supported by coordinated experimental efforts to synthesize and characterize the magnetic properties, including the magnetic anisotropy energy, of these complexes. This will provide a foundation for creating mixed 3d/4d oxo clusters as candidate molecular magnets with large anisotropy energies.

Access to the FLOSIC code

A git repository for the FLOSIC code has been created at quantum.utep.edu The respository is currently being used by our development team and public releases of the FLOSIC code are planned for the near future. The repository will also include training materials including sample input and output files. Supplemental information related to project publications will also be stored in this repository.

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Software tools for data-driven research and their application to thermoelectrics materials discovery

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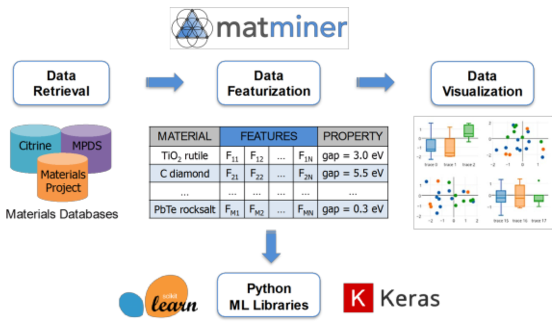
Website: none
Keywords: “thermoelectrics”, “high-throughput density functional theory”, “open source software”, “feature extraction”

Project Scope

This project aims to build software and methodological tools for data-driven materials design and apply those tools towards the design of new thermoelectric materials. The software being developed encompasses implementation and automation of existing methodologies as well as development of new methodologies in the areas of calculation automation and feature extraction for large data set analysis. The approach to thermoelectrics materials discovery includes both high-throughput screening with density functional theory and data mining methods. Success is measured by software and methodological impact as well as progress in the research and discovery of novel thermoelectric formulations.

Relevance to MGI

One of the pillars of the MGI approach is an emphasis on data and software tools. This project creates software tools to generate theoretical data on a large scale, i.e., via millions of simulations executed over a variety of supercomputing resources. It also develops software tools for the analysis of large data sets, specifically implementing feature extraction methods relevant to the materials science domain. By generating large data sets as well as transforming those data sets to make the best use of existing machine learning methods, this project aims to accelerate and change the way in which materials design is done.



MATERIAL	FEATURES				PROPERTY
TiO_2 rutile	F_{11}	F_{12}	...	F_{1N}	gap = 3.0 eV
C diamond	F_{21}	F_{22}	...	F_{2N}	gap = 5.5 eV
...	...	...	...	...	...
PbTe rocksalt	F_{M1}	F_{M2}	...	F_{MN}	gap = 0.3 eV

Figure 1. Schematic of one of the software libraries under development (“matminer”). Matminer can retrieve large data sets from external databases or from internal documents, extract features relevant to the materials science domain (e.g., compositional and structural “fingerprints”), and assist the user with data visualization and compatibility with standard Python-based machine learning libraries. The matminer software is available at *https://www.github.com/hackingmaterials/matminer*

To demonstrate the applicability of this framework, we are collaborating with the experimental groups of Snyder (Northwestern) and White (Dalhousie University) as well the theory group of Hautier (U. Catholique Louvain) to discover and experimentally realize new classes of thermoelectric materials. We have also used our software tools in collaboration with the Pei group (Tongji University) to better understand band convergence in new thermoelectric formulations, including a GeTe derivative with extremely high figure of merit[1] (zT ~ 2.4, device zT ~1.5).

Technical Progress

We have developed and released two software libraries as a result of this award:

- **Atomate** – software to simplify the process of generating data with theoretical methods[2]. Atomate implements common workflows for determining over a dozen materials properties (e.g., band structure, elastic tensor, dielectric constants, etc.) and allows those workflows to be automated at large supercomputing centers. Atomate has been adopted by several research groups worldwide and is now the production software infrastructure for data generation for the Materials Project. Atomate is available at *https://www.github.com/hackingmaterials/atomate*

- **Matminer** – software to retrieve and analyze large materials data sets (Figure 1). Matminer can retrieve data by interfacing with the APIs of several large database providers (Materials Project, Citrine Informatics, Materials Data Facility, MPDS) or load a user's internal data sets. It then assists the user with feature extraction – i.e., the process of converting raw data such as composition, crystal structure, or band structure into a series of physically relevant numbers that can be used to determine patterns in the data. Matminer has implemented 20 different featurization patterns, many of methods developed in the literature but with no open-source implementation, and is capable of generating many thousands of materials descriptors. Matminer also includes a built-in visualization package and interfaces to standard Python-based libraries for machine learning. Thus, matminer serves as a bridge between the materials community and the data science community. Matminer is available at *https://www.github.com/hackingmaterials/matminer*

Apart from software development, we have:

- Generated a large data set of electron transport properties under the constant relaxation time approximation for >45,000 compounds and published the data as open access[3] (downloadable through Dryad at *https://doi.org/10.5061/dryad.gn001*). A dedicated "app" for exploring this data through the Materials Project web site is in development.
- Used the data set above to screen for new thermoelectric materials. Three materials from the screening were experimentally synthesized and tested by colleagues. The first of these, $TmAgTe_2$, reached a figure of merit (zT) of 0.35, with further improvement limited by achievable doping[4]. A second, $YCuTe_2$, reached a zT of 0.75, to our knowledge the highest zT for a computationally designed material[5]. A third quarternary compound was synthesized, but demonstrated low performance due to inability to dope; a report is forthcoming.
- Finally, we have assessed the accuracy of various high-throughput methods to the accuracy of thermoelectrics screening[6]. For example, we found that Seebeck coefficients are better reproduced than the power factor under the constant relaxation time approximation (as expected), but underestimation of the band gap for typical DFT functionals can be problematic for both properties. We have also compiled reports on the thermoelectric potential for less-studied chemistries such as phosphides[7].

Future Plans

Future plans are currently concentrated on development of new crystal structure descriptors for materials data mining as well as improved electron transport models (over a constant relaxation time approximation) that balance accuracy and automation. These developments will be used to continue the search for new thermoelectric materials. We have also been extending our data set of computations to compounds with partial occupancies.

Data Management and Open Access

All the software and data developed by this project is being provided openly. The software is hosted online at Github (all projects listed at: *https://www.github.com/hackingmaterials*) under a Berkeley Software Distribution open source license. The data on electron transport properties has been shared through the Dryad repository (*https://doi.org/10.5061/dryad.gn001*).

Advancing Along the Materials Development Continuum

This project has demonstrated that new and unconventional thermoelectric compositions with moderate zTs can be uncovered through a computational approach. One of the major limitations in achieving even higher zT has been difficulties in estimating achievable doping levels, which has a large effect on the observed experimental properties but cannot be easily determined from calculations. Better methods are needed to estimate the extent to which a material can be doped n- or p-type and may be the subject of future work.

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Computationally guided design of multicomponent materials for catalytic reactions

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Keywords: catalysis, multicomponent, quantum mechanics, kinetic modeling

Project Scope

We are developing multicomponent catalytic materials that allow greater efficiency in energy-demanding reactions. Materials are prepared by nanoscale synthesis techniques to link functional components to catalyze an overall reaction. Close linking of these material components can reduce the formation of unwanted and environmentally hazardous byproducts and decrease the required energy input for important chemical reactions. Predictive multi-scale models are developed to guide the design of linking these components. Multi-component catalyst activity and selectivity are compared with single active site materials.

Relevance to MGI

An alternative approach to catalytic conversion is being developed using multi-component materials. Multi-component materials allow for tailoring of the active site in three dimensions, manipulating activity or selectivity beyond the performance of single component catalysts. Our computationally-guided design framework 1) utilizes atomistic and electronic structure methods to optimize individual catalytic components, and 2) uses a microkinetic model to guide construction of the multi-component material. Synthesis, fabrication, characterization, and reactivity studies validate computational models and realize the enhancements offered by the catalysts.

Technical Progress

Our research efforts towards developing approaches to multi-component catalyst cascade design continue to pursue five specific activity areas:

1) Design of Cooperative Active Sites Using Organic Monolayers

We are focusing on using the developed tools to design cooperative catalytic systems. Numerous important reactions consisting of combinations of steps (e.g., hydrogenation and dehydration) have been found to require bifunctional catalysts with both a late-transition metal component and an acidic component. Here, we developed a new method for preparing and controlling bifunctional sites by employing organic acid-functionalized monolayer films tethered to the support. This approach was used to create a reactive interface between the phosphonic acid SAMs and metal particles, where active site properties such as acid strength were manipulated via tuning of the molecular structure of the organic ligands within the monolayer. After surface modification, the resultant catalysts exhibited markedly improved selectivity and activity toward HDO of aromatic alcohols and phenolics (Figure 1). Moreover, by tuning the organic ligand of the acidic modifier as guided by a basic level of theory, the rate of deactivation was significantly reduced.

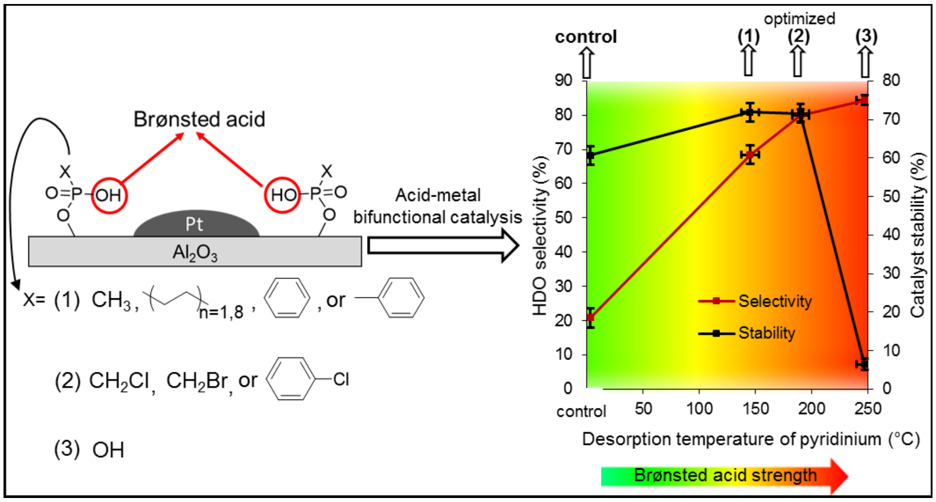

Figure. We used organic ligands to introduce and tune acidity at the interface between metal nanoparticles and their supporting oxide to control activity, selectivity, and stability during hydrodeoxygeantion (HDO) of aromatic oxygenates. (“Catalyst stability” refers to the reaction rates after 80 min of time on stream divided by the initial rates.)

2) Oxide on metal core-shell nanoparticles

One objective of our DMREF-supported work is to improve the selectivity during hydrodeoxygenation of biomass derived alcohols (such as benzyl and furfuryl alcohol) using cascade-type, porous Pd@TiO_2 core-shell catalytic structures that combine the selectivity enhancement possible through site confinement effects in the porous structure of TiO_2 shell with high activity potentially achieved through interfacial Pd/TiO_2 sites. The optimized Pd@TiO_2 catalyst improved the HDO selectivity for benzyl alcohol and furfuryl alcohol to nearly 100% from 50% and 22%, respectively, achieved with TiO_2-supported Pd nanoparticles under equivalent reaction conditions and conversions.

3) Oxidative coupling of methane in electrocatalytic cascades

There is significant interest in the development of direct methane conversion routes. A potential route for direct methane conversion is through a process known as the oxidative coupling of methane (OCM) which was first reported in the early 1980s. A fundamental issue with OCM is that, at the high temperatures applied, undesired over oxidation products such as CO and CO_2 are more thermodynamically favored than the desired C_2 products. We are developing membrane reactor approaches that distribute the oxygen supply to avoid over-oxidation, by designing alternative O^{2-} conducting materials that are also selective for OCM. We have fabricated and tested multicomponent Zr-doped $BaCe_{0.8}Gd_{0.2}O_{3-8}$ (BCG) materials. An important finding of our studies is that that the phase stability of BCG in OCM can be improved by doping with Zr without significantly affecting the C_2 yields obtained.

4) Microkinetic modeling of dual-site catalysts

We have constructed a microkinetic model that we use to consider the potential and limitations for dual-site catalysts to improve catalytic activity and selectivity. This model guides our rationale for designing multicomponent catalysts. This model has been used to conclude that multicomponent catalysts must pair dissimilar material types (metals and oxides, inorganic and organic, etc.) and illustrated how such differences can accelerate reactions at the interface.

These areas vary in their emphasis on synthesis, characterization and experimental testing, and theory/simulation, but these aspects are integrated both within and across these topics.

Future Plans

As our project nears its end, our future goals include further exploiting the various multicomponent material platforms to improve catalytic activity and selectivity. Emphasis on core-shell particles and functional SAM-modified catalysts is exploiting increased control in nanoscale material arrangements, guided by computational catalyst design, to improve catalyst performance.

Broader impact

The research project participants are receiving an integrated research experience with exposure to this integrated approach to materials development. Students participate in project phone calls, sharing their progress with PIs and students with expertise in computation and experiment. Undergraduate research students at our institutions get involved in this collaborative work, including exchange of students between partner institutions. PIs have participated in training workshops internal to our universities, including the GO-GIRLs Workshop at Wayne State, and in international forums on 3 continents.

Data Management and Open Access

Developed multi-scale models will be made available on a project website, and are included as online supplementary material in published papers.

Advancing Along the Materials Development Continuum

Our work has combined experiment and theory to accelerate catalyst development, though our project is not currently involved in any patent development or industrial efforts.

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Extreme Bandgap Semiconductors

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Keywords: Wide Bandgap Semiconductors, AlN, Gallium Oxide, UV Photonics, High Voltage Electronics.

Project Scope

The goal of this DMREF proposal is to develop the materials science of extreme bandgap semiconductors such as BN, AlN, Ga$_2$O$_3$, their alloys and their heterostructures, and to investigate their properties for future applications in power electronics, deep-UV photonics, solid-state qubits, superconductivity, and more.

Relevance to MGI

The goal of this DMREF project is to develop the materials science of extreme bandgap semiconductors: Boron Nitride, Aluminum Nitride, Gallium Oxide, and their alloys and heterostructures, and to investigate their properties for future applications in power electronics, deep-UV emitters, and more. Guided by rigorous mathematical and first-principles theory and modeling, the 4-PI team will explore fundamental questions regarding epitaxial growth, polarization-induced conductivity control, band anti-crossing in highly mismatched materials, effects of isotope engineering on electronic and thermal transport. Specific modeling aims include the predictive calculations of the fundamental vibrational spectra, electronic structure, and optical properties of the investigated xBGS materials.

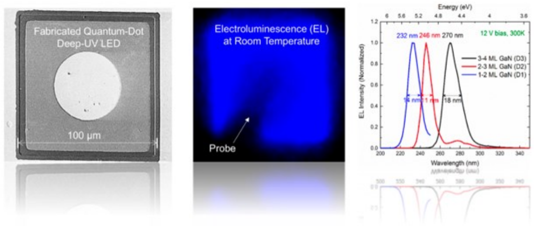

Figure. Deep-Ultraviolet Light-Emitting Diodes demonstrated at the shortest wavelength using ultrathin gallium nitride quantum wells as predicted by first principles theory.

Technical Progress

In Year 1, the DMREF team investigated AlN based extreme bandgap heterostructures grown by molecular beam epitaxy by the Cornell team. Their structural, optical, and electronic properties were explored experimentally, and were guided by first principles theoretical calculations performed by the team at Michigan. Thermal transport setup was installed and used for the measurements of extreme bandgap semiconductors grown at Cornell, provided to the Stanford team, and modeled by the Michigan team. In addition, the electron transport properties of the large bandgap semiconductor monoclinic gallium oxide (Ga$_2$O$_3$) was experimentally and theoretically evaluated. In addition to several publications by the PIs and students + postdoctoral scholars supported by the DMREF, two joint papers have resulted from the project in the first year: one on extreme quantum confined structures, and one on electron transport properties of bulk Ga$_2$O$_3$. **In Year 2,** the DMREF theory effort at Michigan focused on: (1) electronic and optical properties of ultrathin InN and GaN layers, (2) developing energetic calculations of Boron-containing nitride alloys, and (3) a study of the high-field breakdown properties of β-Ga$_2$O$_3$. These 1st principles theoretical work was used to guide experimental work at Cornell to design, grow, and study: (1) the enhancement of external quantum efficiency of short wavelength deep-UV light emitting diodes, (2) growth of Boron-containing nitrides, (3) use of isotopic mixtures of N-14 and N-15 for III-Nitrides and investigate the impact on electronic and optical devices, (4) molecular beam epitaxy growth of Ga$_2$O$_3$ with a focus on in-situ doping using Ge and (Al$_x$Ga$_{1-x}$)$_2$O$_3$ heterostructures, and (5) experimental measurement and modeling of electron transport of Ge doped Ga$_2$O$_3$ thin films. The Stanford team performed a study of the thermal properties of several AlN and GaN and Ga$_2$O$_3$ based structures (bulk layers, superlattices, and heterostructures) grown by MBE at Cornell, and an analytical and first-principles theoretical investigation of thermal and thermoelectric properties was discussed to understand and guide further experiments.

In Year 3 to date, the DMREF theory effort at Michigan The Michigan team has expanded the theoretical prediction of breakdown electric fields in extreme gap nitrides and oxides, and has investigated ultrathin InN wells, and BInN alloys and their stability. Their theoretical predictions of materials stability and solubility, and electrtonic and thermal properties are driving the experimental efforts of epitaxial growth and characterization of the structural, electronic, and photonic properties of the xBGS semiconductors at Cornell, and of thermal conductivity studies at Stanford. In addition, several first demonstrations of high-voltage β-Ga_2O_3 based switches have been realized for the first time in this DMREF at Cornell. The results show significant promise for fundamental advances *and* real-world applications. Several *patent disclosures* have been filed in the final year as a result of this project.

Future Plans

In Year 3, the Michigan team's theoretical first-principle modeling studies will a) Investigate the electronic and optical properties of atomically thin InN, b) Study the thermoelectric and thermal transport properties of beta-Ga_2O_3, and c) Investigate the electronic and optical properties of BGaN and BAlN alloys. The Cornell team will build on the growth of Ga2O3 and its heterostructures to explore the theoretical predictions from the Michigan team, and continue the exploration of the electronic and optical properties of ultrathin heterostructures, and xBGS nitrides. Special emphasis will be placed on the development of Boron containing alloys and BN, which is made possible now with a stable Boron source in the MBE system. These thermal properties of these samples will be explored by the Stanford team by sample exchange, which has been ongoing. The Stanford group will use the 3-omega technique to measure the temperature-dependent thermal conductivity of different nitride samples grown by the Cornell team, including AlN, GaN, InN crystals with different dopant and doping levels, and AlN/GaN superlattice structures. Using the analytical thermal conductivity model, the Stanford team will calculate how impurities (densities measured by the Cornell group) affect the thermal conductivity. The Stanford group will also use the 3-omega technique to measure the thermal boundary resistance between various XBGS materials and their substrates. The Stanford group will measure Seebeck coefficient of AlN/GaN samples, to compare with the theoretical values calculated by the Michigan team. If time permits, scanning thermal microscopy (SThM) will be used to sense the temperature profile and study the thermal properties of 2D material transistors on XBGS substrates.

Broader impact (Only required for NSF projects)

Postdoctoral Scholar (Dr. Amit Verma) supported by the NSF DMREF started an independent career as an Assistant Professor. Undergraduate students (Andrew Devine and Athith Krishna) have joined PhD programs at UCSB and Cornell. Two young women graduate students – Lily Xu at Stanford, and Kelsey Mengle at Michigan are supported by this DMREF program. During Year 1, course videos and materials were recorded for the classes on Compound Semiconductors Materials Science (MSE 5460), and on Lasers and Optoelectronic (ECE 4300) taught at Cornell by PI Jena. These materials including the videos are now available freely on the web, and the PI is under discussions with Prof. Gerhard Klimeck at Purdue University to host these materials on the NanoHUB, another NSF supported project. At Michigan, the educational activities include the incorporation of the research finding of deep-UV emission due to extreme quantum confinement of GaN in the instruction of MSE 242, Physics of Materials, for which the Kioupakis was the instructor during the Winter 2016 academic semester. At Michigan, the educational activities include the incorporation of the research finding of deep-UV emission due to extreme quantum confinement of GaN in the instruction of MSE 242, Physics of Materials, for which the Kioupakis was the instructor during the Winter 2017 academic semester.

Data Management and Open Access

This project has produced computational data for the band structures of atomically thin GaN, AlN, and beta-Ga_2O_3 that have been disseminated in peer-reviewed publications and are being made available on the project's website.

Advancing Along the Materials Development Continuum

The theoretical predictions by the Michigan group in this project led to the experimental demonstration of the shortest wavelength ultraviolet LEDs by the Cornell group. The prediction of high breakdown critical field in Gallium Oxide led to the demonstration of the highest breakdwon voltage Gallium Oxide transistors by the Cornell group. Several patent disclosures have been filed as a result of the research work pertaining to deep-ultraviolet light-emitting diodes, and high voltage nitride and oxide extreme bandgap semiconductor based electronics. The Stanford group has been working with Anasys Instruments to combine the scanning thermal microscopy (SThM) with the 3-omega method in order to determine the thermal resistance and thermal conductivity of the sample under study.

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Analysis and Optimization of Polymer Networks for Emerging Applications

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Keywords: polymer networks, topological defects, junction functionality, mechanical properties, gel point

Project Scope

The objective of this project is to characterize the structure and topology of amorphous polymer networks, study how the structural and topological information translate to bulk materials properties, and either improve the properties and theories of existing materials or design and develop new materials and theories. Specifically, polymer gels and elastomers are made, and the topological defects in the materials are analyzed using experimental, computational, and theoretical tools. The mechanical properties of the materials are also studied, and the relationships between topological defects and mechanical properties are investigated. Theories for predicting the properties of new polymer networks are developed from these studies.

Relevance to MGI

We seek to analyze the structure and topology of polymer networks (Figure 1), understand the impact of these parameters on materials properties, and improve the properties of existing materials or design new materials based on the knowledge and insights. All of these tasks require the combination of experiment, theory, and computation. For example, in order to analyze the topological defects (loops) in networks, we developed new experimental methods that allow for the direct measurement of loops, and the measured loop fractions were validated by simulation and theories. The precise measurement of the loop fractions in networks allowed us to study the impact of loops on mechanical properties quantitatively, which enabled the development of new network elasticity theories. Inspired by the findings, we developed a method to tune the mechanical properties of materials by controlling the amount of loops, which provides a straightforward way to improve the mechanics of common polymer networks. Moreover, we developed a new class of materials assembled from polymer ligands and metal–organic cages (MOCs) as junctions, which considerably increase the network branch functionality, provide multiple handles to tune the materials properties, allow for unique chemical and physical processes within the MOC pores.

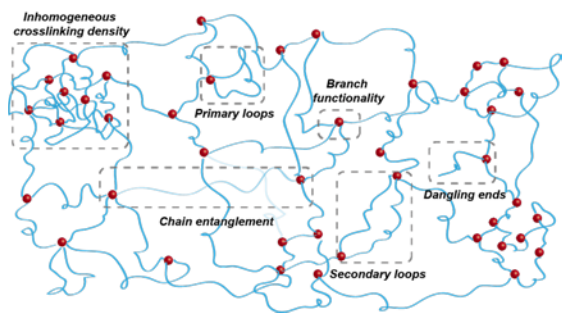

Figure 1. The structural and topological information in a polymer network, including topological defects (e.g., primary loops, secondary loops and higher-order loops), chemical defects (dangling chain ends), chain entanglements, branch functionality and inhomogeneous crosslinking density.

Technical Progress

To predict and understand the properties of polymer networks, it is necessary to quantify network defects. Of the various possible network defects, loops are perhaps the most pervasive and yet difficult to directly measure. We have developed the method, network disassembly spectrometry (NDS), which enabled counting of the simplest loops—primary loops—but higher-order loops, e.g., secondary loops, have remained elusive. In the most recent work, we improved the method by introducing a non-degradable tracer within the NDS framework, enabling the simultaneous measurement of primary and secondary loops in end-linked polymer networks for the first time. With this new “NDS2.0” method, the concentration dependences of the primary and secondary loop fractions were measured; the results agree well with a purely topological theory for network formation from phantom chains. In addition, semi-batch monomer addition is shown to decrease both primary and secondary loops, though the latter to a much smaller extent. Finally, using the measured primary and secondary loop fractions, we were able to predict the shear storage modulus of end-linked polymer gels via real elastic network theory (RENT).

In addition to our past studies on end-linked networks, we have developed a method to count the loops in pendantly functionalized networks for the first time. Pendantly functionalized polymer newtorks are widely used in academia and industry, and our method allowed us to investigate the impact of loops on the elastic modulus of these materials. Currently we are working on a new theoretical model to predict the amount of loops in pendantly functionalized networks.

Accurate prediction of the gel point for real polymer networks is a long-standing challenge in polymer chemistry and physics that is extremely important for applications of gels and elastomers. We applied kinetic Monte Carlo simulation to simultaneously describe network topology and growth kinetics. By accounting for topological defects in the polymer networks, the simulation can quantitatively predict experimental gel point measurements without any fitting parameters. Gel point suppression becomes more severe as the primary loop fraction in the networks increases. A topological homomorphism theory mapping defects onto effective junctions was developed to qualitatively explain the origins of this effect, which accurately captures the gel point suppression in the low loop limit where cooperative effects between topological defects are small.

Gels formed by coupling two different four-arm star polymers lead to polymer networks with high strength and low spatial heterogeneity. However, like all real polymer networks, these materials contain topological defects which affect their properties. We used kinetic graph theory and Monte Carlo simulation to investigate the structure and cyclic defects formed via A–B type end-linking of symmetric tetra-arm star polymer precursors. While loops constituting of odd number of junctions are forbidden by precursor chemistry, the amount and the correlation of secondary loops are found to increase with decreasing precursor concentration. This suppresses gelation, and the delay of gel point was quantitatively predicted by the topological simulations.

Future Plans

Future plans include studying the mechanical properties of polymer networks with trapped entanglements and developing the network elasticity theory that accounts for both trapped entanglements and cyclic defects. In addition, we seek to expand the predictive power of our theoretical and computational models by extending them to networks with dynamic bonding interactions.

Broader impact (Only required for NSF projects)

The outcome of the project enables the better understanding and prediction of materials mechanical properties and facilitates the synthesis of materials with enhanced and finely tuned mechanical properties. The methodology of studying structural topology in polymer networks and its impact on materials properties can be applied to the study of materials in biology, such as the extracellular matrix (ECM) and cartilage, and may open new interdisciplinary research fields. The project provides excellent opportunities for students and postdocs to develop their professional skills for their scientific career paths. The broad dissemination of the project results can advance discovery and understanding, promote teaching and learning, and therefore benefit not only scientific community, but society as a whole.

Data Management and Open Access

We have been working on the development of a “Global Index of Gel Attributes” or “GIGA” website that will provide a database for the structure, composition, topology, and properties of amorphous polymer networks. This page will include apps that enable users to carry out simple calculations of the gel point, loop fraction, and other parameters of polymer network structure and properties.

Advancing Along the Materials Development Continuum

Though there has been extensive advancement in computation-based accelerated design of molecular materials and/or materials with a high degree of order (e.g., crystalline materials), there has been much less progress for amorphous polymer networks even though the latter materials are arguably the most prevalent and important in daily life. Precisely because amorphous materials lack order it is much more difficult to predict their bulk properties quickly from molecular structure alone. Our project has tackled this challenge using a holistic approach that integrates new methods for high-resolution characterization of polymer network topology with new computational and theoretical tools that utilize this information to enable rapid and accurate predictions of network properties from precursors.

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Accelerated Design of Strong, Highly Conductive Carbon Nanotube-based Fibers *via* Electrical Fusion

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Keywords: carbon nanotubes fibers, electrical fusion, conductivity, coarse-grained modeling, machine learning

Project Scope

The weaker inter-nanotube interactions lead to degradation of carbon nanotube properties within their fibers. We exploit a novel process based on electrical fusion to realize local structural transformations between nanotubes within their fibers. Our approach integrates fused fiber processing, mechanical characterization, fiber-scale coarse-grained models, and machine learning algorithms to identify process and structural variables that simultaneously enhance the strength and electrical/thermal conductivity of these fibers. The project has led to development of an in-situ fusion processing technique, a new set of coarse-grained approach for modeling nanotube and/or graphitized fibers, and clustering algorithms that enable predictive design of multifunctional carbon nanotube fibers and yarns.

Relevance to MGI

The interplay between nature and extent of structural transformations and fusion processing variables is crucial for developing predictive capabilities for targeted fiber properties. Nanotube-scale transformations following fusion were identified *via* collaborations between controlled fiber fusion experiments and structural characterization. Mechanical characterization, including a new tear test for the network material (in roving form) and coarse-grained models that explored the effect of structural transformations – graphitization, density, alignment, bundling extent. These studies were used to fine-tune the fusion processing variables – voltage, current, frequency, fusion time – through an iterative loop that identified nanotube alignment and quenched curvature as key variables. The studies also highlighted fiber property degradation due to defect generation at large fusion treatment times. The resultant database of processing and structural variables was subject to clustering and related data-mining algorithms that identified the role of derived variables - instantaneous power and average power, the total energy load, the rest time between pulses, and enabled development of predictive capabilities that allowed design of characteristic time scales of the treatment, and yielded insight into

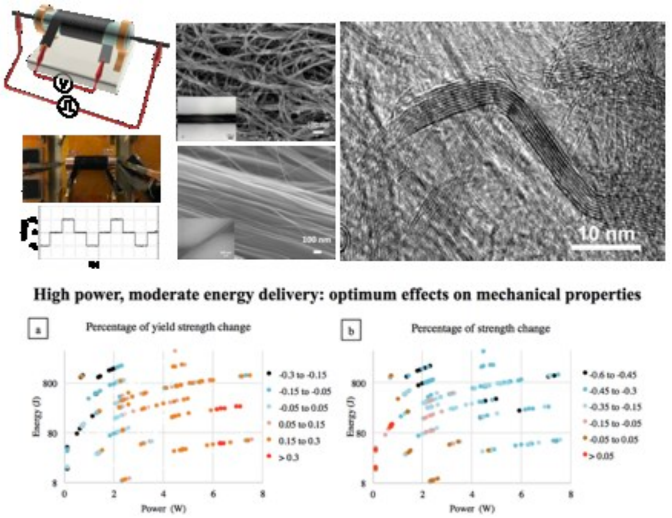

Figure 1. (top left) Image of the electrical fusion furnace. **(top right)** SEM fiber images of before and after fusion showing alignment sand bundling. TEM image showing graphitization. **(bottom)** Mechanical characterization reveals mechanical strength is controlled primarily by input electrical energy/power.

the fundamental processes that lead to fusion. The predictions of coarse-grained models and machine learning algorithms were validated using controlled experiments, leading to accelerated design of processing variables for targeted fiber properties.

Technical Progress

Our final year of this project focused on developing predictive capabilities for fiber properties. Graphitization of double-walled nanotube has emerged as the primary structural transformation during electrical fusion, that also leads to formation of molecular junctions (Fig. 1). Using a combination of mechanical characterization and coarse-grained models, we have developed a comprehensive database that relates the processing variables to mechanical strength and conductivity of these fibers. Supervised learning algorithms allowed us to identify input power and to a lesser extent, energy, as key variables that lead to enhanced strength, and this has been confirmed via structural characterization and experimental validation of these predictions. Using structural characterization as inputs, a new class of coarse-grained modeling efforts with self-consistent graphitization of the fibers have been used to extract the viscoelastic response of these fibers that complement prior studies on alignment, density and bundling extent. These studies show that the graphitization has by far the most dramatic effect on the mechanical strength. The results are in agreement with mechanical characterization studies, and training set algorithms of coarse-grained simulation results and experiments successfully predict the mechanical strength within the tolerance levels associated with the measurements.

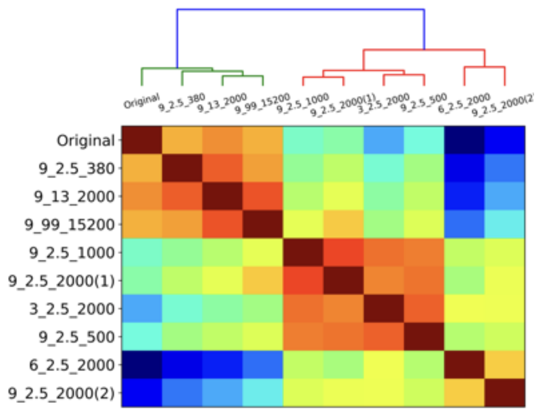

Figure 2. Results of clustering algorithm Raman Spectra of fiber samples subject to varying processing variables. The distance between samples is a measure of the sensitivity of the structural transformation to the fusion variables.

We are also deploying the learning algorithms to develop a fundamental understanding of the processes that lead to fiber fusion. Raman spectra plots of the fused and unfused fibers have been subject to clustering algorithms (Fig. 2) that identify key variables that lead to dramatic changes in the nanoscale structure. For samples that show significant structural transformation, the learning algorithm is being used to identify the frequency range associated with the most changes in the Raman spectra. This method should allow us to uncover novel regions of the frequency spectrum associated with the structural transformations, and offer insight into the nature and extent of these transformations.

Future Plans

Our project has successfully demonstrated an MGI-based approach to develop fibers with optimal multifunctional properties. We plan to extend our efforts in the following areas: i) development of a roll-to-roll process for fiber processing using developed knowledgebase, ii) extending this methodology to other classes of carbon-based nanoscale fibers, in particular graphene nanofibers, iii) targeting applications that rely on the multifunctionality of these fibers such as artificial muscles, thermal engineering via directional heat transport, and self-actuating heterostructured/coaxial nanofibers.

Broader impact (Only required for NSF projects)

This project has generated 5 PhD theses within Northeastern University, - 2 defended, 3 expected within a year. All students were exposed to an MGI-centric approach to material design with significant interactions with industry. Two of these students conducted internships in industries (Tesla and Gravyty), and we believe their exposure within this project was instrumental in their placements. As broad impact, we have given talks within Northeastern undergraduate community (Embark, Society of Women in Engineering) and the materials community (MRS, ASME) that have highlighted the success our project has enjoyed. co-PI Kaeli is involved in NSF-REU programs that has led to further exposure of MGI-based approach in materials research to a wider net of undergraduate students, in particular those with non-materials background.

Data Management and Open Access

The coarse-grained computations required development of novel strategies that incorporated nanotube bundling and graphitization, and these were done under the umbrella of an open source code, LAMMPS. It is our plan to make the relevant subroutines open to public on the completion of this project (late summer, 2018). The database that relates the processing variables, structural variables and multifunctional properties is searchable, but not open for public consumption yet. It is our focus within the coming months to work with open-source platform that i) allows the database to be shared, and ii) and to make it searchable through the web. We are exploring options with collaborators in NIST to realize this.

Advancing Along the Materials Development Continuum

As of now, no patents have been filed, but based on our results, we expect to file at least one patent on fusion processing of nanotube fibers in the coming months. A significant part of this project involved interactions with Mark Schauer and Eitan Zeira of Nanocomp, a company at the forefront of development of nanotube-based high strength fibers. Initially they provided us with their yarn material for some of the fusion experiments and we have co-authored publications with them. In addition, they worked with us on the interactions between the preparation of the starting material and the results of the fusion process. For example, they have chemical/mechanical pretreatments of their yarns that improve the properties of the network by aligning its constituent filaments.

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DMREF: The heterovalent nitride semiconductors and mixed binary-ternary heterostructures

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Keywords: nitride semiconductors, heterostructures, band structure, doping, optoelectronic devices

Project Scope

We aim to accelerate the understanding and control of the growth and properties of the heterovalent ternary nitride semiconductors and mixed ternary-binary heterostructures. Ab-initio calculations of band structure, defects, and optoelectronic and lattice properties help guide the growth experiments, inform the characterization measurements, and provide interactive feedback for modeling of device structures. We focus initially on developing the growth by MOCVD of $ZnGeN_2$ and heterostructures of the $ZnGeN_2$-GaN mixed systems, taking advantage of their close lattice match, close optimal growth temperatures, and their predicted large band offsets, then expand to other materials in this large, expanded group of nitride materials.

Relevance to MGI

Considering the tremendous technological importance of the III-nitrides and approaches to the intrinsic limitations of these materials in some applications, we look toward significant advances in the design of materials properties and discoveries of new functionalities in the closely related but heretofore little-studied II-IV-nitride materials family. The figure shows the band gaps versus lattice constants of some of these ternary compounds, mapped onto those of the III-nitrides, in partial illustration of the wealth of combinations of new materials structures made possible by this expansion. We have the unique capability to grow by MOCVD high quality III-nitride layers and II-IV-nitride layers without cross-contamination, with control of growth parameters not previously made possible. This instrument, designed and constructed as part of this effort, is just now coming online. Meanwhile we have had tight collaboration and feedback on *ab-initio* calculations of fundamental properties with device modeling and with measurements of materials grown by vapor-liquid-solid methods.

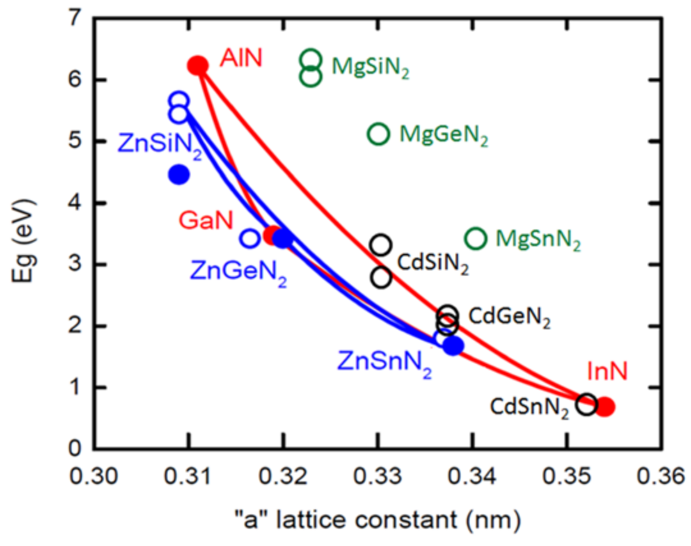

Figure. Band gaps versus lattice spacings of some II-IV-nitrides and the binary nitrides. Open circles are *ab initio* calculations by this group. Where there are two open circles, the lower is an indirect gap. Filled circles are experimentally determined values.

Technical Progress

We have extended *ab-initio* computational studies to the band structures of the Mg-IV-nitrides, the Cd-IV-nitrides, tripling the number of band structures of the II-IV-nitrides calculated accurately by QSGW methods, and calculations for $ZnGeGa_2N_4$ are in progress. For the latter, we found two models that obey the octet rule locally to have significantly lower energy than the models which violate it. We also found that the band gaps in this system were slightly higher than in GaN or $ZnGeN_2$, indicating that size quantization effects more than compensate the large (~1 eV) staggered band offset. We have calculated energies of interstitial and substitutional native defects in $ZnGeN_2$ as well as various potential dopants including Ga, C, Cu, and Ag. Our results indicate that while Ga is a shallow acceptor when on the Ge site, it is compensated by Ga_{Zn}, C prefers the N site substitution over Ge or Zn or interstitial sites but has relatively deep levels. Because the d-levels of Ag lie somewhat deeper than Cu we also tried Ag but still find the levels to be too deep in the gap to give efficient p-type doping. We plan next to explore alkali metals. More involved defect complexes may be required to give efficient p-type doping.

We have continued theoretical and experimental studies of the vibrational modes in $ZnGeN_2$, and have found excellent agreement between theory and experiment in particular in Raman spectroscopy on c-oriented crystals. We also predicted the phonon spectra of the family of Cd-IV-N_2 materials. We have designed and modeled LED structures with enhanced efficiencies in the ultraviolet, blue and green spectral regions using a $ZnGeN_2$ layer inserted into the active region of a III-nitride heterostructure. We have modeled intersubband transitions in GaN-$ZnGeN_2$ heterostructures for applications to quantum cascade laser structures.

The construction of the custom MOCVD instrument was completed in May 2017. Kash and one graduate student received training on operating the instrument in July 2017 prior to shipping of the instrument to OSU in September 2017. Lab renovations and installation at Nanotech West at OSU have been completed and growth tests are underway.

We have created, populated and promoted a publicly accessible database for the heterovalent ternary nitrides and II-IV-nitride heterostructures.

Future Plans

Specific goals and the work plan for the next year are summarized briefly here:

- Achieve MOCVD growth of $ZnGeN_2$ on GaN buffer layers on sapphire substrates
- Improve the crystalline quality and control of stoichiometry of $ZnGeN_2$ films through rapid feedback with relevant characterization tools, including XRD, AFM, PL, Hall measurements and Raman spectroscopy
- Determine intrinsic and extrinsic properties of high quality $ZnGeN_2$, through temperature-dependent and time-dependent PL and PLE, visible and UV absorption, reflectivity, spectroscopic ellipsometry, Raman spectroscopy, and temperature dependent Hall measurements
- Fabricate elementary device structures, *e.g.* Schottky diodes or p-n diodes enabling DLTS and other measurements relevant to defect identification
- Explore GaN-$ZnGeN_2$ mixed systems and site control of Ga for doping of $ZnGeN_2$
- Control the doping of both n-type and p-type $ZnGeN_2$ through tight feedback between growth, characterization and *ab-initio* calculations
- Grow planar GaN-on-$ZnGeN_2$ type-II heterostructures and determine their band offsets experimentally
- Explore MOCVD growth of $ZnSnN_2$ and Mg-IV-nitride films on GaN, InGaN, and other substrates
- Expand the theoretical and computational database of properties of these materials systems
- Refine our models of the defect physics and ordering through interaction between theory and experiment
- Develop tools for visualizing more complete band structure information on our website, in collaboration with other theory groups, currently under consideration for supplementary funding.

Broader impact

Many of the II-IV-nitrides, for example $MgSiN_2$, $MgSnN_2$, $ZnSiN_2$ and $ZnSnN_2$, are composed entirely of abundant and inexpensive elements and as such are potential replacements for energy-critical and expensive alternatives. Development of strategies for synthesis of the heterovalent ternary nitrides and mixed ternary-binary heterostructures by MOCVD, and progress in understanding their properties through *ab-initio* work, coupled closely to modeling and measurement, is contributing an important body of work to the research infrastructure. The project also affords unique opportunities for training of graduate and undergraduate students, contributions to the teaching infrastructure, and public outreach. Outstanding examples are the experience of an experimentalist graduate student with ab-initio calculations of band structures of $ZnGeGa_2N_4$, and calculations of phonon spectra of $BeSiN_2$ and $BeGeN_2$ by an undergraduate. One female PhD student, Lu Han, who participated in this project, successfully defended her dissertation in Feb. 2017 and is now an engineer at Intel. Dissemination of new and archived results via the freely available interactive website-accessed will continue to foster a growing network among research groups, and will be relevant to a broad range of potential applications.

Data Management and Open Access

A website dedicated to the II-IV-nitrides was established. The first-principles computational approach used in this project is the linearized muffin-tin orbital (LMTO) method and its implementation of the quasiparticle self-consistent (QS) *GW* method. These are available through the questaal.org website to which the co-PI W. L. is a contributor. He has also participated as lecturer in hands-on workshops of these methodologies.

Advancing Along the Materials Development Continuum

The custom-designed MOCVD instrument will allow us to explore synthesis of these materials with multiple doping sources, accelerated by guidance from *ab-initio* calculations of defect properties as described above. The close collaboration between the three PIs on theory, MOCVD material synthesis, material characterization, and device fabrication will provide a closed-loop and fast feedbacks between each to accelerate the development of the material discovery. We envision transformative leaps in our understanding and control of these materials and structures and in the availability of information needed for researchers to take advantage of the greatly expanded potential of the nitride semiconductors in the design of new materials properties for a multitude of applications.

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Center for Predictive Simulation of Functional Materials

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Website: https://cpsfm.ornl.gov
Keywords: Quantum Monte Carlo, Electronic Structure, Correlated Materials.

Project Scope

Today, the design of functional materials is greatly hindered by the limited predictive power of established quantum mechanics-based approaches. The strong coupling between charge, spin, orbital, and lattice degrees of freedom that results in desired functionalities also challenges established modeling approaches. For example, functionals for density functional theory calculations are used empirically in practice, while extant quantum many-body approaches do not offer the capabilities, accuracy, and general applicability that is desired. The goal of the *Center for Predictive Simulation of Functional Materials is the development, application, validation, and dissemination of parameter-free methods and open source codes to predict and explain the properties of functional materials for energy applications*. The ability to quantitatively predict, analyze, and therefore design functional materials with tailored properties will accelerate new materials development and bring truly enabling and essential clarity to our modeling and understanding of functional materials.

Relevance to MGI

The Center develops and distributes *robust*, *convergent*, and *generally applicable* electronic structure methods, implemented in the QMCPACK[1] code, that properly and predictively capture the physics of functional materials, by taking advantage of new developments in Quantum Monte Carlo (QMC) techniques. By virtue of their use of only limited and controled approximations, the QMC methods will enable reliable, accurate, and empirical parameter free predictions for correlated materials, including doped or materials with defects, where existing methods lack the necessary predictive power. These methods are also strongly placed to take advantage of today's petascale and tomorrow's exascale supercomputers. The methods may be used directly, to help inform the development of more approximate electronic structure techniques, or e.g., be used for upscaling and derivation of force-fields. Developments are validated in part by experimental studies on PLD-grown, bulk and defective vanadium dioxide, and MBE-grown bulk and potassium doped nickel oxides, which are exemplar correlated or quantum materials. Characterizations include studies at the Advanced Photon Source and Center for Nanophase Materials Sciences. We also validate QMC predictions on finite systems with high-level quantum chemical results.

Technical Progress

Technical progress is driven in part by our initial experiments on VO_2 and NiO where vacancies (VO_2) or K-doping (NiO) are used to tune metal-insulator transitions and act as a sensitive validation of the predictive power of the methodology. After initial bulk [2,3] and defect studies[4], we have begun to study the momentum distribution (Fig. 1), which is a property which requires a full many-body method to access. Unlike previously studied conventional materials, e.g. sodium metal, the momentum distribution in VO_2 lacks a strong discontinuity at the Fermi energy, strongly suggesting non-Fermi liquid behavior.

Methodogical development includes improvements to the calculation of eigenstates, calculating non-ground state properties, and improving the valence Hamiltonians solved by the method. Most significantly, we have developed a new generation of effective core potentials (pseudopotentials) optimized for many-body methods[5]. These aim to reproduce the properties of the all electron Hamiltonian, are fit and tested using only high-accuracy many-body methods, and use a simple Gaussian form suitable for QMC or quantum chemical methods. For the 3d row (Fig. 2), they are a significnatly improvement over previously developed sets.

We identified a new algorithm [6] that significantly improves the efficiency of the Slater determinant updates and potentially doubling the overall speed of a calculation, and replacing an algorithm used since 1977.

Crucial to the improvement in accuracy of QMC algorithms is the use of more sophisticated trial wavefunctions, e.g. via more determinants or higher-order particle correlation functions. We have developed a blocked variant[7] of the linear method for trial wavefunction optimization that is able to optimize tens of thousands of parameters and do so within the memory limits of current generation supercomputers.

While QMC is traditionally a ground state methodology, access to some excited states is critical for widest applicability and utility, e.g. to obtain band gaps in solids. We have developed a new size consistent variational algorithm for excited states [8]. In combination with the new optimizer and other developments, we aim to obtain accurate eigenstates and energies for the lowest excitations in solids.

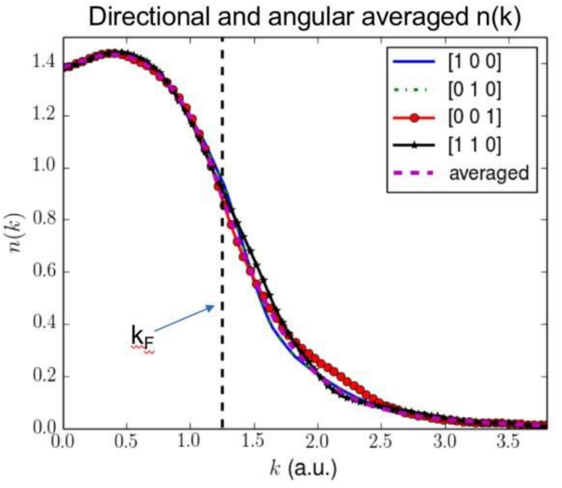

Figure 1. Momentum distrubtions of rutile VO_2 computed by QMC. The lack of a strong discontinuity at k_F indicates non-Fermi liquid behavior in this material and requires a many-body method to access.

Future Plans

We are applying the newly development methods to the materials systems where we have experimental validation (NiO, VO_2) and to related classes of materials where the predictive power is needed. We aim to complete the upper half of the periodic table of new generation ECPs, and will give preference to elements requested by collaborators or through the pseudopotentiallibrary.org site. Addition of spin-orbit will be required for heavier elements and materials.

Once proven in QMC, we will aim to reduce the level of detailed knowledge needed so that the new methods can be used by new users of QMCPACK and for problems, materials, and chemistries not tackled within the Center. We plan to record simple to advanced screencast example tutorials this summer, supplementing the labs and schools already available on youtube.

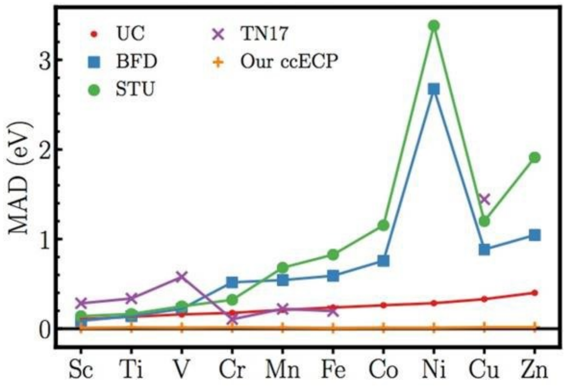

Figure 2. Mean absolute errors of various 3d element pseudopotentials for a broad range of excitations. Our ccECPs [5] and unpublished, have small errors and (not shown here) relatively constant error vs bond length.

Data Management and Open Access

The QMCPACK application is open source and openly developed. It is hosted at https://github.com/QMCPACK/ . Seven releases have been made between October 2016 and March 2018. Extensive datasets for each project publication are archived and published with unique DOIs at the Materials Data Facility https://materialsdatafacility.org/ . Our datasets range from a few MB to 500GB in size. To improve usability, we have also established a new open website for effective core potentials/pseudopotentials for correlated many-body methods https://pseudopotentiallibrary.org/ , either developed via this project or via community contributions.

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Nitride Discovery
Creating the Knowledge Base for Hard Coating Synthesis

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Website: none.
Keywords: Nitrides, Hard coating. Density functional calculations, Transition metal nitrides, Epitaxy.

Project Scope

This project creates a knowledge base on the reaction kinetics for transition metal nitride hard coating synthesis, with the ultimate goal to initiate a transformation from the current evolutionary development of protective coatings to a transformative coatings-by-design approach. Measurements on single-crystal layers and first-principles calculations will determine local equilibria and kinetic barriers for adatom adsorption, reaction, and diffusion for the complete set of 30 binary nitrides. This data builds the basis for a predictive model on the synthesis parameter space for over 500 distinct nitride phases and their off-stoichiometric variants, including phases that have been predicted to exhibit outstanding mechanical properties.

Relevance to MGI

Continuous close cross-fertilization between first-principles predicted phase energetics, x-ray diffraction measurements, and thin film processing is essential to develop the complete nitride synthesis phase space dataset. In particular, (i) simulations determine the effect of point defects on the lattice parameter which is essential to correctly interpret the measured X-ray diffraction results, (ii) the measured composition (nitrogen-to-metal) ratio vs temperature data quantitatively corrects the first-principles thermodynamic prediction for the critical temperature for nitride loss, (iii) thin film deposition and subsequent experimental characterization defines the compositional and structural space that needs to be simulated, (iv) the measured hardness confirms or corrects empirical hardness-vs-elastic-constants correlations that are used to predict hardness from first-principles, (v) computations provide systematic data for all nitrides, including those for which the synthesis phase space is outside of current experimental capabilities.

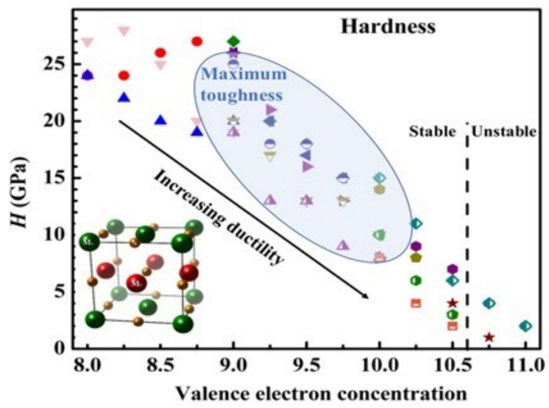

Figure. Predicted hardness vs valence electron concentration in ternary transition metal carbonitrides. A relatively unexplored region in compositional space with a predicted maximum toughness is identified. (Balasubramanian, Khare, Gall, Submitted for publishing, in review process)

Technical Progress

Some major technical achievements and related publications:

(1) *Mechanical properties of ternary carbonitrides* [1, 2] were studied using both experimental and computational approaches. NbC_xN_{1-x}, a novel compound, was synthesized; elastic modulus and hardness were measured throughout a range of temperatures. High hardness indicated great potential for

application in thin film coatings. Therefore, in search of materials with similar or higher hardness than that of NbC_xN_{1-x}, 15 ternary carbonitrides were studied computationally. A thorough database of mechanical and electronic properties was constructed. Not only were several compounds with high hardness discovered, but a direct relationship was also found between hardness and valence electron concentration (VEC), as shown in Figure 1 [2].

(2) *First principles phase diagrams* [3-5] were computed for quasibinary systems TiN-ZrN, TiN-HfN, and ZrN-HfN, allowing prediction of stable and metastable phases for each alloy. Electronic structures and mechanical properties were also computed throughout a range of concentrations. We discovered an increase in hardness through mixing, which could be explained through the solution hardening mechanism. Similar computations were also done for transition metal carbonates and transparent conducting oxides; relevant databases were constructed for each.

(3) *Experimental investigation of cubic WN_x* [6-8] *and related alloys* [9-11] was conducted systematically. The compounds were synthesized, x-ray diffraction data was tabulated, and the nitrogen concentration was measured throughout a range of temperatures. Mechanical and electronic properties were also reported as a function of temperature and nitrogen concentration. To provide more theoretical explanation, WN_x was also studied computationally. Results indicated that defect-free WN was both mechanically and thermodynamically unstable, however, stabilization occurred through introduction of W or N vacancies. Elastic properties were also computed and found to be closely linked to arrangement of t_{2g} orbitals in the electronic structure. Similar methods were implemented to study phase transitions in vanadium oxides and $CdCr_2Se_4$ [12, 13].

Future Plans

(i) The next step towards defining the best synthesis routes of hard nitrides is to study the effects of deviations from stoichiometry, and alloying. These will be accomplished through experimental synthesis as a function of nitrogen partial pressure and temperature (which directly controls the nitrogen chemical potential), and synthesis of newly predicted ternary nitrides from our first-principles computations. Focus will now be on ternary disordered phases involving two metals and nitrogen. Special emphasis on alloying for different applications and phase diagram predictions will be considered. (ii) The public database will be populated further by our own computational and experimental data as well as from the scientific literature.

Broader impact

This project has directly impacted a total of 5 graduate and 2 undergraduate students that have been working collaboratively to determine the best synthesis routes and mechanical properties of transition metal nitrides. They have been trained in materials synthesis, characterization, and computational methods relevant to the hard coating industry. In addition, they maintain a community-driven ceramics database to educate the interested general public about nitride properties and to provide accessible data that is essential to academic and industrial development engineers who design new hard coatings. Open access software has been generated to speed repetitive complex computations of structural, elastic and mechanical properties of single crystal materials, which will impact research in a wide range of ceramics.

Data Management and Open Access

We have created a centralized platform for storage, search and analysis of single crystal data related to structure, composition, elastic and mechanical properties for ceramic materials. Electronic, optical, thermal, tribological and other properties may be added to the database on demand. The database is free, open access, user-friendly and community driven. Data stored in the database is expected to be populated by contributions from the world-wide research community. Responsibility for ownership of results, their veracity and accuracy will be the responsibility of the contributors. For this purpose, a direct online DOI original source citation feature is available. A user may engage with the database as a data contributor with full control of the entered data in terms of addition, correction or deletion. Another way to benefit is to access data contributed by others. In this latter mode, user-specified tabular display and graphical display of trends in searched results is facilitated. Downloading of a sub-set of the searched data is available. Finally, external links to origins of the data in cited papers and contact information about the contributor or paper authors is accessible. The backend data structure has been designed for increase of size and features as demand increases.

Advancing Along the Materials Development Continuum

One of the key advances of this project is the discovery of particularly tough nitrides in a relatively narrow composition range. This was only possible because of the MGI computational approach since the traditional trial-and-error method for optimizing coating hardness never discovered these phases, as their hardness is actually slightly lower than that or neighboring nitride phases. The key challenge for commercialization is the narrow region in compositional and synthesis space. The project is currently exploring alternate synthesis parameters and related compounds which may have a higher likelihood for an accelerated transfer to industrial production.

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DMREF:SusChEM: Simulation-Based Predictive Design of All-Organic Phosphorescent Light-Emitting Molecular Materials

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Keywords: Purely organic phosphors, TDDFT

Project Scope

Although prevalent in OLED applications, organometallic compounds exhibit poor stability at short wavelengths, they are costly, and present environmental threats due their rare-earth metal content. Consequently, the purely organic phosphors we recently discovered by serendipity[1] provide an attractive alternative. However, despite intensive study, reliable design principles for purely organic phosphors are still lacking. In this project we therefore combine computational and experimental techniques in a synergistic design cycle for highly emissive room temperature organic phosphorescent materials, establish an integrated design framework, and derive rational molecular design principles for organic molecular electronic materials in general.

Relevance to MGI

Purely experimental exploration of molecular design requires time-consuming development of chemical synthesis routes, while unequivocal separation of multi-varied influences on materials properties is often challenging. Conversely, atomistic simulations can establish the trends in materials behaviors as a function of chemistry, structure, and processing conditions in a fraction of the time. Computational approaches can clearly pinpoint the origin of specific behaviors, allow one to effortlessly change variables that reveal the underlying mechanisms, and thus provide fundamental understanding. In this project computation is used to accelerate discovery by strategically guiding experiments and by identifying targeted materials design principles.

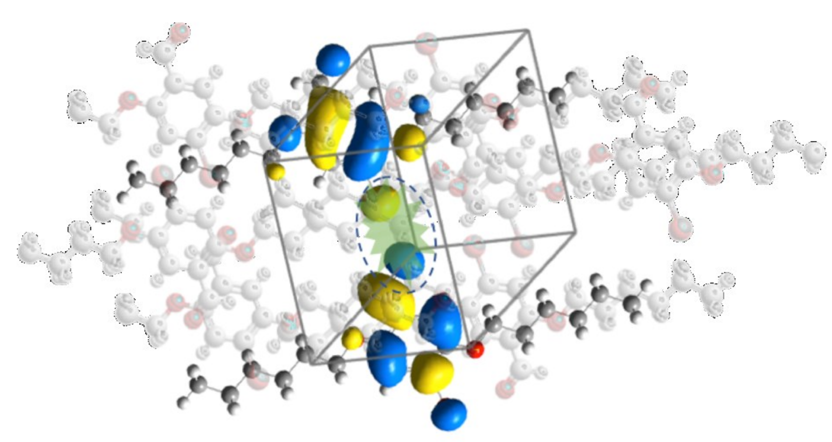

Fig. 1 Molecular orbitals of two Br6A molecules associated with halogen bonding between them. (HOMO on the top and LUMO on the bottom molecule.

Technical Progress

Using TD-DFT calculations, we conclusively demonstrated the existence of halogen bonding in Br6A and other derivatives of this molecule, which strongly suppresses the non-radiative deactivation processes of the phosphorescent excited state by restricting the bond rotation and conformational mobility of the molecule. Furthermore, by sustaining HOMO and LUMO states, bromine facilitates spin–orbit coupling and promotes the decay of the triplet electron that leads to room temperature phosphorescence with high quantum yields (Fig. 1).

To identify general molecular design criteria for purely organic molecular phosphors, we systematically investigated a series of fluorene-core organic phosphor derivatives with different carbonyl groups and substituted for Br all of the other halogen species. Among these, I-based compounds are most sensitive to thermal motion and susceptible to phosphorescence intensity decay. The BrCF3 molecules, which is functionalized with two phenyl side chains and a CF_3 group exhibits a PL quantum yield of 23%. By precisely tuning the distance between purely organic phosphor crystals and plasmonic nanostructures, with a plasmonic band tuned to match that of absorption, surface plasmons can enhance phosphorescence emission by a factor of three.[2,3]

Eliminating the toxicity associated with heavy metal elements makes all-organic phosphorescent materials attractive for bio-medical luminometric sensing applications. Given the high sensitivity of metal free-phosphors to oxygen can be used to probe the bio-activity of cancer or wounds by monitoring oxygen-consumption in the surrounding region. We fabricated polystyrene nanoparticles using poly(2-methyl oxazoline) and PMeOx-based block copolymer. Because the fluorescence of this phosphor is not affected by oxygen, and can thus serve as a reference, ratio-metric read-out is possible.[4]

Triplet states are populated with high probability upon excitation, but very weakly emissive. One approach to improve the emission efficiency is to invoke thermally activated delayed fluorescence (TADF), in which the excited electron migrates from the triplet state to the singlet state. However, one of the challenges is to narrow the emission spectra. We are therefore working on TADF molecules with sharp and narrow emission spectra. By systematically exploring molecular architectures, we have identified molecular structures that show sharp and narrow emission spectra based on predictions using TD-DFT calculations.

To improve our understanding of exciton and polaron pair interactions at interfaces, we have developed a model of excited states based on an effective mass Schroedinger equation. Carrier wave functions are represented by their envelope function, molecule-specific local interactions obtained from DFT calculations are incorporated, and the resulting electrostatic interactions are determined by solving the Poisson equation. We find that the insertion of molecular dipoles at interfaces can improve polaron pair dissociation and that sharp transitions in dielectric permittivity can have a stronger effect on this process than even the electron-hole Coulomb interaction.

Future Plans

We will pursue molecular designs that allow for vibration suppression through internal reinforcement or grafting of moieties that result in steric hindrance limiting vibrational amplitudes. Using computation, we have already identified several molecular architectures that exhibit the desired behaviors. The principal challenge is to identify molecular architectures that can also be realized in the laboratory at a reasonable cost. We endeavor to further advance our understanding of the TADF mechanisms and how they relate to molecular architectures. This effort will also be guided by computational exploration. Finally, we envision to design molecules that simultaneously exhibit fluorescent and phosphorescent emissions and tune their emission characteristics so as to achieve a broad and even emission spectrum, aimed at generating white light sources.

Broader impact (Optional for DOE grants/FWPs)

The new insights into the functional response of molecular materials gained while perfecting metal-free OLED benefits organic electronics in general, and advance technologies such as photovoltaics, sensors, and displays. Most importantly, we develop software tools, data management utilities, and workflows for simulation-based predictive materials design approach that can serve as a new paradigm for materials development. The synergy between experimental and computational techniques of investigation will provide students with a broader perspective on modern approaches in scientific research, a rationale that is also implemented in the courses developed and taught by the PIs.

Data Management and Open Access

In this project we will generate experimental and simulation based data, as well as simulation code and computational workflows. Data curation will be done following the Open Archives Initiative-Protocol for Metadata Harvesting (OAI-PMH) model used in the National Science Digital Library (NSDL). Accordingly, to each data set or image we attach a header, metadata, and optional containers, all encoded in XML format. To identify the appropriate metadata for a given measurement or simulation outcome, we will develop workflow-driven ontologies that help us to determine the ways in which other users in this field might identify or query data. Our metadata will also contain data provenance. Data will be generated, refined, or condensed at different workflow phases. The workflow typically progresses from (i) raw data (spectra, structures, images) to (ii) data prepared for analysis, to (iii) analyzed data (synthesized information, extracted parameters, model descriptions). The metadata structure for the atomistic simulations includes (i) the mathematical description of the underlying model, (ii) documentation as to the meaning and role of each term, (iii) parameter sets for various materials systems for which the model has been optimized, (iv) references publications on the model, (v) sample code to facilitate implementation, (vi) web logs containing questions and answers concerning user experiences.

Advancing Along the Materials Development Continuum

The improved integration and synchronization of computational and experimental aspects of the research workflow in this project allows us to obtain more detailed interpretations of experimental observations, as well as more reliable predictions of molecular designs for efficient all-organic OLED. The MGI objective is achieved by reducing the trial-and-error approach to a large extent. While the identifying appropriate synthesis routes, device fabrication, characterization, property measurement in the laboratory takes of the order of several months, the necessary information can be obtained through computation in a matter of two weeks. Hence, this aspect of materials discovery has been accelerated by a factor of six to ten.

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Extracting thermodynamic parameters of nanoscale structures by integrating physics-based modeling with X-ray scattering

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Keywords: Directed self assembly, X-ray scattering, block copolymer.

Project Scope

The project aims to integrate molecular simulation models of directed assembly of block copolymers into the data analysis of resonant soft X-ray scattering of oriented, periodic block copolymer nanostructures. The project will result in finding molecular simulation parameters that are consistent with the scattering from a real sample. This will allow the extraction of nanoscale thermodynamic properties from the block copolymer and the underlying directed self assembly template. These insights will guide the development of new block copolymers and template structures. The work will build a software framework for applying molecular simulations to the analysis of other metrology methods.

Relevance to MGI

The development of new block copolymers for directed self assembly has a huge parameter space including block copolymer chemistry, additives, processing parameters, and guiding template design. There are too many permutations to explore experimentally. Molecular simulation of the directed self assembly provides some insights, but the models need to be guided by experimental results. Directed self assembly systems developed for next generation lithography have feature sizes too small to characterize with typical methods like transmission electron microscopy. Resonant soft X-ray scattering has been shown to provide information on block copolymers, but the directed self assembly systems are too complex to get unique solutions from the inverse algorithms used to analyze scattering. Integrating molecular modeling into the scattering analysis reduces the parameter space sufficiently that unique solutions can be obtained for the scattering. These solutions are consistent with both the physics-constraints of the molecular simulation and the scattering from a real sample, allowing new insights to be obtained from the scattering. The combination of the scattering, molecular simulation, and well-designed test samples provide enhanced guidance to the design of new block copolymers and templates compared to what any of the methods can provide alone.

Technical Progress

We have applied both theoretically informed coarse graining (1) and self-consistent field theory (2) to the analysis of resonant soft X-ray scattering of block copolymers. The scattering is done on oriented nanostructures so that the measurement is essentially a single crystal diffraction experiment where the crystal is the repeating nanostructure. These measurements have considerably more information than an X-ray scattering measurement on a randomly oriented block copolymer. The enhanced information allowed the extraction of the three dimensional shape of directed block copolymer lamella and the guiding template. We obtained high quality data from a series of block copolymers with small changes in the guiding template structure. The materials simulations were used to fit X-ray scattering. The resulting solutions include information about the interfacial energy between the two blocks and various parts of the underlying template. We were able to determine that the etching process used to pattern the guiding template results in a structure where the sides of the template have a different interfacial energy than the top of the patterned template. This nanoscale variation in interfacial energy is believed to be the key to getting good directed self assembly.

Future Plans

The method of integrating molecular simulation into scattering analysis is being extended to new, more complicated block copolymer systems and to other measurement methods including resonant soft X-ray reflectivity and energy filtered transmission electron microscopy.

Data Management and Open Access

Data and codes are being provided to community through CHiMaD.

Advancing Along the Materials Development Continuum

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Adaptive fine-scale structure design: from theory to fabrication

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Keywords: fine-scale structures, homogenization, shape optimization, additive fabrication

Project Scope

This project is exploring the use of 3D printing to make structured artificial materials with advantageous physical properties. More specifically, the project is developing methods for adapting the fine-scale structure of a manufactured object to its macroscopic mechanical shape and function, specifically elastic properties. While 3D printing processes have restrictions that present design challenges (e.g. the need for support material or self-supporting structures, and limitations on resolution), these processes offer unparalleled flexibility in the choice of structure, making it feasible to explore a large space of possibilities both computationally and experimentally.

Relevance to MGI

This project is integrating theory, computation and experimental measurements. In current work, the formulations we are using are based in part on previous theoretical developments of shape optimization by homogenization. Extensive computation-based searches are used to discover periodic structures approximating target homogenized elastic properties. Sample patterns are produced using stereolithography-based printing. Already at this stage, fabrication informs theory and computation, as not all patterns end up being manufacturable. Elastic properties are measured and compared against those predicted computationally, and the results are used to inform further computational exploration.

Technical Progress

Worst-case stress optimization.

Our recent work involved a complete redesign of the "microscopic" optimization part of our algorithmic pipeline for constructing microstructures with target effective elastic properties.
The original algorithm produced structures that were prone to high stress concentrations. This occurred because the design criterion involved only the macroscopic response to a given load, not the maximum stress in the microstructure. Our original choice of parametric families of structures was insufficiently flexible to address this problem.

Major changes were introduced in our parameterization of the class of printable geometries, in the handling of joints, and in the meshing of the associated PDE problems.
(1) We have demonstrated that for a given point efficient explicit formulas can be derived for the worst-case stress occurring at this point under arbitrary linear deformation of a periodic structure.
(2) The optimization of this worst-case maximal stress is a PDE-constrained optimal design problem. As usual, an adjoint equation is used to determine a descent direction (shape derivative). We found that traditional methods of computing shape derivatives yield highly inaccurate results for functionals approximating maximal stress. We developed a new accurate method based on volume integrals to compute needed shape derivatives.
The structures designed using this new method are dramatically more robust than those produced by our prior algorithm. In numerical tests for periodic structures, the design process typically reduces the maximum stress by a factor of 5 or more, confirmed by mechanical testing.

Expanding the range of achievable elastic properties.

Most of the work to date has focused on structures with relatively simple topologies. However, the range of material properties that can be achieved in this way is inherently limited. We begun exploring the use of structures with more complicated topologies and relationship between topological complexity and the range of achievable material properties. For 2D problems, we have identified two families of structures that approach the theoretical limits on what is possible (the Hashin-Shtrikman bounds) as the parameter controlling topological complexity increases. For positive Poisson ratio we were able, with a relatively simple structure, to match theoretical limits (prior examples with similar properties required sequential laminates, which are cannot be practically manufactured). We plan to explore this topic further, using our shape optimization framework to minimize the topological complexity of the structure (within an appropriate family) for given material properties. Our plans also include attempting to extend these ideas to 3D structures.

A boundary integral approach to structural optimization. We are exploring an alternative approach to PDE constrained shape optimization based on integral equations rather then conventional FEM discretizations. This type of approaches avoids meshing problems entirely (no 3D domain mesh is necessary). These formulations are particularly convenient for certain types of multiphysics problems (fluid + elasticity, elasticity + heat etc)

Future Plans. The key directions we are currently working on include

(1) Making resulting codes and data publicly available (expected in summer 2018)

(2) Development of generalizations of our technology to arbitrary partitions of objects into hexahedral cells; this requires optimization of structures for a range of cell geometries in addition to target material properties.

(3) Extending PDE constraints to model additional physical aspects of optimized structures, e.g., fluid flow through the structure.

Broader impact. Two PhD students supported by the project graduated, one accepting a postdoc position at EPFL continuing his research on optimal shape design there; another student has joined Adobe Research where he works on computational design tools for 3D printing applications. A postdoc in part supported by the project joined University of Colorado at Boulder as an assistant professor. We are currently working with a startup company (nTopology) to integrate some of the developed technologies into their computational design software.

Data Management and Open Access

We have collected a significant amount of data on elastic properties of periodic structures in 2D and 3D in the course of this project. Some of the data are already released We expect that the main outcome of the project will be a collection of methods for generating fine-scale structures with desired parameters; we are already collecting some initial datasets (generated using NYU's HPC facilities) as well as measurements of fabricated sample patterns. The data are stored on the Courant Institute's servers with an off-site back up system and are at this time available to project participants. In addition to publications describing the methodology we develop, we expect to make CAD files describing useful patterns available online, accompanied by associated experimental measurement data. We also will work towards releasing a part of the experimental software we are developing.

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DMREF: Collaborative Research: Designing Optimal Nanoparticle Shapes and Ligand Parameters for Polymer-Grafted Nanoparticle Membranes

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Keywords: Polymers, nanoparticle.

Project Scope

Polymer membranes present an efficient solution for emergent technologies for selective and efficient transport of gases. While a key class of organic membranes is made of glassy polymers, they suffer from the fact that their permeability (i.e., product flux) and selectivity (i.e., purity of the desired species) are inversely correlated. Preliminary work using inorganic NPs chemically grafted into superlattices using polymer chains show that these materials offer unexpected advantages in the context of gas separation membranes..

Relevance to MGI

(i) to develop novel theoretical "design" tools to find the NP shapes and grafting parameters that optimize the permeability and selectivity of relevant gas mixtures; and (ii) to synthesize polymer grafted non-spherical NPs, assembling them into membranes and characterizing their multi-scale structure and dynamics using a suite of tools including advanced scattering techniques (x-ray, neutron) coupled with theory.

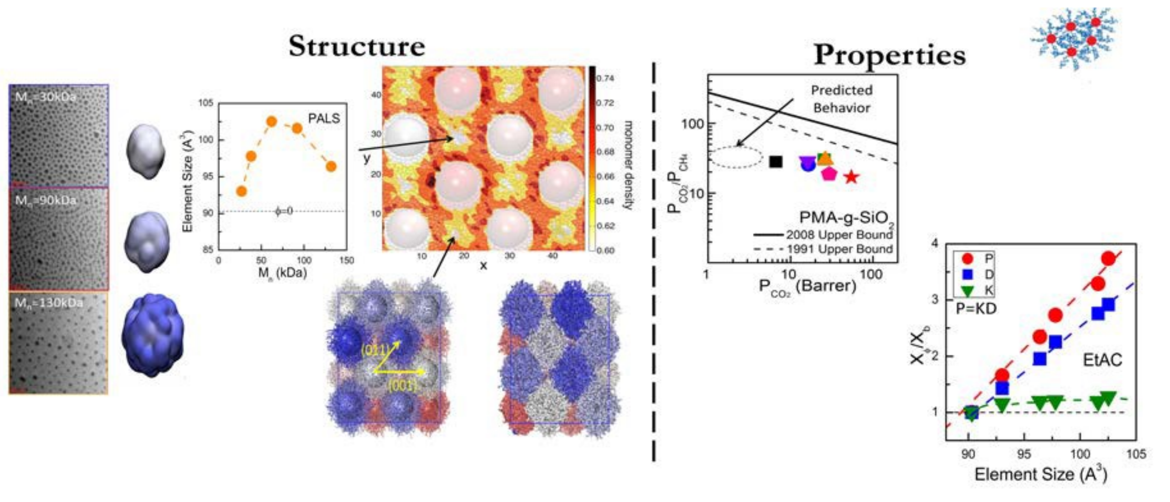

Figure. Please insert a figure that illustrates a key result or concept from this project. This caption should clearly describe the content of the figure. Make sure that all text in the figure is legible. [Figure caption font is Times New Roman, 10 pt.]

Technical Progress

Polymer nanocomposites offer the ability to pick and choose properties of multiple components and combine them into a single material. Often, the resulting properties are highly dependent on the internal structure of the composite, i.e. how the components are arranged together in space. In many instances, optimum performance is achieved when filler particles are uniformly dispersed in a polymer matrix. Good dispersion can be difficult to achieve, however, and is dependent on many factors such as how the components are mixed and processed, as well as the chemical interactions between components, both with each other and themselves. Due to the viscoelastic nature of many polymers, microstructure may change depending on the environment the composite is exposed to. This can render a polymer nanocomposite's properties hard to control and maintain over time. Initially we have focused on determining how microstructure of a polymer nanocomposite affects performance as a separation membrane, using an integrated synthesis, characterization, modeling, prediction approach. When polymer chains are covalently bound to the surface of the nanoparticle fillers, the system spontaneously orders itself into regular arrays, thus cementing the microstructure with uniform dispersion. By altering the polymer chain length and grafting density (# of chains per nanoparticle), both the concentration ratio of nanoparticle to polymer and the inter-particle spacing can be altered. By tuning the self-assembled structures, we have created membranes with superior performance compared to membranes comprised of non-grafted particles physically mixed in a "loose" polymer matrix. We are investigating the underlying physics and polymer dynamics which leads to such extraordinary results.

Based on Molecular Dynamics simulations it is postulated that the self-assembly of the polymer grafted NPs into ordered arrays creates "interstitial spaces" which can only be filled by stretching some of the grafted chains (entropic frustration"). Placing solute molecules in this central region relieves this frustration and yields the improved separation ability. This work is driven by two facts: (i) It is unclear if spherical NPs in fact cause the largest degree of chain frustration, (ii) It is increasingly recognized that non-spherical NPs (e.g., cubes) pack into meta-crystals that are stabilized by vacancies (or order 10%). Such unusual crystals have increased free volume which could improve gas transport.

We have developed the computational machinery to obtain quantitative atomic pair distribution functions (PDFs) from small-angle x-ray scattering signals from the polymer nanocomposite membranes and have begun a series of experiments using laboratory and synchrotron x-ray sources to obtain high-quality data for PDF studies of the nanoparticle distributions in the nanocomposite as a function of grafted polymer chain-length. These are being related to the molecular dynamics predictions of the equilibrated structures, and to the property measurements such as the gas transport.

Future Plans

We wish to develop our theoretical tools to the point where we can have an ability to design spherical nanoparticles that can be tuned to be optimized for a desired separation. To this end we will validate the MD results against measured PDF data for different grafted polymer lengths and develop a feedback loop that allows us to develop better effective particle-particle potentials. We will also seek lower-computational cost proxy models that allow us to study larger systems than are currently possible. The main focus of the proposal is to develop membranes with dispersed non-spherical particles, and to design particle morphologies for optimal gas separation properties. We will begin to synthesize novel membranes with non-spherical particles, explore the synthesis challenges. We will further develop the PDF methods to handle non-spherical form factors for the particles and then characterize the polymer nanocomposite membranes that have been made, and also to validate these results against the theoretical predictions for nanoparticle distributions in the material.

Broader impact (Only required for NSF projects)

Five researchers (one post-doctoral fellow, three graduate students and one undergraduate student) have worked on this project over the last year. The post-doctoral fellow just began his efforts in the area in June '17. Two of three graduate students have already participated in national meetings (APS March Meeting, ICOM meeting). One of these students, who would like to build an academic career, has already taught an undergraduate transport class at Manhattan college in the Fall of '16 and again this Fall.

Data Management and Open Access

The code that we have developed for PDF analysis will be released by Columbia Tech Ventures when it is ready to be released. We will also make our scattering data available with a digital object identifier (doi).

Advancing Along the Materials Development Continuum

The work is at too early of a stage to consider this. However, the technological implications of designer membranes for gas separations is significant and we aim to produce tools that have some predictive capability in this regard.

Publications

Connor R. Bilchak, Eileen Buenning, Makoto Asai, Kai Zhang, Christopher J. Durning, Sanat K. Kumar, Yucheng Huang, Brian C. Benicewicz, David W. Gidley, Shiwang Cheng, Alexei P. Sokolov, Matteo Minelli, and Ferruccio Doghieri **Polymer-Grafted Nanoparticle Membranes with Controllable Free Volume** *Macromolecules* **2017** *50* (18), 7111-7120. DOI: 10.1021/acs.macromol.7b01428 (2018)

Autonomous Materials Research Laboratory: Phase Mapping

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Keywords: machine learning, materials informatics, phase diagram, autonomous

Project Scope

The last few decades have seen significant advancements in materials research tools, allowing researchers to rapidly synthesis and characterize large numbers of samples - a major step toward high-throughput materials discovery. Machine learning has been tasked to aid in converting the collected materials property data into actionable knowledge, and more recently it has been used to assist in experiment design. We are building the next step in machine learning for materials research - an autonomous materials laboratory. The software system controls X-ray diffraction measurement systems at the beamline to identify phase maps from composition spreads with a minimum number of measurements. The algorithm capitalizes on prior knowledge in the form of physics theory and external databases, both theory-based and experiment-based, to hone in on the optimal results.

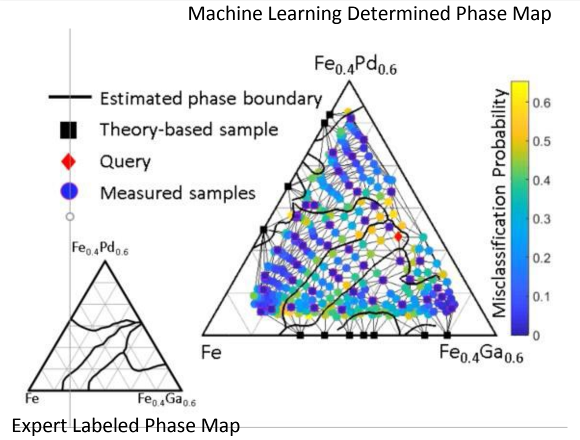

Figure. The autonomous phase mapping system utilizes physics theory, physics databases, and instrument control to rapidly identify a ternary phase map for the Fe-Ga-Pd material system.

Relevance to MGI

The autonomous X-ray diffraction metrology system is able to identify the phase map of a composition spread with 90+ % accuracy using only 10-15 % of the sample, greatly reducing instrument time at the beamline. The system works by integrating the instrument with physics theory and prior data, both experimental and computation-based, through machine learning, which runs measurement design, execution, and analysis. By reducing the number of samples required to identify a phase map by an order of magnitude, the system can play a key role in accelerating materials exploration and optimization.

Technical Progress

The system has improved in accuracy achieved with 10 % of the samples from 80 % to 90+ %. The system has been extended from phase mapping binary and ternary material systems to mapping the composition-temperature phase map of binary systems (see Brian DeCost's poster). Integration of prior structure knowledge has been improved. Accuracy measures now explore both classification accuracy and clustering-based phase map matching.

Future Plans

As this system is capable of experiment design, execution, and analysis through the selection of new materials to investigate, the system is being extended to include material synthesis. The new goal is to build an autonomous materials research laboratory capable of closed loop experiment design, material synthesis, material characterization, and data analysis.

Broader impact (Only required for NSF projects)

The team also works to teach machine learning to materials scientists through the annual ‘Machine Learning for Materials Research Bootcamp & Workshop’: https://www.nanocenter.umd.edu/events/mlmr/

Data Management and Open Access

Data collected will be stored on the Materials Data Curation System and a reference data set will be developed. Developed software will be posted to GitHub for public distribution.

Advancing Along the Materials Development Continuum

The system accelerates phase mapping by an order of magnitude for ternary material systems, suggesting a greater acceleration for more complex systems. We are investigating commercial use of the developed techniques.

References

Publications

Autonomous materials characterization systems: XRD and electrochemical prototypes

Brian L. DeCost, Jason Hattrick-Simpers, Zachary Trautt, Yangang Liang, Ichiro Takeuchi, and A. Gilad Kusne

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Website: none
Keywords: Autonomous systems, Active learning, Gaussian process, X-ray diffraction, electrochemical characterization

Project Scope

We are developing a suite of autonomous materials synthesis and characterization tools to support the MGI goal of accelerated materials design. These tools will leverage tight integration with developing materials data and computational infrastructure, the high-throughput experimental materials collaboratory (HTE-MC) network, and active machine learning methods. This presentation showcases two prototype autonomous systems designed to explore the chemical and physical properties of alloy systems through analysis of composition spread thin films. These systems use active machine learning models to efficiently explore large materials systems by sequentially selecting experiments that will reduce the model's predictive uncertainty.

Relevance to MGI

This project supports the MGI through

- Using machine learning models to drive integrated experiments and theoretical calculations
- Developing explicitly probabilistic models
- Integrating data curation and publication at the point of collection
- Enabling more scalable collaboration between experimental and theoretical researchers via integration with the HTE-MC

Technical Progress

The first autonomous system dynamically maps out structural phase diagrams using sparse X-ray diffraction (XRD) measurements and an in-situ heating stage. This system uses unsupervised clustering to partition a set of XRD spectra according to crystallographic phase. A Gaussian Process classifier extends the clustering results to obtain a probabilistic prediction of the phase diagram. We select a sequence of measurements so as to maximally increase the confidence of the model for the predicted phase diagram by balancing the strength of each predicted point with the model's uncertainty. Our system is nearly an order of magnitude more efficient than dense measurements for the VO_2-NbO_2 system, even when restricting the sampling order to monotonic increases in temperature.

The second system performs sparse scanned-probe electrochemical experiments driven by a Gaussian process model to explore local corrosion in potential corrosion-resistant coating alloys. Our early prototype is capable of identifying the edges of a cylindrical gold sample embedded in a polymer matrix using just 20 cyclic voltammetry measurements, an order of magnitude fewer measurements than a comparable dense scan.

Future Plans

Future work will focus on expanding to other experimental workflows and integrating the synthesis and measurement steps to obtain truly online experimental systems for optimizing functional properties of materials. Active sampling promises to enable efficient exploration of chemical systems with more than three components, with high (or adaptive) resolution in composition and temperature. We intend to incorporate our autonomous materials synthesis and characterization tools into the HTE-MC to provide an open experimental materials science platform for the materials and computer science research community to explore new materials systems and develop novel algorithms.

Broader impact (Only required for NSF projects)

Data Management and Open Access

The autonomous systems we develop will be tightly integrated with existing materials data curation infrastructure. Experimental and computational data will be pushed to a searchable repository as it is collected for downstream open access publication and reuse by the materials community.

Advancing Along the Materials Development Continuum

References

Deriving atomistic structural models of materials with correlated disorder from experimental data

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Website: https://www.nist.gov/programs-projects/measurement-and-prediction-local-structure

Keywords: correlated disorder, local structure, complex modeling, Reverse Monte Carlo

Project Scope

This project seeks to provide materials research community with a methodology and computer software that allow measurement and prediction of atomic arrangements in disordered and nanostructured/nanoscale materials which play an increasingly important role in a wide range of applications. The focus is on the development of a computational framework that combines input from multiple measurement techniques and theory to elucidate an accurate and comprehensive model of material's structure as required for establishing meaningful structure-property relations.

Relevance to MGI

Structure-determination methods that rely on traditional crystallography provide information on average atomic arrangements but ignore local deviations from translational periodicity caused by defects or atomic disorder [1]. As local structural details strongly affect the properties of many advanced materials, methods to measure them are of intense interest and currently comprise a frontier in crystallographic science [1,2]. None of the available techniques alone is sufficient to provide a unique comprehensive solution. We are addressing this challenge by integrating inputs from complementary experimental methods and theory in a computational framework that employs large-scale atomic configurations to fit all the data simultaneously. The project involves the development of data fusion and optimization algorithms, as well as approaches/tools to identify and represent structural features associated with disorder. All these capabilities are being implemented in the publicly available software, which we produce in collaboration with research teams at the neutron centers, SNS at ORNL and ISIS in the UK. The new methodology has already helped to address several long-standing questions about structure-properties relations in key electroceramic systems, providing guidelines that are now actively used in materials discovery and optimization. Concurrently, our developments place new demands on the quality of data generated by neutron and synchrotron facilities, motivating them to improve measurements instrumentation and protocols.

Technical Progress

We have developed a computational infrastructure, implemented in the RMCProfile software, that can fit simultaneously multiple experimental datasets under various geometric and theory-derived constraints. In this approach, a structure is modelled using atomic ensembles (up to hundreds of thousands of atoms) that allow for explicit treatment of local structure without assumptions or effective parameters. The atomic coordinates are adjusted according to a Metropolis-type Reverse Monte Carlo algorithm (RMC) until agreement between experimental and calculated signals is obtained. The resulting configuration represents a snapshot of the structure. The types of data that can be used in this analysis include X-ray and neutron total scattering (Bragg peaks plus diffuse background), extended X-ray absorption fine structure (EXAFS) spectroscopy, and 3-D diffuse scattering, as revealed with single-crystal X-ray, neutron, or electron diffraction. The method provides unprecedented level of structural details relating local chemistry and picometer atomic displacements in complex polycrystalline materials.

The RMC procedure is computationally intensive and the computing time scales as the third power of the number of atoms. Until recently, the models have remained restricted to about 20,000 atoms and length-scales less than three nanometers, although, even then, the computations could take months to converge. Such limitations significantly hampered the applicability of this method because in many advanced materials the determination of structural features that are linked to function requires models that span at least ten nanometers. Last year, we overcame this barrier by outfitting the RMCProfile software with novel algorithms and parallel and GPU computing, which reduced the computational times by up to two orders of magnitude. A major improvement in speed has been achieved by introducing an RMC algorithm that considers several atomic moves simultaneously, as opposed to the standard version in which the atoms are moved one by one. Now, models that contain over 500,000 atoms and interrogate distances up to ten nanometers can be refined within one week. Thus, structural solutions that were deemed impractical become routine. The speed-optimized RMC software also incorporates algorithms that correct the calculated X-ray and neutron total scattering signals for instrument resolution in both reciprocal and real spaces, as required for fitting these data over larger length scales. The newly redesigned software package has already been successfully applied to determine the nanoscale structure in bulk relaxor ferroelectrics and titania nanoparticles for photocatalytic applications.

In addition to the RMC method, we have been also working on methods to treat inevitable systematic errors in average-structure refinements from X-ray and neutron powder diffraction, which pose major challenges if fitting these two types of data simultaneously. Yet, such joint refinements are expected to provide more accurate estimates of structural variables than those derived using single-technique analyses. We have developed a Bayesian-statistics approach for correction of systematic errors in these refinements and implemented it in the popular software package *GSAS-II*. We demonstrated the benefits of this method using structural refinements from the same-sample diffraction data collected using four powder diffractometers that included the synchrotron and laboratory X-ray and two time-of-flight neutron instruments. Structural parameters estimated from standard refinements using the four datasets differed significantly. In all cases, the agreement improved considerably after applying our Bayesian error-correction procedure. We expect that adoption of the new method by the crystallographic community could considerably improve consistency of structural data reported in the literature, which are typically used as a starting point in computational materials design.

Future Plans

Future efforts will be aimed at improving the capabilities for structure determination in nanoparticles, 2D materials, and layered structures with stacking disorder. Another direction is the development of new approaches and algorithms for automated selection and adjustment of weights assigned to individual datasets during joint fits, which remain an Achilles heel for multi-technique analyses. Additionally, despite our recent breakthroughs, computing speed remains a limiting factor, which calls for the development of a new optimization algorithm that would make this speed more scalable with computing powder.

Data Management and Open Access

The software that we develop is made publicly available: e.g., www.rmcprofile.org, https://cran.r-project.org/web/packages/BBEST/, https://github.com/AntonGagin/GSAS_USE, see also https://www.nist.gov/mml/materials-measurement-science-division/materials-structure-and-data-group

Advancing Along the Materials Development Continuum

This project accelerates materials discovery and development by providing methodology and software tools for accurate and comprehensive multiscale determination of atomic arrangements in complex materials, the knowledge of which is a prerequisite for understanding and modeling of materials properties and performance. Additionally, the project develops data fusion approaches and algorithms that may benefit similar efforts in other areas of materials research.

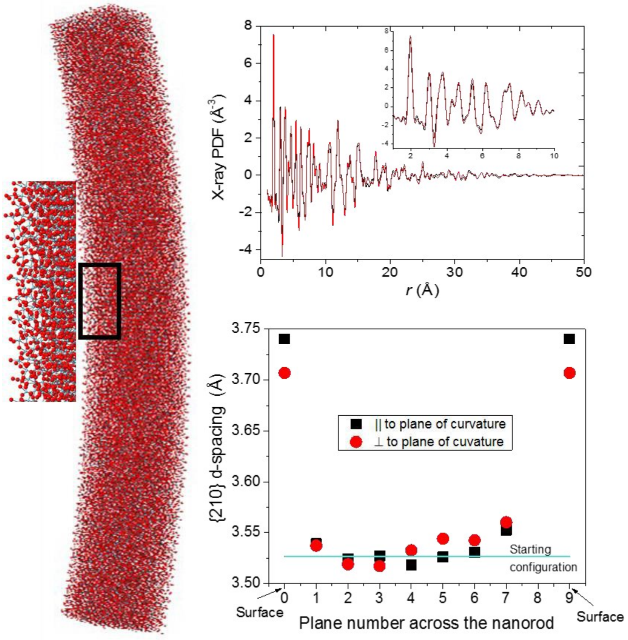

Fig. 1: An atomistic model of a brookite TiO_2 nanorod (left), 4 nm by 40 nm, determined by fitting the X-ray total scattering data in reciprocal and real (top right) space forms. These nanorods that are studied in collaboration with Prof. Cargnello's group at Stanford University exhibit superior photocatalytic properties, the origins of which remain yet to be explained. The nanorods are faceted on {210} planes and the nanorod axis is parallel to [001] direction. According to the electron microscopy data, the nanorods are bent with a curvature radius of ≈90 nm. Detailed refinements of such large models (≈60,000 atoms) from X-ray data have been enabled by our recent advances in the Reverse Monte Carlo software. This approach provides hitherto inaccessible information on spatial distributions of structural distortions in nanoparticles (bottom right), highlighting, for example, differences between the surface and core structures.

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Material Design Toolkit: towards a computational framework for materials design

Shengyen Li, Carelyn Campbell, Ursula Kattner, Steven Mates, Mark Stoudt

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Website: https://mgi.nist.gov/materials-design-toolkit
Keywords: Meso-scale simulation, CALPHAD, Material design, Machine Learning, Structural Material

A python-based framework, Material Design Toolkit (MDT), has been developed to assist the decision making in a multi-objective material design project that integrates experimental data, simulation models and computational tools. To demonstrate aspects of this framework it has been used to better understand the nonequilibrium behavior of a steel during a Kolsky bar experiment, where rapid heating, cooling and deformation produce unexpected microstructures and material behavior. For this application, it is important to be able to predict the volume fraction and stability of the austenite phase as a function of thermal and deformation profiles. To predict the austenite formation the MDT framework is used to combine experimental dilatometry, scanning electron microscopy, and high-strain rate Kolsky bar compression test data with existing models to predict the phase transformation behavior and some alloy properties. A comparison of the predicted phase transformations and yield stresses to the experimental observations will be presented.

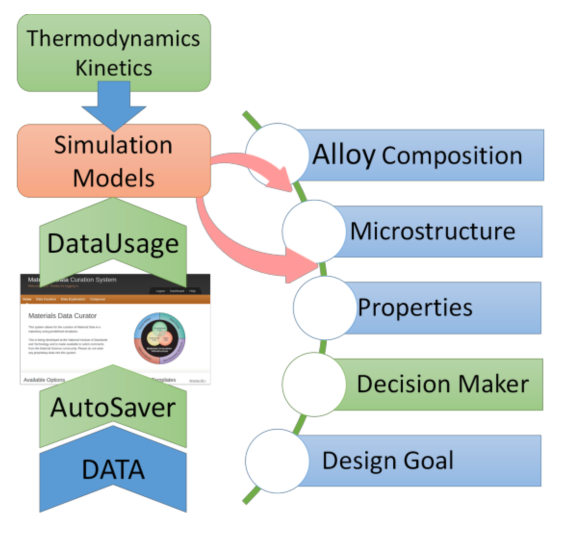

Figure. The computational workflow for material design constructed by material design toolkit; the Autosaver and DataUsage functions are developed to create a smooth data flow for ICME framework; the simulation models are implemented to interpret the relations from composition, processing, structure to properties for decision making to achieve the design goal.

Project Scope

Material Design Toolkit (MDT) is an Integrated Computational Material Engineering (ICME) framework using Python to assist the decision making for material design. There are three elements in MDT including data management, simulation models, and a decision maker. Data management modules enable the saving and retrieving of data from Materials Data Curation System, MDCS, using a REST-API. The additional functionality transforms the raw data into appropriate forms for various input into a variety of composition-processing-structure-performance relations. The hierarchical model is integrated with the decision maker to optimize the composition with the processing conditions to achieve the design goal.

Technical Progress

There are three phases of MDT project in NIST. Since 2014, the data management functions have been implemented to provide smooth data connections for the elements within the ICME framework. In 2017, the project moved to phase 2 and focused on the improvement of the decision maker. It uses the ensemble machine learning model with different sampling strategies, such as the Monte Carlo method, to suggest the solutions in high dimensional variable space for design problems. The machine learning model maps out the presented data and provides the probability density function of the solution space for the chosen sampling strategy to pick the candidate samples. These samples are evaluated by the following ICME framework and the results are used to retrain the machine learning model for higher accuracy. The efficiency of this recurrent learning process is intensely improved by number of search iterations.

Future Plans

Physics-based hierarchical models are more robust but require great efforts to assess and formulate the model parameters in comparison to the statistical models. The next phase of MDT is building a hybrid framework based on physics-based models with the support from machine learning functions to manage the model parameters. An integration with modern optimization tools and machine learning functions can minimize the manual inputs for model training and generate a better description of the model parameters to reduce model uncertainty.

Data Management and Open Access

The data including experimental and computational results are saved as XML files to one of the MDCS instances in NIST network. The data will be uploaded with the research publications to public interfaces such as NIST repositories (http://hdl.handle.net/11256/946).

Advancing Along the Materials Development Continuum

MDT is designed to assist the decision making based on the simulation models and the present data. The simulation models provide the relations from alloy composition through three-link chain model to material performance and the information is used to train the decision maker that suggests the design variables for the following evaluations according to the design objectives. This closed searching loop specifies the potential solutions including chemical composition and processing conditions for experimentalist to reduce the number of design iterations.

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Computational Design of Topological Disorder and Emergent Properties of Polymers using Stochastic Reaction-Diffusion Simulation

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Website: https://mgi.nist.gov/computational-design-photopolymerized-materials
Keywords: polymers, reaction-diffusion, stochasticity, disorder, phonons

Project Scope

The aim of this project is to computationally map polymer fabrication parameter to material properties. We are developing methods and associated computational software using the principles of stochastic reaction-diffusion, effective medium theory, and quantum Green's function techniques, to identify the effect of reaction chemistry and fabrication parameters on the spatial configuration of the polymer network, and on resultant properties. The software will accelerate the design of polymeric materials with targeted properties. As a use case the project focuses on photopolymerization, which is extensively used in 3D printing, lithography, and biomedical applications.

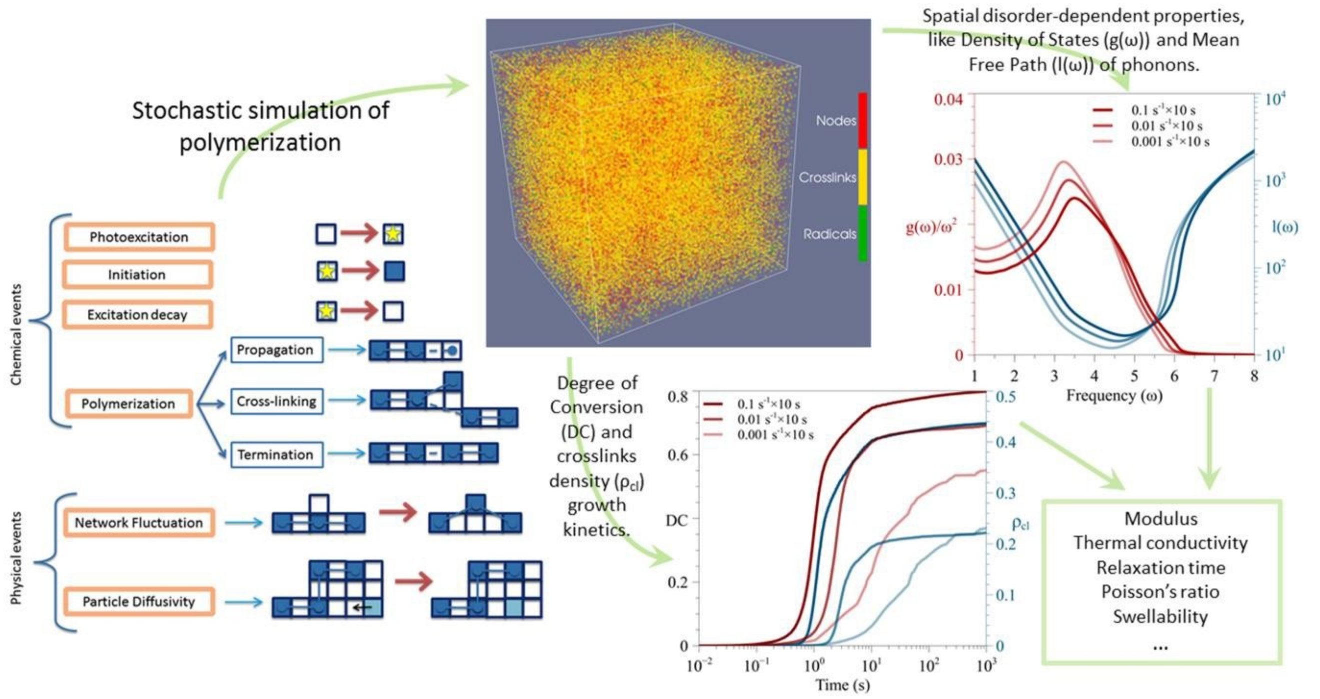

Figure. We simulate the evolution of a lattice polymer network as competing polymerization and fluctuation processes. The growth in network size, crosslinks, and spatial disorder as a function of control parameters are obtained from simulation. The spatially disordered network is used to determine the phonon Green's function and other material properties.

Relevance to MGI

The fabrication parameter space for polymer design is vast, and a computational approach is necessary to explore and realize the full potential of fabrication technologies. The methods developed for this project connects the well-established computational fields of coarse-grained polymer modeling, stochastic reaction-diffusion, percolation theory, and quantum Green's function calculations in new ways, which opens opportunities for new parametric simulations, thereby expanding the scope of polymeric material design. Experimental observations both from within and outside of NIST are being used to validate the software's ability to correlate fabrication control parameter to emergent material behavior. The Biomaterials Group at NIST has considerable experience in experimental characterization of photocured polymers. The combined computational and experimental effort has also produced new measurement strategies to determine the rate of transformation of a photopolymerizing material as a function of the photocuring environment. Hence, this project is producing both software for simulation and for novel analysis of experimental data.

Technical Progress

We have developed scientific software to simulate the reaction-diffusion process of photocured polymer network growth using a coarse-grained polymer model. Generally, a photocuring process consists of three classes of variables, the resin of monomers, the initiators, and the curing light source. Our software can simulate resin mixture of multiple monomers, varying in functionality and rate constants, multiples types of initiator systems, and curing light transients that are used in practice. Each simulation produces a sample stochastic trajectory of network growth during polymerization. We obtain a highly-resolved picture of polymerization kinetics, quantifying the degree of conversion (DC), growth in crosslink density, and drop in the diffusivity of the medium. We can determine the evolution of the spatial heterogeneity of the network due to competing polymerization and fluctuation events. Hence, the heterogeneity in network structure as a function of the reaction rate constants or viscosity of the polymerizing resin can be determined. This simulation method captures the salient features of photopolymerization, like auto acceleration and post cure polymerization. The slow diffusion of radicals in the jammed polymer network is known to cause a significant rise in the modulus over a long span of time. We have used this method to simulate post cure polymerization over the duration of a day to determine the slow increase in crosslink density. The disordered network structure that is produced from stochastic simulation is used to calculate the Green's function of the collective modes of vibrations (phonons). The vibrational density of states (DOS), mean free path, and velocity of phonons are obtained. A key feature of DOS is the 'boson peak', and the effect of crosslinker concentration and initiation rate constant on the 'boson peak' is identified. Using the initiation rate constant as a typical control parameter we have shown how, starting from the same resin, we can create polymers with different material properties.

We have also developed an experimental method to determine the evolution of relaxation time during the fast process of photopolymerization. Simultaneous measurements of DC, polymerization temperature, polymerization stress, and deformation is used to quantify the τ-vs-DC curves as a function of curing light intensity. We further show that the shifts in the τ-vs-DC curves carries information about the extent of clustering of crosslinks in the network.

Future Plans

We have planned two future directions for this work: (1) expanding the scope of stochastic reaction-diffusion simulation to other types of polymerization processes, and (2) developing new computational methods to determine more conductive and failure properties of the disordered polymer network. The first part involves introducing new reaction mechanisms like reversible crosslinking, and possibly include polymerization of composites. The second part involves furthering the analysis of the disordered network to obtain properties like fracture toughness and charge transport.

Data Management and Open Access

All scientific software produced from this project will be available from the NIST MGI site on Computational Design of Photopolymerized Materials (https://mgi.nist.gov/computational-design-photopolymerized-materials) for free, with sufficient documentation. The computational tools have been developed in Python, using the freely available Python packages, and users will not need any commercial packages for execution. The software related to the analysis of the experimental data is already available.

Advancing Along the Materials Development Continuum

A key aspect of the method and the scientific software developed for this project is the classification of the input parameters in a way that is familiar to those who are designing new polymeric materials in research and in industry. Hence, the progress from an experimental design to a computationally-guided design practice will be a seamless one. Measurements of quantities like the density of states and crosslink heterogeneity are often challenging. So the simulation software will also increase the ease with which material designers can explore new resin compositions and curing protocols. In a similar way, the experimental work builds upon existing measurement techniques, by theoretically justifying the necessary set of quantities that should be measured and by presenting a new method of analysis.

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Ab initio Theory and Computation of Multiple-Particle Correlated Excitations in Materials at C2SEPEM: Trions and Biexcitons

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Keywords: Interacting-particle Green's functions, multiple-particle excitations/spectroscopies, time-dependent phenomena, algorithms/codes for high-performance computing, BerkeleyGW

Project Scope and Scientific Topic of Talk

The mission of the Center for Computational Study of Excited-State Phenomena in Energy Materials (C2SEPEM) is to develop theories, methods, and general software to elucidate and predict excited-state phenomena in energy-related materials. C2SEPEM performs research on first-principles many-body perturbation theory and advanced algorithms, as well as their experimental validation and efficient implementation to high performance computers. Studies on quasiparticle excitations, optical spectra, trion and bi-exciton formation, exciton-exciton interactions, nonlinear optical processes, time-dependent phenomena, and more are carried out for bulk and reduced dimensional systems. In this talk, we report recent progress on the *ab initio* theory and computation of multiple-particle correlated excitations. We present our new formalism and computational methods, and results on trions and bi-excitons in carbon nanotubes. We also discuss an application to the decay of a photoexcited singlet exciton to two triplet excitons, discovering a purely Coulomb channel for singlet fission in molecular crystals.

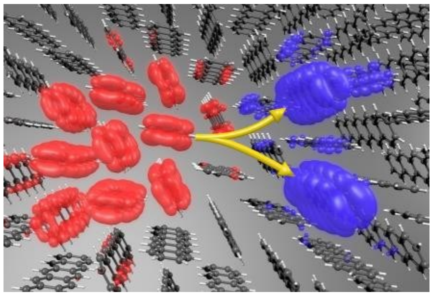
Relevance to MGI

Excited-state phenomena in a material typically give rise to its defining attributes and determine its usefulness. These phenomena are particularly important in processes of energy generation, transport and storage. However, *ab initio* methods for them, especially for multiple-particle correlated excitations and ultra-fast electron dynamics, have been under explored and hence limiting their studies in real materials. The methods and software developed at C2SEPEM (through a team of physical scientists, applied mathematicians and computational scientists) aim to fill this gap, and are relevant to the predictive study of complex materials and validated through close collaboration with experimental groups. The end result will be an integrated open-source software package (BerkeleyGW) with capabilities to predict and understand a variety of excited-state phenomena from first principles.

Technical Progress

The C2SEPEM was established in October, 2016. Its activities cover advances in the development and applications of theories, methods and codes in the areas of multiple-particle correlated excitations, time-dependent phenomena, algorithms for high performance computing, and large-scale excited-state properties calculations. Experimental validations are carried out as an important component as well. Fifteen papers have been published or submitted acknowledging the Center including 1 *Science*, 2 *Phys. Rev. Lett.*, 3 *Phys. Rev. B*, 1 *Phys. Rev. M*, 1

J. Chem. Theory. Comput., 1 *J. Chem. Phys.*, 1 *J. Am Chem. Soc.*, 1 *SIAM J. Matrix Anal. and Appl.*, etc. Some selected results are:



Ab initio many-electron calculations revealed a new mechanism (via a purely Coulomb process) for decay of a singlet exciton (red) into two triplet excitons. Predicted decay rate into 2 triplets of opposite center-of-mass momentum in solid pentacene is in good agreement with experiment.

- Development of many-body perturbation theory and the methods and codes for 3- and 4-particle correlated excitations which address phenomena such as exciton-exciton interactions, formation of biexcitons and trions, singlet exciton fission, etc., with applications to trions and biexcitons in carbon nanotubes.
- Development of *ab initio* methods for and the discovery of a new purely Coulomb mechanism for singlet fission in solid pentacene.
- Development of time-dependent GW (TD-GW) approach and codes for optical spectroscopy, pump-probe phenomena, and nonlinear optics. Applications with an adiabatic approximation to optical absorption were made and first time-propagation calculations of nonlinear optical coefficients were done.
- Code optimization and new algorithms have led to linear scaling of BerkeleyGW to 500,000 cores and large-scale GW calculations with ~2,000 atoms in ~2 minutes on the full Cori supercomputer with 50% of peak performance.
- GW and GW-BSE calculations on the quasiparticle states and optical properties of divacancy in SiC, a promising system for quantum information.
- Elucidation of the influences of chalcogen vacancies on the optical properties of monolayer transition metal dichalcogenide (TMD) systems.
- Development of stochastic GW methods for quasiparticle density of states, lifetimes, and couplings to plasmons for systems with > 1,000 atoms.
- Experiments have been performed to validate our theories/methods/codes for defects in monolayer TMD, singlet fission, and substrate screening effects on 2D materials.

Future Plans

Planned activities are focused in: 1) theories and methods for excited-state phenomena in energy materials; 2) advanced algorithms and new codes for the community; 3) verification and validation; 4) pilot projects demonstrating impact of the new methods with experimental validation. Area 1 concerns with the understanding and development of new ideas and methods, aiming at performing predictive calculations and making discovery of new phenomena and properties. Area 2 concerns with creating advanced algorithms and codes so that the methods developed in area 1 may be efficiently employed in high performance computers, especially for exascale applications. Area 3 concerns with the verification of the codes developed and the validation of our theoretical and computational methods through experiments. Area 4 concerns with performing specific studies on materials of current interest to demonstrate the impact and versatility of the new methods/codes.

Data Management and Open Access

All software developed as part of C2SEPEM are made available to the community using open source distribution licenses (the Open Source Initiative (OSI)) under the BerkeleyGW project and will be freely available through the BerkeleyGW website (www.berkeleygw.org) for registered users. The BerkeleyGW code itself is distributed with an open-source BSD license. Community input to the codes are solicited through workshops and meetings, and through the users forum on the BerkeleyGW website. Many of the methods developed and the resulting codes and libraries will be general and relevant for the chemistry, condensed matter physics, and materials science communities. C2SEPEM's goal is to deliver robust software, separate well-defined portable libraries and software tools in an open source manner such that it allows the components to be integrated into codes outside of the Center, thereby maximizing the impact of the development efforts. The Center's data management framework will support the complete data lifecycle: requirements, collection, processing and validation, archiving and sharing, access and dissemination.

Advancing Along the Materials Development Continuum

C2SEPEM develops *ab initio* theories, methods and codes for excited-state properties and phenomena that are not adequately addressed for real materials from first principles currently. Such predictive methodologies and studies fill an important gap in the spectrum of tools for the theoretical and computational study of materials. The codes developed, as mentioned above, will be made available freely to all researchers.

10 Selected Publications

1. Gabriel Antonius and Steven G. Louie, “Temperature-Induced Topological Phase Transitions: Promoted versus Suppressed Nontrivial Topology,” Phys. Rev. Lett. **117**, 246401 (2016).
2. Felipe H. da Jornada, Diana Y. Qiu, and Steven G. Louie, "Non-uniform sampling schemes of the Brillouin zone for many-electron perturbation theory calculations in reduced dimensionality," Phys. Rev. B **95**, 035109 (2017).
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DMREF: Rapid Design and Engineering of Materials Systems for Nanomanufacturing via Directed Self-Assembly

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Keywords: block copolymers, self-assembly, meso-scale, stochastic simulation

Project Scope

This project endeavors to (1) develop a design platform that tightly couples experiment and modeling of block co-polymers with dissimilar blocks (high x), and (2) use this platform to design new materials with smaller features. To address this challenge we are combining an accurate meso-scale energetic model, high speed GPU processors, and a novel stochastic simulation method. The successful completion of this work will include the accurate prediction of structure property relationships for these high x block copolymers and the use of these relationships to design new self-assembled systems with smaller features.

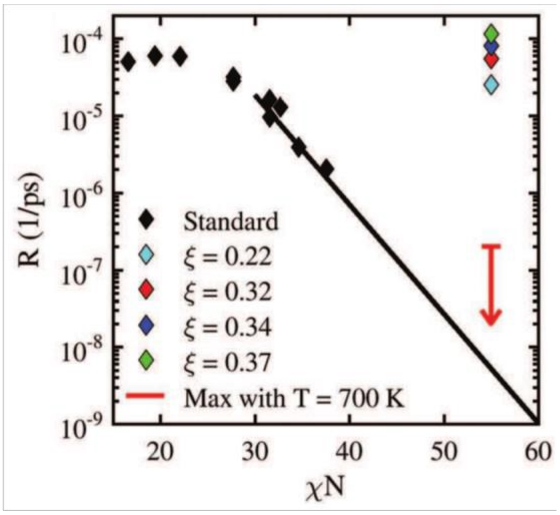

Figure. Simulated annealing rate of defects in block copolymer self assembled lamellae as a function of χN and the strength of stochastic fluctuations (ξ) in PCND. [1]

Relevance to MGI

The relevance to MGI is derived from the direct integration of experimental characterization of block copolymer directed self-assembly and simulation of the same. We have synthesized block copolymers (BCPs) at the high and low end of the spectrum for directed self-assembly (DSA). This spectrum is defined by the thermodynamic interaction of the two segments in the block copolymer, which is often described by the Flory-Huggins heat of mixing parameter χ. We already carried out simulations of BCPs at various values of χ, and we are currently carrying out molecular dynamics simulations of the specific high and low χ BCPs that have been synthesized. In order to carry out the simulations of the high χ BCPs we have overcome a major theoretical obstacle. Because the energetic barrier of the two different blocks diffusing past each other is so high (for high χ polymers), these do not equilibrate in a reasonable time frame. We have applied a new simulation method to analyze defect annealing in such high χ polymers called Protracted Colored Noise Dynamics (PCND) to achieve a simulation speed up of over four orders of magnitude to make these simulations possible (see Figure). More than just determining the theoretical connection between χ and the DSA or BCPS for making nanoscale features, we have investigated issues relevant to the application of BCPs to DSA for producing the next generation of nanoscale features in microelectronic devices. For example, previously we determined the appropriate range of BCP polydispersity that would results in acceptable line edge roughness in DSA produced lamellae. This is of critical importance in the application of DSA. Recently, we have investigated the effect of doping BCPs with homopolymer to fine-tune the lamellar dimensions. This approach is currently being used in the microelectronics industry.

Technical Progress

Our biggest advance is in producing simulations that will allow the simulation of the high χ block copolymers of interest in this project. Because block copolymers will only separate into stable lamellae if the product of χ and the degree of polymerization (χN) is sufficiently high, only high χ block copolymers will achieve the smallest dimensions for templating nanometer scale devices. However, high χ block copolymers diffuse very slowly due to the repulsive interactions between the segments. As seen in the black symbols in the Figure above, the rate of annealing of defects in the lamellae of such block copolymers becomes very slow as χN increases. To overcome this, we have applied a simulation method we developed previously called Protracted Colored Noise Dynamics (PCND). This speed up the simulations by up to four orders of magnitude (see Figure).[1] This is accomplished by adding stochastic noise to the backbone contour of the polymers (colored noise) to increase polymer reptation and consequently the local diffusivity.[2] We have identified both the amount of stochastic noise and its time scale in PCND that will allow block copolymers equilibrate to stable lamellae.

Other recent simulation efforts have examined the effect of doping BCPs with homopolymers of the same BCP segments. This is being explored by the microelectronics industries to fine-tune the lamellar dimensions. Our simulations have shown that this is an effective method of fine-tuning, but results in increased line edge roughness when more that approximately 10% homopolymer is added.[3] Because the high χ BCPs will contain an inherent energetic asymmetry we have also simulated the effect of this asymmetry on BCP DSA.[4]

Additionally we have completed synthesis of both low and high χ block copolymers to examine the effect of χ on the behavior of block copolymers in this range. The low χ block copolymer has already been characterized and illustrates DSA behavior that is consistent with our previous simulations.[5] The high χ block copolymer, poly(styrene-*block*-hydroxy ethyl methacrylate) has such a high value of χ that we are awaiting small angle x-ray diffraction results at the appropriate temperature to confirm this value. However, we have been able to confirm that the χ value is higher than the other polymers that have been previously synthesized.

Future Plans

Now that we have the appropriate tools that can simulate the behavior of high χ, and an experimentally synthesized high χ BCP we will finish this project by simulating the behavior of this high χ BCP. Our work so far has indicated that higher χ BCPs form smaller lamellae with less defects, but the annealing time of these defects is also longer. Our aim is to determine what changes in structure or process might overcome this issue to help design the next generation of nanoscale materials.

Broader impact (Only required for NSF projects)

All the personnel, including graduate students, undergraduate students, and faculty have collaborated in a multidisciplinary environment that completely integrated simulation and experiment. All those trained under this grant have extensive experience in the integration of these valuable tools. The importance of this project has been conveyed to the public via a section on polymer simulations in a humorous STEM outreach tour. This has been performed for venues including the colleges, science festivals and fringe festivals.

Data Management and Open Access

Both experimental and simulation results are being organized on a single data server at the Georgia Institute of Technology. Given that the original PI of the project has moved to University of South Florida, we are currently exploring whether University of South Florida or the Georgia Institute of Technology would make the best venue for the public-facing version of this project's website. While all the experimental data will be published in the literature, digitized versions of relevant characterization results (e.g. small angle scattering) will be included in this repository. Both equilibrium structures and molecular dynamics trajectories will be included in this repository that are readable by the commonly used public domain programs HOOMD and VMD.

Advancing Along the Materials Development Continuum

The biggest hurdle to applying DSA of BCPs to produce the next generation of nanoscale devices is the tradeoff between defect population and defect annealing time. We now have to simulation tools and synthetic results to explore this tradeoff in high χ BCPs and are in the process of doing so. Such an investigation will ultimately prove if DSA technology using BCPs can produce a new generation of nanoscale devices.

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Publications

1. A.J. Peters, B.D. Nation, D. Nicoloso, P.J. Ludovice, and C.L. Henderson, *Protracted Colored Noise Dynamics Applied to Linear Polymer Systems*, Macromolecular Theory and *Simulations* **27**, 1700062 (2018).
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pyPRISM: A Computational Tool for Liquid-State Theory Calculations of Macromolecular Materials

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Keywords: liquid-state theory, polymer, scattering, software

Project Scope

pyPRISM is a Python-based, open-source framework aimed at both theorists and experimentalists across academia and industry for conducting Polymer Reference Interaction Site Model (PRISM) theory calculations. PRISM theory describes the equilibrium spatial-correlations and thermodynamics of liquid-like polymer systems including melts, blends, solutions, polyelectrolytes, and nanocomposites. The goal of this framework is to reduce the barrier to correctly using PRISM theory and to provide a platform for rapid calculations of the structure and thermodynamics of polymeric fluids. In addition to the tool, extensive documentation, tutorial, and knowledgebase materials are being developed to make pyPRISM accessible to a broad audience.

Relevance to MGI

PRISM theory directly interfaces with experiments, molecular simulation, and other theoretical methods. It can forward-predict or be fit to experimental structure factors, so pyPRISM can be used as a generalized model to describe neutron and X-ray scattering for polymer melts, solutions, and nanocomposites. Additionally, PRISM theory can use the results of scattering experiments as input, allowing for experimentally-informed theoretical calculations. PRISM theory can predict the structure of concentrated systems using input from computationally-cheap, single-molecule simulations, thereby greatly speeding up the property prediction process. By lowering the barrier to using PRISM theory with pyPRISM, we are facilitating MGI workflows which can leverage PRISM theory to enhance computational, experimental, or theoretical studies. Projects that adopt pyPRISM will have many avenues to either speed up their property prediction process or produce predictions that were inaccessible without PRISM theory. Furthermore, the pyPRISM platform will catalyze new PRISM innovations by providing a consistent and stable platform for the community to work from. Finally, the combination of a neutron source (NCNR https://nist.gov/ncnr), an industrial neutron scattering consortium (*n*Soft https://nist.gov/nsoft), and PRISM theory's direct link to neutron and X-ray scattering measurements make NIST an ideal location to develop pyPRISM and apply MGI principles to industrially-driven materials discovery and design.

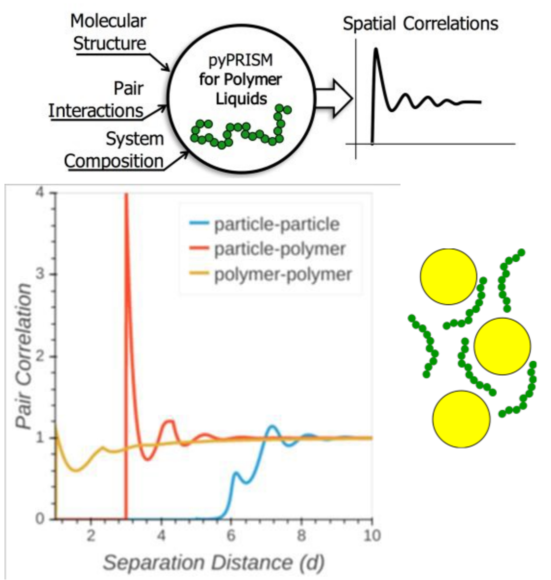

Figure. pyPRISM graphic (top) and example results for polymer composite (bottom).

Technical Progress

In the six months since the inception of this project, we have focused on developing the software behind the pyPRISM tool. The pyPRISM codebase was designed with software engineering principles to be safe, maintainable, and extendable. This means that it has comprehensive unit and integration tests designed under the test-driven development paradigm. Furthermore, the code was structured to make it easier for non-expert coders to add new features to the codebase, i.e., most common additions to the code require copying a single file and making minor modifications.

Our primary goal with pyPRISM is to lower the barrier to *correctly* using PRISM theory. This mission goes beyond software, as users must not only be educated in how to use the tool but also how to understand and leverage PRISM theory. To this end, we have developed extensive documentation and tutorial materials, which are hosted at http://pyPRISM.readthedocs.io. These materials teach users the basics of PRISM theory and how to set up both simple and complex calculations *via* case-studies which reproduce data from the literature. All tutorial materials can be viewed statically online or downloaded as live, editable Jupyter notebooks. The tutorial materials have also been deployed in a guided format at the 2017 *n*Soft Annual Meeting at NIST, in which representatives from member companies participated in live pyPRISM training.

Finally, we currently have a paper under review with the American Chemical Society (ACS) journal *Macromolecules* which serves as an overview of the pyPRISM tool and a review of the PRISM theory literature.

Future Plans

In association with industrial and academic partners, we are currently developing projects which span industries from biopharmaceuticals to polyolefins to personal care products. The *n*Soft consortium will provide a pipeline between NIST and industry that allows us to find industrially-relevant problems for which pyPRISM can help close the materials discovery loop. In all of these studies, MGI principles and tight integration between experiment, theory, and simulation will play a crucial role in their success.

Beyond these projects, we will expand the capabilities of pyPRISM. This includes extensions which would allow pyPRISM to predict the structure of currently inaccessible systems such as associating polymer blends or oriented liquid crystals, as well as extensions to the fundamental PRISM theory. We also intend to develop features that assist users in non-predictive tasks such as the coarse-graining of atomistic force-fields or the modeling of scattering data. Finally, we will develop expanded workflow utilities that simplify linking PRISM to other techniques such as molecular dynamics, thermodynamic perturbation theory, or self-consistent field theory.

Data Management and Open Access

pyPRISM will be released as an open-source codebase under the NIST software license upon acceptance of our article by *Macromolecules* in early CY2018. At that time, pyPRISM will be available for commercial and non-commercial uses. The codebase will be hosted at github.com/usnistgov/pyPRISM and documentation at pyprism.readthedocs.io/. In addition, using the MDCS platform (mgi.nist.gov/materials-data-curation-system), we will construct a public database of curated PRISM calculations and scattering curves that can be used for machine-learning and A.I. focused studies.

Advancing Along the Materials Development Continuum

pyPRISM was developed at NIST in partnership with Procter and Gamble, *n*Soft, and Professor Arthi Jayaraman's group at the University of Delaware. While pyPRISM is too new to have had quantifiable impact on materials development, it is designed to enhance many materials studies. Unlike detailed molecular simulations which can take days or weeks to finish, solutions to PRISM theory can be solved for in seconds. Using pyPRISM, a library of polymer architectures, chemistries, and blend formulations can be rapidly screened for specific structural or thermodynamic properties, greatly reducing the number of candidates that need to be synthesized. Alternatively, when combined with simulation and experiment, pyPRISM can help determine the structure of already synthesized materials to better inform the next iteration on their design. The pyPRISM tool brings the rapid and high-quality property predictions of PRISM theory to the world of MGI by creating an open and accessible platform for its use.

Publications

1. T. B. Martin, T. E. Gartner III, R. L. Jones, C. R. Snyder, A. Jayaraman, *pyPRISM: A Computational Tool for Liquid State Theory Calculations of Macromolecular Materials* (under review at Macromolecules)

Nanoscale Temperature Manipulation via Plasmonic Fano Interferences

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Keywords: thermo-plasmonics theory/simulation, photothermal contrast single-particle absorption spectroscopy, photothermal imaging, super-resolution microscopy

Project Scope. A consequence of thermal diffusion is that heat, even when applied to a localized region of space, has the tendency to spread out. This implies that the degree of spatial correlation between the heat power supplied and the temperature change that it induces is likely to be small. Yet, the ability to control heat flow and thus temperature at <50 nm dimensions has important implications for a host of applications. The goal of our DMREF project is to overcome thermal diffusion through the theoretical design and experimental realization of a new class of plasmonic nanopatterned materials composed of Ag, Au, Cu, and Al that are capable of directing temperature increases to precise nanoscopic regions of space by exploiting optical Fano interferences [1]. The outcome of this work will provide microscopic insights to the design of novel materials that can place nanoscopic temperature increases at precise locations in 1-, 2-, and 3-dimensions. To accomplish this work, we are developing theoretical and computational models of optically-driven heat diffusion, as well as novel single-particle photothermal absorption spectroscopy, photothermal imaging, and super-resolution microscopy.

Relevance to MGI. Plasmonics theory/simulation, nanolithography, photothermal spectroscopy, and super-resolution microscopy are deeply integrated throughout our DMREF project. Through our bi-weekly Skype meetings there is continual feedback between students, postdocs, and faculty across all team components. All public talks that present DMREF-sponsored research combine data from

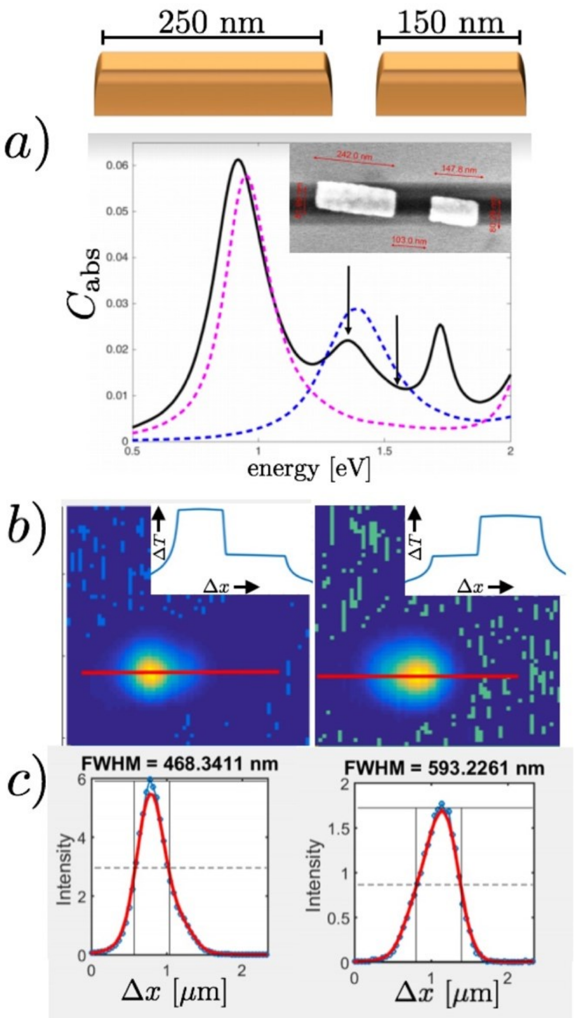

Figure. Theory-driven workflow illustrating our ability to manipulate temperature increases in a gold nanorod dimer. (a) Computationally optimized nanorod dimer with variable gaps ranging from 10-100 nm. The inset shows one such gold dimer fabricated via nanolithography on a silica substrate and immersed in glycerol. The absorption efficiency reports the spectral locations of the dimer's plasmonic normal modes, with the two lowest energy peaks corresponding to the dipole-dipole bonding and antibonding modes. (b) The inset shows the predicted temperature profile of the dimer, computed via *T*-DDA. Photothermal PSFs imaged at these normal modes indicate a leftward/rightward biasing. (c) Transects of these photothermal PSFs indeed confirm the temperature bias as predicted by theory.

both theory and experiment, and highlight the continual feedback between all three teams. This continual feedback is greatly accelerating our materials research development as we are able to quickly prescreen for desired materials via simulation, fabricate and characterize those that are theoretically but not necessarily experimentally "best", and then re-optimize around the latter constraints, thus completing the cycle. In addition, our complete datasets and all numerical (optical, thermal, and microscopy) codes are freely available online (see below) in effort to equip the larger materials community with advanced tools and techniques related to managing temperature at the nanoscale via plasmonic heating.

Technical Progress. In the first seven months of our DMREF collaboration, we have already made enormous progress. Beginning with theory, we have predicted a large set of plasmonic nanostructures that should offer the ability to controllably nanolocalize temperature increases below the diffraction limit. Such structures vary from nanoparticle dimers and one-dimensional chains of nanoparticles to complex two-dimensional, multimaterial nanostructures, the simplest of which is the nanorod homodimer where left versus right temperature control is predicted (see Figure). The rod dimer is composed of gold and is fabricated on a silica substrate and immersed in glycerol. The experimental team has fabricated such dimer structures of varying gap size, measured the absorption spectrum [2-4] of each dimer individually (which by itself is a significant experimental challenge), and imaged photothermal point spread functions that show heat localization on individual nanorods within the dimer. Interestingly, not only were predictions about heterodimers proven correct, but in addition, the experiment noticed that individual nanorods have the ability to asymmetrically heat their environments—that is, the temperature in the medium adjacent the rod ends is hotter than in the middle. This points to an additional degree of temperature control that was not anticipated and is now being investigated by the theory team.

Future Plans. We will optimize the materials genome of our plasmonic nanostructures to drive larger temperature gradients with increased control of temperature nanolocalization in one, two, and even three dimensions. Degrees of freedom to optimize are the shape, size, orientation, materials composition, and assembly of plasmonic nanoparticles from ~10-500 nm in dimension. Varying the polarization state and wavelength of the excitation field will allow us to drive optical interferences of normal modes that are predicted to lead to even larger temperature gradients and controllability [1]. Exploring such optical interferences at the nanoscale will form the basis for future investigation.

Broader impact. Our team is actively involved in training the next generation of materials researchers through education of our graduate students and postdoctoral fellows as well as through our outreach activities to our scientific community and general public. For example, Link is the Chair of the Gordon Research Conference on Noble Metal Nanoparticles in Summer 2018 (https://www.grc.org/noble-metal-nanoparticles-conference/2018/) and Willets organized a symposium on "Energy and Charge Transfer at the Nanoscale" at the Spring 2018 ACS National meeting, at which both Link and Masiello were speakers. In addition, Masiello and Link are editors of the current issue of *Chemical Reviews* on *Plasmonics in Chemistry* appearing online on 3/28/18 (https://pubs.acs.org/journal/chreay). Willets is also the editor of a recent issue of *Chemical Reviews* on *Super-Resolution and Single-Molecule Imaging* (https://pubs.acs.org/toc/chreay/117/11?ref=feature). In addition, all three PIs bring their DMREF students and postdocs to national meetings such as ACS and GRC to discuss team projects in person.

Data Management and Open Access. Iteration between the different project components to converge on the target material is of critical importance to the success of our project and necessitates regular open communication between all researchers involved. The three PIs and their groups meet bi-weekly by Skype and maintain and an online database of all data, figures, and graphics on a Google Drive account. Our thermal discrete-dipole approximation (*T*-DDA) and photothermal point spread function codes are both freely available at the following permanent digital Uniform Resource Identifiers (URIs): http://hdl.handle.net/1773/41637 and http://hdl.handle.net/1773/41638, respectively. All data appearing in all published work will be made publicly available at a similar permanent digital location (TBD).

Advancing Along the Materials Development Continuum. We anticipate that our strategies for actively-controllable nanoscale temperature manipulation will have significant impact upon heat-assisted magnetic recording for improved data storage. For example, Seagate Technology has been working to use laser illumination of plasmonic materials to locally heat, and thus individually address, densely-packed magnetic nanostructures, thereby generating a sizable increase in data storage capability. However, thermal diffusion within the plasmonic material limits how tightly localized the heat source is able to concentrate local temperature increases, causing cross-talk across magnetic grain boundaries and limiting the packing density of magnetic storage media. Our DMREF team has discovered a class of plasmonic nanomaterials that can confine temperature increases to highly localized regions of space in spite of thermal diffusion. Such plasmonic nanomaterials hold great promise in improving the performance of these devices and may someday allow for increased data storage capacity.

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Publications

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Graphene based Origami and Kirigami Metamaterials

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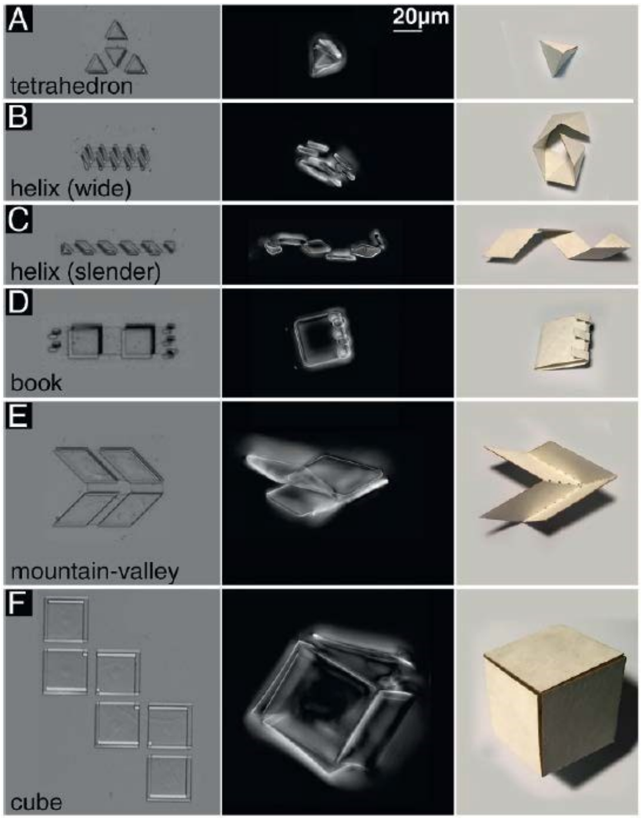
Keywords: Graphene, Origami, Kirigami, Electronic membranes, Mechanical Metamaterials

Project Scope:
Origami and kirigami, the arts of folding and cutting paper, offer a powerful new pathway to nanoscale materials design. Drawing inspiration from optical and acoustic metamaterials, it is proposed to develop a framework for designing and fabricating atomic membrane origami and kirigami mechanical metamaterials. Using lithographic techniques, graphene sheets will be perforated and cut to create modules with prescribed mechanical properties. These modules will be assembled to create mechanical meta-materials whose response to applied stresses, temperature, and other environmental signals can be tailored.

Relevance to MGI
Adopting a single platform, graphene, along with cuts following kirigami and origami principles, we can tailor emergent mechanical behaviors so that material properties can be designed. This addresses a major need for materials with tunable mechanical properties for construction of micro- and nano-scale machines. Developing such materials will have fundamental impacts on micro-engineering, enabling the manufacture of a range of components from micron-scale actuators for soft robotics to active biomimetic materials for artificial tissues.



Graphene–glass bimorphs can be used to fabricate numerous 3D structures at the micrometer scale. These include, but are not limited to, tetrahedron (A), helices of controllable pitch (B and C), high-angle folds and clasps (D), basic origami motifs with bidirectional folding (E), and boxes (F). In Left, we show the device flattened and still attached to the release layer. After they are etched, the bimorphs self-assemble to their targeted 3D geometries (Center). Images of the folded devices were obtained by focal plane stacking. All of the figures in Center are at the same scale. For com-parison, we present paper models of the target geometry in Right.

Technical Progress
On the experimental front, we finished developing our technique for creating atomically thin graphene bimorphs that can bend/fold graphene (See Figure). We can now deposit nm-thick silicone dioxide or metal layers by atomic layer deposition and subsequently transfer graphene onto these layers to create the world's thinnest bimorphs. These bimorphs show reproducible bending in a controlled and dramatic fashion in response to a variety of stimuli including heat, pH, ion concentration, etc. This is an exciting step forward with many potential applications. This work was published in PNAS.

2) The Platinum graphene biomorphs are voltage sensitive. Using a probe to manipulate the bimorph and apply a relative voltage between the bimorph and the surrounding solution drives Hydrogen and Hydronium ions into and

out of the platinum. This ion absorption and desorption reaction leads to actuation. We find that these devices can be actuated from nearly flat samples to bent helices with a radius of curvature smaller than 3 μm. We also demonstrated that only 200 mV are necessary to drive the transition to the fully bent state. Moreover, the data show that with voltage actuation it is also feasible to dial in, with precision, any intermediate bent state.

3) We have shown how to integrate photovoltaic devices to drive the voltage based actuations. Our Silicone photo diodes are able to produce 700 mV which is sufficient to drive the bending of our Platinum graphene bimorphs.

4) We have continued conducting experiments with paper based models of our kirigami unit cells. We have confirmed various scalings predicted by the analytic calculations developed by our theory team led by Nelson and Bowick. The advantage of our theoretical calculations is that they bypass finite element simulations that are prohibitive for calculating the behavior of arbitrary kirigami motifs. We are now testing the predictions out on more complicated kirigami motifs including ones with slits parallel and perpendicular to the radial direction.

5) On the theoretical/modeling front, the team has used a combination of the theory of thin elastic plates and large-scale numerical simulations to study effects of thermal fluctuations in the elastic properties of clamped graphene strips and flaps. A renormalization group analysis of flexural phonons reveals that elongated ribbons behave like highly anisotropic polymers, where the two-dimensional nature of ribbons is reflected in non-trivial power law scalings of the persistence length and effective bending and twisting rigidities with the ribbon width.

Future Plans

We are now wrapping up our projects and preparing the final publications.

Broader impact (Only required for NSF projects)

The PIs are promoting the results in a wide range of venues both technical and public. The Cornell team ran a symposium titled: **Atomic Origami: a Technology Platform for Nanoscale Machines, Sensors, and Robots?** The symposium was well attended by members of the scientific and industrial communities including representatives from Corning, Xerox, Applied Materials. Cohen proposed an invited session for this year's APS March meeting on Atomic Origami at which our postdoc Marc Miskin and David Nelson were invited speakers. The Cornell team has also followed through on its proposal to develop a course on scientific presentations. The course is titled "Finding your scientific voice" and was taught in the spring of 2017. The response was overwhelmingly positive and the course received a 4.7/5 rating.

In the last year, McEuen has given invited talks about this work at multiple workshops/conferences, including the annual meeting of the AVS as well as public lectures at University at Buffalo and Vanderbuilt, and a talk at the Matter Design Computation: The Art of Building From Nano To Macro Conference at Cornell. Together these have reached hundreds of both scientific researchers and non-specialists. Cohen has discussed these results in departmental colloquia, the March Meeting, as well as invited contribution to the Gordon Research Conference on Thin Film Mechanics and at the metamaterials conference (Metamorphose VI) in Greece. Cohen's work on origami was on display at the Chi Mei Museum of art in Taiwan. Over 130,000 visitors viewed this work. In addition he gave a talk about the work we are conducting to a public audience. This talk was recorded and can be found at the link below. https://www.youtube.com/watch?v=iWJ81AJR6oE . In the past year, David Nelson has given invited talks on" "Thermalized Sheets and Shells: Curvature Matters" related to this work at Dept. of Physics, ETH, Zurich, Switzerland; and the KFA (Atomic Energy Center) in Julich, Germany. Bowick gave an invited talk at the meeting "Mathematical Modeling of 2D Materials" at the Institute for Mathematics and its Applications at the University of Minnesota, Minneapolis. Overall, these lectures have reached out to everyone from non-experts to scientific researchers to policymakers on the growing importance and excitement in the research areas supported by this grant.

Data Management and Open Access

As publications are pushed out, we are sharing the codes and recipes used for the studies so that they become available to the broader scientific community. In addition, all the PIs as well as the students and postdocs are delivering talks based on their work in this project. We provide access to all experimental techniques on request. We also provide graphene samples to a number of groups on campus. We anticipate that the publications on our work will garner quite a bit of attention. The high profile of the work will inspire others to pursue these lines of studies. The advantage that other researchers will have is that we will have worked out many of the major stumbling blocks for getting our designs and devices to work. In particular, once recipes are established, the final products can be made very reproducibly. As such we anticipate wide scale adoption of the methods and techniques we are developing.

Advancing Along the Materials Development Continuum

What constitutes a new “Material” here corresponds to modifications of a graphene sheet, in two ways. The first is a pattern of cuts. The second is an additional “smart” layer on the graphene to create bimorphs that can respond to external stimuli. The MGI, comnbining theory, design, manufacture, and testing in a closed loop is speeding up our ability to explore the possible phase space of these materials. For example, the tight interaction between our theory and experiments has been vital for developing the work on the square frames. A theoretical framework of screened charges was developed to enable rapid and efficient calculation in complicated arrays of slits and holes. The experiments on paper frames were able to verify much of the theoretical predictions as well as push the theorists to refine their theory. We have now converged on results that everyone agrees with and are in the process of writing up our results for publications. By understanding these fundamental properties of both the unit cells and their repeated metamaterial forms, combined with the smart response, will make possible a broad new class of smart 2D materials. These materials have potential applications in a number of areas, the most obvious being sensing. As the technology develops, we will seek out specific applications and partners for commercialization.

Publications

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DMREF: Collaborative Research: Synthesis, Characterization, and Modeling of Complex Amorphous Semiconductors for Future Device Applications

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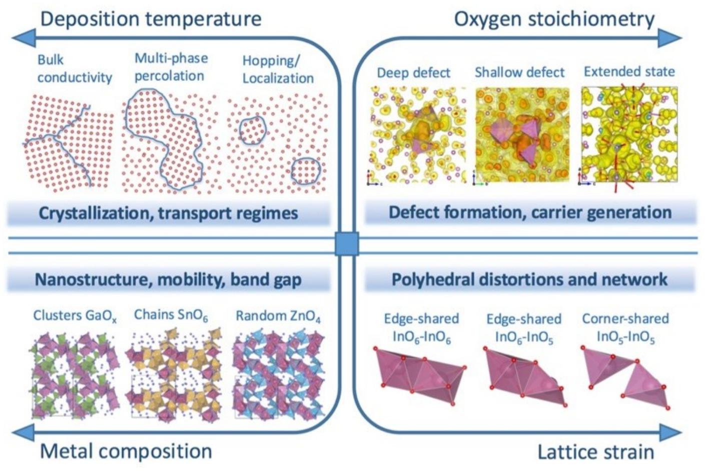
Website: none.
Keywords: amorphous oxide and chalcogenide semiconductors, thin films, ab-initio molecular dynamics, transient photoconductivity response.

Project Scope

The main objective of this project is to gather, decipher, integrate, organize, and disseminate large experimental and computer-generated data that accurately describes the structure and properties of a large class of complex amorphous semiconducting oxide and chalcogenide materials. The integrated materials data along with open-source statistical machine-learning software to be developed within the project, will be made accessible as a Materials Genome Node of the Global Materials Network to multiply our work impact, accelerate the discovery of new materials with unique features and performance and to help produce new optimized products at a much faster pace and reduced cost.



4-D parameter space of amorphous oxide semiconductors is too large for empirical sample-by-sample approach due to large number of constituents and diverse deposition conditions.

Relevance to MGI

An integrated framework has been developed by our Team to study In-based prototype amorphous oxide semiconductors. Within the framework, theory and experiment are linked within three major core units: (i) synthesis and molecular dynamics simulations; (ii) property measurements and density functional calculations; and (iii) structural characterization and statistics analysis of modeled structures. At every step, the link between experiment and theory is via parameter alignment and in-depth comparison. The crosslinked channels between the three core units provide the information transfer and feedback not only between the units but also toward the central part of the integrated framework where a unified predictive theoretical model is developed. In this project, we will not only advance the core units of the framework via improved control of growth parameters, improved quantitative characterization, and multi-scale modeling, but will also develop ways for efficient utilization of the framework to study complex amorphous oxides and chalcogenides. Specifically, we plan to (1) employ transient behavior measurements and to combine the results with time-dependent modeling; (2) develop approaches for growth under external stimuli and for large-scale modeling; and (3) formulate an integrated database with rigorously tabulated parameters and incorporate open-source user-friendly software for comprehensive structural analysis.

Technical Progress

One of the major goals of the project is to develop a community standard for the data itself. To establish a reliable link between experiment and theory, the experimental and computational parameters (e.g. variables for synthesis and modeling or measured and calculated properties) need to be aligned via in-depth comparison. Such an alignment has been achieved by our Team for the experimental deposition temperature and theoretical quench rate in the molecular dynamics simulations, and the results helped explain the observed 3-fold peak in the carrier mobility of amorphous indium oxide [1,2]. Our next goal is to align the experimental partial pressure of the O_2 gas used during film deposition with theoretical oxygen stoichiometry in simulated structures. For the latter, novel theoretical approaches for non-stoichiometric-melt cooling and time- and temperature-dependent statistical analysis codes are being developed. This will enable a systematic comparison of the calculated and experimentally observed trends in the structure and properties that occur in response to variations in oxygen content. Our preliminary theoretical results for amorphous In-Ga-O reveal high sensitivity of Ga coordination to oxygen stoichiometry of the oxide. This opens up a possibility to control the number of free carriers as required for thin film transistor applications and to optimize carrier mobility governed by the spatial distribution of Ga atoms and transformations in the Ga coordination.

Future Plans

Building on the success of our integrated theoretical and experimental framework, our team is uniquely poised to develop complete, standardized deposition-structure-property relationships for a large class of amorphous semiconductors. Specifically, we will: (1) systematically study and develop a searchable database for amorphous post-transition metal oxides, including ternary and quaternary oxides, with their structure, properties, and long term stability rigorously tabulated; (2) explore ways to enhance the materials conductivity by inserting non-traditional metallic cations to form a-In-X-O with X = Ag, Cd, or Sb; (3) expand our efforts beyond the oxides by studying amorphous mixed oxide-chalcogenides and multi-cation chalcogenides within the same integrated framework; and (4) extend our investigations into the dynamic responses of the materials under external stimuli, such as light illumination, field-effect, heat, and mechanical stress.

Broader impact

The Global Materials Network (GMN) for Young Researchers, launched under NSF support and led by co-PI R.P.H. Chang, will be promoted for the amorphous semiconductor genome community. The mission of GMN is to establish a network of topical materials nodes interlinked around the world for research collaboration that solve global problems facing mankind. A node on complex amorphous oxides and chalcogenides will be created and led by our graduate students as part of the GMN international collaboration to enable new discoveries and product development under the Materials Genome Initiative.

Data Management and Open Access

We will work closely with our collaborators at NIST to adopt the existing MG database technology at NIST for data curation and maintenance in order to develop a convenient format for dissemination of the integrated experimental and computer-generated data. The PIs plan to release the Amorphous Structure Analysis (AStA) as open source and build a user community around the language by ensuring that interested researchers are able to contribute to AStA codebase.

Advancing Along the Materials Development Continuum

Development of realistic approaches for non-stoichiometric-melt cooling and time-dependent statistical analysis will enable studies of defect formation and dynamics, ion diffusion, structural evolution and stretched-exponential relaxation, phase transformation, and crystallization processes, bringing the computer-aided design of amorphous materials to a new level. As the project progresses forward, we plan to interact with companies and NSF-SBIR and I-Corps programs to translate our work into a commercially relevant technology.

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Publications

None.

Advanced Water Splitting Materials for Hydrogen Generation Research Consortium (HydroGEN)
A DOE Efficiency and Renewable Energy Energy Materials Network Consortium

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Website: https://www.h2awsm.org/
Keywords: Hydrogen, Water-splitting,

Project Scope

Hydrogen is an energy carrier that can be produced from diverse domestic resources including renewable electricity, nuclear energy, and fossil fuels. Advanced water splitting (AWS) technologies including high- and low-temperature electrolysis (HTE, LTE), photoelectrochecmical (PEC) and solar thermochemical (STCH), are versatile pathways that will play a significant role to in enabling high volume, clean, sustainable hydrogen production. Recently, the Fuel Cell Technologies Office (FCTO) launched the HydroGEN consortium in an effort to accelerate the materials development and discovery critical to these promising AWS technologies. Currently there are 20 active projects utilizing the expertise and capabilities housed at the six core national laboratories that compromise HydroGEN (the National Renewable Energy Laboratory (NREL)- lead, Sandia National Laboratory (SNL), Lawrence Berkeley National Laboratory (LBNL), Idaho National Laboratory (INL), Lawrence Livermore National Laboratory (LLNL), and Savanah River National Laboratory (SRNL)). HydroGEN endeavors to effectively enable the widespread commercialization of hydrogen and fuel cell technologies in line with the H2@Scale initiative and meet the ultimate cost target for production set by the U.S. Department of Energy (DOE) at $2/kg.

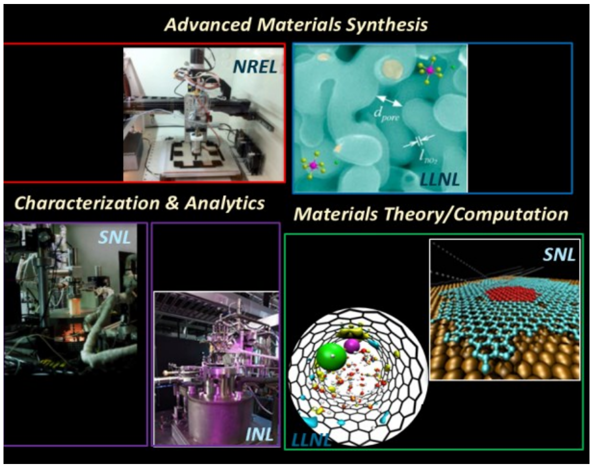

Figure 1. HydroGEN capability node examples including: characterization to evaluate kinetics of catalytic materials under real-world operating conditions (+ extreme temperatures in HTE and STCH), cutting edge multi-physics modeling of solid-liquid interfaces, relevant LTE and PEC, and advanced atomic layer deposition (ALD) synthesis capabilities for precise nano-engineering of catalytic surfaces.

Relevance to MGI

HydroGEN was formed through the DOE's Energy Materials Network (EMN) framework and offers a suite of more than 80 capability nodes to help accelerate the discovery and development of AWS materials spanning computational tools and modeling, materials synthesis, characterization, process manufacturing and scale-up, and analysis. Each node combines a tool or instrument, a technique, and a node leader with experience in utilizing their capability for one or more of the AWS technologies. Detailed descriptions of all the HydroGEN nodes are available in a searchable format on the HydrogGEN website (https://www.h2awsm.org/capabilities), including information such as the host National Lab, the capability experts, and a synopsis of the node's unique aspects and capability bounds. By design, the nodes are cross-cutting, and any given node may be useful for one or several AWS technologies. Some example nodes are provided in Figure 1. Leveraging these capabilities across the AWS community is expected to advance the maturity and technology readiness levels of these hydrogen production pathways as well as enable a foundational understanding of materials critical to these technologies.

Technical Progress

This month, 18 HydroGEN projects have completed their first year and meet their first year's technical targets, while 2 new high temperature electrolysis projects kicked off at the end of FY 2018. Some highlights from HydroGEN projects across the four AWS technologies are provided here.

In low-temperature electrolysis Proton Onsite met and exceeded near-term performance targets of 1.85V (achieved 1.8 V) at 2.0 A/cm^2, using Proton-synthesized high activity IrRu oxide catalysts of different compositions. The Proton PEM water electrolysis cell also demonstrated 800 hours of durability at 2 A/cm^2, operating at 80°C and 30 bar. This project utilized NREL's *ex-situ* characterization node towards a better understanding of IrRu oxide catalysts stability. Proton's improved cell efficiency is a step towards achieving its PEM water electrolysis cell efficiency goal of 43 kWh/kg (1.7 V at 90°C) and at a cost of \$2/kg H_2. .

For photoelectrochemical water splitting Rutgers University demonstrated that PGM-free Ni_5P_4 hydrogen evolution catalysts/TiN on p-$GaInP_2$ have performance on par with (onset potential and saturated current density) and stability greater than PGM catalysts (PtRu/p-$GaInP_2$). To produce these catalyst assemblies Rutgers utilized NREL's III-V Semiconductor Epi-Structure and Device Design and Fabrication node with metal-organic vapor-phase epitaxy (MOVPE) tools and results were obtained through the Characterization of Semiconductor Bulk and Interfacial Properties node.

In collaboration with SNL's stagnation flow reactor (SFR) node, The University of Colorado, Boulder (CU) was able to experimentally measure solar thermochemical water splitting kinetics and use it as critical feedback to develop rapid kinetic screening techniques of materials. CU and SNL demonstrated 3 solar thermochemical (STCH) water splitting materials. with > 200 μmol H_2/g/cycle at $T_{red} < 1450°C$ and $\Delta T < 400°C$.

In the High-temperature electrolysis area, Northwestern University's cobalt-substituted $SrTi_{0.3}Fe_{0.7}O_3$ catalyst with YSZ electrolyte, in collaboration with LBNL's Metal-Supported Solid Oxide Cell node, demonstrated a metal-supported SOEC for the first time in electrolysis mode. This is a promising initial performance for efficient and cost-effective SOEC.

Future Plans

HydroGEN looks forward to growing its membership of industry, university and laboratory collaborators that can partner with member-laboratory experts by way of CRADAs and potential future FOAs. Moving forward, HydroGEN will expand its presence in the AWS community through working group meetings and participation at relevant professional meetings. The HydroGEN nodes were created to support the efforts of the AWS community, but also to derive guidance from it. Ongoing stakeholder engagement and input is viewed as critical to the continual evaluation of the capability nodes and potential capability gaps within the consortium. The HydroGEN nodes will be regularly updated and reevaluated based on the needs of the AWS community.

Data Management and Open Access

HydroGEN has developed a secured Data Hub (https://datahub.h2awsm.org/), which enables and encourages the sharing of data within and across projects. It is a secure project space for team members to upload, view, share and download project data and currently comprises 128 users and 3889 data files. The goal is to make the digital data generated within HydroGEN accessible, so the data can be shared and leveraged throughout the EMNs and in future programs.

The Data Hub was created and maintained by a dedicated data team. The HydroGEN data infrastructure was built using standardized, open source tools and enables the capture, storage, analysis, and visualization of both experimental and computational datasets that are generated in HydroGEN projects. Data is accessible via a searchable database and, where appropriate, will be available to the scientific community and public.

Advancing Along the Materials Development Continuum

HydroGEN is aimed at accelerating the material-to-market process by integrating the phases of the R&D. The EMN framework, on which it was built, streamlines the process to work with national labs by developing standard, non-negotiable, and mutually agreed upon technology transfer agreements (TT/A). The EMN has an Intellectual Property Management Plan, a standard non-disclosure agreement (NDA) that has been pre-signed by all six core labs, a single-lab and multi-lab cooperative research and development agreement (CRADA), and a material transfer agreement (MTA). The template for these standard agreements is available at the "Work With Us" HydroGEN's website. HydroGEN also has a dedicated TT/A team to develop these standard agreements and facilitate this process efficiently. In addition, HydroGEN offers a clear, single point of engagement through the HydroGEN website and email (h2awsm@nrel.gov). This contact directs interested parties to the appropriate laboratory capabilities and streamlines access through a catalog of technology transfer agreements, as appropriate.

Selected Publications

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Extracting real time material evolution information at a synchrotron using machine learning methods

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Keywords: Synchrotron X-rays, diffraction, unsupervised learning, light source, transient behavior

CHESS Overview

CHESS is one of only two high-energy synchrotron sources in the U.S. (of only five in the world) that can produce intense beams of high-energy X-rays (20-100 keV) having a wavelength short enough, and an incident flux high enough, that diffraction and spectroscopy can be performed in real-time in a non-destructive way on dense/hard materials or through the walls of a chemical reaction vessels or thin-film deposition chambers. To perform *in-situ* and *operando* studies on a wide array of materials CHESS has developed unique focusing and tunable X-ray optics, innovative reaction vessels, load frames, furnaces, and dual-color spectrometers, synchronous data collection and analysis techniques, and specialty X-ray detectors that can capture diffraction and/or tomographic images in the milli-, micro- and nanosecond timeframe. CHESS holds annual hands-on workshops, produces and broadcasts tutorial courses, and hosts summer research experiences to bring new scientists, engineers and students into the user community.

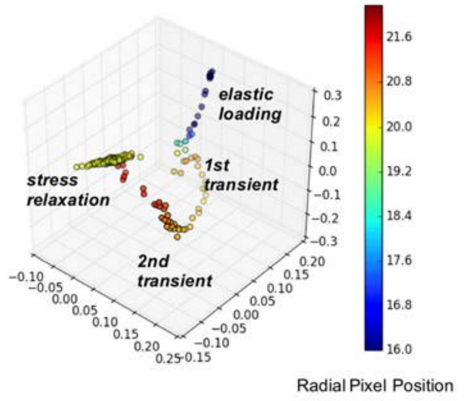

Figure 1. Transients in the elastic-plastic deformation of a commercially pure tensile sample loaded *in-situ* identified by operating directly on the raw HEXD data using Locally Linear Embedding.

Real Time Characterization using Synchrotron X-rays

The ability to tune the wavelength, size and flux of an X-ray beam at a synchrotron creates the potential for a broad spectrum of non-destructible material characterization experiments from absorption-based methods such as computed tomography (CT) to scattering methods such as high energy X-ray diffraction (HEXD) and small angle X-ray scattering (SAXS). Interpreting X-ray data involves turning detector "images" into information regarding the internal material structure. Data reduction methods vary from one X-ray technique and detector to the next, but the underlying truth is that X-ray detectors are able to collect data at ever increasing rates, resolution and range. This, along with the enormous flux of X-rays that are possible at CHESS, make it possible to "watch" dynamic evolution processes associated with material synthesis or in-service performance. Thousands of conventional *ex-situ* experiments are conducted at CHESS every year, but its *in-situ* and *in-operando* capability and mission to train novice users is what make CHESS truly unique for DMREF-based users. The enormous data sets produced during an *in-situ* experiment along with the goal of extracting the most important aspects of material behavior or structure evolution has created an unprecedented opportunity for employing machine learning methods on X-ray data. As an example, in the next section we describe the use of unsupervised learning on raw diffraction images to reveal the underlying elastic-plastic deformation mode of titanium during an *in-situ* HEXD experiment.

The Elastic-Plastic Transition of CP-Ti

During a typical HEXD experiment, the distortion and re-orientation of every crystal within a deforming metallic sample is extracted by carefully tracking the diffraction peaks (spots) collected at the detector. The sample loading is halted and the sample rotated to obtain data from each plane within each crystal. In a recent experiment, we collected 40,000 detector images at 500 Hz as the CP-Ti sample was loaded **continuously**, deformed elastically, then developed fully plastic deformation. The evolution of the diffraction spots - a consequence of elastic straining and the dislocation motion and storage associated plasticity – could be seen in the evolving diffraction spots, but could any real, quantitative information be extracted directly from data taken at this rate without full rotation? We applied the unsupervised learning technique of Locally Linear Embedding (LLE) directly to the raw detector images; instead of examining the data peak by peak, an enormous vector of data was created using the intensity collected at each pixel over the entire experiment. The manifold resulting in the LLE analysis of this vector is shown in Figure 1, with each symbol corresponding to hundreds of consecutive diffraction images and colored according to average radial peak position (an indicator of average lattice strain in the direction of the applied load). LLE renders an ordering of symbols in time, and reveals four distinct regimes: elastic loading, transients of micro-plastic yield (1) and stress relaxation (2), and finally post-yield with plastic flow throughout the sample. LLE provides concise representation of the mechanical response directly from diffraction images. The mechanical response is assessed directly from diffraction data through unsupervised learning. This experiment will change the way we do HEXD.

Outlook / Future

Fundamentally, CHESS provides users with an unprecedented ability to characterize the temporally evolving and spatially resolved internal state of a material sample. While the above results clearly indicate the richness of the information embedded in the data collected at CHESS, the truly revolutionary advances to be made will arise from the interpretation of these data using a combination of advanced physical models and state-of-the-art machine learning methods. For example, LLE demonstrates that the deformation dynamics “live” on a low dimensional manifold. However, building on ideas in [1], parameterizing that structure in terms of process-relevant quantities, as would be required, for example, to develop models useful for closed loop control, requires the use of **supervised** learning methods. The training data for these methods can be derived from a limited number of well-chosen experiments as well as more diverse outputs of high-resolution simulations coupling the evolving material sample and the diffraction experiments. In addition to modeling with an eye toward process control, fundamental processes in materials science are also amenable to quantification using these tools. For example, non-equilibrium phase evolutions that evolve on time scales short even relative to the capabilities of the CHESS detectors give rise to inherently stochastic data governed by Poisson statistics. Model-based methods originally developed in the context of medical and geophysical imaging problems [2] are being adapted at CHESS to extract from such limited data information regarding the spatial evolution of phase structure over time. Notably, the use of probabilistic techniques will allow for both the estimation of the “most likely” phase trajectories as well as the quantification of uncertainty associated with these estimates [3].

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DMREF-GOALI: Mechanistic and Microstructure-Based Design Approach for Rapid Prototyping of Superalloys

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Website: Under construction.

Keywords: Superalloys, deformation mechanisms, microscopy, creep, microtwinning

Project Scope

Breaking away from traditional, incremental superalloy development, a new design paradigm is being implemented in this GOALI program with GE using a novel materials data analytics applied to an integrated experiment/modeling exploration of "simplified" six-component compositions. Advanced *ex situ* and *in situ* mechanical testing, microstructure characterization, DFT, phase-field, and crystal plasticity modeling are being used to develop an atomic-level understanding of alloying effects of deformation mechanisms. A novel, rapid-prototyping approach enables nimble exploration of the inter-related effects of composition, microstructure, deformation mechanisms and creep response, and producing a seven-component powder metallurgy alloy with improved creep capability over current commercial alloys.

Relevance to MGI

Mechanical testing and characterization results are being integrated in three alloy variant feedback loops with first-principles, phase field and crystal plasticity models, and validated with advanced characterization at each length-scale, to develop quantitative and predictive understanding of alloying and microstructure effects on creep. Non-linear dimensional reduction to aid the design of experiments and physics-based modeling, and to assess the results, in order to predict additional rounds of alloys that will be designed to enhance the fidelity and reduce the uncertainty of the models.

Technical Progress

Following up on our groundbreaking discovery of the "phase transformation strengthening" mechanism during the first year of the DMREF program (Publication [1]), Mills and co-workers have continued to probe local segregation effects at stacking faults, twins, and dislocation cores using advanced scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDS) techniques. The analysis reveals the presence of Co and Cr rich Cottrell atmospheres around leading dislocations responsible for the creation of SISFs, SESFs, and microtwins. An assessment of the kinetics of these processes indicates that movement of Cottrell atmospheres is the rate limiting process during creep. There appears to be a direct relationship between alloy content and fault segregation. The alloys with highest Ta, Ti, and Nb of the four alloys we have explored so far is the only one that forms ri phase along SESFs, apparently preventing the deleterious microtwinning deformation mode.

Motivated by these observations, systematic DFT calculations by Ghazisaeidi and coworkers have determined the interaction energy between a variety of relevant solutes and stable stacking faults in y'. Our calculations show no significant segregation to SISF, SESF or twin boundaries, in contrast to experimental observations. This apparent discrepancy indicates that segregation must involve precursor structures involving wrong nearest neighbors that are attractive to solutes. In addition, we show that the underlying reason for segregation is not dure to solute size misfit; but, rather, is due to the enhanced bonding between the solutes and their nearest neighbor Ni atoms.

Motivated by the rich variety of deformation mechanisms found in recent TEM observations after creep at intermediate temperatures, Wang, Niezgoda, and coworkers are combining ab initio calculation and phase field simulations at the elementary defect level to aid our understanding of stress, temperature, microstructure, and alloy composition effects on these mechanisms. We have further developed a computational framework that couples dynamically a dislocation-based crystal plasticity model for creep (developed in previous year) with a phase field model for yly' microstructure evolution. Model inputs include alloy-specific materials parameters calibrated against experiments, and enables exploring the interplay between plastic deformation and microstructure evolution, which are difficult to separate in experiments. Finally, a physics-based model for primary creep of superalloys has been developed, aiming at providing a homogenized constitutive relationship at macroscale. Application to data for two superalloys enable demonstration that critical materials parameters (the dislocation drag coefficient and activation volume) can be unambiguously determined from the model parameters.

Future Plans

The initial matrix of six-component alloy compositions has been developed in consultation with GE Global, produced, and provided to the program. These compositions provide large variation on crucial elemental constituents (including Ti, Ta, and Nb which appear to be integral to the formation of nanoscale ri phase at stacking faults), while maintaining similar y' volume fraction and y' solvus temperature based on predictions using Thermocalc. Quantitative microstructure characterization is being conducted using SEM, EBSD, TEM and STEM, with specific attention on determining compositions that exhibit nanoscale ri phase. The quantitative characterization results are being used as input for phase-field modeling and materials informatics analysis which will lead to production of a second round of alloys from GE Global later in 2018.

Broader impact (Only required for NSF projects)

Coordinated application of computational and experimental tools are providing a roadmap for future alloy development strategies for these critical materials. The graduate students are acquiring a cross-disciplinary education involving microscopy, image processing, and advanced multi-scale modeling approaches. The students and faculty are engaging with GE Global Research staff and facilities in the program. Semi-annual visits at GE at OSU commenced this fall. The PIs will provide opportunities for undergraduate students to participate in interdisciplinary senior capstone projects that involve atomistic and continuum simulations and microscopy. We have also established close, collaborative interactions with three world-leading groups in Germany, France and England.

Data Management and Open Access

The team is exploring making the data analytics tools available through Citrine Informatics Citrination platform (https://citrination.com). PIs Niezgoda and Wang are collaborating with Citrine on a DOE NETL ICME project, and are leveraging these interactions for this DMREF in order to provide Citrince resources that can be utilized for data hosting and analysis. Source code for the developed software will also be maintained by the PIs in an open repository (presently under development). We are also exploring distribution by Bluequartz as plugins/filters for DREAM.3D (http://www.icmrl.com).

Advancing Along the Materials Development Continuum

There appears to be a direct relationship between alloy content and fault segregation. Inhibition of the deleterious creep mechanism of microtwinning via the formation of ri phase along SESFs is a present focus for alloy exploration. Our GOALI partner (GE Global) is keenly interested in this result, and the next series of model alloys will allow us to understand which of these elements are essential in ri phase formation, with important implications for future alloy development.

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Computationally Driven-Genetically Enginereed Materials

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Keywords: coiled-coil proteins, Rosetta, fibers, theranostic agent, non-canonical amino acids

Project Scope: Theranostic materials are emerging as promising targeted therapeutic scaffolds. These materials take advantage of the high capacity biomaterials to deliver drugs of interest in combination with various imaging modalities. In this project, we intend to develop theranostic coiled-coil protein fibers through computational design and experimental analysis with the objective to predictably: 1) control the self-assembly into fibers on the mesoscale with functional capability of small molecule recognition; 2) integrate non-canonical fluorinated amino acids (FAAs) that encode thermostability and traceability; and 3) biomineralize and organize Fe_3O_4NPs onto the protein fiber substrates leading to image-ready bio-nanocomposites with magnetic properties.

Relevance to MGI: This is a collaborative effort between the groups of **Montclare** (PI), **Bonneau** (co-PI) and **Wadghiri** (co-PI). **Montclare** has expertise in protein-engineered biomaterials and her group is responsible for the experimental methods to produce, screen and characterize materials. **Bonneau** and **Renfrew** (senior personnel) have expertise in Rosetta-based computational design of proteins. **Wadghiri** leads the preclinical imaging core, developing radiofrequency probes tunable to proton and fluorine as well as setup for high-throughput MRI screening. **Montclare** will fabricate, purify and assess the proposed coiled-coil protein fibers for initial high-throughput fluorescence screening upon binding to various small molecules, which will then be further characterized for fiber formation from nano- to mesoscale. Based on the experimental results, **Bonneau** and **Renfrew** will design the next iteration through computation and this cyclic design process will provide a fundamental understanding on protein fiber assembly. **Wadghiri** and **Montclare** will investigate the non-canonical amino acids (NCAAs) in the protein fiber for detecting (^{19}F or iron oxide) via MR relaxometry and imaging. Through computation, protein engineering and chemical biology, we will be able to precisely control the dimensions, robustness and physicochemical properties of protein-engineered fibers in a systematic and high-throughput fashion to fabricate fibrous biomaterials for potential use in theranostic applications.

Technical Progress: Objective 1. Recently, we developed the protein, Q, from cartilage oligomeric matrix protein coiled-coil, which is capable of assembling into nanofibers and mesofibers upon binding curcumin at pH 4 [1]. We are exploring the ability of Q to bind other small molecules including photo-isomerizable azo-benzene-containing ligands, such as DENAQ [2]. Using these insights and established hypothesis that nano- and potentially meso-scale fibril assembly is directed through the patterning of hydrophobic and charged surface patches, we are now optimizing the Q sequence surfaces by Rosetta by maintaining the positions required for helix formation. Directly modeling all of the residues in a meso-scale fibril at an atomic level required for accurate modeling is computationally intractable. This work will expand on new ways of modeling fibril structure using a framework where the parameters of the helices and their interactions are described parametrically.

Objective 2. To improve the stability and assembly of the helical fibers, we designed Q bearing trifluoroleucine (TFL) and residue specific incorporation of TFL in Q resulted in highly helical conformation with a 13 °C increase in T_m . We are now performing Rosetta-based design of stable, soluble fluorinated Q+TFL variants capable of encapsulating small molecules, while also exhibiting a strong signal for ^{19}F MRI. In parallel with TFL, we are also generating Q+hexafluoroleucine (HFL) variants for better thermostability and enhanced ^{19}F MRI signal. This work includes the development of new ways of scoring NCAAs in Rosetta (such as the fluorinated amino acids (FAAs) needed for enhanced ^{19}F MRI signal). It also leverages a new 'split-unfolded' reference scoring function needed for protein design with FAAs (this scoring function component is needed to balance the types of side chains used in design, and for the 20 canonical amino acids is derived from a statistical treatment of the PDB; whereas we must derive it from a statistical treatment of simulations).

Objective 3. We aim to coat the surface of protein fibers with spatially organized Fe_3O_4 nanoparticles through biomineralization to create traceable bio-nanocomposites with defined magnetic properties. We generated a Q variant bearing azidohomoalanines (AHAs) to control the spacing of propargylglycine-CMms6 peptides (for Fe_3O_4 mineralization) by [3+2] cycloaddition. This Q+CMms6 conjugate has been imaged via T_1-, T_2-, and T_2*-weighted MRI at 7-Tesla. The hybrid biomaterial exhibits a ratio of relaxivity values r_2/r_1 value of 123.01, 2.33-fold higher than that of Feraheme (FDA approved standard) and a nearly 8-fold higher r_2^*/r_2 ratio, suggesting that it has a weak T_1 effect compared to Feraheme at 7T, but it does perform as an effective and sensitive darkening agent for T_2- and T_2*-weighted imaging, particularly for T_2*.We are now developing a computational approach to determine the ideal placement for the AHAs in the Q fiber. Here the design goals (encoded into a Rosetta design protocol) additionally include the spacing of surface side chains interacting with the nanoparticle as well as the packing and presentation of these side chains on the fiber surface (to facilitate quaternary assembly of the fibers into larger, more robust, structures).

Future Plans: Objective 1: The development of a robust high-throughput screen for protein fiber assembly is critical for the rapid identification of functional materials. After computational designing of different constructs of Q, fiber assembly will be analyzed by various conditions using high-throughput 96-well plates. As we have demonstrated that Q fibers can bind curcumin and the photoisomerizable ligand DENAQ, exhibiting fluorescence of the fiber, we will screen via fluorescence spectroscopy and microscopy. This will enable the rapid screening for functional fibers capable of binding and encapsulating the small molecules. Those with a fluorescence value equivalent or better will be further characterized via confocal microscopy, binding to other small hydrophobic molecules and EM analysis. The knowledge obtained from characterization will be used to improve upon our design followed by more comprehensive fiber morphological studies.

Objective 2: We will perform high-throughput screen for protein fiber assembly by incorporating TFL/HFL in Rosetta-designed Q variants. We intend to perform experiments in 96-well plate and focus on fiber stability at elevated temperature. Fiber formation will be carried out in the presence of curcumin and screened for fluorescence and traceability by fluorescence microscopy and ^{19}F MR, respectively. We will further characterize positive constructs from computational design using SEM and TEM for fiber assembly and dimensions. Data obtained from fully characterized fluorinated proteins will be used to refine computational designs.

Objective 3: The designed proteins will be expressed in the presence of AHA, purified, crosslinked into fiber assemblies and then will be subjected for conjugation via click chemistry to Prg-CMms6 in 96-well plates. Iron oxide crystallization experiments and MRI experiments will be performed to characterize the relaxivity effect induced by the Fe_3O_4-bound protein using ^{1}H imaging. We will further characterize the positive constructs with MRI signal from the screen using TEM, energy dispersive X-ray spectrometer (EDAX) and magnetometry.

Broader impact (Only required for NSF projects): The proposed biomimetic fibrous materials are comprised of proteins and as a result, they hold tremendous promise for application in medicine as theranostic scaffolds for regenerative medicine. More importantly, we will transform the paradigm for biomaterials design through the marriage of state-of-the-art computational protein design and innovative approaches to rapidly screen for materials properties especially for imaging, reducing the time and expense for developing functional materials. The experimental characterization will then feedback into the computational algorithms to help refine our understanding for protein fiber assembly and inorganic nanomaterial crystallization, in accordance with the Materials Genome Initiative.

The broader impacts of this proposal are centered on the expanding biomaterials outreach to K-12 through NYU Scientific Outreach and Research (SOAR) Program. We aim to recruit upper class undergraduate students as paid fellows to develop a sequence of modules that exposes the students of "Urban Assembly Institute for Math and Science for Young Women" (UAI) to biomaterials by exploring amino acids, peptides, secondary structure, templation of magnetic nanoparticles and imaging. In collaboration with InSchoolApps, we will adopt the Next Generation Science Standards (NGSS) that centers on a cross-disciplinary framework for K-12 science and engineering education. The goal is to scientifically impact these young women in a way that links all these disciplines together while also relating the work to practical real-world applications such as imaging and biomedicine. All of these lessons will be integrated into the curriculum and published as we have done for others to employ in the K-12 classroom.

Data Management and Open Access: All software tools and databases developed with this mechanism of support will be open source and distributed under one of the open-source licenses (codes developed to date have primarily used the LGPL and GPL licenses, although newer licenses offer several advantages). Developments to Rosetta will employ the RosettaCommons (https://www.rosettacommons.org) to share Rosetta code developments supported by this proposal with industry, government, and academic labs (with thousands of groups already using this code in many settings). Rosetta is already freely available to non-profit and academic labs and widely licensed to Industry. Software will be developed to the point that it will be usable by others and will include enough documentation to be usable and modifiable by people who did not develop the code (this process of helping other to use our code will be aided by the Rosetta-commons and our yearly developers meeting which is open to the public).

Advancing Along the Materials Development Continuum: Through a feedback loop design involving computation and experimentation coupled to the development of biomaterials screening, we are able to more rapidly discover and develop functional biomaterials. We have parented these coiled-coil protein assemblies [3] and as we further optimize sequences and function, we will continue to protect the intellectual property. In order for these biomaterials to become more commercially relevant, we need to optimize the signal intensities for imaging modalities as well as investigate their biocompatibility.

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DMREF: High Throughput Design of Metallic Glasses with Physically Motivated Descriptors

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Website: none.
Keywords: Metallic glass, machine learning, descriptors, high-throughput, molecular simulation

Project Scope

The objectives of the proposed work are to develop an extensible iterative materials informatics framework (Figure 1) for predicting the glass-forming ability of metal alloys, and then to apply that framework to develop Al- and Mg-based alloys with improved glass forming ability (GFA). The approach includes combinatorial 3D printing synthesis, rapid optical, microscopy, thermal, and nanomechanical characterization, and high-throughput molecular dynamics (MD) and machine-learning. This work will produce large-scale databases with both measures of GFA and extensive thermophysical data from simulations, and integrate them to generate physical descriptor driven machine-learning models for iterative new metallic glass search and discovery.

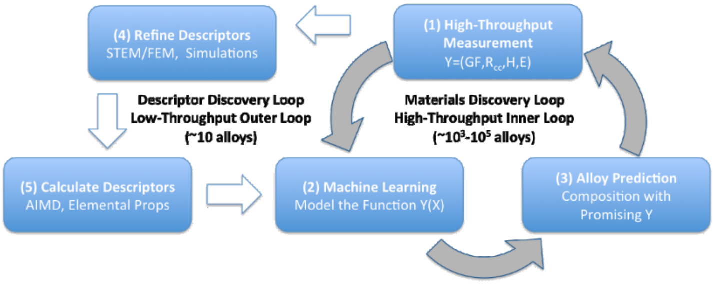

Figure 1: Dual-loop iterative materials design approach. The inner "materials discovery" loop (steps 1, 2, and 3) allows for effective training of a machine learning model through rapid interaction with high-throughput experiments and characterization. The outer "descriptor discovery" loop (steps 1, 4, 5, 2) iterates low- to medium-throughput methods to improve descriptors and practical measures for true GFA

Relevance to MGI

This project develops a powerful approach to tight iterative integration of experiment, modeling, and informatics, as shown in dual-loop approach in Figure 1. The project pushes into new domains of high-throughput synthesis with application of Laser Engineered Net Shaping (LENS) additive methods for Mg- and Al- metallic glass synthesis and thermodynamic characterization with flash Differential Scanning Calorimetry (DSC). We also integrate cutting-edge fluctuation electron microscopy with machine learning and computer vision enabled approaches for structure determination and analysis to yield new GFA descriptors. Finally, integrating these descriptors with high-throughput MD and machine learning will allow unprecedented correlation between GFA and calculated glass and liquid thermokinetics and structure that cannot be obtained from just experimental data. These correlations will then provide a foundation for predicting new glasses, which can be exploited for targeted experiments. Databases of GFA from the LENS experiments and thermokinetics from MD will be made available and be of value for many other researchers in the metallic glass field.

Technical Progress

This project only started in October 2017 so we are just beginning the work. We have the LENS system working with up to 4 elements and have purchased Mg and alloying element powders. Initial tests are optimizing processing parameters (maximum cooling rate, powder flow, and cycle time) to enable safe, *in situ* alloying. We are also using ab initio informed CALPHAD models to search for target Mg-based glasses that will partially devitrify to Mg bcc phases, a critical property to support both high strength and good ductility. Detailed characterization will begin after samples have been synthesized. Critical cooling rates and thermophysical properties from interatomic potential MD have been calculated for over 80 alloys and used in a machine learning model which already shows significant correlation with key GFA descriptors. Significant progress has also been made building on previous work. Specifically, we have used interatomic potential MD to better understand mechanisms of Al-Sm glass formation,[1] which will help guide descriptor selection in future machine learning. We have also determined a strong correlation between MD predicted fraction of icosahedral clusters and GFA in Al-based glasses. This correlation was used to predict a new high Sm Al-Sm glass, which was then synthesized and shown to form a glass under melt spinning.[2] This correlation has also been extended to ternary Al-Sm-X alloys based on ab initio MD predictions, as shown in Figure 2. Such correlation can now be used to screen new elements for promising GFA in Al-Sm-X glasses using just ab initio MD input.

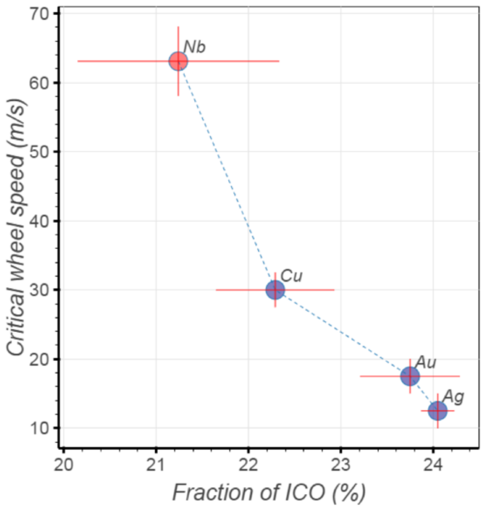

Figure 2: Glass forming ability (as represented by critical wheel speed in melt spinning) vs. fraction of icosahedral clusters (ICO) predicted by ab initio molecular dynamics. Data for multiple metals M in $Al_{92}Sm_7M_2$. This type of correlation enables prediction of GFA directly from ab initio MD, opening up new opportunities for computational materials design.

Future Plans

Our planned steps over the next year are to

1. Continue path to synthesis of Mg-based glasses with the LENS system, followed by flash DSC characterization of the selected promising compounds.
2. Initiate synthesis and flash DSC characterization of promising Mg-based glasses identified from CALPHAD to have probably partial devitrification to bcc Mg.
3. Initiate search for new structure-based descriptors from electron microscopy and advanced structure determination and analysis methods.
4. Extend MD simulations of critical cooling rates and thermokinetic and structure properties of melts and quenched glasses and explore correlation of GFA with thermodynamic, kinetic, structural, and elemental descriptors in machine learning models.

Broader impact

This project will provide a novel dual-loop iterative design approach that can be adopted by other scientists, unique thermodynamic and kinetic data and software tools that will be of fundamental value for researchers throughout the metallic glass community, and new Al- and Mg-based glasses with improved GFA that will enable a wide range of technological applications. This grant will also support the PIs training multiple graduate students and postdocs in state-of-the-art experimental and computational techniques. In particular, these student/postdocs will learn to use high-throughput methods and work as a team to integrate them into an iterative materials design loop. We are dedicated to engaging undergraduates in this project and will be integrating them with both experimental and research efforts. In particular, PI Morgan has initiated the Informatics Skunkworks,[3] an organization that works with undergraduates to realize the potential of informatics for science and engineering. This grant will further support a strong machine learning effort focused on amorphous alloys in the Informatics Skunkworks, which presently has four active undergraduate researchers. This grant will also help support the participants (PIs, students, and post-doc) contributing their time and expertise to multiple science outreach activities to the community, including the biannual UW hosted Engineering Expo, where Co-PI Voyles will host a high-resolution STEM demo and Co-PI Thoma will host a demonstration of 3D printing and other tools of advanced manufacturing.

Data Management and Open Access

In addition to publications, all raw and processed data from this work will be permanently archived and available to the public in easily accessible and searchable forms through the Materials Commons and the Materials Data Facility. The databases of GFA and simulated structural data will be a valuable resource for the metallic glass community and, more broadly, for other materials and mechanical engineers seeking metallic glasses for particular applications. Codes that enable efficient application of machine learning to materials problems will be developed as part of this work and will be shared as an integrated package through the Python package server and Github.

Advancing Along the Materials Development Continuum

The long-term goal of the approaches being developed here is to enable computational prediction of candidate alloy GFA. If successful, this will greatly accelerate development of new metallic glasses, enhancing existing areas of application such as packaging, arterial stents, water purification, and MEMS gears and springs, as well as enabling new applications. The MGI approach taken here is essential to develop these methods and a successful tool would represent the strong integration of computation with experiment that is at the heart of the MGI.

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2. G. Bokas, L. Zhao, H. Sheng, J. Perepezko, I. S. Synthesis of Sm-Al metallic glasses designed by molecular dynamics simulations. *J. Mater. Sci. (Under Review)* (2018).

DMREF: Design of Nanoscale Alloy Catalysts from First Principles

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Keywords: CO_2 reduction, copper, alloy nanoparticles, electrocatalyst

Project Scope

We are developing and validating a way to design alloy catalysts using density functional theory and the cluster expansion approach. The project is divided into two thrusts. *1)* Computational and experimental studies are combined to develop and validate a method for predicting the atomic structures of pure metal and alloy catalysts. *2)* Predicting the structure-property relationships of these catalysts, which are compared to and validated by electrocatalytic studies for CO_2 reduction. The integration of these two thrusts will lead to a rational approach towards the design of advanced catalytic materials for complex chemical processes.

Relevance to MGI

The predictions generated by our computational models are compared to experimental data on metal and alloy nanocatalysts. Based on these comparisons, we are iteratively refining both our computational approach and synthesis methods to improve our ability to make reliable predictions that can be used for nanoparticle design. Towards this end, we are developing methods to predict both how synthetic methods affect the atomic structures of the catalysts and how the activity, durability and selectivity of the catalysts correlate to their atomic structures.

Technical Progress

Thrust 1. We have developed cluster expansions for Cu-Pt nanoparticles, enabling us to rapidly predict the energies, c, and lattice parameters of nanoparticles as a function of composition, particles size, and temperature. The predicted shapes and lattice parameters are in good agreement with TEM images and XRD data on synthesized nanoparticles (Fig. 1a and 1b). To achieve good agreement between the experimental characterization of the surface composition and cluster expansion predictions we have for the first time developed a nanoparticle cluster expansion that explicitly includes adsorbed oxygen on the surface, demonstrating both the

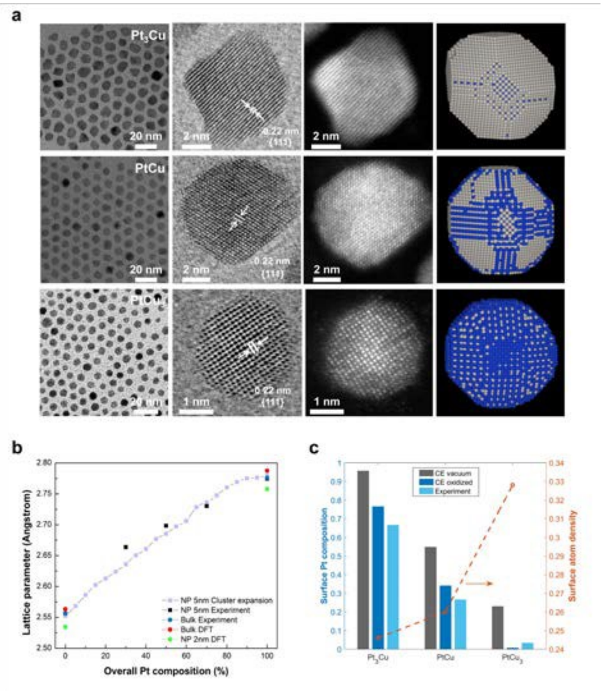

Figure 1. (a) Shapes of Cu-Pt nanoparticles from TEM and cluster expansion calculation (Cu blue, Pt gray); (b) Lattice parameters of Cu- Pt nanoparticles in comparison with experimental data; (c) Corresponding surface compositions in vacuum and oxidizing environment.

importance and feasibility of accounting for the chemical environment when predicting the structure of alloy nanoparticles. (Fig. 1c).

Thrust 2. We have built up an electrolysis cell for the electrocatalytic studies of CO_2 reduction and examined both Cu-based nanoparticle and nanowire catalysts. The gas and liquid-phase products were analyzed by a gas chromatography (GC) equipped with a mass spectrometer (MS) detector and nuclear magnetic resonance (NMR). In particular, we have developed the synthesis of highly dense Cu nanowires (Fig. 2a and 2b) and found them to be highly active and selective for CO_2 reduction, requiring an overpotential of only –0.3 V to reach 1 mA/cm^2 electrode current density and achieving Faradaic efficiency toward CO as high as ~60% (Fig. 2c). Further studies of CO reduction using these Cu nanowires demonstrated >50% selectivity toward ethanol at potentials more positive than -0.5 V (vs. RHE). The performances of these Cu nanowire electrocatalysts are among the best activities/selectivities for the low-overpotential electroreduction of CO_2 and CO. To better understand the reason for the catalytic activities of these nanowires and enable the rational design of improved catalysts, we have combined DFT calculations coupled with temperature-programmed CO desorption (CO-TPD) and OH_{ad} electrosorption experiments. Our combined experimental-computational approach indicates that the metastable (110) surface or a closely related surface feature is responsible for the relatively low overpotentials for both CO_2 reduction and CO reduction to C_2 products. Moreover, for CO_2 reduction mechanism, a kinetic model reveals competition between CO(g) evolution and *CO poisoning depending on the surface structures and electrode potential (Fig. 2d and 2e).

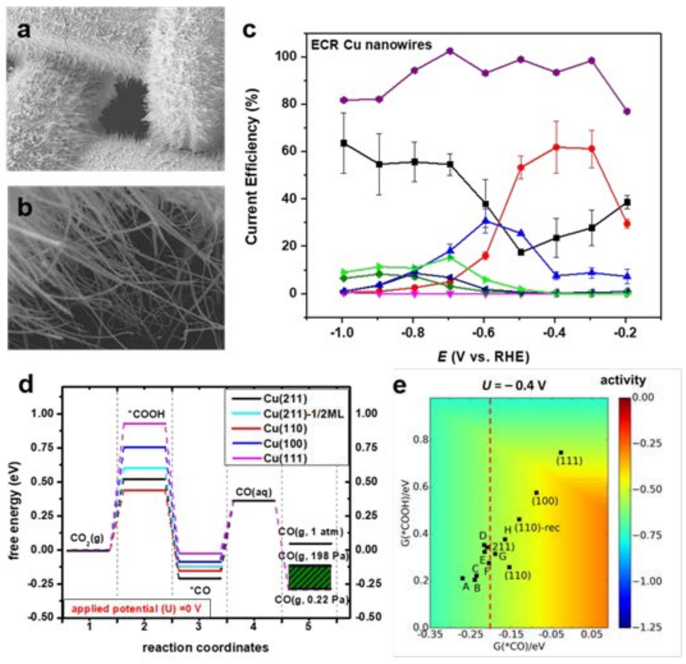

Figure 2. (a, b) SEM images of Cu nanowires grown on Cu mesh by electrochemical reduction of CuO nanowires. (c) Faradaic efficiencies (FEs) of various products obtained from CO_2 reduction on the electrochemically reduced Cu nanowires. (d) The free energy diagrams of CO_2 reduction on various Cu facets. (e) Trends in CO_2 reduction activity at -0.4 V, plotted as a function of both *CO and *COH binding energies. The points A-H represent (310), (210), (332), (322), (311)-rec, (221), (331) and (311) facets, respectively. The dashed line indicates the *CO binding energy corresponding to the rightmost peak on the CO-TPD of HR-150 and HR-300 (15h) nanowires.

Future Plans

We are continuing our efforts to understand how the surface structures of Cu nanowires relate to their catalytic properties by combining experiments and calculations to identify an unlabeled peak in the OH electrosorption data; developing cluster expansion models of CO and H adsorbed on various Cu facets to better understand the competition between the hydrogen evolution reaction and CO_2/CO reduction; and beginning joint computational and experimental studies on the structure and catalytic properties of Cu-alloy surfaces, which is used to guide the further development of Cu-based electrocatalysts for selective reduction of CO_2 to valuable hydrocarbon products.

Broader impact

The development of viable catalysts for CO_2 reduction could enable the synthesis of hydrocarbon fuels from CO_2 powered by off-peak electricity, simultaneously increasing global fuel supply and reducing one of the primary causes of global warming. The PIs meet regularly with the Ph.D. students working on this project to mentor them and discuss research results and strategies. The project team has hosted seven female high school students from largely minority Baltimore City public schools, who have gained valuable research experience by working closely with the graduate students and PIs.

Data Management and Open Access

The computational and experimental data generated during this project are being archived and made available for sharing, as are the computational tools developed for this project. Detailed descriptions of the computational and synthesis methods used have been and will continue to be published in peer-reviewed literature and student theses.

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Electrocatalysis Consortium (ElectroCat)
A DOE Energy Efficiency and Renewable Energy Energy Materials Network Consortium

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Website: www.electrocat.org
Keywords: electrocatalysis, fuel cells, oxygen reduction reaction, ORR, high throughput

Project Scope

The ElectroCat (Electrocatalysis) Consortium is aimed at addressing the primary challenge to widespread implementation of fuel cell electric vehicles (FCEVs) and other fuel cell energy conversion devices. The precious metal electrocatalysts that are the current standard in fuel cell systems are expensive and restrict the ability to develop fuel cells that are cost-competitive with traditional hydrocarbon-based power sources. ElectroCat is addressing this barrier by accelerating the development and deployment of platinum group metal-free (PGM-free) electrocatalysts in fuel cells. To do this, the consortium is employing a systematic approach in which potential catalysts are synthesized and analyzed rapidly and comprehensively using high-throughput, combinatorial methods. These in turn are guided by computational work and the fundamental electrocatalysis and materials knowledge housed across the national laboratory network. Streamlined data sharing with industry and academic partners is critical to the ElectroCat approach, rapidly building an understanding of PGM-free electrocatalysts across the field, and ultimately enabling the incorporation of those materials into next-generation fuel cells.

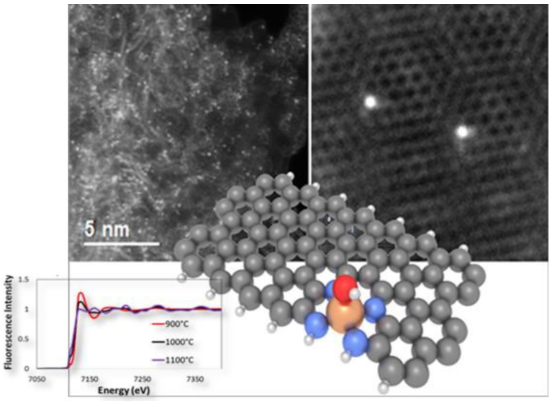

Figure 1. Potential active site(s) in PGM-free Fe-N-C catalyst are visualized with scanning transmission electron microscopy, characterized by X-ray absorption spectroscopy, and computationally correlated with specific lattice-level carbon structures.[1]

Relevance to MGI

ElectroCat is developing effective PGM-free catalysts for fuel cells using the Materials Genome Initiative approach. To speed the development and implementation , potential catalysts are synthesized and analyzed rapidly and comprehensively using high-throughput, combinatorial methods that are guided by high-throughput computational studies, advanced materials characterization, and fundamental knowledge of electrocatalysis and materials science. The effort benefits greatly from the efficient collaboration of national laboratories that have core competencies in PGM-free catalyst development and in high-throughput fuel cell catalyst development and analysis. The consortium approach involves industry and university players and provides them unprecedented and rapid access to the unique capabilities at these national laboratories, furthering meaningful progress towards the deployment of PGM-free catalysts and electrodes.

Technical Progress

Since ElectroCat began 1.5 years ago, its work has increased the catalytic activity of PGM-free catalysts for the oxygen reduction reaction by approximately a factor of five. Similarly, the performance of fuel cells made with PGM-free catalysts has also been increased by 40% over this time. Through its characterization efforts, the consortium has obtained direct microscopic and X-ray spectroscopic evidence that iron sites in the most promising class of catalysts are atomically dispersed and that the majority of these sites are on the surface of the catalyst, and are thus able to bind the oxygen molecule. Through its high-throughput tasks, the consortium has developed and utilized high-throughput software to calculate a durability descriptor for PGM-free cathode catalysts and has screened the durability of more than 25 potential active sites. Furthermore, we have utilized a high-throughput robotic system to synthesize 40 variations of the atomically-dispersed catalyst, screened the oxygen reduction reaction of these catalysts in a high-throughput fashion using a multi-channel flow cell developed in-house, and characterized the atomic structure of all 40 samples using X-ray absorption spectroscopy. A catalyst composition with potentially twice the activity of the baseline catalyst material has been identified through this effort.

Future Plans

The near-term focus of ElectroCat is on improving the performance of the atomically-dispersed catalyst in the fuel cell environment by improving electrode structure and on determining and addressing the limitations to the lifetime of these catalysts in this environment. Another near-term focus is active site identification and scale-up of the catalysts showing promising activity in the combinatorial studies.

Data Management and Open Access

A publically-accessible data hub has been established to support collaborative science through an accessible, searchable data resource. The data hub allows secure sharing of data among the project team members and advanced search across all data, facilitates access to advanced data tools for analysis, and makes selected datasets publically available. Project spaces have been created for the core national laboratory team and the four university, industry, and national laboratory awarded projects currently working with the consortium. The hub leverages the Globus platform and is linked to the Center for Hierarchical Materials Design (CHiMaD). The ElectroCat data hub is at: https://datahub.electrocat.org/.

Advancing Along the Materials Development Continuum

Developing effective PGM-free catalysts at an accelerated pace requires a systematic approach that includes the employment of high-throughput combinatorial methods and computational methodologies to direct discovery and development. As such, leveraging the consortium model through ElectroCat will provide an valuable space for developing the tools necessary to solve this material challenge, streamlining data sharing with relevant industry and academic teams and rapidly building an understanding of PGM-free catalyst materials, and for ultimately enabling the incorporation of PGM-free catalysts and electrodes into next-generation fuel cells.

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Publications

1. H. T. Chung, D. A. Cullen, D. Higgins, B. T. Sneed, E. F. Holby, K. L. More, P. Zelenay, "Direct Atomic-Level Insight into the Active Sites of a High-Performance PGM free ORR Catalyst;" Science, 357 (6350), 479-484, 2017.

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DMREF: Accelerating the Discovery and Development of Nanoporous 2D Materials (N2DMs) and Membranes for Advanced Separations

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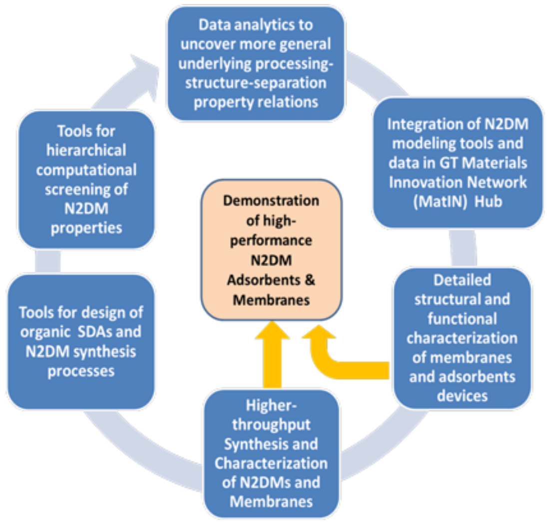
Keywords: nanoporous, 2D zeolite, separations, membrane, adsorption

Project Scope

To dramatically accelerate discovery of nanoporous oxides particularly for new separation applications, we propose a novel approach focusing on *Nanoporous 2D Materials* (N2DMs). N2DMs retain desirable structural features of conventional 3D zeolites, but have important advantages: a nanoscopic 2D sheet-like structure that overcomes diffusion limitations, and facile membrane fabrication by coating processes. Our approach interlinks multiscale modeling of N2DMs, development of novel N2DM data analytics methodologies, and material/membrane synthesis and characterization experiments. Metrics of success will be development of a large database of N2DMs, screening tools for N2DM separation applications, and demonstration of N2DM membranes for gas and hydrocarbon separations.



Workflow of a “genomic”-based approach to discovery and development of functional nanoporous 2D materials (N2DMs) and membranes.

Relevance to MGI

Our strategy exemplifies a “genomics”-enabled approach (see Figure) and has five key elements: (1) *In silico* N2DM structure database generation, (2) Hierarchical models and data-driven structure-property analytics of N2DMs for membrane-based separation), (3) *In silico* prediction and analytics of N2DM synthesis-structure relations, (4) Experimental synthesis and structure-property relations in N2DMs and membranes, and (5) Creation of a collaboration and informatics platform for N2DMs *via* sharing and evaluation of large datasets, code and protocol repositories, and open-source-format data repositories.

Technical Progress

We have made large progress towards the above goals. In the area of N2DM synthesis, we have obtained new insights on the effects of N2DM composition on their interactions with molecular species, by using their catalytic activity for bulky molecules as a probe of their structural properties. In the area of membrane fabrication with N2DMs, we have successfully fabricated membranes of two desirable N2DM materials on scalable ceramic hollow fiber support materials. This step provides the basis for pursuing a scalable and benign fabrication route to N2DM membranes. On the computational and data science front, we have created a massive database of more than 50,000 N2DM structures based upon the 200+ existing 3D zeolite structures. We overcame a number of obstacles in creating N2DM structures starting from 3D materials. We have also developed efficient and automated algorithms to calculate the structural and functional features of these N2DMs. This creates the basis for screening N2DMs for separation applications. Finally, we have set up a GitHub-based collaboration and informatics platform for the database of N2DMs.

Future Plans

We have three major goals in 2018-2019: (1) Obtain comprehensive computational screening data on diffusion and adsorption in N2DMs, use them to identify promising materials, and apply data science approaches to deduce key structure-property relations from the large dataset. (2) Develop a new fabrication process for N2DM membranes that is entirely free of demanding steps like hydrothermal growth. This is based upon our recent demonstration of N2DM coatings on hollow fiber supports. In upcoming work, we will develop low-temperature, benign methods to seal the nanoscopic gaps between the N2DM layers and obtain high selectivity for gas and hydrocarbon separations. (3) Establish a publicly available database and collection of informatics tools for N2DMs.

Broader impact

We are producing a cadre of STEM workforce members with unique MGI-enabled capabilities for materials development to drive a sustainable economy, who will be readily absorbed into US industry and academia. Our program has substantially ‘MGI-enabled’ the GT educational curriculum and exposed a large number of students to next-generation materials design and discovery, *via* new course materials on the theme of ‘Nanoporous Materials Genomics’ developed and taught by PI Nair starting in Fall 2017. Our program has created excellent avenues for interdisciplinary training of students across four academic units at Georgia Tech, *via* a strongly collaborative mentoring and co-advising environment for all of 3 PhD-track and 2 UG researchers.

Data Management and Open Access

Research data will be generated, stored and disseminated through the MatIN hub (http://materials.gatech.edu/matin) at Georgia Tech. Stored data will be archived according to usual Institute standards by adopting most recent computer techniques in storage architecture and database organization. This will include measurement datasets as well as simulation data from simulation packages, geometrical and digital input and output files for simulations, visualization plots, and so forth. This data will also be disseminated in peer-reviewed journal publications, theses, book chapters and other print or electronic publishing formats, as well as conference presentations/ abstracts/proceedings. The data will be backed up continuously. PI Nair and co-PI Kalidindi will be responsible for oversight in collecting data, storage data, and making data available to the research community.

Accelerating Materials Discovery & Development

The successful accelerated development of N2DMs and N2DM membranes is expected to attract and facilitate new industrial collaborations, thus adding a new dimension to our strong partnership with industry and significantly accelerating new economic impacts of nanoporous materials in the energy, chemicals, and environmental sectors.

Publications

Three publications are currently in preparation for submission in the first half of 2018.

Predictive Multiscale Modeling of the Mechanical Properties of Polymers 3D Printed Using Fused Filament Fabrication

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Peter Olmsted: Department of Physics, Georgetown University, Peter.Olmsted@georgetown.edu.
Keywords: process modeling, fused deposition modeling, thermoplastic, 3D printing, mechanical properties.

Project Scope

Fused filament fabrication (FFF), also known as fused deposition modeling, is one of the most widely used and rapidly growing additive manufacturing process. Our goal is to uncover the relationships between key processing, tool-path, and feedstock material parameters and the anisotropy, strength, and toughness of printed materials. We will study polycarbonate (PC) as the model material, but the findings will form a basis for understanding more complex materials. The research outcomes will provide methodologies and computational tools for the analysis-driven, accelerated design of FFF products with enhanced mechanical properties.

Relevance to MGI

Our research approach treats the printed material at four structural length scales: (1) the chain conformational and entanglement structure, (2) the fiber and weld structure, (3) the raster structure of welded fibers, and (4) the printed part. At each scale, the effects of the printing parameters on the structure and mechanical properties of the printed materials will be evaluated using an integrated approach with iterative feedback between printing, experiments, and computational modeling. We will develop a multi-scale modeling framework to downscale the temperature history from thermal analysis of the printed part and upscale mechanical properties of lower scale models to evaluate residual stresses in the part. Simulations at each length scale will be validated by innovative experiments developed at JHU, NIST and ARL.

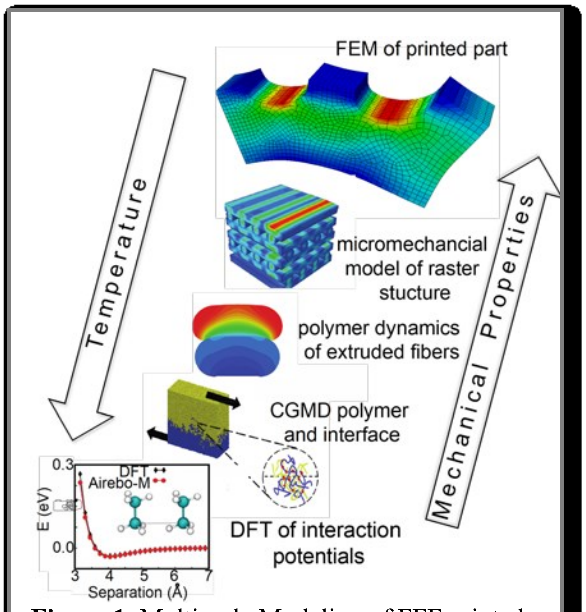

Figure 1. Multiscale Modeling of FFF printed materials

Technical Progress

Molecular dynamics (MD) study of chain diffusion: Extrusion in FFF is typically fast enough to produce significant chain alignment in filaments. MD simulations with a generic polymer glass potential were used to determine if alignment affects the rate of welding to previously printed layers by producing a substantial reduction in entanglements, which should increase interdiffusion rates, or by producing a large entropic force driving chains towards spherical conformations that may enhance welding. Results show that neither of these effects enhances weld strength. Entropy drives chain retraction in the tube, but this does not speed interdiffusion since the tubes are aligned along the interface. There is also no indication of accelerated interdiffusion due to entanglement loss. However, alignment can enhance weld strength by reducing the tensile yield stress of polymer filaments in the direction perpendicular to the alignment. At times less than the Rouse time, this can greatly enhance the fracture energy of welds by moving failure away from the interface and into the aligned filament. At longer times the strength of welded bonds is nearly independent of the initial alignment. *Polymer dynamics simulations:* Simulations of filament extrusion, using an in-house finite element algorithm based on the Rolie-Poly constitutive model for polymer melts calculated the molecular configuration and entanglement density through the diameter of the filament. The calculations used a new continuum equation for the dynamics of entanglements and re-entanglements of polymers during and after the flow associated with FFF. The results were used to estimate the interdiffusion time and weld strength. Results show that the amount of disentanglements can influence the weld strength. *Measuring the feedstock and weld material properties:* We have established a common family of PC feedstock materials developed by ARL, with different molecular weight (MW) and polydispersity index (PI), for experiments at JHU, NIST, and ARL. Our groups have also developed a set of experimental protocols to characterize the molecular structure and physical properties of the filaments using NMR spectroscopy, GPC, DSC, DMA, and uniaxial tension/compression tests. We have measured the Tg, temperature-dependent heat capacity and thermal expansion coefficient, and the temperature-dependent and rate-dependent large deformation stress response of PC filaments through the glass transition. The data will be used to parameterize constitutive models to simulate extrusion, mechanical behavior of the printed materials, and fracture behavior of the welds. *Measuring temperature history and structure:* IR measurements showed that filament extrusion raises the temperature only of the layer directly beneath to above Tg. This rapid temperature drop may have important implications for the weld strength and residual stresses. Micro-CT data revealed the presence micron-size bubbles/voids in the printed filament in addition to the large voids between filaments. The bubbles are caused by the evaporation of moisture within PC filaments.

Future Plans

Future work will focus on integrating the simulations across length scales and developing experiments to validate model predictions. MD studies will examine other modes of failure, develop more chemically accurate simulations of the PC materials used in experiments and provide interfacial fracture and strength properties for finite element simulations of peeling and tearing. These will be compared to peel tests being developed at JHU and NIST to measure the interfacial energy and strength of the welds between printed filaments for different printing conditions. The thermomechanical properties measured will be used to simulate the printing of raster structures to calculate the temperature history and residual stresses. These will be validated by IR measurements at JHU and experiments developed at NIST using polarized light imaging. We are building an environmental chamber that controls temperature and minimize humidity, and developing a drying process of the feedstock material to reduce warping from residual stresses and minimize the presence of voids in the printed filament.

Broader impact

The research project provides hands-on research education for students at all levels that integrate 3D printing, experiments, theory, and computation. PhD students work closely with each other across groups to design experiments and simulations that integrate with each other and across length scales. Results are shared during monthly project meetings attended by all groups, and by NIST and ARL collaborators. PhD students are assisted by Masters and undergraduate students recruited at JHU and Morgan State University through the Extreme Science Internship Program. We plan to request supplemental funding for REU and Masters students from underrepresented groups, and begin to host high school research interns through the Women in Science and Engineering and similar programs with Baltimore City public and private schools.

Data Management and Open Access

The project will involve extensive experiments and computer simulations across different length scales using open source (e.g. LAMMPS) and commercial (ABAQUS) codes. The main outcomes of the project will be materials data, simulations results and computational codes. The analyzed data will be disseminated to the scientific community in peer-reviewed publications. After publication, copies of files pertaining to metadata, analyzed data and corresponding primary data (or files needed to recreate it), will be made available to members of the scientific community upon request. The data will be shared via a public folder on JH Box cloud storage. Software modules written to enhance the open-source software (LAMMPS and Tahoe) will be provided to the developers for incorporation in future releases. ABAQUS user subroutines will be made available upon request.

Advancing Along the Materials Development Continuum

The fundamental knowledge uncovered by this project will enable analysis-driven design and optimization of the printing parameters and part geometry and the development of standards to evaluate the print quality. To that end, PI Nguyen joined the AM-Bench Scientific Committee. The role of the committee is to advise on the development of rigorous benchmark tests for modelers to test their simulations.

Publications

C. McIlroy and P. D. Olmsted (2017). Disentanglement Effects on Welding Behaviour of Polymer Melts during the Fused-Filament-Fabrication Method for Additive Manufacturing. *Polymer*. **128**:376-391.

C. McIlroy and P. D. Olmsted (2017). Deformation of an Amorphous Polymer During the Fused-Filament-Fabrication Method for Additive Manufacturing. *Journal of Rheology*. **61**:379-397.

R. Xiao, G. Ghazaryan, T. A. Tervoort, T. D. Nguyen (2017). Modeling Energy Storage and Structural Evolution During Finite Viscoplastic Deformation of Glassy Polymers. *Physical Review E*. **95**:063001.

Paired Ionic-Electronic Conductors in Spatially Confined Self-Assembling Rod-Coil Block Copolymers and Bolaamphiphiles

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Keywords: modeling, synthesis, characterization, self-assembly, mixed conduction.

Project Scope

This project's goal is to develop and study organic materials that conduct both electronic and ionic charges for a wide range of applications including rechargeable batteries, electrochemical transistors, and bioelectronic devices. We couple organic substituents capable of electronic conductivity (polythiophenes) with ionic conductivity (poly(ethylene glycol) with ionic dopants) in self-organizing materials. We design, model, synthesize, assemble and characterize electronic-ionic conductors ranging from oligothiophene-oligoethylene glycol small molecules to macromolecules.

Relevance to MGI

Although mixed conduction materials offer extraordinary opportunities, research has been limited by the availability of synthetic routes, the complexity of their morphology-phase behavior and the challenges in understanding interactions across the electronically-ionically conducting interfaces. Due to the enormity of the design space for such materials, our research relies on intimate collaborations between predictive theory and simulation, model-assisted materials synthesis, processing and advanced characterization to identify effective mixed conduction materials, to integrate and then to deploy them in prototype devices. The Escobedo Lab is developing force fields, computational methods, and a machine learning framework for discovery of such novel dual conducting materials. The Ober Lab, and the Luscombe Lab are involved in the synthesis of selected small molecule and polymeric derivatives respectively. These synthesized materials are characterized by the Nealey Lab and Patel Lab for morphology and conductivity properties. This characterization acts as a tool for validation and future development of materials by providing feedback to the modeling and re-design efforts.

Technical Progress

Due to the novelty of this general class of organic materials, no suitable set of force field parameters was available for all-atom or coarse grain simulations. Using DFT and maximum entropy methods we have developed of atomistic (AA) and coarse grain (CG) force field potential for this class of materials. Using a CG system which replicates the chemistry of thiophene and ethylene glycol derivatives we could dynamically self-assemble the system into morphologies seen experimentally. Although the morphology is captured adequately, AA simulations are needed to predict ionic conduction. Hence, we developed a Reverse Coarse Graining (RCG) Software which converts a CG system to an AA system. This multi-scale simulation approach allows us to capture morphologies which are not accessible using AA simulations due to computational limitations without losing key intricate details needed for calculating properties like ionic mobility and electronic conductivity which are blurred out in CG models.

For small molecule derivatives, we successfully synthesized a low molar mass liquid crystalline material 4T/PEO4 which consists of an electronic conduction portion, quarterthiophene, and an ionic conduction portion, tetra(ethylene glycol). Using both structural characterization and molecular dynamics simulation, we show that 4T/PEO4 can spontaneously form smectic morphologies in which both ion and electron conduction pathways exist within the materials. Additionally, upon blending with ionic dopant (lithium bis(trifluoromethanesulfonyl)imide, LiTFSI) and electronic dopant, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), a film of 4T/PEO4 exhibits remarkable ionic and electronic conductivities in the solid state.

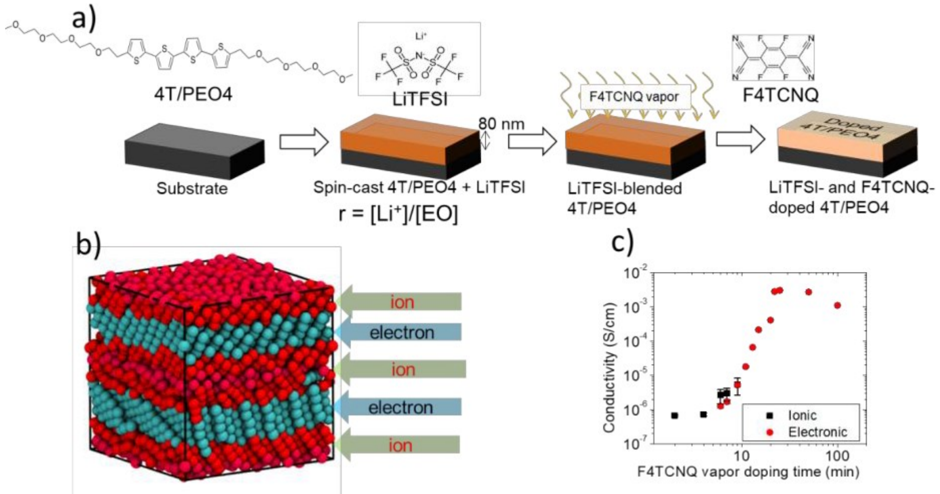

Figure 1. (a) LiTFSI and F4TCNQ doping scheme of 4T/PEO4 (b) simulated self-assembled structure of coarse-grained 4T/PEO4 and (c) mixed ion/electron conduction of 4T/PEO4-LiTFSI blend film as a function of F4TCNQ vapor doping time.

In the case of polymeric macromolecular systems, we use atomistic molecular dynamics to predict ionic conductivity in derivatives of P3HT and successfully prepared the high performing candidates. While there are many studies concerning the electronic conductivity of P3HT-like molecules, the mobility of ions in these materials is not well understood. We have studied various molecules with different ethylene glycol content and architecture. For each polymer, we calculated the ionic conductivity in the crystalline and amorphous phases to observe the impact of side chain design on ionic mobility. We found that a decrease in crystallinity of polythiophene dramatically reduces the mobility of the ion due to a reduction in percolating pathway for ionic diffusion. We use an inverse design approach to identify good ion-conducting side-chain architectures and propose that it consists of two ethylene glycol units separated by three methylene groups. This architecture incorporates the percolation of the ethylene glycol segment near the backbone, and the faster chain segment mobility of a PEO segment at the chain end, thus giving the best ionic mobility. To verify this effect, we have successfully synthesized polythiophene with side chains as tri-ethylene glycol. We expect to characterize these materials experimentally in the near future.

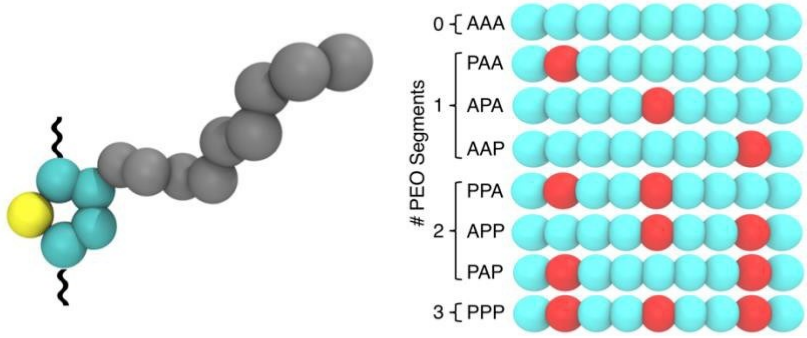

Figure 2. Various P3HT derivatives studied for ionic conductivity in crystalline and amorphous state.

Future Plans

In mixed conductors, interactions across the ionic and electronic conducting domains are of fundamental importance yet remain poorly understood. To tackle this challenge, we will continue to develop new series of 4T/PEO4 derivates nT/(EO)m, in which both n and m are systematically varied to generate materials with different ionic/electronic conducting channel width. Additionally, we will also vary the grafting position of ethylene glycol unit on thiophene to alter the materials' self-assembly behavior. Subsequently, we will use directed self-assembly techniques to precisely align the electronic and ion conduction domains into functioning prototype devices to study their structure as well as the conduction characteristics. We plan to use CG simulations to predict the self-assembly of the materials with the addition of ionic and electronic dopants before shortlisting the most promising systems for which to run AA simulations to predict their electronic and ionic conductivity. The high performing candidates from the simulation results will be selected for synthesis and subsequently used for self-assembly and characterization studies.

For the polymeric thiophene derivatives, we are exploring various chemistries using a permutation of 10 different functional groups. This combinatorial space entails over 10,000 possible chemistries for the side group. We are in the process of training a neural network to predict the ionic conductivity for these systems and later predict the side chain architecture with the highest ionic conductivity for Li^+. We note that calculating ionic conductivities involves several computational challenges, including the estimation of the salt dissociation rate, for which we have developed a modified umbrella sampling methodology that calculates the dissociation free energy of the salt in the material of interest. Overall, our machine learning assisted approach for the identification of high performance is expected to significantly accelerate the discovery of dual conducting organic materials.

Broader impact (Only required for NSF projects)

The new insights into the molecular packing of the rod-coil copolymers and small molecules and its effects on ionic-electronic conductivity benefits organic electronics in general, and advanced technologies such as thermoelectric devices, memristors, organic transistors, and batteries. More importantly, the involved students are exposed to the synergy among key elements of a comprehensive materials design cycle comprising modeling, synthesis, assembly, and characterization. We have also developed computational techniques and software that will serve in accelerating the material discovery initiative.

Data Management and Open Access

The reverse coarse graining software in this project is still under development and refinement, it will be released on the project website soon. The force field parameters will be made available in the Supporting Information section of future publications, so that it is open access.

Advancing Along the Materials Development Continuum

Principally development of organic mixed ionic-electronic conductors depends on only two components, one for electronic conduction and the other ionic conduction. However, the molecular packing of each of the component in the presence of the other is a non-trivial problem. We are using high throughput techniques where we use molecular modeling coupled with machine learning as a guide for our synthesis for successful discovery of new materials with high strength, ionic and electronic conductivity for future device application.

Publications

1. Giridharagopal, R.; Flagg, L. Q.; Harrison, J. S.; Ziffer, M. E.; Onorato, J.; Luscombe, C. K.; Ginger, D. S, "Electrochemical strain microscopy probes morphology-induced variations in ion uptake and performance in organic electrochemical transistors," Nature Materials, **16**, 737 (2017).
2. Y Sun, P Padmanabhan, M Misra, F Escobedo, “Molecular dynamics simulation of thermotropic bolaamphiphiles with a swallow-tail lateral chain: Formation of cubic network phases”, Soft Matter **13,** 8542 (2017).

DMREF: Collaborative Research: The Synthesis Genome, Data Mining for Synthesis of New Materials.

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Website: synthesiproject.org

Keywords: materials synthesis, machine learning, natural language processing, inorganic oxides

Project Scope

The objective of the research is to build predictive tools for materials synthesis leveraging natural language processing techniques coupled with thermochemical information. The database we are developing is populated by recipes extracted automatically from experimental sections in published literature. Then this database can be used to identify patterns for existing materials that can be extended to new materials or to develop hypotheses of what drives synthesis. Case studies thus far have focused on inorganic oxides used in batteries and thermoelectrics. Our goal is to disseminate a database of synthesis information for inorganic materials extracted from scientific literature.

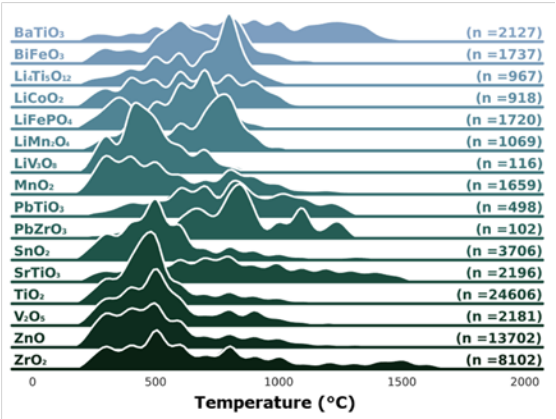

Figure. Temperature histograms for several oxide materials to demonstrate the breadth and capability of the database we have developed. Each histogram represent the temperatures used in the syntheses of the named oxide across the number of papers indicated on the right (n=number of papers).

Relevance to MGI

MGI's success to date in accelerating materials design has begun moving the bottleneck in materials development towards the synthesis of novel compounds, gating the momentum and efficiency gained in the design process by trial-and-error synthesis techniques. This delay in going from promising materials concept to validation, optimization, and scale-up is a significant burden to the commercialization of novel energy materials. Shortening the duration of materials synthesis would lead to more rapid iteration between materials design efforts and their testing, thereby not only shortening materials development time, but also spurring more efforts towards novel, high risk materials design concepts. The complexity of materials synthesis demands an interdisciplinary approach, one that can integrate the body of experimental knowledge already acquired with modern predictive ab-initio tools along with experimental work. Consistent with the spirit of the MGI program we aim to combine modern data extraction and analysis methods—to capture historic experimental data—with data mining and first principles computed data to take the next step in accelerated materials design by extracting, rationalizing, and predicting the synthesis of inorganic compounds.

Technical Progress

To date, we have achieved automated extraction of recipes from over 1.2 million published scientific articles, thus enabling the first demonstration for body text extraction, focused on synthesis of inorganic materials using primarily machine learning approaches. Articles are retrieved with a combination of APIs and publisher agreements; a significant portion of our corpus is closed-access, therefore requiring publisher agreements. Relevant synthesis text and reaction conditions are extracted from articles using deep learning techniques, such as word2vec and, more recently, recurrent and convolutional neural network approaches. Annotated data is used to supplement these unsupervised approaches as well as test the accuracy of the extraction. Currently we assume a linear ordering of operations within the relevant text, which has proven to be a reasonable assumption for this domain based on comparison to unsupervised generative models. Our accuracy measured by F1 score for token classification of 85%, with highest accuracy on identifying materials and operations. This database has enabled comprehensive search across all materials and types of synthesis. At a high level our key accomplishments have been to demonstrate the viability of the database as a way to learn about synthesis parameters for oxides. Our current work is to couple these insights with thermochemical data by linking them directly to data within the Materials Project. This will enable a higher level of resolution in our data mining. We have examined the synthesis conditions for various metal oxides across more than twelve thousand manuscripts. As an example, we applied machine learning methods to predict the critical parameters needed to synthesize titania nanotubes via hydrothermal methods and verify this result against known mechanisms. By training a decision tree across 22,065 journal articles, a hierarchy of single-variable divisions for titania nanotube formation is selected from a pool of 27 synthesis variables (e.g., annealing temperature, drying time). The root node in the decision tree splits the dataset by NaOH concentration, and the distributions of the data projected onto this univariate axis confirm that the majority of recipes use NaOH at concentrations of either 1 M or 10 M.

We have also used a variational autoencoder to compress sparse synthesis representations into a lower dimensional space, which is found to improve the performance of machine learning tasks. To realize this screening framework even in cases where there are few literature data, we devised a novel data augmentation methodology that incorporates literature synthesis data from related materials systems. We apply this variational autoencoder framework to generate potential $SrTiO_3$ synthesis parameter sets, propose driving factors for brookite TiO_2 formation, and identify correlations between alkali ion intercalation and MnO_2 polymorph selection. Domain opportunities for machine learning within the field of materials science synthesis include scarce data, sparse vectors, strong priors, and variation in phase and morphology.

Future Plans

We will continue to refine the database by improving our accuracy metrics along the entire software pipeline, by adding additional materials systems through more articles (and patents). We have also begun to extract information from tables and from the results sections of published manuscripts. We have begun to extract recipes for zeolite materials as this is a system that the team can perform experimental confirmation of newly generated synthesis conditions.

Broader impact (Only required for NSF projects)

We have had two key aims in our broader impacts efforts, the first to continue to develop our infrastructure to make this knowledge accessible to the public (describe in the next section) and the second is around education. The MIT team has led the educational activities. We have participated in two programs where we have conveyed the philosophy of the MGI program as well as our research findings. MIT Splash invites thousands of high school students from across the country to MIT for a weekend every fall. At Splash 2016, the Synthesis Project team presented a lecture and tutorial on materials informatics to 16 high school students. The average class feedback score was 5.00/5.00 from students (with a global average of 4.01/5.00 for all classes). MIT Spark is a similar program, run in the spring for middle school students. We presented a similar materials informatics tutorial to 43 middle school students, and received an average class feedback score of 4.67/5.00 (with a global average of 3.91 for all classes). Materials used in the lecture are included here: https://github.com/eddotman/intro-to-materials-informatics] The MIT team is working with MIT's Teaching and Learning Laboratory to develop a module that can be used by others. We are using these materials to plan for a hackathon type event in collaboration between UMA and MIT.

Data Management and Open Access

First as part of our publications we have made data accessible both the word2vec embeddings and the portion of our code base that is not specifically related to the publications (as per our agreements with publishers). The code used to download journal articles for large scale text-mining is available at [www.github.com/olivettigroup/article-downloader]. The code used to compute and analyze the data is available at [www.github.com/olivettigroup/sdata-data-plots/]. Additionally, the compiled Word2Vec embedding vector model is available at [www.github.com/olivettigroup/materials-word-embeddings/]. The underlying machine learning libraries used in this project are all open-source: Tensorflow, SpaCy, and scikit-learn. A detailed web-accessible Python tutorial for loading and analyzing the dataset is available at [https://github.com/olivettigroup/sdata-data-plots/blob/master/SDATA-data-plots.ipynb]. We have also developed a beta-test for our results to also be disseminated through the Materials Project. We are enabling snippets of relevant synthesis paragraphs (along with DOI article links) to be presented on the Materials Project website.

Advancing Along the Materials Development Continuum

We believe that the iterative approach we have enabled by development and dissemination of the text extraction approach can accelerate materials development over what would be possible without this approach. Our findings thus far have been to demonstrate the framework and in our final year the aim is to more directly contribute to development for a series of novel materials. We have been approached by several industrial partners interested in our pipeline for particular materials systems, so we can pursue specific cases with these firms.

Publications

1. E. Kim, K. Huang, A. Saunders, A. McCallum, G. Ceder, E. Olivetti, *A Data-driven Framework for Materials Synthesis Discovery*, Chemistry of Materials **29**, (2017).
2. E. Kim, K. Huang, S. Jegelka, E. Olivetti, *Virtual screening of inorganic materials synthesis parameters with deep learning,* npj Computational Materials **53**, (2017).
3. E. Kim, K. Huang, A. Tomala, S. Matthews, E. Strubell, A. Saunders, A. McCallum. E. Olivetti, *Machine-learned and Codified Synthesis Parameters of Oxide Materials*. Scientific Data. (2017).4, 170127.
4. Mysore, Sheshera, et al. *Automatically Extracting Action Graphs from Materials Science Synthesis Procedures.* arXiv:1711.06872. Workshop on Machine Learning for Molecules and Materials at NIPS 2017. (2017).

Integration of computation and experiments to design a versatile platform for crystal engineering

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Website: Under development

Keywords: nanoporous zeolites, crystal growth modifiers, binding energies, calorimetry

Project Scope

Designing crystalline materials with tailored properties is critical to industries spanning (petro)chemicals to pharmaceuticals and electronics. One technique that is utilized to control crystal properties is the use of modifiers, which are molecular additives that adsorb on specific crystal faces and alter anisotropic rate(s) of growth. This project integrates zeolite synthesis, characterization, modeling (density functional theory and molecular simulation), and machine learning to develop an experimentally-validated computational platform (Crystal-MoD) for high-throughput screening of growth modifiers.

Relevance to MGI

Crystal-MoD will be an experimentally validated platform for elucidating structure-activity relationships and high-throughput statistical screening of crystal growth modifier compounds. The platform is initially being developed to design zeolite materials for catalytic applications and later will be extended to a wide range of crystalline materials including metal-organic frameworks, metal oxides, and biominerals. It will be derived from physics-based methods for modeling of crystal surfaces (DFT) and simulating modifier adsorption (molecular dynamics with explicit solvent). These methods are combined to computationally search through chemical space and screen on the order of several thousand compounds for attributes associated with modifier efficacy (i.e., favorable adsorption energies). These computationally screened compound libraries will be used to train and cross-validate a separate quantitative structure-activity relationship (QSAR) model for each zeolite structure for rapidly screening large, open-source databases with millions of commercially available substances. The platform will rapidly accelerate growth modifier discovery by supplanting time-consuming and expensive empirical approaches for crystal design with robust, predictive methods. The overall predictive capability of the platform will be carefully scrutinized by performing zeolite synthesis studies to assess the efficacy of modifiers identified using the QSAR models. Classical simulation force fields will be validated and refined using data from calorimetry experiments.

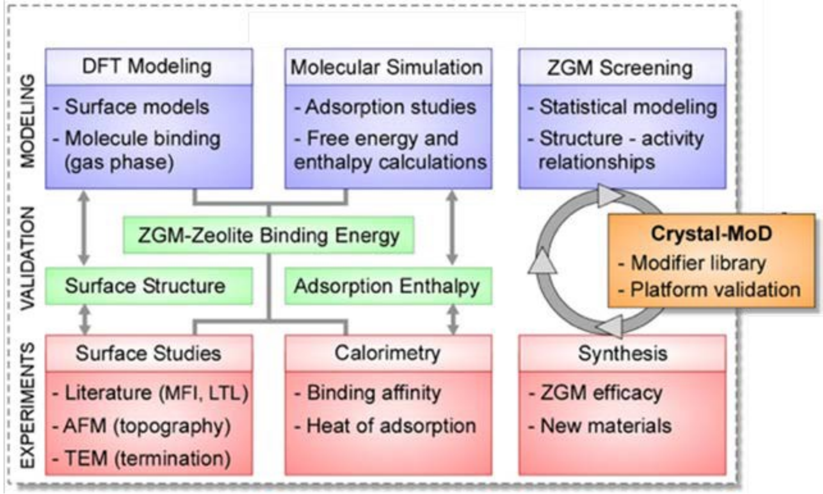

Figure 1. Crystal-MoD: An experimentally validated computational platform for accelerating rational zeolite design using zeolite growth modifiers (ZGMs).

Technical Progress

We have performed combined experimental and computational studies to investigate the adsorption of crystal growth modifiers on LTL and TON framework zeolites, which have 1D porous networks. The combination of restricted mass transport in 1D zeolites coupled with large aspect ratios impose internal diffusion limitations that negatively impact their performance in catalysis. Hence, the performance characteristics of these materials can be greatly improved by devising protocols that reduce the diffusion path length, either by altering the aspect ratio and/or reducing the size of zeolite crystals. Our experiments demonstrate that the crystal morphologies of LTL and TON can be tuned by introducing growth modifiers during synthesis. Strikingly, we find strong correlations between the hydrophobic character of the growth modifiers and their efficacy in altering the aspect ratio of LTL. Conversely, no such trend is observed for TON framework zeolites. To rationalize this behavior, we have performed molecular dynamics simulations to study the structuring of water near zeolite surfaces. These simulations reveal that the local density of water near the surface increases in regions where the density of exposed of silanol groups is high. This behavior is expected because the silanol groups can act as both hydrogen bond acceptors and donors with water. In these high density regions, however, we find that water forms structured layers in which the molecules exhibit low translational mobility. These structured layers serve as barriers that can inhibit hydrophilic growth modifier compounds from adsorbing to the surface and forming hydrogen bonds with the exposed silanol groups, thereby reducing their efficacy.

We have also utilized heat of wetting (calorimetry) measurements to quantify the heat flow associated with the wetting (adsorption, pore filling) of basic aqueous solutions containing growth modifiers. The results demonstrate substantial differences between the heat of wetting of the same growth modifier on TON or LTL. We also find that the heats of wetting in the absence and presence of growth modifiers are remarkably similar, suggesting that the modifiers interact weakly with the zeolite surfaces. This observation is consistent with estimates of adsorption free energies computed using umbrella sampling molecular dynamics simulations. The simulations also reveal that hydrogen bond formation with surface silanols is the primary mechanism for growth modifier adsorption, thus explaining the low heats of wetting and adsorption free energies. Importantly, we find that the simulations are able to semi-quantitatively capture the experimentally observed trends, indicating that existing classical force fields and sampling methods are well-suited for computationally screening growth modifiers based on adsorption energies.

Future Plans

We are focusing on leveraging the fundamental insights gained from our initial studies to develop a computational platform that can rapidly screen growth modifiers based on adsorption energies. This platform will use the computational methods (umbrella sampling molecular dynamics) and force fields that have already been validated against experimental calorimetry measurements and density functional theory calculations in our initial studies. Additional experiments will also be performed to construct databases of growth modifiers for other zeolites (e.g., MFI) than can be used to perform blind validation tests of the computational platform.

Broader impact

The PIs at the University of Houston (UH) have recruited three graduate students for this project, and two graduate students have been recruited at Penn State. The PIs have also solicited active participation from two UH female undergraduates and one physically disabled UH student. The PIs organized the 2017 Texas Soft Matter meeting at UH and the annual meeting of the Southwest Catalysis Society; findings from this project were highlighted at both meetings.

Data Management and Open Access

The PIs are currently constructing a web-based platform to highlight key findings from this project and provide open access to the generated data. The website will also include tutorials on using open-source simulation software to perform the classical and density functional theory simulations used in this project.

Advancing Along the Materials Development Continuum

Zeolite growth modifiers offer a commercially viable route to tailor material properties without significantly impacting the economics of catalyst manufacturing. Computational screening of modifiers will identify inexpensive, commercially available molecules as ideal targets for industrial scale zeolite synthesis. The additional advantage that modifiers can be incorporated in existing synthesis processes with the possibility for recovery and recycling of the organics post-synthesis will facilitated the facile integration of this technology in zeolite crystallization. Moreover, the resulting improvement in catalyst performance, such as enhanced selectivity of desired products or longer on stream lifetime, can lead to significant cost savings in catalytic applications that offset the expenses associated with the use of modifiers in catalyst processing.

The PIs all have projects funded by industries that employ zeolites as catalysts, which will be used as a starting point for exploring pursuing future commercialization. The initial modifiers screened in this project is based on a previously filed patent application; however, this DMREF project is expected to uncover additional (more effective) modifiers that will be the basis of future patent applications.

Publications

A. Chawla, R. Li, R. Jain, R. J. Clark, J. G. Sutjianto, J. C. Palmer, and J. D. Rimer, *Cooperative effects of inorganic and organic structure-directing agents in ZSM-5 crystallization*, Molecular Systems Design and Engineering **3**, 159-170 (2018).

S. He, J. C. Palmer, and G. Qin, *A non-equilibrium molecular dynamics study of methane transport in clay nano-pores,* Microporous and Mesoporous Materials **249**, 88-96 (2017).

Uncertainty Quantification for Molecular Dynamics

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Co-Principal Investigators: Andrew Dienstfrey, NIST, andrew.dienstfrey@nist.gov
Website: https://math.nist.gov/~PPatrone/UQ/ (soon to launch)
Keywords: Uncertainty quantification, molecular dynamics, materials science

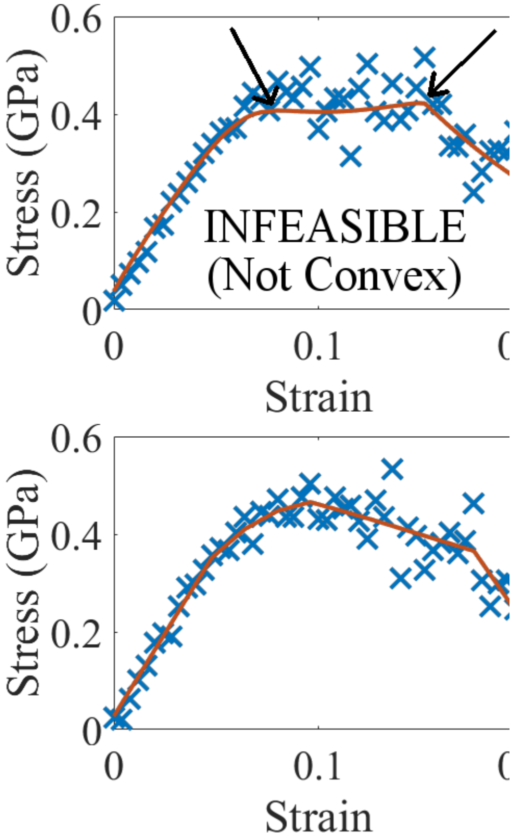
Project Scope

Molecular modeling remains a powerful tool for predicting the properties of novel and untested materials. Despite this, simulation tools such as molecular dynamics (MD) are often accompanied by various sources of uncertainty not found in the experimental realm. This project aims to: (I) identify and better understand the sources of such uncertainties; (II) develop analytical and numerical techniques for quantifying them; and (III) establish tools and publications to more broadly disseminate research results. Ultimately the broader goal of this work is to help build confidence in simulations to facilitate more widespread adoption for materials development.

Relevance to MGI

Reducing time-to-market of new materials is a key component of increasing US competitiveness in a variety of industries. While the traditional paradigm of make-it-and-break-it has led to systematic and robust methods for characterizing and qualifying materials, the cost and time associated with such approaches are naturally in conflict with the need for high-throughput tools. To address this problem, the scientific community is beginning to turn towards simulations (e.g. MD) as a lower-cost alternative to materials discovery. However, such methods suffer from a variety of uncertainties arising, e.g., from: modeling choices associated with force-fields; finite-size and time effects; limited ability to sample molecular configurations; and subjective data analyses. Ultimately these issues have slowed the adoption of simulations as scientists wait to gain a better understanding of their capabilities and limitations.

The UQ work comprising this project is therefore an important part of enabling computationally informed materials-discovery paradigms in support of MGI goals. In more detail, scientists and their managers often face expensive decisions regarding allocation of monetary and experimental resources. UQ is thus critical component of modeling since it facilitates decision-making by increasing confidence in simulated predictions. Ultimately, such tools help to reduce waste, increase throughput, and thereby facilitate more rapid time-to-market of new materials.



Example of data analysis for stress-strain data. Determining the global maximum (i.e. yield) of simulated data can be difficult because there is no universal function for a stress-strain curve. By recasting the problem in terms of convex optimization, we can test the hypothesis that the data has a unique maximum and thereby find it.

Technical Progress

The uncertainty quantification (UQ) comprising this project aims to provide the necessary tools to vet simulations and identify possible insertion points in materials discovery workflows. In particular, we have focused on several different issues that modelers face, especially in the aerospace, composites, and energy industries: verification of simulation protocols, best-practices for data analysis and UQ thereof, validation against experimental data, and calibration of model inputs (e.g. force-fields).

Regarding the first three issues, we have developed and published several analyses on verification, data analysis, and uncertainty quantification of glass-transition temperature and yield-strain for thermoset polymers, which are used in the construction of aerospace composites. Notably, recent work has also demonstrated that such analyses can be extended to linear polymers (e.g. polypropylene) and other materials of interest to the oil and energy industries. Moreover, simulation protocols developed in the course of this work are now being validated against experimental data through collaborations with NIST. More recently, we have also addressed general issues associated with best-practices for: (I) sampling time-series and estimating uncertainties in correlated data; and (II) constructing statistical descriptors (e.g. radial distribution functions or RDFs) for condensed matter systems in terms of a spectral Monte Carlo (SMC) analysis (right).

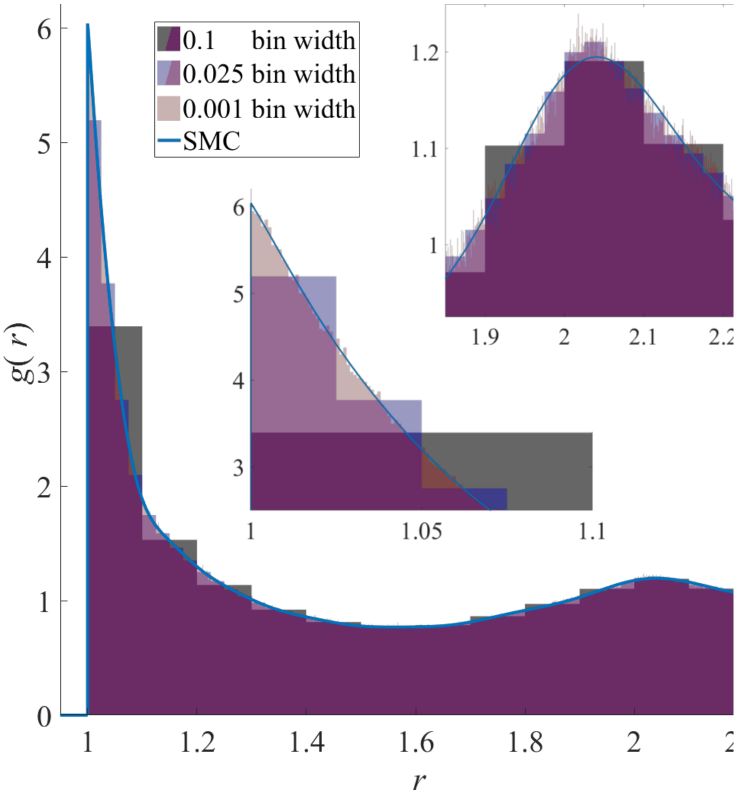


Illustration of Spectral Monte Carlo (SMC) reconstruction of an RDF compared to histograms with various bin-widths.

As regards calibration of model inputs, our work has focused mainly on creation of coarse-grained force-fields, as atomistic potentials are often proprietary and/or unable to be changed in commercial software packages. In this vein, we have addressed fundamental issues associated with the that are valid for a variety of thermodynamic state-points. Work on this project is on-going, but we anticipate several publications and demonstration of the first transferable and calibration-free coarse-grained force-field that also yields *a priori* estimates of its error relative to an underlying atomistic potential.

Future Plans

As discussed above, we anticipate further results in coarse-graining and calibration of associated potentials. Moreover, on-going work with industrial collaborators aims to extend the verification and UQ analyses to different material properties such as thermal conductivity and viscosity predictions. Here we anticipate extensions of the SMC approach for RDFs will be provide useful perspectives for analyzing data in such contexts. Moreover, on-going work with Solvay (formerly Cytec) aims to better understand the time-temperature superposition principle of polymer systems and develop simulation approaches that leverage this principle to characterize time-dependent responses of composites.

Data Management and Open Access

Publications are the primary vehicle for disseminating research results. In this vein, we have published X articles (see references), and a teaching article on best practices for MD is also in preparation. Moreover, the book series *Reviews in Computational Chemistry* commissioned a book chapter on UQ for MD, which is in publication. Notably, this book chapter is accompanied by simulation and analysis scripts that are soon to be available on a publicly available NIST server (https://math.nist.gov/~PPatrone/UQ/).

Advancing Along the Materials Development Continuum

The work done in this project is actively being used by the materials development community in a variety of companies, including: Boeing, Solvay (formerly Cytec), an energy company, and Schrodinger. Notably, the latter has already incorporated some of our UQ analyses (e.g. for glass-transition temperature analyses) into their commercial software package. Moreover, the SMC analysis for RDFs is (to the best of our understanding) actively being developed into the open-source MD package HOOMD-blue by a graduate student at Boise State University.

Publications

P. N Patrone, A. Dienstfrey, A. R. Browning, S. Tucker, S. Christensen, Uncertainty quantification in molecular dynamics studies of the glass transition temperature, Polymer **87**, 246-259 (2016).

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P. N. Patrone, Estimation and uncertainty quantification of yield via strain recovery simulations, in Proceedings of the Composites and Advanced Materials Expo (CAMX), Anaheim CA, September 27 2016.

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Thin Film Biofabrication for Integrated Bio-Electronics

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Keywords: Bioelectronics, Electrochemistry, Polysaccharides, Self-assembly, Synthetic biology.

Project Scope

Biology and electronics are both expert at processing information, yet their molecular and electronic signaling modalities are incompatible. Our broad goal is to enable bio-device communication. To achieve this broad goal, we are: (1) creating thin film electrofabrication technologies to build the bio-device interface; (2) enabling communication across this interface through redox mechanisms that shares features of both molecular and electronic modalities; and (3) engineering synbio constructs for redox-based communication.

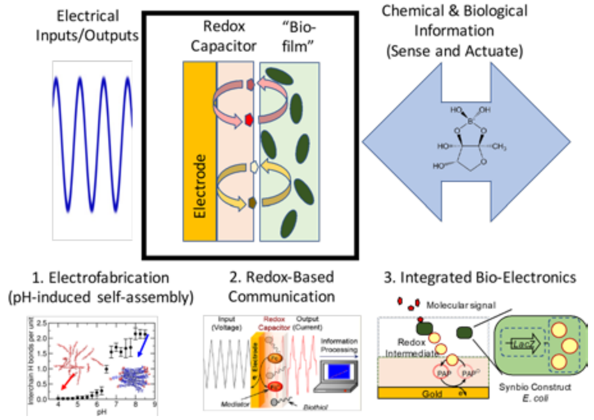

Figure. The goal of bridging bio-device communication is being achieved by: (i) assembling functional hydrogel films at electrode interface; (ii) enabling redox-based communication across this bio-device interface; and (iii) engineering biology to transduce information between molecular and electronic modalities.

Relevance to MGI

Objective 1 (electrofabrication) requires integration of theory and experiment to understand how electrical inputs can induce stimuli-responsive self-assembly to generate hydrogels with complex structures and tailored properties. Modeling both supports and motivates experimentation, while novel experimental methods (e.g., quantitative polarized light microscopy and Brillouin spectroscopy) provide richer insights of self-assembly. Objective 2 (redox-communication) involves the development of new materials (redox-capacitor) and characterization methods (mediated electrochemical probing). These materials and methods are being adapted by others for the development of functional materials for medical and national security applications. Objective 3 (engineering biology to span bio-electronic communication) cross-trains experimentalists in biology, microfabrication and electrochemistry. Our cross-training program spans traditional academic boundaries, extends across national borders, and includes partnerships with national laboratories.

Technical Progress

Objective 1. Molecular modeling: reproduces experimentally-determined pH-dependence (pKa) and subtle features of self-assembly (salt effects); provides insights of self-assembled structures (a crystalline domains has a hydrophobic core and hydrophilic solvent-exposed exterior); indicates that structural differences (core vs exterior) yield pKa-differences for chitosan's amines; and demonstrate that the self-assembly is highly stable (deep free energy wells). Experiment shows that: complex electrical inputs can induce chitosan chains to orient (macromolecular level) and complex microstructures to emerge; a subtle interplay between the imposed electrical current and field control the emergence of structure; and chitosan films can be crosslinked by two independent reversible crosslinking mechanisms (crystalline domains and electrostatically crosslinked domains) and films can be fabricated to have stable gradients in structure and properties, and these can be erased and reprogrammed.

Objective 2. An electrochemical reverse engineering methodology is being developed to discern redox-based molecular information based on their electrical features (this can be contrasted by –omics that discern molecular information from granular details of molecular composition). This method relies on mediated electrochemical probing that is analogous to sonar in that we: probe a local environment for redox-activities (we probe using diffusible mediators vs sonar's use of sound waves); impose complex inputs (we impose voltage inputs that switch the mediators' redox state vs sonar's use of transmitted sound), and we analyze responses using signal processing (we detect mediator currents vs sonar's detection of the reflected sound). We have shown that an electrofabricated redox-capacitor (catechol-chitosan film): amplifies, rectifies and gates output mediator currents to enable characterization of a local redox information; allows multiple mediators to probe specific redox windows; and enables electrical inputs to be tuned to probe for specific information. This methodology has been extended (from our use for bioelectronics) to the characterization: of melanin-based materials for understanding their biological activities and potential technological applications; and the development of biomimetic antimicrobial bandages.

Objective 3. We are using advanced biological methods (molecular biology, protein engineering and synthetic biology) to understand how biology perceives, responds and transmits redox-based molecular information with the ultimate goal of using this knowledge to understand how to detect biological redox activities (to sense) and how to impose redox inputs to guide biological responses (to actuate). We have: created synbio constructs that can recognize a non-redox-active biological signal (a bacterial quorum sensing signaling molecule), and transduce this recognition through a genetic circuit that generates a redox output (a redox-active intermediate molecule) that can be detected by electrochemistry; and integrated this synbio construct into a dual film system (synbio-containing "biofilm" and redox-capacitor film) for the conversion of molecular information into redox outputs.

Future Plans

We envision continuing research along the same 3 general objectives of the current research. First, we plan to continue integrating modeling with experiment to create hydrogel systems with increasingly complex internal structure with the goal of controlling the "flow" of molecular information. Our goal is to mimic biology's use of structures (e.g., vesicles and compartments) to control the organization and delivery of molecular information (needed to overcome the randomizing effects of diffusion). Second, we plan to expand redox-probing methods to integrate increasingly sophisticated information processing strategies (e.g., signal processing and machine learning) to enable the autonomous, self-guided "extraction" of redox-based information. Our goal is to access biologically-relevant redox information through its electrical features (accessible through electrochemistry) rather than focusing on granular molecular details and we envision this will accelerate biomarker discovery. Finally, we plan to continue learning how biology perceives, processes and transmits redox-based information. Our goal is to apply this knowledge to enable probing of the redox-"landscape" of complex biological systems (e.g., couple redox probing with capsular endoscopy to enable a more complete understanding of the microbiome).

Broader Impact (Only required for NSF projects)

We have supported several graduate students throughout this project. These students are embedded within a rich learning environment in laboratories that: are actively engaged in multidisciplinary research; incorporate contributions from researchers at various stages of their careers (ranging from undergraduates to visiting professors); engage partners from national labs (e.g., NIST, FDA, Naval Research Lab and the Army Research Lab); and integrate contributions from foreign collaborators (e.g., from China and Italy). These trans-cultural experiences prepare students for careers in an ever more diverse and dynamic workforce.

Data Management and Open Access

The work is disseminated by presentations and publication in national/international forums.

Advancing Along the Materials Development Continuum

The modeling (Objective 1) is enhancing interpretation of experiment and suggesting experiments: this accelerates our ability to control materials structure. Mediated electrochemical probing (Objective 2) is enabling a more nuanced understanding of redox-active (but non-conducting) materials: this tool is expanding capabilities to build materials for bio-electronics, medicine (antimicrobial wound dressings) and protection. The synthetic biology research (Objective 3) is yielding new insights of how biology perceives and responds to redox-based stimuli (e.g., oxidative stress): this knowledge can be applied to facilitate the use of electronics to sense biological dysfunctions (e.g., pathologies) and enable redox-based cues to actuate biological responses. Overall, this research is stimulating collaborations that span disciplines and borders, and impacting the research in our national laboratories.

Publications (10 most important)

Objective #1. Assembling functional hydrogel films

Modeling pH-responsive Self-assembly

B.H. Morrow, G.F. Payne, J. Shen. pH-Responsive Self-assembly of Polysaccharide through a Rugged Energy Landscape. *Journal of the American Chemical Society*, **137,** 13024-13030 (2015).

C.-C. Tsai, B.H. Morrow, W. Chen, G.F. Payne, J. Shen. Toward Understanding the Environmental Control of Hydrogel Film Properties: How Salt Modulates the Flexibility of Chitosan Chains. *Macromolecules*, **50**: 5946-5952. (2017).

Experimental Demonstration of Controlling Structure and Function

H.M. He, X. D. Cao, H. Dong, T.Ma, G. F. Payne. Reversible Programing of Soft Matter with Reconfigurable Mechanical Properties. *Advanced Functional Materials*. **27**, 1605665. (2017).

K. Yan, Y. Liu, J. Zhang, S.O. Correa, W. Shang, C.-C. Tsai, W.E. Bentley, J. Shen, G. Scarcelli, C.B. Raub, X.-W. Shi, G.F. Payne. Electrical Programming of Soft Matter: Using Temporally Varying Electrical Inputs To Spatially Control Self Assembly. *Biomacromolecules*, **19:** 364-373. (2018).

Objective #2. Enabling redox-based communication

Signal Processing to Access Molecular and Biological Information

Z.C. Liu; Y. Liu, E. Kim, W.E. Bentley, G.F. Payne. Electrochemical Probing through a Redox Capacitor to Acquire Chemical Information of Bio-thiols. *Analytical Chemistry*. **88(14),** 7213-7221 (2016)

Y. Liu, J. Li, T. Tschirhart, J.L. Terrell, E. Kim, C.-Y. Tsao, D.L. Kelly, W.E. Bentley, G.F. Payne. Connecting Biology to Electronics: Molecular Communication via Redox Modality. *Advanced Healthcare Materials,* **6(24):** Article 1700789. (2017).

Reverse Engineering Methodology for Characterizing Redox Properties of Materials

E. Kim, L. Panzella, R. Micillo, W.E. Bentley, A. Napolitano, G.F. Payne. Reverse Engineering Applied to Red Human Hair Pheomelanin Reveals Redox-buffering as a Pro-oxidant Mechanism. *Scientific Reports*, **5** Article 18447. (2015).

E. Kim; M. Kang, T. Tschirhart, M. Malo, E. Dadachova, G. Cao, J.J. Yin, W.E. Bentley, Z. Wang, G.F. Payne. Spectroelectrochemical Reverse Engineering Demonstrates that Melanin's Redox and Radical Scavenging Activities Are Linked. *Biomacromolecules*, **18(12):** 4084-4098 (2017).

Objective #3. Engineering biology to transduce information between molecular and electronic modalities

J.L. Terrell, H.C. Wu, C.-Y. Tsao, N.B. Barber, M.D. Servinsky, G.F. Payne, W.E. Bentley. Nano-guided cell networks as conveyors of molecular communication. *Nature Communications*, **6,** Article number: 8500 (2015).

Y. Liu, C.-Y. Tsao, E. Kim, T. Tschirhart, J.L.Terrell, W.E. Bentley, G.F. Payne. Using a Redox Modality to Connect Synthetic Biology to Electronics: Hydrogel Based Chemo-electro Signal Transduction for Molecular Communication. *Advanced Healthcare Materials,* **6**, 160098 (2017).

SCAN Meta-GGA: An Accurate, Efficient and Physically Sound Density Functional for Wide Classes of Materials

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Keywords: density functionals, exchange-correlation energy, cuprates, self-interaction error

Project Scope and Relevance to MGI: High-throughput first-principles materials searches, including *ab initio* molecular dynamics, which are the key to the success of the MGI, require accurate and computationally efficient methods. Density functionals in wide current use such as the local density approximation and the generalized gradient approximation achieve limited accuracy and fail altogether in some classes of materials (e.g. half-filled cuprates). A major goal of the Center of Computational Design of Functional Layered Materials (CCDM) at Temple University is to design and validate a more accurate semilocal functional that is based on sound underlying physical considerations and applicable to wide classes of materials.

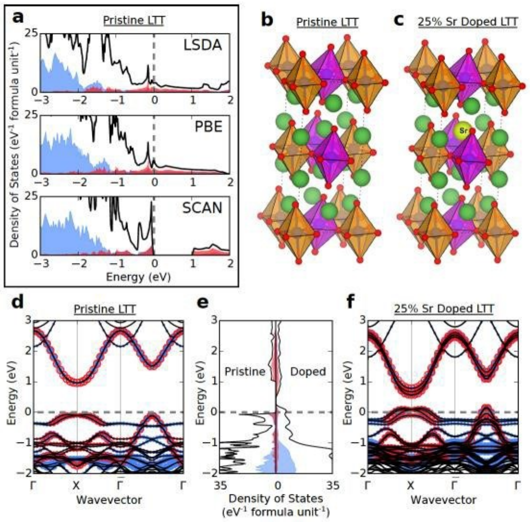

Figure 1: Comparison of the crystal, magnetic and electronic structures of pristine La_2CuO_4 (LCO) and doped $La_{1.75}Sr_{0.25}CuO_4$ (LSCO). (a) Density of states (DOS) illustrating the incorrect metallic prediction of LSDA and PBE(GGA). SCAN-based relaxed crystal structures of (b) pristine and (c) doped low-temperature tetragonal phases of LSCO where Cu, O, La and Sr positions are marked with blue, red, green and yellow spheres, respectively. The related AFM structure is highlighted by coloring the octahedra orange(pink) for spin up(down). (c-e) Effect of 25% Sr doping on the SCAN based electronic structure, for (d) pristine LCO and (f) 25% Sr doped LSCO.

Technical Progress: Density functional theory is widely used to model and understand electronic structures and properties of materials in chemical, physical and engineering sciences. The current standard for functionals is the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) in which the exchange-correlation energy density is constructed from the local electron spin densities and their gradients. The PBE was constructed in 1996 to satisfy 11 exact constraints. In 2014, the key PBE paper was identified as the 16th most-cited scholarly article of all time in all fields. The SCAN (strongly-constrained and appropriately-normed) meta-GGA, which adds the spin-dependent orbital kinetic energy density to the list of ingredients, was constructed in 2015 to satisfy all 17 known exact constraints that a meta-GGA can satisfy. The freedom afforded by the inclusion of the kinetic energy density allows SCAN to fit to additional appropriate norms, non-bonded systems such as atoms in which SCAN can be accurate for the exchange and correlation energies separately, and not just for their sum as in bonded systems. Without being fitted to any particular type of bonding, SCAN accurately predicts diverse kinds of bonding, including even the effects of intermediate-range van der Waals interaction. (Long-range corrections are available.) Extensive work at the CCDM has shown that SCAN provides a significant improvement over PBE for defects in semiconductors, surface properties of metals, ice and liquid water, the subtle structural distortions in ferroelectrics, the formation energies and structural predictions for solids including transition-metal oxides, and the critical pressures for structural phase transitions in semiconductors. Remarkably, as shown in Figure 1, SCAN is the only density functional that correctly predicts not only the pristine La_2CuO_4 (LCO) cuprate to be an antiferromagnetic insulator but also the transition to a metallic state with doping. At a typically much lower computational cost, and without empiricism, SCAN does some things better (and others not as well) as the hybrid functionals that mix fractions of GGA and exact exchange. Notably, the SCAN functional is currently in process for replacing PBE 1996 in the Materials Project.

Future Plan: A limitation of GGAs and meta-GGAs is that they cannot be exact for the exchange energies of all possible one-electron densities. They make a self-interaction error, which Perdew and Zunger (PZ) proposed in 1981 to remove via an orbital-by-orbital subtraction. For size consistency, localized orbitals are needed. The Fermi-Löwdin orbitals (FLOs), a simple unitary transformation of the occupied canonical orbitals, are an appealing choice. SCAN may be particularly well-suited to PZ self-interaction correction (SIC) since it recognizes and satisfies exact constraints for one-electron densities. [Freedom from self-interaction error is also a property of the quasi-particle self-energy operator.] The PZ SIC leads to total energies which, in open systems, produce a nearly linear variation of the total energy between adjacent electron numbers. This piece-wise linearity was later realized to be an exact feature of the density functional theory, and its violation was identified as the reason why GGAs and meta-GGAs overly delocalize electrons. Yang and collaborators have developed a self-consistent localized orbital scaling correction (LOSC) that can impose linearity in fractional electron number, as well as a second exact constraint of energy constancy with fractional spin. Those two constraints are combined in a single "flat-plane condition". Hybrid functionals only achieve a rough linearity with fractional electron number, and at a computational cost higher than LOSC. We will combine the nonlocal corrections, including PZ-FLO-SIC and LOSC, with SCAN to correct the self-interaction error, which we expect will significantly improve the description of strong correlation effects and thus provide the next generation of first-principles modeling of wide classes of materials.

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DMREF-A Combined Experiment and Simulation Approach to the Design of New Bulk Metallic Glasses

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Co-Principal Investigator, Paul M. Voyles, Department of Materials Science and Engineering, University of Wisconsin-Madison, voyles@wisc.edu.

Website: None

Keywords: Bulk Metallic Glass Design, Nucleation Kinetics, Glass Structure, Liquid Dynamics

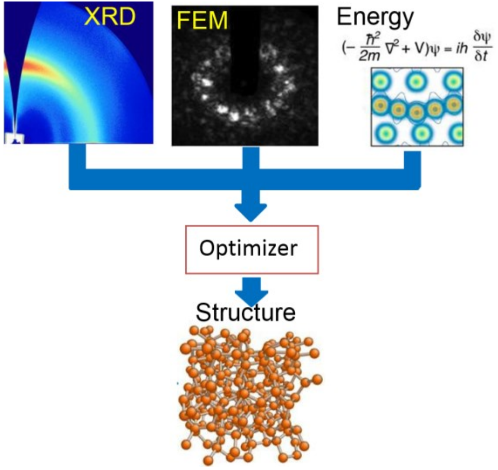
Project Scope

We are using experiments on crystal nucleation and amorphous structure tightly coupled with simulations on atom dynamics and transport to obtain new insight into the contributions from alloying additions to stabilizing aluminum based metallic glasses. This strategy is being used to develop a new methodology for designing new bulkier Al based metallic glasses, including a software package for structure determination combining accurate atomic interactions and measurements on short- and medium-range structure into a genetic algorithm refinement.

Relevance to MGI

Part of the vision of the Materials Genome Initiative is to create new tools for materials design a t the intersection of simulations, data and experiments. We have released two software packages for structure determination of complex materials that occupy that intersection.

Understanding structure is one of the nodes of the processing-structure-properties-performance tetrahedron at the heart of materials engineering. But for structurally complex materials, like glasses and nanostructures, a single data set is often insufficient to determine the structure. Our vision is to develop methods and software that use everything we know about a material–multiple experimental data sets and simulated total energies–to determine the structure. We have used the se tools to study the structure of metallic glasses, but they have much broader application across materials design. The optimizer is based upon a fitness function: Fitness = $\alpha\chi^2$ + E/atom, where χ^2 is the error in the modeled vs. the true data, α is a weighting function, E/atom is the energy per atom, and Fitness is the total fitness of the structure being considered. The tool has been tested on a crystalline nanoparticle and is being extended to amorphous structures.

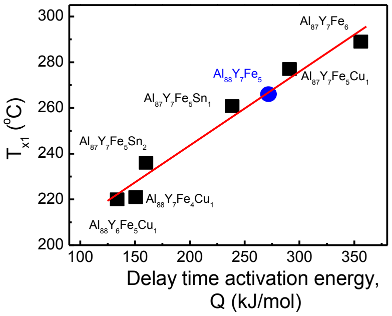


Structure optimization combines all of our knowledge from both experiments and simulations in a computational optimization framework to determine the structure of complex materials.
https://github.com/paul-voyles/femsim-hrmc
https://github.com/uw-cmg/StructOpt modular

Technical Progress

A key challenge to achieving Al base metallic glass in bulk volumes is the suppression of primary crystallization that is initiated by the medium range order in the glass structure. We have found that selected minor levels of solute substitution such as Cu in Al-Y-Fe alloys have a large effect on the primary crystallization onset, Tx to either promote or suppress the reaction (top figure). We have shown that the solute effect changes the delay time during which clusters grow to a critical size for nucleation by modifying the activation energy for cluster growth (. These findings offer critical guidance in selecting solute substitutions to suppress crystallization to enable bulk glass formation. In fact, by following the trend in the figure we have obtained Al-base glasses with new record sizes.

We have also discovered the first Sm-rich glass in the Al-Sm system. In FEM, $Al_{25}Sm_{75}$ has a shifted main peak plus additional peaks vs. quenched $Al_{92}Sm_8$ which indicates a new structure. This new structure is more like the structure of cold-rolled $Al_{92}Sm_8$. DSC measurements reveal significantly different glass stability. The identification of two different amorphous structures in the same system demonstrates that we can "tune" structure with composition, and that the cold-rolled, high-Al content glass may give access to more stable glass structures.



Comparison of Qdelay time and Tx for minor-alloying in AlYFe glasses

Voyles and Morgan have developed an integrated genetic algorithm optimization tool called StructOpt that can determine complex atomic structure by matching forward modeling to experimental data and simultaneously minimizing the energy. We have tested the first version on Au nanoparticles and are now developing the tool for FEM data and amorphous structures.

Szlufarska and Perepezko are applying integrated molecular modeling and experiments to understand Sm effects on Al-Sm glass formation. The modeling results indicate that as the Sm concentration increases the delay time for Al nucleation and decreases the nucleation rate inside the supercooled liquid. I As the Al crystal grows, Sm atoms get enriched in the glassy matrix, which results in the enhancement of Icosahedral ordering and the decrease in atomic diffusivity, thus making the glassy matrix more stable. Voyles and Perepezko have used an existing hybrid reverse Monte-Carlo (HRMC) structural refinement tool to create models of $Al_{92}Sm_8$ glass with realistic MRO consisting of nanoscale regions with approximately FCC structure which will be incorporated in future simulation studies of crystallization kinetics.

Szlufarska is using machine learning (linear fitting, neural networks, Gaussian kernel ridge regression) to interpolate/extrapolate glass forming properties such as crystallization temperature (T_x) as a function of composition. Preliminary results based upon data from over 80 Al-X alloys, (X alloys of Fe, Y, Ni, La, Ti, Co, Cu, Sn, Ga, B, and Ce) reveal a good fit between the predicted and observed T_x. Voyles and collaborators have developed a new descriptor for MG glass structure based on first-neighbor atomic clusters rotated and aligned using a point-pattern matching approach.

Amorphous $Ni_{60}Nb_{40}$ samples were synthesized by cold rolling and by melt spinning. The atomic structures of the two samples have indistinguishable SRO, but quite different MRO. Compared with the as spun sample, less icosahedral-like and more bcc Nb-like Voronoi polyhedra exist in the as rolled $Ni_{60}Nb_{40}$, that cluster to make bcc-like MRO.. The structure of the amorphous alloy influences both the T_x and crystal products: the as-rolled sample has a significantly lower T_x and produces metastable Ni-rich phases on crystallization

Future Plans

We will use coupled experiments and simulations to understand the atomic structure and dynamics underlying glass-formation and crystal nucleation as a function of composition in Al-metallic glasses. The structures will be incorporated into MD simulations of crystallization delay time and nucleation rate, giving atomistic-level insight into the interactions of pre-existing MRO structure with crystallization kinetics. Based on those connections, we will test minor additions to the Al-rich compositions to find additions that mimic the structure and dynamics characteristic of bulk glasses, first in simulations, then in experiment. Further structure determination and simulations will close the design loop,. New software tools for more rapid, larger-scale structure determination using GA and better structural diagnostics will enhance this effort and enable other researchers to directly benefit from our project outputs. This simulation-experiment iterative design loop will be supplemented by materials informatics approaches to suggest the most promising minor additions and base alloys for the iterative design loop.

Broader impact

StructOpt is available under open source licensing as part of the MAterials Simulation Toolkit (MAST), and can be obtained from https://pypi.python.org/pypi/MAST. An undergraduate student from UW-Madison participated by developing FEM data analysis software for release to the broader community as both a software tool and online application on the MaterialHub (materialshub.org). That software has been adopted by researchers at the Universities of Muenster and Glasgow. Undergraduates are involved in FEM software development and machine learning work. Machine learning activities have helped initiated our *Informatics Skunkworks*, a group dedicated to engaging undergraduates in the application of informatics tools in the physical sciences. The Skunkworks now has over 12 undergraduate researchers from two Wisconsin systems schools.

Data Management and Open Access

EM data sets for various MGs and data analysis software have been posted at http://tem.msae.wisc.edu/papers. The FEM data analysis software is available as on online application using nanohub tools on the MaterialHub (materialshub.org). StructOpt is available under open source licensing as part of the MAterials Simulation Toolkit (MAST), and can be obtained from https://pypi.python.org/pypi/MAST.

Accelerating Materials Discovery & Development

Amorphous aluminum alloys have excellent corrosion resistance and superior mechanical properties. When they are treated to induce a primary crystallization reaction, the resulting microstructure of a high density of aluminum nanocrystals in an amorphous matrix exhibits a specific strength (tensile strength/density) that exceeds the level of high strength steel by more than a factor of two. However, to date, amorphous aluminum alloys can only be produced in ribbon form by rapid solidification and this restriction limits the potential applications. Our work based upon the MGI approach has provided a key insight that by controlling the MRO and the delay time for nucleation by appropriate solute additions we can achieve bulk glass volumes. It will then be possible to use conventional commercial processing methods such as die casting to manufacture structural components. Our structure determination and structure analysis software tools and materials informatics database will be useful to other researchers seeking to develop metallic glasses in other alloy systems and for other applications.

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NSF DMREF: Designing Insulating Topological Insulators

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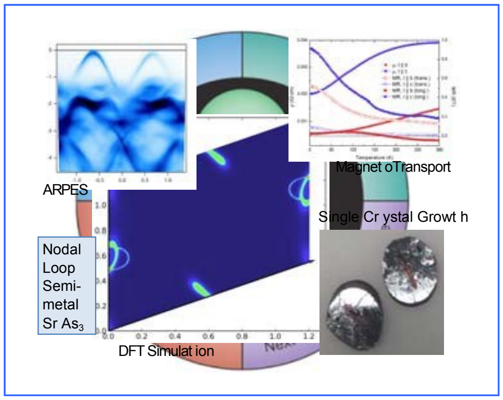
Website: *Materials Archive Portal*: https://materials.soe.ucsc.edu
Keywords: Crystal growth; osmates; pnictide antiperovskites, ARPES, alkaline earth triarsenides.

Project Scope

We look to advance the design and characterization of topological materials, bringing together theory & computation, two synthesis labs, and magnetotransport and ARPES characterization that feed back on theory and synthesis. A key feature of this project is the teaming with other MGI-related facilities, as follows. Results from a computational survey of seventy-five alkaline earth pnictide antiperovskites were entered into the *Materials Project* at LBNL; some were determined to be possible topological insulators. A community resource *Crystal Sample Archive* hosted at UCSC is being extended in functionality. Design of Chern insulating oxide bilayers has led to formal collaboration with the NSF Materials Innovation Platform PARADIM, and magnetotransport characterization at UCSC is leading to further sample growth by PARADIM.

Relevance to MGI

(1) Computation revealing $SrAs_3$ to be a nodal loop semimetal (NLS) spawned single crystal synthesis followed by magnetotransport and ARPES characterization. This project required four of the five PIs. Twinned crystals of triclinic $CaAs_3$, with the lowest symmetry possible for a NLS, were synthesized, as were single crystals of $SrAs_3$. **(2)** Computational design of Chern insulating perovskite bilayers with (111) orientation stimulated formal collaboration with the NSF Materials Innovation Platform PARADIM. Samples have been MBE grown via a formal collaboration with the **(3)** Synthesis and characterization on new iridate, tungstate, molybdate, and osmate compounds has revealed, among other results, the honeycomb lattice compound Li_2OsO_3, the first osmate in this structure that hosts prospective Kitaev spin liquid phases. A four PI collaboration of synthesis (Oregon State), magnetotransport (UCSC), xray spectroscopy (Colorado/ANL) and DFT studies (UCD) point toward Os moments with much itinerant character. No magnetic order was observed down to 0.2K, but a spin-freezing crossover was observed at 0.5K, likely the result of magnetic frustration caused by Li-Os intermixing.



Closing the MGI Loop. Lower left panel: DFT calculation (Davis) of the surface projection of the nodal loop of degeneracies (fine blue line) that exists in the absence of spin-orbit coupling [SOC] and Fermi surface of $SrAs_3$ after SOC is included (fuzzy green regions). Lower right panel: large single crystals grown at NHMFL. Upper right panel: magnetotransport data (Santa Cruz) along two axes of the monoclinic structure of $SrAs_3$. Upper left panel: ARPES data (Colorado) on the a-c surface cleavage plane, illustrating the upper valence band contacting the Fermi level.

Technical Progress: four examples

Topological nodal loop semimetals. After our computational study revealed $SrAs_3$ and $CaAs_3$ to be nodal loop (topological) semimetals with the loop of degeneracies being intersected by the Fermi level, both have been synthesized, in single crystal and twinned crystal samples, respectively. In a collaboration involving four PIs, $SrAs_3$ was characterized by x-ray diffraction, magnetotransport studies, and ARPES spectroscopy, and analyzed through density functional theory studies of the nodal loop, the Fermi surfaces that arise due to spin-orbit coupling, and the topological surface states. High quality cleaved surfaces facilitated ARPES characterization. Extensive twinning triclinic $CaAs_3$ crystals renders characterization inconclusive; however, with inversion only (space group Ᵽ1) it is a unique example in having the lowest symmetry possible for a nodal loop system. $CaAs_3$ thereby becomes the primal "hydrogen atom" of nodal loop semimetals.

Wide gap Chern Mott insulating phases achieved by design.. Chern insulators topological ferromagnets that are important both as a novel electronic phase and for potentially useful boundary charge and spin currents. Honeycomb lattice systems occupied by heavy transition metal ions have been proposed as Chern insulators, but finding concrete examples has been challenging due to an assortment of broken symmetry phases (charge, spin, orbital order) that thwart the topological character. Building on our accumulated theoretical database of the 3*d* series, we tuned spin-orbit and interaction strength together with strain to design two Chern insulator systems with bandgaps up to 130. A trade-off between larger spin-orbit coupling and strong interactions ws adjusted to stabilize the Chern insulating phase. A formal collaboration was formed with the *NSF/MIP PARADIM* (Cornell) to grow layer-by-layer our predicted ruthenate bilayer Chern insulator. Magnetotransport data of the initial samples was obtained at our UCSC site, with the feedback leading to new synthesis routes. Computational studies are being extended to analogous trilayers.

Synthesis, characterization, simulation of new 5d oxide compounds. Persistence resulted in synthesis of the first honeycomb osmate Li_2OsO_3, thus changing the band filling compared to isostructural iridates (below). XPS data provided the mean Os valence and transport revealed an anomalously small moment, without ordering. A spin freezing transition at 0.5K may be related to Li-Os site disorder, with this behavior illuminated with first principles calculations, closing the loop on collaboration by four PIs. Three studies probed Ir's tendency to localize valence electrons through spin orbit coupling and electronic interactions, coupled with a tendency towards itineracy. In one study, Rh was substituted for Ir in Li_2IrO_3, the proposed Kitaev quantum spin liquid platform. Characterization revealed a strong reduction of the effective magnetic moment on the Rh-rich side of the series. Certain alloy regimes display a very large Seebeck coefficient reaching 400 μV/K.

Computational Survey of a New Class of Antiperovskites. The alkaline earth (Ae) pnictide (Pn) antiperovskite class (viz. $BiNCa_3$) was shown not long ago to harbor topological insulator phases under uniaxial strain. The entire class of 5x5x3 compounds PnPn'Ae_3 has been studied by DFT methods, obtaining: equilibrium volumes, relative stabilities, electronic structure including bandgap or band overlap. The most promising examples will be pursued for possible synthesis in bulk (within the team) or as strained thin films (by outside collaborators).

Future Plans

(1) Formal collaboration with *NSF/MIP PARADIM* is being extended by incorporating their summer 2018 students into the project. In addition, the bilayer materials are being generalized to look at (111) trilayers, which form a "dice lattice." **(2)** For Ir- and Os-based pyrochlore and honeycomb materials, growth in sealed environments will be implemented; this has been shown to yield better stoichiometry for rare-earth iridate pyrochlores. With precision control of the stoichiometry, we will explore the effect of charged impurities on magnetotransport. The goal is to achieve low conductivity needed to enable trap spectroscopy with electrical gates. To further explore the effect of SOC on electron localization, we will pursue other osmate compounds, in particular Os-pyrochlores, to unravel the peculiar reduction in magnetism discovered in Li_2OsO_3. **(3)** Our work on tetradymite phases, in particular $Pb_2Bi_2Se_5$ (not yet reported), demonstrated non-congruent phase formation. Since phase stability is related indirectly to defect formation, it is important to determine the region of stability for this structure and thus we will explore neighboring members of the Pb-Bi chalcogenide family of phases, $Pb_2Bi_2Se_5$ being one example. **(4)** Relevant to the DMREF/MGI data initiative, we will expand the number of participants in the *Crystal Sample Archive*. A beta version of this database of extant crystalline samples can be found at https://materials.soe.ucsc.edu/home. **(5)** Since the pnictide antiperovskite class shows promise of TI candidates, axially strained materials will be studied computationally for promising behavior; preliminary results suggest multi-Weyl behavior (discovered earlier computationally at Davis) does occur, in which case samples grown epitaxially on appropriate substrates will be pursued (with *PARADIM* or more informally).

Broader Impacts

(1) One of the PIs (WEP) co-authored the "Back Page" essay "Hard Line on Sanctions Harms Science Diplomacy" in the March 2018 issue of *APS News*, describing being denied by the U.S. Treasury Department to travel to a conference in Tehran. One of the two talks to be given would have been on DMREF-supported research. **(2)** This project has fostered and supported the training of ten students in techniques in the computation-synthesis-characterization feedback loop emphasized by MGI. **(3)** Five invited conference talks, a colloquium, two seminars, and several conference contributed talks have been presented on our collaborative research and results. **(4)** One of the PIs presented a plenary talk at the "1st Principles Modeling" Winter School, January 2017, focused on MGI methodology and held at the National High Magnetic Field Laboratory. Around 25 young scientists heard lectures and received hands-on training in the use of (largely density functional based) simulation methods.

Data Management and Open Access

This DITI project was specifically not founded on high throughput – large dataset computational explorations, an approach covered by many other DMREF projects. The project is founded rather on close synthesis-characterization-theory coupling that provides rapid focus on promising materials classes. A foundation is the *Materials Advancement Portal* (A. Ramirez, UCSC) database of samples. Computationally, high throughput computations were not our computational focus since that method is broadly applied in many other projects. However, a computational survey of 75 alkaline earth–pnictide compounds (a few existing, most proposed) was carried out, published, and posted on the Materials Project (MP) hosted at LBNL. The calculations, if more information is needed than is available on the MP site, can be readily reproduced from information in our publications and their Supplemental Materials.

Advancing Along the Materials Development Continuum

The MGI emphasis of computation, synthesis, characterization, and when applicable, demonstration of principle, is thoroughly internalized within our project. On several projects computation and synthesis has proceeded in parallel, with mutual feedback. A broad-based study of the novel honeycomb osmate Li2OsO3, coauthored by four of the PIs, has been submitted, and the SrAs3 work intimately involves four PIs as well. The community is benefiting from the *Materials Advancement Portal* hosted by one of the PIs. The project personnel are committed to speeding the design, discovery, and demonstration of potential applications, of novel topological materials.

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Data Discovery with The Materials Resource Registry.

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Website: https://materials.registry.nist.gov/
Keywords: data science, data discovery, data curation, resource registry

Project Scope

This project has brought together materials scientists, information technology experts, and software developers to build and populate the Materials Resource Registry (MRR) aimed at connecting materials science researchers with published data relevant to their work. The registry allows scientists to find resources such as data repositories, databases, data portals, services, tools, and software through targeted searches and faceted browsing. It also allows researchers who share their data assets to create metadata descriptions to add to the registry so that others may discover them. The registry deployed at NIST is actually part of a federation with a partner registry deployed at the Materials Data Facility. The two registries share their records with each other so that both may provide a comprehensive view of all available data. Other institutions may join the federation by deploy our open registry software.

FIZ/NIST Inorganic Crystal Structure Database
National Institute of Standards and Technology (NIST) and Fachinformationszentrum Karlsruhe (FIZ)
https://www.nist.gov/srd/nist-standard-reference-database-84
"The Inorganic Crystal Structure Database (ICSD) is produced cooperatively by the Fachinformationszentrum Karlsruhe (FIZ) and the National Institute of Standards and Technology (NIST). The ICSD is a comprehensive collection of crystal structure data of inorganic compounds containing more than 120,000 entries and covering the literature from 1913 to... show more

Structural Materials Data Demonstration Project Database
ASM International
http://mio.asminternational.org/smddp/
Subject keyword(s): multi-scale microstructure, phase, diffusion, and mechanical property data for Al 6061 and Al-Mg-Si alloys
The Structural Materials Data Demonstration Project Database is a public data resource established, along with a companion repository, to facilitate the development and demonstration of best practices and protocols for capturing and sharing multi-scale experimental and computational data for structural materials in support of the Materials Genome I... show more

Experimental Molar Volume/Thermal Expansion Data DSpace Repository
National Institute of Standards and Technology (NIST)
http://hdl.handle.net/11256/46
Subject keyword(s): molar volume, thermal expansion
This collection contains experimental data on the molar volume and thermal expansion of materials (primarily metallic systems)

Virtual Vault for Pseudopotentials
National Nanotechnology Infrastructure Network
http://www.nnin.org/research-support/computation/nnin-computation-nanotechnology-resources/virtual-vaults
Subject keyword(s): pseudopotentials, electronic structure
"This website is an NNIN resource to provide information on pseudopotential relevant for electronic structure calculations of molecules, materials, and nanostructures."

EAM potentials (Howard Sheng)

Figure 1. Search results page from MRR

Relevance to MGI

One of the key challenges MGI is tackling is "making digital data accessible" [1], and so the initiative is driving growth in amount and diversity of materials science data available over the web. With this increasing digital wealth comes a challenge for the scientist: how does one learn that particular data exists? The MRR addresses this problem directly by providing a tool that direct scientists to the data they need. It also provides a means for data producers to advertise the availability of their data to the world.

Technical Progress

We have successfully deployed two instances of the registry which automatically share their records with each other. The instance operated by the Materials Data Facility specializes in managing records from the Facility and its partners from the Center for Hierarchical Materials Design (CHiMaD). The NIST instance specialized in data resources from NIST; however, it also allows data providers from the broader research community to register their resources. Today, the registries together describe 340 resources including databases, repositories, portals and other websites, and software.

A key feature of the latest version is the integration of the Materials Science Vocabulary developed as part of this project (with inputs gathered through the Research Data Alliance's International Materials Resource Registries Working Group). This controlled vocabulary is used to describe the scientific subject, attributes, and context of a data resources, capturing such information as the type of data it is, the type of material studied, structural features, and experimental techniques used. With this vocabulary plugged into the registry, publishers can quickly "click off" the attributes that are applicable to their resource. This allows users looking for data to easily drill down into the search results based on the attributes through faceted browsing.

Future Plans

First and foremost, we plan to further expand the contents of the registry and, consequently, its value as a resource to researchers. Through the community we built in collaboration with the RDA, we plan to engage other international projects to encourage and support their deploying their own registry to participate in the federation.

Development of the software continues as well. As new partners become interested in the registry, there is an opportunity to leverage community contributions to the code. Thus, we plan to put into place more open source development practices. We want to expand the registry's support for XML schemas and, in particular, address the challenges of schema evolution. We also want to incorporate additional "FAIR" (Findable-Identifiable-Interoperable-Reusable) practices, particularly with improved support of persistent identifiers and data linking.

Data Management and Open Access

The registry encourages open access by creating the necessary demand for re-usable data. By enabling scientists to find useful data that to generate useful results, we expect to see greater benefits flowing to the original provider as well through data citations.

Advancing Along the Materials Development Continuum

By building on previous results through digital data analysis and re-use, a materials scientist or engineer gains a leg up in the development process. This is particularly important for industry which must turn research results into practical products; having access to the digital data behind those results can help bridge the gap between research and commercialization.

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DMREF: Collaborative Research: Semiconductor Heterostructure Platform for Active Nonlocal Plasmonic and Hyperbolic Materials

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Evgenii E. Narimanov: Department of Electrical and Computer Engineering, Purdue University, evgenii@purdue.edu
Claire Gmachl: Electrical Engineering Department, Princeton University, cgmachl@princeton.edu
Website: none
Keywords: Metamaterials, designer metals, optical nonlocality, quantum plasmonics.

Project Scope

The goals of the project is to understand the quantum-to-classical transition in optical response of highly doped semiconductor- ("designer metals[1]-") based metamaterials and use this understanding to develop a new material platform for photonic and optoelectronic applications. The project involves integrated analytical, numerical, and experimental tasks, advancing solid state theory, electromagnetism, thermal transport, and materials science. The ultimate goal of the project is the development of new theory-driven electro-optical material platform with designer passive (refraction/transmission) and active (light generation) components.

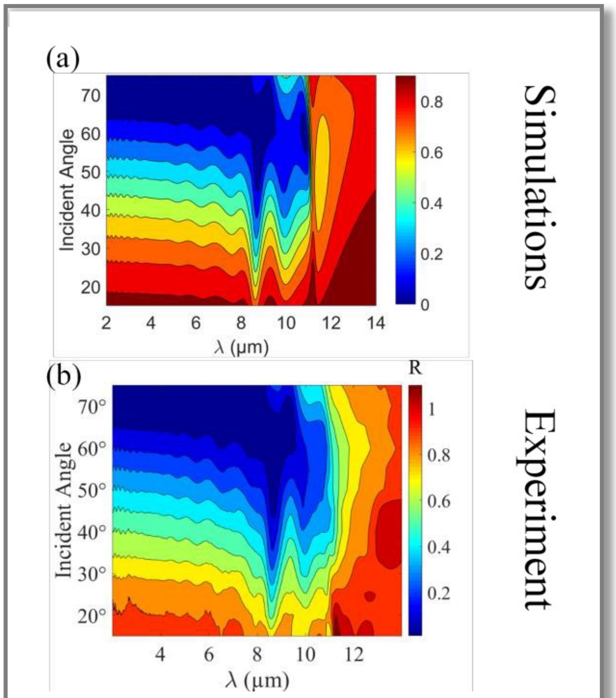

Figure. Please Reflection (characterized by the ratio of TM-polarized to TE-polarized signal) from the designer-metal-based metamaterial; comparison between theoretical (a) and experimental (b) data

Relevance to MGI

The project aims to advance the MGI goals of doubling the speed of materials discovery and creating the world-class materials workforce by bringing together an interdisciplinary teams with computational (V. Podolskiy), analytical (E. Narimanov) and experimental (D. Wasserman & C. Gmachl) expertise. In the research process, the results of growth and characterization efforts developed by the experimental teams feed directly into analytical and numerical results developed by the theory teams. Respectively, the modelling and analytical efforts will feed into experiment by driving the best experimental configurations to be analyzed given the plurality of data. Close interaction between different members of interdisciplinary team provides unique opportunities for the students participating in the project.

Technical Progress

In the first year of the project our experimental teams have grown a set of samples with identical overall thickness and overall doping but with different number of layers and thickness of individual layers. Analysis of spectroscopy data clearly points to the deviations from Drude theory (thought to be a gold-standard for designer metals[1]). Theory group has developed a nonlocal correction to Drude model that should describe the transition regime. Numerical team has implemented the new theory and is in the process of validating it. From the preliminary data it appears that the new theoretical formalism will be able to describe electromagnetic response of ~30nm-thick (and thicker) designer metal layers. The properties of thinner layers appear to be significantly affected by the level quantization and will need development of a different theory.

In a separate project, the team has developed robust computational technique for calculating diffraction of light through structured interfaces. In the context of this project, the computational technique was used to understand the fundamental limitations of light extraction from high-index media, an important problem that our team will face in future.

Future Plans

In the upcoming year we are planning to finalize theoretical understanding of the electromagnetic response of thin designer metal layers, using computational paradigm that is currently being developed by Podolskiy and Narimanov groups. Simultaneously, we are planning to develop computational modelling of light emission in structured layered materials containing designer metal layers and verify this modelling tool with experiments. Once completed, the tool will be used to understand the electro-optical interactions in active nonlocal designer metal systems.

Broader impact (Only required for NSF projects)

Over the first year of the project, the team has already setup productive research atmosphere between the members of the team. After several telecom meetings we have scheduled the first inter-team visit of a graduate student.

Several team members already actively employ undergraduates and high school students in MGI research and the remaining team members have advertised summer research positions and capstone projects to the undergraduate communities at respective universities.

Finally, a software developed by the computational team is available for free download for non-for-profit use.

Data Management and Open Access

The software for analysis of light diffraction by complex periodic structures is available on V. Podolskiy's www [2]. As publications get accepted, supporting codes are published on the same www. Post-processed experimental data is included in publications and is available in non-processed form upon request.

Advancing Along the Materials Development Continuum

V. Podolskiy along with his graduate student undertook the I-Corps project that resulted in development of the diffraction-calculation software, mentioned above. Over the course I-Corps we have identified the target customer base for the software, consisting of researchers at the Universities, National Labs, and major defense contractors. The software is copyrighted and is currently available for download for free for non-for-profit use.

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DMREF: Accelerating the Design and Synthesis of Multicomponent, Multiphase Metallic Single Crystals

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Keywords: Alloy design, Co-Al-W, oxidation, single crystals, multicomponent, crystal growth

Project Scope

Novel complementary computational and experimental tools developed are being integrated with existing tools to address fundamental barriers that challenge the design and synthesis of a new class of $L1_2$-strengthened cobalt-base alloys. New approaches being developed include (i) a self-consistent thermodynamic framework for alloy design that rigorously couples first principles calculations, multicomponent thermodynamics, internal stresses and diffusion; (ii) new parallelized, sharp interface computational methods that can predict the behavior of multicomponent alloys in a single crystal growth environment; (iii) new approaches for rapid characterization of the material structure and properties (iv) new microstructure-level computational approaches for predicting mechanical properties.

Relevance to MGI

The program is developing new capabilities that substantially enhance the iterative feedback process between design, characterization and synthesis, rapidly expanding the knowledge base for this new class of single crystal materials that could impact a broad array of advanced high temperature propulsion systems. The tools have enabled a non-linear exploration of compositional space to identify compositions with a favorable suite of properties that can be synthesized as single crystals.

Technical Progress

During the past year a combinatorial approach for exploration of compositional domains with high oxidation resistance has been employed to identify alloys that form protective ⟨-Al_2O_3. In conjunction with this we have developed a rapid screening method for detection of ⟨-Al_2O_3 based on Photo Stimulated Luminescence Spectroscopy (PSLS). Fig. 1 shows three libraries of alloys and the domains over which favorable oxidation resistance is present. Alloys with highly favorable combinations of mechanical properties *and* oxidation resistance have been identified.

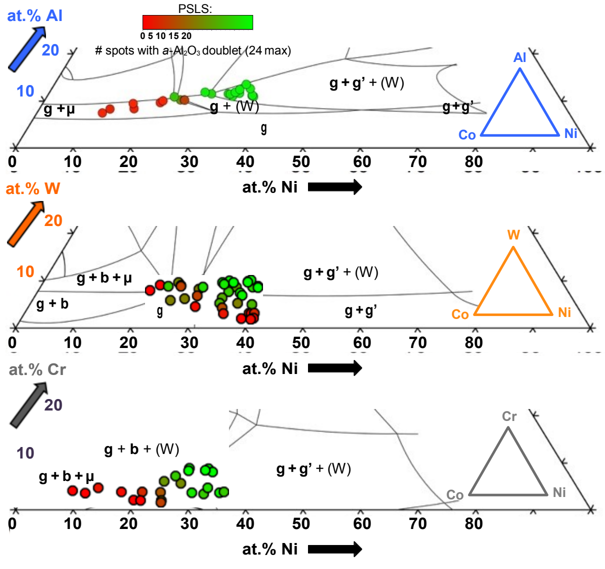

Figure 1: Oxidation PSLS results from the three combinatorial libraries plotted on predicted ternary phase diagrams. Each diagram is an isoconcentrate section, though constant 8.7W – 2.2Cr – 3.5Ta at%, 11.0Al – 2.2Cr – 3.5Ta at%, and 10.0Al – 8.5W – 3.5Ta at% respectively, all at 1100°C. More strongly alumina-forming regions are shown in green, located at greater Al, Cr, W, and Ni contents.

A cluster expansion model (CASM) has been developed for the Ni-Al-W ternary system for fcc, bcc, and hcp parent lattices. We have constructed ternary cluster expansions for parent fcc, bcc, and hcp crystal structures in the Co-Al-W system, allowing the Co-Ni compositional space to be explored. A first-principles based assessment of superlattice instrinsic stacking fault energies at finite temperature has been conducted. This is a critical property for tuning high temperature strength that is extremely difficult measure. Alloys predicted to have the highest fault energies have been design and grown as single crystals for property measurements.

We have solved the problem of applying the Robin boundary condition for multicomponent solidification simulations and the dendritic structure of ternary Co-Al-W alloys has been modeled. Finally, a new approach to modeling deformation of the two-phase microstructure that accounts for strong strain localization / precipitate shearing has been developed.

Future Plans

We will continue to develop computational and experimental approaches that enable exploration of higher dimensions of multicomponent compositional space. In the upcoming year we specifically plan for:

- Extension of the thermodynamic models to explore Co-Ni quaternary and quinary superalloy compositions
- Incorporation of the effect of dilute alloying additions and vacancies into existing thermodynamic models
- Kinetic Monte Carlo simulations to obtain diffusion information on existing cluster expansions
- Use thermodynamic cluster expansion results to model kinetic behavior in Co-base superalloys
- Growth of single crystals of new alloys that possesses both oxidation and creep resistance and perform validation experiments with single crystal samples
- Develop dislocation-informed mechanical models
- Conduct cyclic fatigue experiments on promising compositions
- Validation of the algorithms for simulating solidification of ternary alloys

Broader impacts

The program is offering an intellectually rich, diverse and stimulating environment where students are (i) working on scientifically challenging problems with clear and substantial potential for technological impact, (ii) are being mentored by an interdisciplinary team of academic and industrial experts in the field, and (iii) have had opportunities for research internships in industry and at academic institutions in Europe.

- All students benefit from regular group meetings of the DMREF faculty and student group, all located at UCSB.
- All students have presented their research to faculty and UCSB graduate students within the weekly Structural Materials Seminar.
- Ph.D. student Rob Rhein has continued a collaboration with Professor Yunzhi Wang at the Ohio State University for integrating UCSB model results with OSU capabilities on phase field-based dislocation modeling.
- Ph.D. students Colin Stewart and Rob Rhein presented their research at the 13th International Conference on Superalloys in September of 2016 and at the TMS Annual meeting in San Diego, CA in February 2017.
- Ph.D. student Mike Titus started on the faculty of Purdue University as an Assistant Professor in 2017.
- Ph.D. student Colin Stewart completed a summer internship with Arconic (Alcoa) and was invited to deliver a lecture at the Air Force Materials Laboratory in August of 2017.
- Postdoctoral researcher Wesley Jackson has accepted a position at Pratt and Whitney in 2017.
- Professor Gunther Eggeler of the Ruhr University in Bochum has planned an extended research visit to UCSB in Academic year 2016 and 2017.

Data Management and Open Access

The first principles and statistical mechanics CASM code developed by Van der Ven is available at GitHub; https://github.com/prisms-center/CASMcode. Thermodynamic data generated in the program is now commercially available in the Pandat / Computherm Co alloy database. The code developed by Begley for design of coatings systems for these materials is at https://engineering.ucsb.edu/~begley/LayerSlayer.html. All other experimental data has been or will be published in archival journals.

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Tackling Disorder and Ensemble Broadening in Materials Made of Semiconductor Nanostructures.

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Keywords: semiconductor nanostructures, quantum wells, anisotropic nanomaterials, colloidal, disorder.

Project Scope

Elimination of disorder and polydispersity is arguably one of the most important challenges in nanoscience. We have launched a joint experimental and computational study toward synthesis, characterization, and modeling of the materials comprising II-VI semiconductors with negligibly small inhomogeneous broadening. We examine routes to and effects of eliminating energetic disorder, and by focusing on inhomogeneity of characteristic hopping transport, Förster resonance energy transfer (FRET), and Auger processes will uncover new fundamental properties and fully unlock the technological potential of bottom-up engineered functional materials. Our preliminary results show that elimination of inhomogeneous broadening leads to transformative improvements in material properties.

Relevance to MGI

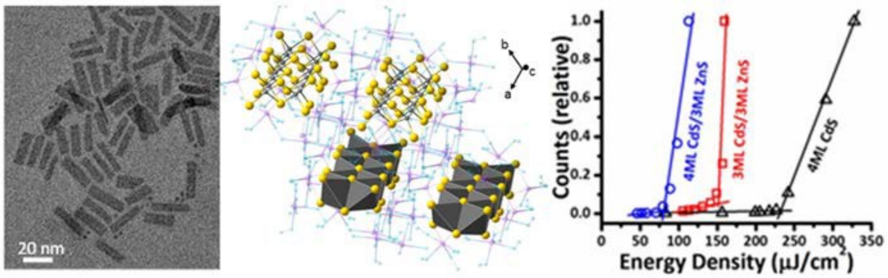

Figure. Nanomaterial types presenting negligible ensemble broadening constitute the focus of this research effort. Materials include (left) colloidal nanoplatelet quantum well materials of perfectly controlled thickness and (center) unprecedented inorganic molecular nanowires with controlled morphology. Material properties such as electronic structure, excited state properties, as well as (right) optical amplification, here for CdS nanoplatelets are focus areas of measurement and modeling.

In exploration of a fundamentally interesting materials class, this project closely integrates experiment, computation, and theory through close interaction of principle investigators on the team. Via monthly conferences and videoconferences as well as occasional in-person meetings at conferences, recent progress and concepts in each lab are shared and attacked collaboratively. Efforts in the team focus principally on 2-dimensional colloidal quantum wells of CdSe that are respectively synthesized, probed, and modeled by the researchers and involved students. Students within the two experimental groups on occasion work in each other's labs in the form of hands-on participation. Characterization data is passed to those performing theory as inputs for modeling physical behavior. Such interactions enhance the project outcomes in that rapidly evolving thinking in this material class is propelled by latest insights and new findings. Newly synthesized materials enter into advanced characterizations and modeling more rapidly and seamlessly than would occur outside the collective effort. The result is more thorough, insightful advances that result on reduced timescales, which is then disseminated to help develop the fundamental knowledge base in the broader academic community.

Technical Progress

During the first year of the project, we carried out extensive research in synthesis, characterization, and theory of CdSe nanostructures including nanoplatelets as well as unprecedented molecular nanowires. In parallel with synthesis of novel nanostructures with particularly small inhomogeneous broadening as well as core-shell variants of these materials, we are examining the electronic structure of both individual particles and ensembles of these systems. Further, optical gain and lasing phenomena are being examined so as to determine the fundamental benefits of negligible ensemble broadening, but also the origin of the unusual exciton lifetime behavior in these materials, which becomes shorter lived with reduced temperature, unlike spherical particles of the same composition.

Understanding electronic structure of CdSe nanoplatelets: Scanning tunneling spectroscopy (STS) was performed, compared with optical absorption spectra, and investigated with theoretical models of this material. Measured excitonic gaps are smaller than both carrier tunneling gaps and theoretical calculations, as expected, due to electron-hole binding energy of ~180meV. The measured tunneling gaps are consistently larger than the corresponding calculated ones. The origin of this is still not clear. Possible explanations: (a) the effect of voltage division in the experiments. b) The difference in binding energies. (c) Charging effect. The separation of light hole to heavy hole optical transitions as manifested in the absorption spectra (second to first transition in the optical measurements), are about 80-100 meV smaller than those extracted from the STS data and calculations. This large difference cannot be due to the effect of voltage division alone, which (according to the 3-5% estimate above) can account for 10 meV at most, nor can it be due to the different binding energies of the light/split-off and heavy holes (we have calculated the difference between the binding energies of the light and heavy holes and found these to be smaller than 20 meV). More recently, we estimated the charging energies of the heave hole and electron and found significant differences (platelets show significant dielectric confinement). The light/split-off hole charging energy is expected to be between that of the heave hole and that of the electron, which would explain the 80-100 meV difference described above.

Novel synthesis of inorganic, molecular wires: We investigated the structure and properties of soluble chalcogenidocadmates, a molecular form of cadmium chalcogenides with unprecedented one-dimensional bonding motifs (as noted in the above figure). The single crystal x-ray structure reveals that sodium selenocadmate consists of infinite one-dimensional wires of $(Cd_2Se_3)_n^{2n-}$ charge balanced by Na^+ and stabilized by coordinating solvent molecules. Exchanging the sodium cation with tetraethylammonium or didodecyldimethylammonium expands the versatility of selenocadmate by improving its solubility in a variety of polar and nonpolar solvents without changing the anion structure and properties. The introduction of a micelle-forming cationic surfactant allows for the templating of selenocadmate, or the analogous telluride species, to create ordered organic-inorganic hybrid CdSe or CdTe mesostructures. Finally, the interaction of selenocadmate "wires" with Cd^{2+} ions creates an unprecedented gel-like form of stoichiometric CdSe. We also demonstrate that these low-dimensional CdSe species show characteristic semiconductor behavior, and can be used in photodetectors and field-effect transistors.

Gain and Lasing in CdS Nanoplatelet Films: We demonstrated amplified spontaneous emission (ASE) and lasing in the challenging violet-to-blue (430-490 nm) spectral region using CdS and newly-synthesized core/shell CdS/ZnS nanoplatelets via colloidal atomic layer deposition. This material exhibits distinct, excitonic absorption spectra, yet fairly weak band-edge photoluminescence. Via comparisons of transient absorption and ultrafast photoluminescence, we clearly relate that the weak band-edge emission arises from fast, efficient hole trapping for 4, 3/3 and 4/3 CdS and CdS/ZnS monolayer thickness ensembles. Owing to negligible dispersion in thickness, large measured absorption cross-sections of 2.8×10^{-14} cm^{-2}, and rather slow (150 to 300 ps) biexciton Auger lifetime that we characterize in Figures 6b an 6c using fluence-dependent transient absorption measurementsIn spite of this, low ASE thresholds observed originate from. Under higher-fluence excitation, ASE kinetically outcompetes trapping. Using nanoplatelets as the gain medium, lasing is observed in a linear optical cavity with high stability.

Future Plans

Future efforts will focus on routes to maintaining negligible inhomogeneity for nanoplatelet structures upon adgrowth of shell materials that permit further manipulation of electronic structure. Relatedly, we will investigate whether characterization methods that seem to relate build-up of heterogeneous response actually relate to other intrinsic features of the materials. Characterizations of electronic structure in both static and transient characterizations, such as STS and transient absorption, will be pursued as functions of temperature and material features. Carrier transport will be investigated vs temperature in order to evaluate effects of negligible site energy variations.

Broader impact

Funds at University of Chicago have been used to provide partial support for two graduate students advised by Prof. Dmitri Talapin. Mr. Igor Fedin, 5th year graduate student worked on synthesis and characterization of nanoplatelet structures, and has since obtained his PhD. He also trained 2nd year student Ms. Maggie Hudson who worked on synthesis of novel semiconducting molecular wires and 1st year graduate student Mr. Wooje Cho who will continued Igor's work on the platelet nanostructures.

At Northwestern, funds support 50% each of two 2nd year graduate students under advising of Prof. Richard Schaller. Ms. Samantha Harvey, and Mr. Nic Watkins, each hired last year. Each student is involved in transient spectroscopic studies of 2D semiconductor nanoplatelet materials.

At UC Berkeley, the project supports one post-doctoral scholar, Dr. Weifeng Hu, hired last year. He is mainly concerned with the development of more accurate techniques to study the electronic properties of confined structures. In addition, a third year student is involved in the development of an approach to calculate Auger processes in correlated nanoplatelets (student partially supported by external funds).

Understanding derived from this collaborative effort rapidly enters the classroom, where each of the principle investigators teaches both undergraduate and graduate courses that relate nanomaterials understanding. Further, the broader community and public are educated about these materials efforts and derived understanding at local, national and international venues where the principle investigators present the supported work.

Data Management and Open Access

Significant data is provided in the publications listed below and the corresponding supplementary information. Additional supporting data is available upon request. Computer codes to perform electronic structure calculations are also available upon request. These include Auger calculations for correlated biexcitonic states as well as stochastic calculations of the density of states and the band edge electronic and excitonic properties. We wish to point out that the computational approach is tailored for CdSe nanoplatelets, since this is an excellent test bed to understand and realize novel conceptual issues. Generalization of the approach to other materials is an ongoing project in the Rabani group.

Advancing Along the Materials Development Continuum

The goal of the project is to develop new semiconductor nanostructures reducing disorder and ensemble broadening for diverse optical gain applications. This is an ambitious goal that requires deep understanding of the chemistry of nanoplatelets and nanowires, as well as developing physical insights using advanced optical and theoretical/computational tools. Our team combines such expertise in the spirit of MGI with emphasis on the development of controlled nanostructured materials. This requires close collaboration between the teams, where experimental results are used to guide and also validate the theory and vice versa. This combination offers a platform to ask and answer fundamental question as well as practical developments, not foreseen by the individual components.

Publications

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DMREF: Collaborative Research: Accelerated Development of Damage Tolerant and Oxidation Resistant Alumina-Forming MAX Phases

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Website: none

Keywords: MAX phase solid solutions, Structural materials, Materials for extreme environments, Bayesian Framework, Cohesive zone model.

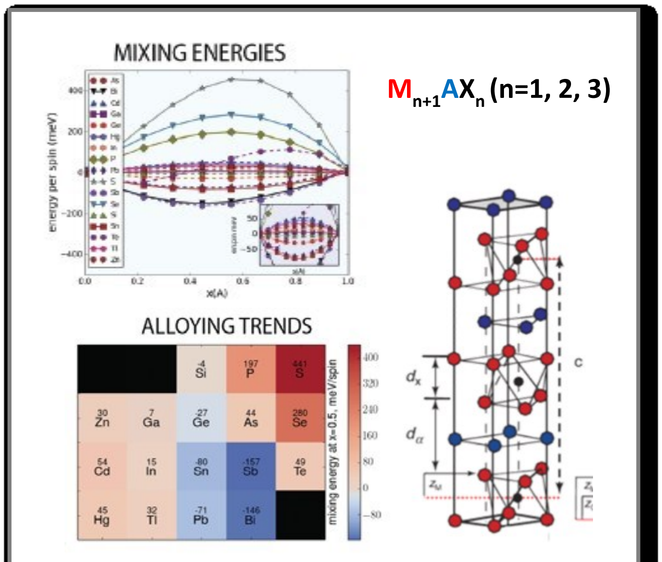

Figure 1. (left) Mixing energies and alloying trends in $Ti_2(Al_{1-x},A_x)C$ determined using cluster expansion approach, for A=Si, P, S, Zn, Cd, Ga, etc. [3] (right) unit cell of M_2AlC phase. [2]

Project Scope

This project focuses on accelerated development and design of alumina-forming MAX solid solution alloys with outstanding mechanical properties and oxidation resistance for applications up to 1500°C through the implementation of a materials discovery/development methodology that seamlessly integrates (i) prior knowledge, (ii) computational simulations at atomistic and continuum scales, and (iii) experimental synthesis and characterization. The underlying hypothesis of the proposed work is that the oxidation resistance, high temperature mechanical properties and damage tolerance of MAX, that are at par compared to existing high temperature structural materials, can be further improved by solid solution substitution on M and/or A site [1,2].

Relevance to MGI

Full experimental exploration of the MAX solid solution design space is practically an impossible task because of the large number (over 6 million) of possible compositions. The realistic way to approach this challenge is the optimal design of (computational and physical) experiments that balances the need to explore the materials design space with the need to exploit it in order to identify and synthesize promising MAX phase compositions with optimal properties for high temperature applications, that includes good oxidation and creep resistance and high temperature strength. This framework offers the two-fold benefit of increasing the knowledge about the materials space while maximizing the value of the information of each experiment/computation leading to accelerated progress in a manner consistent with the goals of the Materials Genome Initiative (MGI).

Technical Progress

Since the beginning of the project in August 2017, we have developed preliminary computational cluster expansion framework to probe stability of different MAX phase solid solution, with substitution on M and A site

[3-5]. We are currently synthesizing some of the initially identified stable solid solutions that contain Al on the A such as $Ti_2(Al_{1-x},A_x)C$, where A=Sn, Ge, Bi, Sb, Figure 1. Characterization of oxidation kinetics of different MAX solid solutions is also ongoing, as well as characterization of the effect of solid solution substitution on mechanical properties. DFT approach has been developed to evaluate cleavage and shear stresses along M-A that are crucial for understanding mechanical response of MAX phases [6]. The initial cohesive zone based model of the layered material is being developed to understand competition of shear, cleavage and kinking in single crystal MAX phases under constrained conditions. The DFT calculations and experimental characterization that will provided necessary input to the continuum-based model and verification experiments are also under development at this moment.

Future Plans

Building on the preliminary results, the PIs will (1) develop physics-based predictors for the formation of protective alumina layers on the MAX phases; (2) develop micromechanics models for the MAX phases and identify the compositional and structural parameters that control their intrinsic mechanical properties, including those at elevated temperatures; (3) design of Bayesian calibration protocols for parameter identification; (4) implement and deploy Efficient Global Optimization protocols for the efficient discovery of MAX solid solutions with optimal mechanical properties, including tensile creep, under high temperature oxidizing conditions and; (5) validate the proposed framework through material synthesis, characterization and mechanical testing. This will guide fundamental knowledge and protocols to design optimal compositions and microstructures of the MAX phases for high temperature application. The overall framework relies on striking the perfect balance between the exploration and the exploitation of the MAX phase design space, and as such, the PIs posit that it offers a promising strategy for the optimal discovery and development of materials that can be generalized to other problems, particularly when the size of the materials design space precludes more traditional approaches.

Broader impact (Only required for NSF projects)

The broader education impact centers on (i) specialized multidisciplinary training for graduate students on integrating materials informatics, atomistic and continuum modeling and simulations, and experiments in materials design; (ii) enriching students' educational experience thorough collaborative research and exchange of students between collaborating institutions; (iii) engagement of undergraduate and graduate students from underrepresented groups through Pathways to the Doctorate, and an NSF-funded NRT and REU programs at Texas A&M University; (iv) development of demonstrations and design problems for "Materials informatics" and "Materials Design Studio" courses at Texas A&M University; and (v) organization of the international Summer School on Computational Materials Science across Scales (https://cms3.tamu.edu/) at Texas A&M University for graduate students, postdocs and industrial researchers from all around the world.

Data Management and Open Access

Currently obtained experimental data in the forms of graphs (XRD, TEM) and tables (processing condition, lattice parameters, etc.) are documented both in hard copies of original laboratory notebooks and in computer data files. The computational data are stored in dictionary format (json files) for later data curation purpose. Access to these data is currently available upon request. The PIs are working on making all data publicly accessible via Citrination, the web-based data platform for materials, chemical, and device information offered by Citrine Informatics. Also, Materials Model and Data Management System (MMDMS) is being currently constructed at Texas A&M University to host these data, making them more available and accessible to community.

Advancing Along the Materials Development Continuum

In the initial stages of the project, the PIs and collaborators have already developed a framework to efficiently explore composition space of the MAX phase solid solutions. The framework has been used to identify novel MAX phase solid solutions. Discovery of these promising MAX phase alloys through costly Edisonian-type approaches would have taken considerably longer time.

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Publications

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Materials Innovation Platform: 2D Crystal Consortium (2DCC)

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Website: https://2dcc.psu.edu
Keywords: 2D chalcogenides; thin films; bulk crystal growth; reactive force fields; first-principles computation

Project Scope: The 2DCC is focused on advancing the state of the art in the crystal growth of bulk chalcogenides and two-dimensional (2D) thin-film chalcogenides through transformational research and mid-scale facilities investments in bulk crystal growth and thin films and integration of theory/simulation with experiment. 2DCC's in-house research team focuses on advancing our knowledge and understanding of synthetic routes and approaches aimed at applications of 2D chalcogenides in current and next-generation electronic device architectures. Researchers from across the U.S. can access the 2DCC's growth facilities and expertise in theory/modeling, synthesis, and characterization as an on-site user at Penn State University or request standard characterized samples through our external user program.

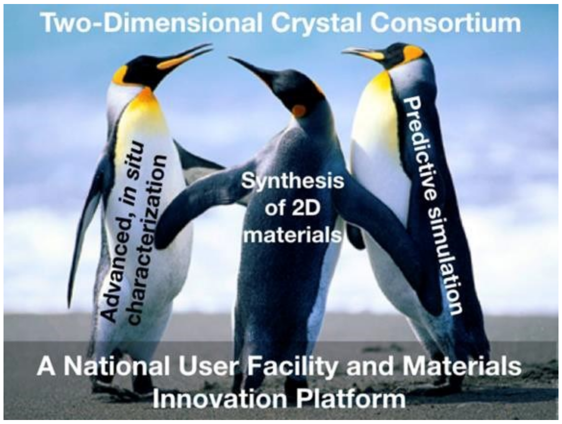

Figure 1. The 2DCC platform integrates theory and simulation with experimental efforts in 2D materials synthesis and in-situ characterization for both in-house research and external user projects.

Relevance to MGI: The 2DCC platform facilitates research that integrates theory and simulation with experimental efforts in 2D materials synthesis and characterization in a closed-loop feedback process. The theory/simulation effort develops key simulation capabilities of general use at the 2DCC and beyond in modeling and understanding growth of 2D chalcogenides. Reactive force field development, guided by first-principles expertise, expands the capabilities of force fields to handle precursor chemistry and substrate interactions. Additional efforts employ computational fluid dynamic simulations to model mass and heat transport to the substrate surface, and develop theoretical tools and results for the interpretation of *in situ* and *ex situ* characterization probes (e.g. optical spectra, scanned probe, electron microscopy). An over-arching goal of the platform is to develop simulation tools that will enable key insights into growth kinetics within broader thermodynamic constraints and to make both tools and results available for broad use, both anticipating future experimental needs and reacting to current experimental challenges.

Technical Progress: The 2DCC research efforts are broadly directed at advancing the science of 2D chalcogenide thin-film synthesis by molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), as well as bulk crystal growth of these materials\, with theory/simulation playing an important role in guiding and supporting experimental activities. Current research in thin films includes epitaxial processes for the MBE growth and doping of Bi_2Se_3 and $(Bi,Sb)_2Te_3$ heterostructures for studies of topological phenomena and wafer-scale MOCVD growth and characterization of $(Mo,W)(S,Se)_2$ monolayers and heterostructures. Bulk growth activities are developing reproducible processes for high purity crystals and exploration of novel chalcogenide compounds for quantum science. Theory and simulation in the 2DCC are centered around identifying new synthetic targets, developing new synthesis strategies, optimizing synthetic conditions, and assisting in the interpretation of in situ and ex situ characterization, all serving the goal of accelerating the design, discovery and development of transformative wafer-scale 2D materials. Our comprehensive approach integrates phase-field modeling, reactive force fields, first-principles computation, and high-throughput data-driven discovery. Recent advances include a means to obtain ordered atomically thin striping in transition metal dichalcogenide alloys, direct topographic control of grain boundary geometry, accelerated atomistic MD simulation of the nucleation and growth of 2D TMD flakes, mechanisms of defect-mediated epitaxy enhancement, progressive enhancements in the scope and precision of reactive force fields, preliminary integrated CFD simulations of reaction chambers, theoretical support of rapid Raman and PL-based characterization including resonant and excitonic effects, and new methods of inducing spatially controlled interlayer interactions. This work supports existing 2DCC users, develops enhanced tools for future users, and identifies new potential growth targets for both in-house and user research.

Future Plans: Research efforts within the 2DCC thin films facility will begin to focus on in-situ characterization as the signature MBE and MOCVD equipment comes on-line. This includes the use of *in situ* angle resolved photoemission spectroscopy (ARPES) and four-probe cryogenic scanning transmission microscopy (STM) to probe the topography and electronic structure of 2D layers formed by MBE, real-time spectroscopic ellipsometry to monitor growth rates and optical properties of ultrathin films in MBE and MOCVD and *in situ* Raman and photoluminescence spectroscopy to characterize 2D layers in MOCVD. These characterization capabilities will facilitate research aimed at understanding fundamental mechanisms of nucleation and growth of 2D chalcogenides and the optical and electronic properties of pristine 2D surfaces. Growth modeling will include reactive force-field simulation of nucleation events that respect the orientational preferences discovered from first-principles and extend grain boundary control techniques to other chalcogenides under controllable synthesis environments to further increase orientation fidelity and investigate mechanisms of monolayer growth enhancement and defect characterization and control.

Broader impact: The 2DCC's active Education, Outreach and Diversity (EOD) program focuses on activities that are synergistic with 2DCC research, promote professional development of technical staff and the broader community of 2D materials practitioners, and promote usage of the facility by a diverse user base both locally and nationally. Outreach activities include the annual "Graphene and Beyond" workshop that includes tutorials, invited presentations and industrial engagement focused on 2D materials and devices, hosting of a monthly webinar series highlighting recent advances in 2D materials research, development of training videos for external users of the 2DCC facility, participation in the Materials Research Facilities Network (MRFN) that provides travel and housing support for faculty from minority-serving and primarily undergraduate institutions, and operation of a STEPFORWARD program that facilitates 2DCC faculty and staff visits to non-R1 institutions to engage the broader research community and build the user base.

Data Management and Open Access: The 2DCC is developing a comprehensive application infrastructure to capture "lifetime" data on all samples grown in the facility, including real-time data streams and associated simulations and computation, make it available to users, and release to the wider community on a timely basis. All information on growth protocols developed at the 2DCC will be released to the public. Recent advances in expanding the number of chemical elements that can be handled by empirical reactive force fields are currently being packaged into the publically available ReaxFF code package for distribution to the community. Additional tools that enhance interpretation of characterization data from optical spectroscopies (as described in section 5) are also being prepared for medium-term community availability. As part of a supplementary NSF-supported effort, the 2DCC will be one of two central nodes of a recently launched the DMR 2D Data Framework initiative, bringing together key materials informatics expertise from Stanford, U Florida, Ames, and CUS Northridge. This collaborative effort will also coalesce an existing extensive but distributed data infrastructure for computational results on equilibrium properties of 2D materials and extend it to handle more complex circumstances with spatial and temporal structure (i.e. defects, interfaces, and growth kinetics), in close collaboration across the Framework.

Advancing Along the Materials Development Continuum: The 2DCC is a national user facility that advances the MOCVD and MBE growth of wafer-scale 2D chalcogenide-based materials and their bulk counterparts. A total of 50 user project proposals have been received in the first two years of operations, including both sample requests and on-site visitors. The user facility model of the MIP platform, which includes both experiment and theory/simulation facilities, enables external researchers to more readily access computational tools and expertise and integrate these approaches into their experimental research efforts. Computational insights are integrated into the synthetic protocols, including identification of new means to control in-plane heterostructures and 2D flake orientational epitaxy in service of future device applications. The crystal growth protocols developed by the 2DCC are accessible to industrial researchers through the 2DCC external user program and through ATOMIC, a related NSF industry-university cooperative research center (IUCRC) at Penn State which focuses on applications of 2D materials and related atomically thin multifunctional coatings. Industrial participation in workshops (Graphene and Beyond) provides a further mechanism to potential commercialization.

Selected Recent Publications

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Microstructure-sensitive Crystal Plasticity in the OOF Finite Element Modeling tool.

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Website: www.ctcms.nist.gov/oof
Keywords: Crystal plasticity, finite element methods

Project Scope

The OOF finite element tool is a long-standing, open-source software tool designed to make sophisticated finite element functionality accessible to a materials science audience. The goal of this project is to add anisotropic plasticity, called “crystal plasticity”, to the solid-mechanics suite of the OOF tool, permitting materials-science users to model a greater range of materials, and to undertake structure-property explorations of more interesting and potentially useful microstructures.

Relevance to MGI

Adding improved solid-mechanics modeling capabilities to the OOF tool is part of the MGI effort to integrate experiments, computation, and theory. Broadly speaking, the OOF tool facilitates the exploration of structure-property relationships in microstructures derived from either simulation, or from visualization of experimental samples, providing a link from microscopy or small-length-scale modeling to mesoscale modeling. Users performing parametric studies with OOF, or exploring the behavior of custom constitutive rules, can link computation to the underlying theory from which the custom constitutive rules are derived.

For the specific case of crystal plasticity, we will provide a tool to rapidly assess the behavior of various candidate plastic response models in real microstructures, proving a length-scale bridge from the microscopic description of dislocation dynamics to the mesoscopic continuum scale, where interactions between deforming grains at different orientations, and possibly of different materials, govern the response of a material sample. Sufficiently careful virtual experiments can differentiate between the effect of dislocation behavior and the effect of overall material texture in plastic deformation, behaviors which are conflated in many other continuum models. At its most ambitious, this effort could provide a bridge from dislocation behavior to the forming behavior of sheet material at the macroscale.

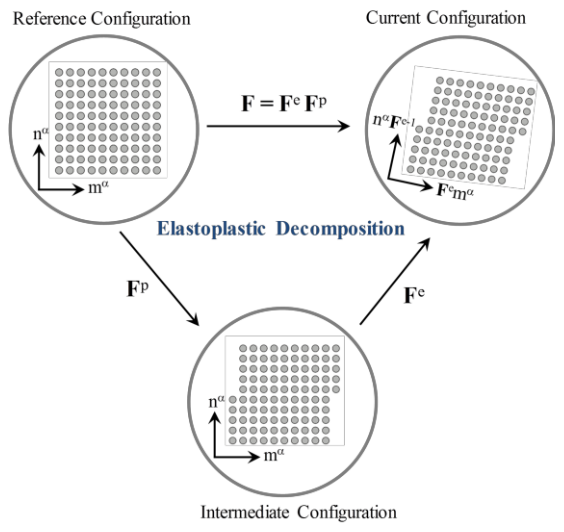

Figure. The decomposition of the deformation field is a core aspect of crystal plasticity finite element methods, and is the source of many of the challenges in integrating this functionality into the OOF tool.

Technical Progress

We have completed the construction of a prototype code which is specific to crystal plasticity, but emulates the OOF software architecture, providing the capability to swap in different plastic constitutive models, documenting the emerging software interface, and ensuring that the prototype code has the virtues of modularity and generalizability which give the OOF scheme its value. The prototype code does not have the microstructure-sensitive mesh construction capability of OOF, but in using the same mesh and element scheme, will provide for straightforward porting of the prototype scheme into the actual OOF code.

A number of important lessons have been learned during this process. While the initial OOF architecture did not anticipate history-dependent dynamics such as arise in the context of plasticity, we were able to construct a storage and retrieval scheme for intermediate data without having to refactor the OOF solver code as a whole. Crystal plasticity requires careful attention to the space in which various computations take place, a feature that the computational solid-mechanics community implements by means of various computational conventions, which do not lend themselves to modular decomposition or extension. This "impedance mismatch" between the engineering-based approach of the solid-mechanics community and the applied-math approach of the OOF architecture has been the principal challenge, surmounted at the cost of a larger code-base.

Once the modular, extensible crystal-plastic scheme embodied by the prototype code is incorporated into the main OOF code, the prototype code will remain valuable as a test-bed for new constitutive rules, and a source of regression comparisons for the OOF implementation.

Future Plans

It remains to complete the incorporation of the crystal plasticity scheme embodied by the prototype code into the OOF codebase itself. Once this process is complete, we will be able to explore the behavior of various candidate plastic constitutive rules, and compare against both lower-length-scale models, such as defect-containing molecular dynamics simulations, and higher-length-scale models, such as those implemented by commercial finite element software for large parts. We will then be able to identify and quantify important dislocation mechanisms active in these systems, providing hints to materials designers on how to obtain desirable mechanical properties.

We also have plans to integrate the OOF tool into emerging digital workflows. The software was originally conceived as a stand-alone product in which users would perform structure-property explorations of interest to them. In the context of the MGI, this model is at best incomplete, and we plan to accommodate users who wish to use OOF as a model evaluation step in a larger, possibly closed-loop materials design workflow. OOF must be able to read and write microstructure and property data from popular tools in the community, such as Dream3D and the Materials Project.

Data Management and Open Access

The OOF software is already open-source, and is available on github.

An additional lesson learned during the early stage of the crystal-plasticity effort, however, was the insufficiency of merely having one's code be accessible – code the size and complexity of OOF is not inherently comprehensible, even to subject-matter experts in finite elements or practitioners in the C++ and Python programming languages in which OOF is written. We have therefore undertaken to improve the low-level technical documentation of the property programming interface to the OOF code, as well as the documentation of the OOF solver machinery itself, to better enable the community to take advantage of the software's capabilities.

We also imagine that a community of users may arise who wish to share microstructures and property data. While we have no specific plans for a repository of such data, we are paying close attention to our colleagues' work in developing schemas and tools like the Materials Data Curation System to solve this problem, and plan to provide suitable metadata for users who wish to combine OOF data with MGI data management tools.

Advancing Along the Materials Development Continuum

OOF is a length-scale-bridging tool that is generally usable by a large audience of materials science users. We have no plans for commercialization, but are committed to maintaining the availability of the software for any purpose.

Publications

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Grain Growth Beyond Isotropic Models: Microstructure Evolution with Experimentally Derived Interface Properties

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Website: none.

Keywords: Grain Growth, Grain Boundaries, Microstructure, High Energy Diffraction Microscopy.

Project Scope

The goal of this project is to test the hypothesis that it is possible to predict how microstructures evolve on a grain-by-grain basis using 3D mesoscale simulations with rules for interface motion that incorporate experimentally determined interface properties. Using near field-high energy diffraction microscopy (nf-HEDM) data, we will specify both the structure and the properties needed to instantiate a phase field model for growth. Comparisons between the simulated and measured growth will allow us to identify properties incorrectly measured or mechanisms not reproduced by the model.

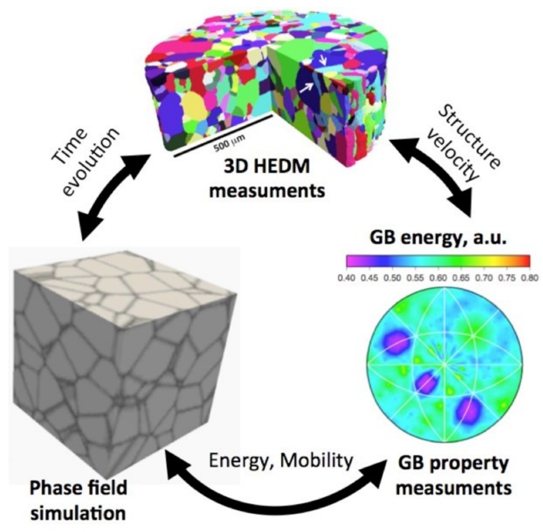

Figure. Illustration of the three main project activities and the feedback of information from one to the other.

Relevance to MGI

To predict how microstructures evolve on a grain-by-grain basis using 3D mesoscale simulations, we are using a feedback cycle that allows the models to be refined until they are able to predict the outcome of the experiment, as illustrated in the figure. The cycle begins with experimental observations by nf-HEDM, and then the extraction of interfacial properties. From the energies and velocities of grain boundaries, we will determine the mobilities. This will provide both the structure and the properties to instantiate a phase field model for growth. Comparison between the observations and simulations will be used to modify both the models and experiments.

Technical Progress

A method was developed to measure the distribution of grain boundary curvatures as a function of five independent crystallographic parameters from 3D electron backscattered diffraction data. The method was first validated using ideal shapes to find appropriate parameters for the microstructure reconstruction and limits of applicability. The methods were then used to measure both local curvatures and integral mean curvatures of an austenitic steel, a ferritic steel, and $SrTiO_3$. We have also developed software tools to analyze the changes in the shapes and sizes of grains in nf-HEDM data. When a microstructure is measured and reconstructed at multiple anneal states, we know that (ignoring rare exceptions) the grains in the final state were also in the preceding state. However, there are no completely unambiguous characteristics to identify the same grain at both time states. Furthermore, because there are thousands of grains in each state, the method to link the grains needs to be automated. We have developed software that uses characteristics of the grains such as position, orientation, and size to identify the same crystal in multiple time steps. We have used this to analyze 3D data from α-Fe and Ni. We have also begun the formulation and implementation of a phase-field tool using Fourier techniques. As a part of this effort, an initial step has involved the development of fast methods to solve the evolution equations using mixed explicit / implicit methods. In particular, the Recursive Projection Method (RPM) has been adapted for to enable dealing effectively with high contrast settings using an adaptive splitting into fixed point and Newton iterations.

Future Plans

We are planning to combine curvature measurements with observed changes in grain size with time to determine if curvature is a robust indicator for grain boundary velocity. We will also be developing tools to extract interface velocities from the 3D data. When we combine this with the knowledge of curvature and energy, it will be possible to measure mobility over all five crystallographic variables. This will be needed as input to the grain growth models. In the arena of simulations, we will develop the fast 3D phase field model for microstructure evolution.

Broader impact

We held a 3D microstructure workshop that took place July 17-18, 2017. The workshop consisted of three types of presentations. Roughly one third of the presentations were about state of the art 3D materials research. Another third of the presentations were tutorials illustrating the capabilities and uses of Dream.3D. The final third of the workshop consisted of practical sessions in which participants worked on individual projects with the guidance of the speakers. The 50 participants learned about 3D microstructures investigation tools, including those being developed as part of this project. The professionals who attended were from industry and from government labs. The graduate students and post docs who attended came from universities in the United States and Europe.

Data Management and Open Access

The primary data, as well as processed data sets which are deemed to be of sufficient quality, will be made available for sharing with other researchers by means of the grain boundary data archive (http://mimp.materials.cmu.edu/~gr20/Grain_Boundary_Data_Archive/). The main software tool that will be used to analyze the data is DREAM.3D, an open source tool available to all at: http://dream3d.bluequartz.net/. Other, more specialized analysis software will be also available at the Grain Boundary Data Archive.

Advancing Along the Materials Development Continuum

The PI received follow-on funding from ArcelorMittal to apply the tools being developed in this project to understand microstructure evolution in welds in advanced high strength steels for vehicular applications.

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Search for Magneto-Electronic Complex Fluoride-based Interfaces with Novel Properties.

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Keywords: oxyfluorides, multiferroics, DFT, MBE.

Project Scope

We proposed to systematically study complex fluoride thin films and heterostructures, in which the different origin of multiferroic properties as well as the larger electronegativity of fluorine can result in enhanced magnetoelectric effects. The research consists of a synergistic collaboration between computational and experimental scientists. The computational work employs state-of-the art, first-principles techniques to determine the most likely structures to have large magnetoelectric responses. These fluoride materials are synthesized using a unique molecular beam epitaxy growth system specifically designed for this purpose. Experimental characterization in the macro-, micro-, and nanoscopic length scales regime is carried out and the results are compared to the theoretical predications.

Relevance to MGI

The strong computational - experimental partnership achieved to search for interface electronic and multiferroic states in complex fluoride compounds and heterostructures is designed to discover new materials that can be used in electronic devices that are more power efficient and faster than current technology. These devices could result in energy-efficient electronic control of magnetic information.

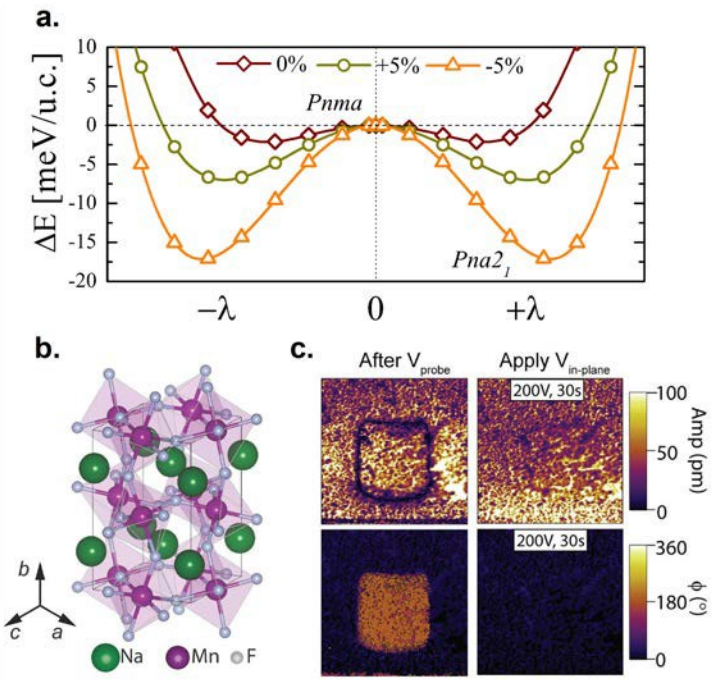

Figure. Theoretical prediction (a) of the ferroelectric phase in the fluoroperovskite $NaMnF_3$ (b) and its later experimental confirmation in the $NaMnF_3/SrTiO_3$ (001) epitaxial thin-films.

Technical Progress

As a first approach, using density functional theory we studied the effect of the epitaxial strain on the structural, electronic, and magnetic properties in the fluoride perovskite $NaMnF_3$. A multiferroic-induced state was predicted for $NaMnF_3$ under epitaxial strain at compressive or tensile strain. A non-linear behavior of ferroelectric instability, and then, a non-linear piezoelectric response as a function of epitaxial strain was found. The later completely different in contrast with the findings reported in perovskite oxides. Additionally, an out-of-plane polarization was observed again in opposite trend such as has been found in oxides. A cooperative FE ordering between Na and Mn sites was found for compressive strain against a pure *A*-site geometrically driven ferroelectricity at tensile values of orthorhombic ac-strain. Magnetic ordering reveals a non-collinear ground state under the $G_zA_xF_y$ representation. And even more interesting, and non-linear magnetoelectric coupling was found in this material under the strained $Pna2_1$ ground state. From the experimental point of view, we grew the $NaMnF_3$ thin films on the $SrTiO_3$ (001) substrates. Using piezoresponse force microscopy, we verified the FE character of the NMF films. Though $NaMnF_3$ proved to be quite difficult to be epitaxially grown.

Moving forward, we have analyzed by means of first-principles calculations the electronic and structural properties of oxyfluorides $(KTaO_3)_n/(KMF_3)_l$ with M = Zn and Ni superlattices with alternating *p*- and *n*-type interfaces. We found that the orbital levels symmetry at the interfaces is strongly as a function of the O–M–F coordination. The polar catastrophe phenomenon also takes place in the oxyfluoride interfaces. Unexpectedly, we found that less number of layers is needed in order to achieve the insulator-to-metal transition in comparison to $SrTiO_3/LaAlO_3$ [1,2]. Our calculations indicate that the magnetism in the $KTaO_3/KNiF_3$ exhibits a moment magnitude modulation across the entire fluoride film. Nevertheless, the magnetic structure keeps the *G*-type AFM such as in the bulk former compound. Surprisingly, we observed a large k^3-Rashba type splitting in at the oxyfluoride interfaces, at least four times larger than the one reported in oxide-oxide $SrTiO_3/LaAlO_3$ interface and twice of the $KTaO_3$-based transistor [3].

Finally, we have studied the $BaMF_4$ family of compounds and found a multiferroic behavior with an orbital ordered state, induced by the Jahn-Teller distortion, in the $BaCuF_4$ with a $Cmc2_1$ symmetry ground state. Our calculations indicate a quasi-1D AFM magnetic ordering in addition to a ferroelectricity with a polarization of Ps = 8.40 μC/crn^2. This FE order is induced by a condensation of a polar mode that involves CuF_6 octahedral rotations and Ba-polar displacements along b-axis. Moreover, we are observed a feasible way to control the magnetic order by switching the ferroelectric polarization achieving a strong magnetoelectric coupling.

We are also growing the $NaNiF_3$ (NNF) compound, an antiferromagnet with weak ferromagnetism with a high transition temperature (~150 K). We have grown high quality thin films on [001] STO and demonstrated the existence of weak ferromagnetism. Ferromagnetic thin films grown in-situ on NNF show exchange bias only in the perpendicular direction. We plan on studying the possibility of induced magnetoelectric coupling using strain, detected optically through exchange bias after field cooling in an electric field.

Future Plans

From the theoretical point of view, we will expand our consideration of materials to ABF_4. We expect to offer a clear picture on this type of materials. Then we will consider interfaces with different oxides with different or similar stoichiometry.

Experimentally speaking, we will study the properties of $NaNiF_3$ with different substrates as we have done for $NaMnF_3$. Calculations supporting the magnetic behavior and providing information about the magnetic exchange couplings will be included.

Based on the good response we got from the community to our PyProcar script (used to perform band structure analysis), we will create a more professional python package, which will be more modular and it will allow to include more features in the future (as the analysis of the optical transition in the full Brillouin zone, projection of the band structure to specific layer in the material, etc). We will also create an interface to do similar analysis for the results from the Software ABINIT (www.abinit.org). This new implementation will broaden our pool ofusers.

Broader impact

New Technologies: This project relies on a computational/experimental partnership to search for interface electronic and multiferroic states in complex fluoride compounds and heterostructures. In some cases, we expect their magnetoelectric properties to be superior to those observed in oxide compounds. Once verified, we anticipate that these new materials and the knowledge about the mechanism responsible for their behavior will lead to the design and implementation of electronic devices that are more power efficient and faster than current technology. This may be possible, for example, if we discover enhanced multiferroic properties that allow for efficient electronic control of magnetic information.

New Materials Design Software: Romero and his group are developing user- friendly software package to perform band structure analysis. This software called PyProcar has been downloaded more than 800 times. We recently have redesigned the project and in the next few days we will upload the new package, which include more features. At the same, we have continued our development of our package PyChemia, which is an interface with DFT codes. We have created interfaces with VASP, ABINIT, FIREFLY and ELK. These new interfaces no only allow the user to run calculations based on these packages but also facilitate the interpretation of data. The interfaces also allow to use structural search methods, as it is the case of Firefly. The methodology we have introduced in the course of this project.

Data Management and Open Access

The Web page has been moved to a different server and before the meeting, we will have an uploaded version with more information and interfaces to public structural databases. The data will be freely available in this Web server.

Accelerating Materials Discovery & Development

The goals described in the original proposal were basically completed. From the theoretical side, a full study of study of ABF_3 compounds were performed and two of them were selected for the experimental study. For $NaMnF_3$, a ferroelectric behavior was experimentally corroborated with an incipient magnetoelectric response. No clear magnetoelectric response was measured. This could be related to the difficulty to grow the material, though we have considered different substrates. This indicates that in order to improve the quality of the crystals, we need to perform a better selection of the substrate. Another material that has been theoretically and experimentally studied in $NaNiF_3$, where a high magnetic transition has been measured. This provides enough information to the theoreticians to improve the methodology used to describe this strongly correlated material.

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Recent Publications from this proposal

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Predictive Modeling of Polymer-Derived Ceramics: Discovering Methods for the Design and Fabrication of Complex Disordered Solids

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Keywords: Amorphous, Ceramics, Electronics, HRMC, ANN

Project Scope

Toward the long-term goal of creating an integrated program for the design of complex disordered solids, this new project aims to develop a general methodology for accurately simulating the atomic structure of substructure-containing amorphous solids and mapping resultant structures/properties back to fabrication conditions, ultimately enabling a design capability. The effort focuses on developing an *ab initio* molecular dynamics (AIMD) and hybrid reverse Monte Carlo (HRMC) simulation, augmented by *ab initio* energy constraints, that couples with experimental feedback, using a series of thin-film amorphous preceramic polymers, a-BC:H, a-SiBCN:H, and a-SiCO:H, as suitably complex and technologically relevant case studies.

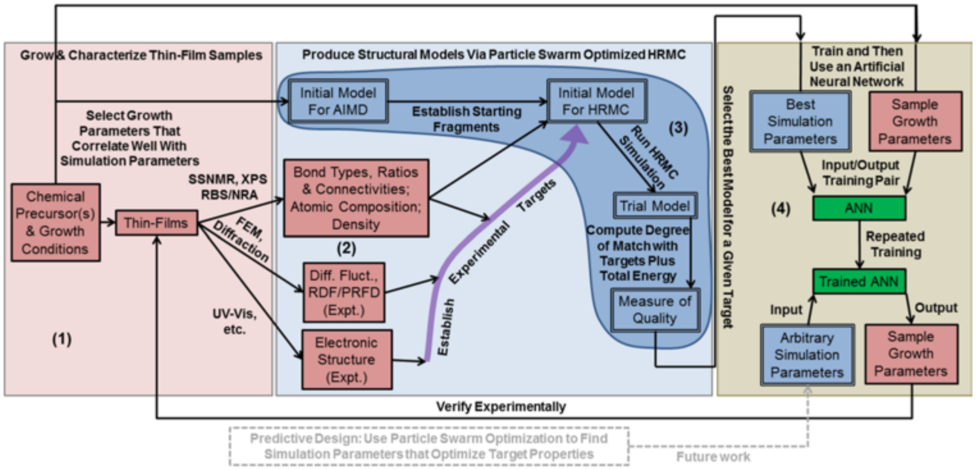

Figure. The project includes (left) growth and characterization, (middle) iterative modeling, and (right) design training and validation. Single-frame red boxes represent experimental samples and data, while double-framed blue boxes represent computational products. The shaded region in the middle represents the application of particle swarm optimization. The general flow can be understood as: (1) growth of samples varied by composition and growth procedures; (2) experimental structural characterization; (3) iterative model simulation using characterization data; (4) ANN training to link simulation and growth parameters followed by predictive application of the ANN.

Relevance to MGI

The first step in any computational materials design is the generation of realistic structural models, a task that is rendered much more difficult in the case of complex disordered solids. The investigators advance the state of the art, and surmount traditional challenges associated with identifying non-global potential energy minima for materials produced under non-thermodynamic conditions and aligning simulation and growth process timescales, by developing novel algorithms for linking growth conditions and characterization information to atomistic simulation, and for mapping fabrication conditions to desired properties. The project combines state of the art computational techniques (AIMD, HRMC) with modern optimization algorithms (*e.g.* artificial neural networks (ANNs), particle swarm optimization (PSO)), in conjunction with specialized experimental characterization techniques, such as nuclear magnetic resonance (NMR) and fluctuation microscopy. The unique utility of modern solid-state NMR techniques to obtain specific bonding and connectivity information and the sensitive medium-range order information available from fluctuation microscopy will be combined with neutron diffraction and more routine physical/electronic structure characterization methods to provide input and constraints for the simulations. The HRMC modeling efforts are optimized via PSO and subsequently used to train an ANN (see Figure).

Technical Progress

The summary of technical progress since the start of the project in November 2017 is described below.

Materials synthesis: The synthesis of ^{13}C-labeled *o*-carborane to be used for NMR experiments is nearly complete. The use of ^{11}B-labeled *o*-carborane for neutron diffraction experiments is being investigated. A series of unlabeled *o*-carborane films has been synthesized to systematically measure and use as a dataset for the project.

Characterization: A new-generation fast pixelated detector for scanning transmission microscopy has been used for the first time to characterize the detailed structure of amorphous hydrogenated boron carbide films. This new detector dramatically advances the capability of fluctuation microscopy, as it enables continuous acquisition of nanodiffraction patterns from a large area of the amorphous sample, providing information on the details of the medium range ordering (MRO), including the size, type, connection, and volume fraction of the ordering, at the nano- to meso-scale with unprecedented precision. The user proposal for the beam time on the Spallation Neutron Source at the Oak Ridge National Laboratory has been submitted for June-Dec 2018 period.

Computation: HRMC code is being modified to incorporate the calculation of fluctuation microscopy data and to simulate the electron diffraction data using the Multislice algorithm. This should result in higher precision in the atomic positions and more unique nano- to meso-scale structure in the simulated model. The fully functional HRMC algorithm is still being developed, but in the meantime, we are optimizing parameters for MD simulations to speed the creation of initial models for the HRMC algorithm that are already at least partially consistent with the MRO information acquired using fluctuation microscopy. This is an important process because it will provide insights into the length scale limits of the optimized structure in MD, which will help us determine the weighting ratio between components in the HRMC simulation (*e.g.* geometric constraints vs. NMR. vs. fluctuation microscopy).

Management: Software platforms (*e.g.* GitHub) have been investigated for shared data storage and formatting. Literatures and lab notebooks are shared among PIs and students working on this project via online resources (Mendeley). The progress has been discussed through regular online biweekly meetings, and several on site meetings have been held involving all PIs since the beginning of the project. The PIs are organizing a symposium “Synergy in multi scale modeling and experiments to resolve complex disordered solids” in MS&T 2018 Conference to share and discuss our findings with the research community.

Future Plans

The long-term goal our project is the development of an integrated program for the design of complex disordered solids that satisfy the performance requirements of advanced applications. Our current short term (~1 yr) plans to meet this goal include the following: (1) We will form connections between experimental characterization and simulated data to guide the construction of realistic polymer derived ceramic models. Our working hypothesis is that establishing a procedure based on preparing a large-scale simulation composition via smaller scale AIMD followed by progressively improved matching of experimental data via HRMC will lead to viable structural models of samples with known growth parameters. (2) We will establish methods and algorithms for linking the combination of simulation/growth parameters and model/sample properties to attain a predictive capacity. Our working hypothesis for this aim is that a relationship between the simulation procedures used to obtain a given model and the growth procedures used to produce a material sample with matching properties can be embodied within an ANN. Once trained, the ANN will be able to predict the synthesis directives that are necessary to grow a sample with the arbitrarily simulated structure. It is important to note that although specific, computationally inexpensive physical properties will be calculated from the models and compared with experimental data as a part of the structural modeling and verification process, the scope of this work is expressly constrained to the fundamental issue of generating structural models and mapping these to processing conditions and not optimizing material properties themselves. Our goal is to be able to predict sample structures and related derived properties on the basis of processing conditions.

Broader impact (Only required for NSF projects)

This effort will benefit technology and society by advancing the science of design of complex disordered solids through the development of intelligent algorithms that link growth conditions and atomic structure to enable predictive design. Further, new insight into the specific case study materials will be relevant to a number of areas, including dielectric and patterning materials for nanoelectronics, radiation detection, micro- and nano-electromechanical systems, as well as various specialized coatings and engineering materials. This project integrates research and education through the traditional scientific mentoring of graduate and undergraduate students as well as through participation in ‘Project SEED.’ Project SEED is an internship program, sponsored by the American Chemical Society, that offers financially disadvantaged high school students an opportunity to work in a research laboratory over the summer. This is the type of program that can alter education/career trajectories and open otherwise closed doors, permanently changing the lives of these young people. Finally, the results of the project will be disseminated to a broader audience, through both student-generated Wikipedia content as well as the open-source distribution of packaged and documented source code.

Data Management and Open Access

Central to our data management plan is the University of Missouri System’s Open Access permanent digital repository, MOspace (http://library.umkc.edu/mospace), which uses the open source DSpace institutional repository application. Metadata assigned to items submitted to MOspace are searchable by Google Scholar and other search engines, which makes the data easily accessible to other researchers and the general public. In addition to MOspace, computer source code that is developed in connection with the project will be stored on the internet-based distributed development environment called Github (https://github.com/), and all of the code will be made available according to the Educational Community License v2 open source license. Github is designed for distributed development and regular updating of computer code.

Advancing Along the Materials Development Continuum

We expect that this effort will have major scientific and technological benefits to society by advancing the science of computational modeling and design of complex disordered solids. The iterative make–measure–model paradigm described here is not in itself new, nor are many of the characterization and simulation techniques to be employed. The novelty of the proposed effort, however, lies in developing the algorithms and rule-sets that will tie together growth, characterization, and simulation such that truly realistic models can be produced, as well as in developing strategies for mapping (not necessarily reproducing) fabrication conditions and desired properties, and it is this that takes the proposed effort from evolutionary to potentially revolutionary. Additionally, we will make progress in understanding the specific technologically relevant materials we have chosen as case studies for developing our methods.

Discovery and Design of Additives for Novel Polymer Morphology and Performance

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Keywords: nucleation kinetics, polyolefin, molecular dynamics, optimization, morphology

Project Scope

The overarching vision of this project is the development of a paradigm for accelerated materials discovery and design through the synergistic application of molecular simulation and experimental evaluation. The instantiation of this paradigm here is the discovery and development of foreign additives for polyolefins that serve to alter the crystallization behavior, and thus the semicrystalline morphology of the resulting material, in predictable ways. The outcome of such effort will be newly tailored additives and semicrystalline materials with exceptional combinations of thermal, mechanical, and optical properties.

Relevance to MGI

This project is a collaboration between academia and industry to create a new method of materials research, involving the application of (i) molecular level simulation, (ii) experimental validation, (iii) materials design and optimization, and (iv) industrial application, to identify essential relationships between molecular structure, morphology, and performance (see figure). In this project, this paradigm will be realized through the discovery and design of additives (e.g., nucleating agents, clarifiers, nanofillers) that alter the morphology of polyethylenes and polypropylenes, and thereby their properties as well. Molecular simulations will be used to conduct broad screenings of additive classes and will be validated experimentally in select cases by measurement of heterogeneous nucleation kinetics. Evolutionary strategies and related methods will be used to design and optimize candidates within and across additive classes. Best-in-class candidates will be identified for subsequent synthesis, development, and characterization of semicrystalline morphology and properties within the laboratories of ExxonMobil, the industrial collaborator.

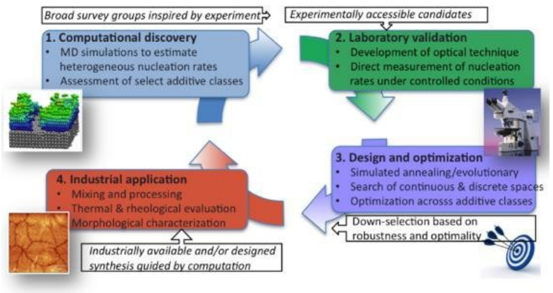

Figure. Schematic illustration of iterative process involving discovery through computational assessments, validation of computational indicators, design and optimization for rapid improvement, and industrial application.

Technical Progress

This project is in its first year. To date, the development of experimental techniques to measure heterogeneous nucleation kinetics and validate the available molecular simulation results is the main accomplishment. Experiments using polarized light microscopy to observe crystallization have demonstrated surface nucleation within an ensemble of micron-sized polyethylene droplets on an amorphous polystyrene substrate, following the approach of Dalnoki-Veress and co-workers.[1] Motivated by the simulation work of Bourque et al.,[2] in which heterogeneous nucleation of an oligoethylene (*n*-pentacontane) by a family of tetrahedrally coordinated crystalline substrates was simulated, gallium arsenide was chosen as a crystalline substrate to be tested experimentally. However, accurate characterization of polyethylene nucleation has been more difficult on this substrate, as the birefringence of crystalline droplets on gallium arsenide is less pronounced than those observed in experiments on polystyrene. Image analysis techniques are being developed to detect birefringence more sensitively. It is also hypothesized that droplets may become too thin to observe birefringence optically, due to wetting during melt equilibration. A balance is currently being sought between minimizing wetting and removing melt memory effects.

Future Plans

This project has three major objectives:

1. Broad examination of surface nucleation using multiple and diverse classes of additives, through the implementation of high-throughput screening and optimization algorithms
2. Direct experimental measurement of nucleation kinetics
3. Industrial application and implementation of selected additive classes to validate heuristics and to relate kinetics to measurable elements of morphology and properties.

In the first objective, physics-based surveys of additive classes by molecular simulation and kinetic modeling will be used to identify trends and to determine mechanisms of activity within each class. Established design algorithms such as simulated annealing and evolutionary algorithms will be implemented for rapid and robust optimization and design purposes. These methods will also be applied to other polymers such as oligopropylene.

In the second objective, experimental measurements will be extended to substrates of known nucleating agent efficiency, such as graphene, various organic crystals, mica, and talc, as well as on substrates examined only *in silico*. Experimental measurements will also be used to validate simulated heterogeneous nucleation rates directly. Once linear polyethylene has been studied, the experimental methodology will be extended to other polyolefins such as polypropylene and/or polyethylene with short chain branching.

In the third objective, morphological and property observations such as crystallite size, crystal number density, crystallization rate, and mechanical strength and toughness will be rationalized with the heterogeneous nucleation efficiency for the substrate measured *in silico*, as well as with observed surface nucleation rates when available. This understanding thus obtained will be used to design and synthesize next-generation nanocomposites, such as polyethylene-graphene, with superior properties. New additives will be synthesized or fabricated based on the most promising candidates identified by materials genomic surveys conducted by simulation.

Broader impact

Advanced materials and their manufacture are essential to economic development, national security, and quality of life. The design of additives to produce lightweight polyolefins that are stiffer and tougher than those currently available will benefit societal and economic requirements for energy and material conservation. By advancing a new paradigm for materials discovery and development that can accelerate the development cycle for new materials by orders of magnitude, this program contributes to U.S. competitiveness in advanced materials. Increased competitiveness and innovative practices are known to translate into job creation within the U.S. manufacturing economy. Industrial collaboration provides a mechanism to realize these benefits.

This project further serves society through the education and professional development of young engineers and scientists, and through the dissemination of results at national and international venues. The project will develop outreach to college undergraduates around the country through established Research Experience for Undergraduates programs at MIT, which promote the participation of underrepresented minority students. Pedagogical aids such as molecular dynamics animations will be developed for teachers seeking ways to “bring to life” such phenomena for their students.

Data Management and Open Access

Digital data from both experimental and computational work generated in this project will be retained in three forms during the lifetime of the project. All non-confidential data will be made publicly available at the earliest reasonable time, with the exception of publications and presentations that are subject to a period of review by the industrial partner for removal of proprietary information. All publicly released data will be made available upon request to the MIT PI. Re-use of public data will be allowed except where assignment of copyright no longer resides with the PIs, for example, scientific publications. After the conclusion of the program, all data will be retained on MIT's archive DSpace@MIT (http://libraries.mit.edu/dspace-mit/) for the maximum allowed period, which is currently permanent. Due to the early stages of this project, no data has been released yet for public sharing.

Advancing Along the Materials Development Continuum

At present, the industrial design and selection of nucleating agents and additives is still largely a matter of empiricism. However, by using experimental observations to guide computational investigations of new additives, and by using the results of computational studies to construct the basic language for material behavior, this project can trim down and focus subsequent experimental efforts into the most productive and informative directions. State-of-the-art optimization approaches that are efficient, broad, and high-throughput will also open the possibility of finding the optimal additive(s) to produce a specific combination of crystallization kinetics and resulting morphology for a given polymer. This synergy between computation and experiment will substantially reduce both the time and cost to deploy novel materials for targeted applications. The industrial partner in this GOALI project has the resources to develop and commercialize best-in-class additives that result in nanocomposites that meet or exceed its design requirements.

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Operation of Lithium-Oxygen Batteries with Long Cycle Life in a Realistic Air Atmosphere

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Keywords: Molybdenum disulfide, Li oxygen battery, Li air battery, Ionic liquid, Lithium anode

Project Scope

Lithium-air (Li-air) batteries are considered as a potential alternative to Li-ion batteries for transportation applications due to their high theoretical specific energy. However, these batteries suffer from a poor cycle life in the presence of the actual air components, such as nitrogen, oxygen, carbon dioxide, and moisture, as well as volumetric issues with use of pure oxygen. Here, we report a system comprised of a lithium carbonate based protected anode, molybdenum disulfide cathode, and ionic liquid/dimethyl sulfoxide electrolyte that work together as a real Li-air battery with a long life of up to 700 cycles. Density functional theory, classical and ab-initio molecular dynamic simulations and various characterization techniques are used to provide insight into how this system operates in air.

Relevance to MGI

In this study, we used an integration of material synthesis, battery experiments, in-situ/ex-situ characterization, classical and ab-initio molecular dynamics (MD) simulations and density functional theory (DFT) calculations to design a new architecture for Li-air battery system to operate in a simulated air environment with a long life of up to 700 cycles. Through use of a closed, iterative feedback loop between MD/DFT and experiments, we found a novel synergy between ionic liquid/dimethyl sulfoxide and molybdenum disulfide cathode that prevents reaction of H_2O and CO_2 molecules in the air with either LiO_2 or Li_2O_2 discharge products. In-situ scanning transmission electron microscopy (STEM) and differential electrochemical mass spectroscopy along with ex-situ XPS, XRD and Raman characterizations were used to gain invaluable supporting information for the simulation part and design of experiments. On the anode side, combination of in-situ material synthesis, in situ electron energy loss spectroscopy (EELS) and ex-situ Raman and XPS, and DFT calculations were used to design and directly synthesis a novel carbon rich lithium carbonate passivation layer on top of pure lithium anode. This layer provide a selective channel for the Li ion transport with an average of 99.97% lithium retention per cycle. Moreover, it prevents air compounds to reach the anode surface, thus protecting the lithium anode surface from oxidation.

Technical Progress

Li_2CO_3 as the anode protection layer was synthesized in a custom-made electrochemical cell encapsulated with pure CO_2 and run in a constant current density of 500 mA/g for 10 continuous discharge and charge cycles in a one-hour time-lapse. The scanning electron microscopy (SEM) image of the anode surface (Figure 1a) reveals a dense network of rod-shape structures on the anode surface. Raman spectroscopy shows distinct peaks at 717, 743, 1088, and 1456 cm^{-1} for this coating (Figure 1b), which are characteristic peaks of Li_2CO_3. Moreover, the X-ray Photoelectron Spectroscopy (XPS) results shown in Figure 1c-d for Li 1s, C 1s, and O 1s show peaks at 55.2, 289.3, and 531.5 eV, respectively, further confirming the presence of Li_2CO_3. The composition of the synthesized Li_2CO_3 layer was further characterized by electron energy loss spectroscopy (EELS). Li *K*-, O *K*- and C *K*-edges obtained from EELS of platelet-like particles extracted from the anode are presented in Figures 1e.

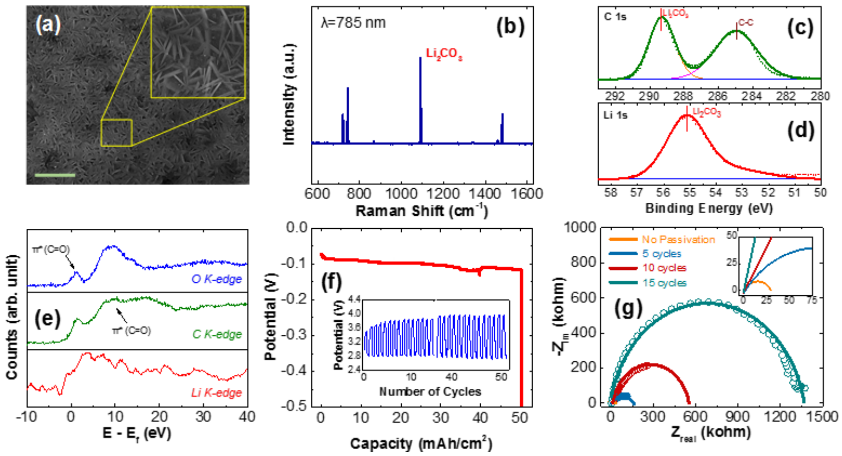

Figure 1: Protected anode. (a) Scanning Electron Microscope (SEM) image of the surface of the protected anode (scale bars: 1 µm). **(b)** Raman spectra of the protected anode surface, excited by a 785 nm laser. **(c)** X-ray photoelectron spectroscopy (XPS) spectra of the protected anode surface in Li 1s and **(d)** C 1s regions. **(e)** EELS spectra for Li *K*-, C *K*-, and O *K*-edges of the anode SEI layer consistent with the compound lithium carbonate. **(f)** Exhaustive stripping of protected lithium using current density of 0.5 mA/cm^2. Inset figure shows the cycling test of the protected anode in the air environment under the current rate of 500 mA/g. **(g)** Electrochemical Impedance Spectroscopy (EIS) of passivated anode after 5, 10, and 15 cycles of exposing to pure CO_2 environment compared to the anode without passivation.

Next, a custom-made Swagelok type Li-air battery cell was assembled in an Argon (Ar) filled glove-box using the MoS_2 NFs cathode, a lithium anode with the protective coating, and ~35 µL of 25% of EMIM-BF_4 and 75% of DMSO electrolyte. This composition of electrolyte provides the maximum oxygen reduction and evolution reactions studied in a three-electrode electrochemical cell. A custom-made air stream consisting of ~79% N_2, ~21% O_2, 500 ppm CO_2, and relative humidity (RH) of 45% at 25°C was used for the battery experiments. Figure 2a shows the long-term discharging and charging profiles up to the capacity of 500 mAh/g by applying a constant current density of 500 mA/g. The charge at the first cycle was started at 2.92V, which is very close to the reversible thermodynamic potential of Li_2O_2 formation (2.96V vs Li/Li+) and reaches the potential of 3.75V at the capacity of 500 mAh/g. The potential gap for the first cycle of the Li-air system is 0.88V, which increases to 1.3V after 50 cycles followed by a gradual increase to 1.62V after 550 cycles. We did not observe any failure of the battery tested up to 700 cycles. Figure 2b demonstrates the dependence of the number of Li-air cycles on the number of cycles used to make the protective coating for the anode. The results indicate a dramatic increase in the number of Li-air cycles when the coating is included compared to when no coating is used. With no coating the Li-air cell fails after 11 cycles. With the addition of the protective coating (10 deposition cycles) the Li-air cell can cycle up to 700 cycles. Raman spectroscopy and XPS were performed on the cathode surface to study the discharge products and cell chemistry from different cycles. The Raman results (Figure 2c) show the presence of only a Li_2O_2 peak at 788 cm^{-1} during discharge process and the peak disappeared during charging process. We did not detect any peaks related to LiOH (485 cm^{-1}), Li_2CO_3 (1088 cm^{-1}), or LiO_2 (1125 cm^{-1}) in the Raman spectra suggesting that Li_2O_2 is the only product during the discharging process. Results from XPS analysis (Figures 2d-f) and differential electrochemical mass spectrometry (Figures 2g) further confirm the presence of Li_2O_2 as the product of discharge reaction. The ex-situ and in-situ characterizations indicating that CO_2 and H_2O do not cause any detrimental reactions, are further confirmed with Swagelok experiments (Figure 2h) which demonstrate similar results for both Li-oxygen and Li-air systems, suggesting that the discharge and charge chemistries of our Li-air battery are the same as that of the Li-O2 system.

To explain why CO_2, H_2O and N_2 do not participate in the reactions on both cathode and anode sides, we performed classical and ab-initio MD simulations and DFT calculations to study all types of reactions involving these compounds in the Li-air cell that could result in the formation of undesired reaction. Our study indicate that unique combination of electrolyte mixture with MoS2 cathode and lithium carbonate protected anode make a selective chemistry for O_2 reaction, by preventing other side reactions.

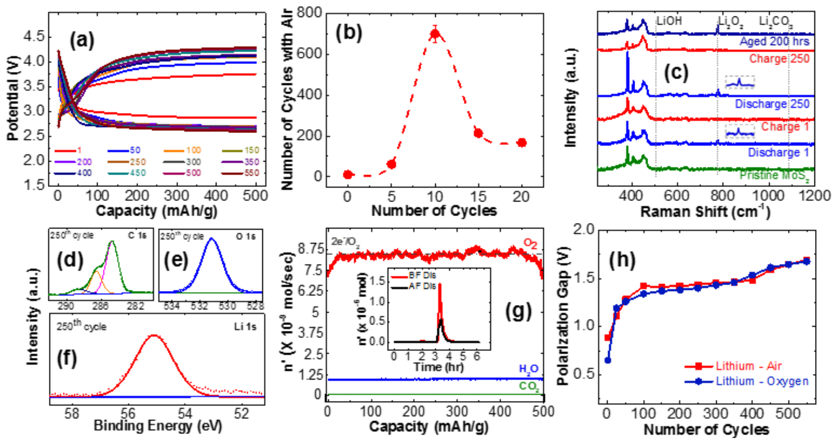

Figure 2: (a) Discharging and charging voltage profile of the Li-air battery after 550 cycles. (b) The effect of the anode protection cycling length on the life cycle of the Lithium-air battery. (c) Raman spectra of the cathode surface after discharge and charge process. (-ed) X-ray photoelectron spectroscopy (XPS) spectra of the cathode surface. (g) Differential Electrochemical Mass Spectrometry (DEMS) profiles of the cell during discharge and charge cycles. (h) Polarization gap (V) of the Li-air battery compared to Li-O_2 battery with the same operating condition as a function of the number of cycles.

Future Plans

In a next step, we plan to examine different transition metal dichalcogenides (TMDs) and ionic liquid materials and study their synergetic behavior for oxygen reduction and evolution reactions. Moreover, we will test their performance within Li-air systems. The effects of doping and alloying will also be studied. In particular, we will use-in-situ characterization, such as STEM imaging and EELS to examine the effects of different alloys on the edge atomic structure of the particles and the particle/electrolyte interfaces.

Broader impact (Only required for NSF projects)

PIs from UIC will collaborate with existing UIC programs such as the NSF-REU program and the Minority Engineering Recruitment and Retention Program (MERRP) to actively involve undergraduate students in the proposed research. PI Salehi-Khojin will serve as a faculty member in Next Generation Electrochemistry (NGenE) summer school, UIC, 2018. NGenE brings 25 advanced graduate students together from across the country for five days to identify and elaborate the most important unsolved challenges associated with the electrochemical systems. During this summer school Salehi-Khojin will present our recent Li-air battery results to the participants. Co-PI Klie has been the editor and publisher of the Journal of Undergraduate Research at UIC (http://jur.uic.edu), which publishes 10-12 undergraduate research papers every year. Co-PI Mishra co-organized a “Transmission Electron Microscopy” workshop at Washington University through the Institute of Materials Science and Engineering from Nov 6-10, 2017 (https://imse.wustl.edu/events/transmission-electron-microscopy-workshop). He also gave a talk on “Single-atom dynamics in scanning transmission electron microscopy” as part of the workshop. Mishra group will also be involving two Washington University undergraduate students to work during summer 2018.

Data Management and Open Access

The data for this study is available online on Nature website and have been stored on PIs computers and UIC Box. All experimental and theoretical modeling data will be preserved through data back systems at UIC and Washington University at St. Louis.

Advancing Along the Materials Development Continuum

One of the goals of the proposed research is to identify TMD alloys with improved catalytic activity and stability. Rather than taking a trial-and-error based approach of identifying promising alloys, we are using first-principles DFT calculations to discover miscible single-phase TMD alloys. Concurrently, we are carrying out a systematic joint experimental and theoretical study to evaluate the ORR activity of a series of TMDs and identify descriptors that can subsequently be applied to discover better alloys.

Publications

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Biologically-Interfaced Single Layer Devices

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Website: www.uwgemsec.com
Keywords: SAP-SLAM, solid-binding peptides, coherent bio/nano interfaces,

Project Scope:

The overarching goal of this project is to "biologically integrate interfaces with single layer devices". The goal is achieved by directing electronic, magnetic, optical, phononic and photonic transport and interaction properties *via* doping and signal transduction, by the controlled ordered structures of self-assembled peptide systems (SAP) on two-dimensional (2D) single layer atomic materials (SLAM). In this integrated and iterative experimental-computational project, we benefit from the opportunities provided by the combination of diverse recent developments of engineered solid binding peptides that can form organized molecular networks, and advances in single layer materials with simple structures and rich electronics. The development of experimental test-beds form the foundational strategies in a wide range of highly potent and practical bionanodevices of the future.

Relevance to MGI:

The three task areas in the project integrate experiments, computations, and theory through the use of a closed, iterative feedback loop. Ten major phenomena are involved in the generation of SAP/SLAM devices: (i) Peptide conformation in water and folding on the solid surface; (ii) Binding to solid; (iii) Surface diffusion; (iv) Intermolecular interactions leading to self-assembly; (v) Long-range ordered nanostructures; (vi) Coherent interface formation leading to molecular recognition of single layer crystal by the peptide, (vii) Signal transduction across the bio/nano coherent interface, leading to the (viii) Change in the biochemical properties of the peptide, and (ix) The physical properties of the solid substrate, leading to (x) Rules for genetic design of bio-enabled solid state device function. In short, the hybrid systems, that constitute self-assembling peptides and 2D atomic solids, in Task-1 (Overney & Sarikaya), are constructed by integrating the carefully designed experiments with hierarchical computational modeling, in Task-2 (Daggett & Ustundag), to predict the best outcome, carried out by iterative test-bed measurements based on new physics, in Task-3 (Xu, Overney, Ustundag, & Sarikaya), with a feed-back loop. The generic devices, e.g., transistors, integrated sensors, and capacitors, are aimed to have predictable behavior, and experimentally tested *via* carefully designed measurements. The interactive and iterative nature of the project in experimental results lead to the definition of the modeling approaches enhancing the project outcomes through the predictive design of relevant peptide sequences that are likely to develop coherent interfaces allowing test-bed measurements with the appropriate SAP/SLAM system. These will then lead to new devices, including e.g., graphene FET, PL measurements, and hybrid devices accelerating, e.g., the design of bionanosensors for early cancer detection , biomolecular fuel cells, and for biomimetic PVs, to name a few.

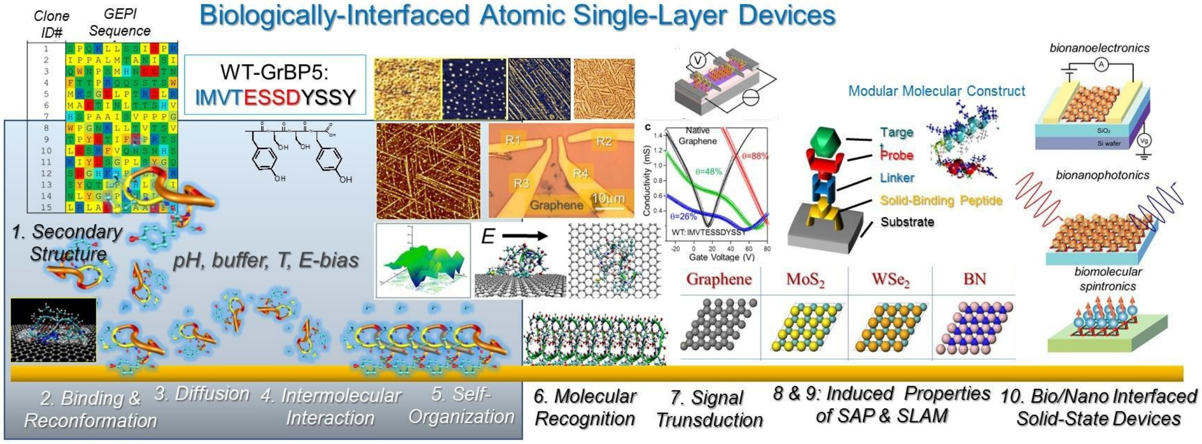

Fig. 1: A schematics showing the ten different iterative steps involved in the project.

Technical Progress

The progress has been in all 3 tasks (Fig.2). Following its tradition of having the most abundant and well characterized solid-binding peptides (GEPI) in the literature, GEMSEC lab under MGI project so far genetically selected ~100 new peptides for MoS_2 and created 30+ new mutants for graphene based on GrBP5 (one of 80 experimental), a dodecapeptide known to self-assemble on graphene forming molecular nanowires (Fig.2a,b). *Via* bioinformatics, the team has developed a new algorithm for creating similarity matrices to *de novo* design peptides with predictable behavior. Using MD, MC and MD approaches, refolding and docking behavior of peptides on solid surfaces under variety of (bio)chemical and electromagnetic fields are underway (2c). Test-bed devices, e.g., graphene FET and PL, have been developed (2d).

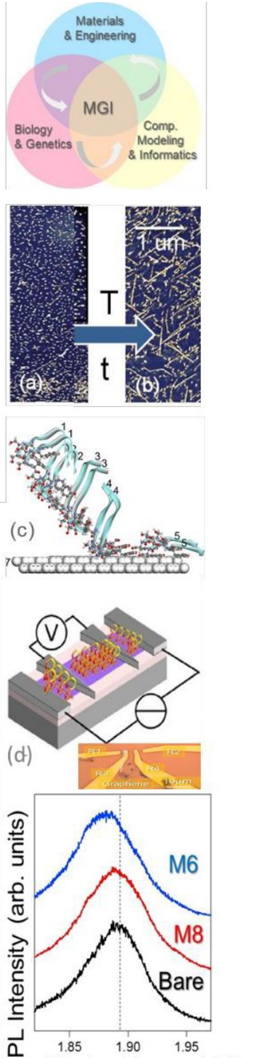

Figure 2

Future Plans

In Task-I, the progress includes selecting peptides for $MoSe_2$ and for BN, a semiconductor and an insulator, respectively. Standardized binding, surface diffusion, physical characteristics tests as well as self-assembly studies under a variety of physical and chemical conditions will continue for generating the quality data essential for the machine learning software developed in the labs. For this, both atomic/molecular scale imaging and local spectroscopy techniques are adapted for big data collection and analytics. DFT algorithms as well as other approaches, e.g., charge-patch, are developed in Task-II for foundational physical and electronic structures of coherent bio/nano interfaces. In Task-III, test-bed measurements are extended to cryogenic measurements and in different hybrid materials and test platforms. These iterative studies are all designed for producing big data to feed into ML/AI algorithms that will form the foundation of predictably designed, biologically-enabled future solid-state devices.

Broader Impact

BI is being implemented in 5 different areas: (i) Recruiting UG research (15) and grad students who are normally NOT associated with MSE (6), i.e., CSE, informatics, neuroscience; (ii) GEMSEC Lab-Organized (via MGI) Materials Summer (day) Camp (1 week each) for Middle School & High School students; (iii) *Science-Tuesdays*, monthly science café at Bulldog News (top news-stand in Seattle); (iv) One patent filing, two provisionas, one start-up Co.; (iv) Interactions with industry in big data, data analytics, data streaming, ML and AI (incl., Microsoft, Real Networks, AI2, and Amazon).

Data Management and Open Access

Raw data are initially being stored internally; vetted, analyzed, validated, and metadata will be available in publications, thesis and dissertations at UW Libraries and at GEMSEC web site (www.uwgensec.com). Links to existing codes and data analytics architectures can also be found at the same website; new codes and all relevant experimental parameters, tool schematics, etc. will be made available as soon as feasible, after vetted for IP purposes, which includes computational codes, AI and ML algorithms, and visualization protocols.

Advancing Along Materials Development Continuum

The MGI project, by its nature, is accelerating research leading to materials discovery not only by providing difficult to achieve strategic lessons for designing complex bio/nano hybrid interface for future devices (the team's ultimate goal), but also providing new experimental and computational tools which are accelerating the everyday materials research. For example, the lab traditionally used FFT to evaluate images for LRO, semi-ordered or amorphous organization of peptides on surfaces. The lab is now using wavelet transform, making it possible to evaluate quantitatively the pattern formation in ordered or disordered structures of any or all cases identifying the underlying physical phenomena to the biochemical mechanisms. The team is working closely with Comotion, UW's commercialization center and has formed partnerships with centers and groups at UW (e.g., eScience Inst) and is working closely with local industry to develop its first product in data streaming.

Publications (partial list): *Sci. Rep* (2016), doi:10.1038/srep33778; *Langmuir* (2018)DOI: 10.1021/acs.langmuir.7b02231; *ACS Biomater*., (2018), dx.doi.org/10.1021/acsbiomaterials.7b00959.

DMREF: Collaborative Research: An integrated multiscale modeling and experimental approach to design fouling-resistant membranes

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Keywords: Water purification, membranes, molecular dynamics, computational fluid dynamics, multiscale

Project Scope

The main goal of this project is to develop the multiscale mathematical framework to predict fouling behavior on the surfaces of membranes with different geometric patterns and chemical coatings. It is well understood that reduction in membrane permeability due to fouling is one of the largest costs associated with membrane processes in water treatment. The fouling propensity of a membrane depends greatly on its surface properties such as chemistry and roughness. The discovery that sub-micron patterning of a membrane surface can improve its fouling resistance provides an orthogonal membrane design parameter. Our research hypotheses are that (i) certain combinations of geometric patterns and chemical coatings will significantly reduce membrane fouling and (ii) experimentally-trained multiscale computational models will accelerate the discovery of novel chemical and topological surface modifications.

Relevance to MGI

The grand vision of this project aligns with the MGI: we will use a collaborative experimental and modeling approach to accelerate the development of advanced membranes to address the societal need for clean water produced with low energy input. Investigations will examine the roles of pattern geometry and feature sizes, surface chemistry, foulant type, and operating conditions on membrane fouling. We combine the expertise of four co-PIs: Husson group -- experimentally generating patterned membranes and performing chemical modification of these membranes; Ladner group -- two-dimensional models of patterned membranes using COMSOL to perform computational fluid dynamics (CFD) simulations, Sarupria group -- molecular modeling of membranes and foulant interactions and Battiato group -- analytical and corresponding numerical tools to relate macroscopic membrane fouling performance to microstructure properties, as well as operating conditions. Our collective expertise we enable us to build a multiscale framework to predict membrane fouling behavior. Collectively, our joint effort has led to identifying appropriate systems to study and development of frameworks that enable information transfer across the different scales. The modeling tools we develop will enable us and other U.S. institutions, businesses, and organizations to reduce the time and resources needed to bring new membrane materials to market. While we anticipate the discovery of several novel membrane designs during this project, the broader impact will be the development of the underpinning modeling tools that will enable future innovations, far beyond the test matrix studied here.

Technical Progress

(1) Factors that contribute to differences in patterning of thin-film composite membranes.
- Variations in patternability among TFC membranes with the same support material and active layer chemistry appear to be a result of differences in humectant/concentration used by the manufacturers.
- Replacing the original humectant(s) with a standard humectant results in uniform patternability within a TFC class (i.e, membranes having the same active layer and support chemistries).
- Membrane properties such as surface Young's modulus, polyamide layer thickness, polyamide crosslinking density, surface roughness, surface free energy, and permeance/salt rejection do not correlate to patternability (i.e., peak height).

(2) Effects of colloidal particle surface chemistry on membrane fouling.

- Threshold flux measurements on patterned and pristine membranes using different crossflow velocities revealed that hydrodynamics at the membrane surface plays an important role on controlling colloidal fouling.
- Foulant chemistry plays a role on the threshold flux at low crossflow velocity.
- The role that patterning plays on fouling by colloidal nanoparticles unexpectedly appears to depend on particle chemistry.

(3) CFD models to evaluate fluid flow profiles in the space above the membrane with different surface features.

- CFD models were built to simulate membranes patterned in the lab with a silicone stamp and to evaluate fluid flow profiles in the space above the membrane with different surface features. The surface features varied in size from 5 to 120 µm with a pattern depth of roughly 2 µm with surface features features including lines, circles, rectangles, triangles and some irregular shapes.
- Velocity profiles have shown that the surface features alter the fluid path, resulting in a lower velocity in between features, but a faster velocity on the elevated regions. Local turbulence and shear stress are generated, however, in almost all of the geometries evaluated (so far) the patterns lead to increased concentration polarization. (Concentration polarization is a buildup of salt near the membrane surface but does not include adsorption).
- Concentration polarization is mitigated only when the patterns are large enough that the fluid flow feels a constriction between the pattern and the opposite wall. This is an important insight because it leads us to believe that hydrodynamic scouring of the membrane is not what produces the fouling mitigation seen in experiments. Scouring could be important and useful, but only with large (~mm scale) surface features.

(4) CFD simulations to evaluate the foulant adsorption behavior of membranes with geometric patterns.

- Langmuir adsorption model was used directly, then was modified to add a shear term whereby higher shear led to faster desorption. Including the shear term made the results more realistic.
- The adsorptive fouling process was simulated for both flat and sinusoidal membrane surfaces with five different heights. Sinusoidal membranes with taller pattern heights tended to show lower flux decline. Membranes with random roughness had worse flux decline than sinusoidal and flat, suggesting that a regular membrane pattern can mitigate the effects of fouling. Exact geometry was less important than the repetitive undulating nature of the patterns.
- With a combination of image processing tools and CFD methods, the Stanford group was able to accurately reproduce the spatial fouling patterns experimentally measured at Clemson (Ladner) on channels of various sinusoidal shapes and for different operating conditions.
- To the best of our knowledge, this is the first code able to capture the spatio-temporal evolution of foulant, as well as system-scale quantities (e.g. permeate flux and global pressure drop) while accounting for full coupling between hydrodynamics, solute transport and concentration polarization effects, and foulant deposition and membrane clogging.
- Local modification of the flow streamlines has a great impact on foulant deposition: specifically streamlines convergence in proximity of the membrane (i.e. high local shear) decreases fouling.

(5) Performing molecular simulations to study foulant-membrane interactions.

- We are developing the code to generate the molecular structure of polyamide membranes which are consistent with the membranes used in the accompanying experimental studies.
- We are following the strategy developed by Kolev and Freger. In this methodology, the process begins with simulations of TMC and MPD monomers and TMC-MPD dimers. The monomers were allowed to react with only the growing clusters. After the reactions were identified, the steric constraints were relaxed through a series of energy minimization and short constant volume and temperature simulations. This process is designed to mimic the polymerization process. Further ad hoc criteria are included to enhance the reaction rate when it drops below a certain value due to decreased “diffusion” of the monomers into the growing clusters due to dense cross-linking.
- The practical implementation of this algorithm while syncing it with the simulation software used for our MD simulations is non-trivial. We have developed an extensive code in Python integrated with SQLite to enable an automated process to perform this entire cycle of – reaction, minimization, short NVT simulation, and repeat.

Future Plans

Husson group will continue to study the different patterned membranes and foulants (starting to study Generation 3 as per our proposal). Ladner and Battiato group will work to enhance their models especially through incorporation of surface reactivity. This will be done through phenomenological models and also through integration with molecular dynamics simulations. Sarupria group will quantify the binding of foulant and membrane to feed into the CFD models. We will continue to work collaboratively to validate our predictions at various scales with experiments and for consistency amongst each other.

Broader impact (Only required for NSF projects)

The project has brought together four different research groups and provided an excellent multidisciplinary environment for education and training. The research project has provided training to 6 graduate students at Clemson University and a postdoc at Stanford. This project has also led to communication between faculty in Environmental engineering with Chemical engineering in developing module-based course on teaching computational fluid dynamics to multiple engineering disciplines. Further outreach efforts are directed towards educating undergraduate and high school students about membrane-based water purification and separation technologies. The project outcomes have been communicated through conference presentations and publications.

Membranes are used in many applications such as seawater desalination, wastewater treatment, and water reuse. Membrane fouling in these applications causes a transient flux decline or pressure increase and a decrease in salt rejection. Fouled membranes require chemical cleaning, which shortens the membrane life and greatly increases membrane operating cost. When membrane fouling occurs, the price of water and sewage could go up as a result of chemical cleaning and pumping costs to maintain constant flux operation. Reduction of fouling with our innovative strategy could have substantial broader impact by improving process efficiency.

Data Management and Open Access

The codes developed will be shared once they have been validated and are ready for release through Github repository.

Advancing Along the Materials Development Continuum

We use a collaborative experimental and modeling approach to accelerate the development of advanced membranes to address the societal need for clean water produced with low energy input. The membrane design space – i.e., the number of chemical modifications possible and the variety of surface patterns possible – makes it unrealistic to scan the available options experimentally and discover the specific modifications that would result in the most effective antifouling properties. This renders computationally-aided design imperative. Our work will be transformational because it will deliver a computational framework that enables rapid screening of many modifications to short-list the most promising ones for further experimental testing. This approach will enable us and other U.S. institutions, businesses, and organizations to reduce the time and resources needed to bring new membrane materials to market.

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None

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Chemical Catalysis for Bioenergy Consortium (ChemCatBio): A DOE Energy Efficiency and Renewable Energy Energy Materials Network Consortium

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Website: https://www.chemcatbio.org/
Keywords: bioenergy, biofuels, bioproducts, thermochemical conversion, biomass

Project Scope

The Chemical Catalysis for Bioenergy Consortium (ChemCatBio) leverages unique U.S. Department of Energy (DOE) national lab capabilities to address technical risks associated with accelerating the development of catalysts and related technologies for the commercialization of biomass-derived fuels and chemicals, leading to enhanced energy security and national leadership in the global bioeconomy. The U.S. presently produces about 15 billion gallons corn ethanol added to gasoline, and about 2 billion gallons soy biodiesel added to diesel fuel. The Billion Ton Bioeconomy would sustainably produce approximately 35 more billion gallons biofuels, from lignocellulosic, non-food sources including agricultural residues, energy crops, waste resources, and forestry resources. ChemCatBio is a research and development consortium dedicated to identifying and overcoming catalysis challenges for biomass conversion processes.

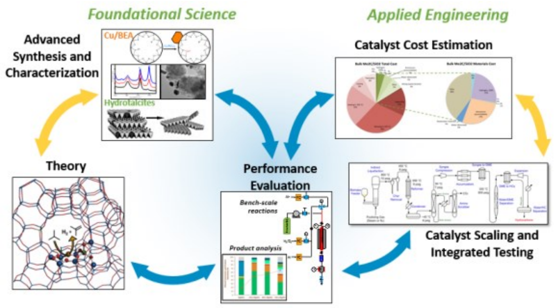

Figure. ChemCatBio aims to establish an integrated and collaborative portfolio of catalytic technologies and enabling capabilities

ChemCatBio brings together multiple DOE labs along with industrial partners to rapidly transition R&D discoveries into commercial processes and grow the bioeconomy in the United States. The consortium provides access to more than 50 unique, world-class capabilities and expertise in materials theory & computation, synthesis, characterization & analysis to accelerate the development of new biofuel catalysts, and has published 84 peer-reviewed manuscripts in the last 2 years.

Relevance to MGI

To address challenges related to biomass conversion, ChemCatBio utilizes a consortia approach which allows national lab, industry, and university stakeholders to rapidly exchange information and utilize national lab capabilities. Current research encompasses the following three core topics: 1) upgrading of synthesis gas and synthesis gas-derived intermediates; 2) hydroprocessing of fast pyrolysis and catalytic fast pyrolysis bio-oils; and 3) upgrading of lignin, carbohydrates, and other biologically derived intermediates. The consortium also pursues work in three enabling areas: 1) advanced characterization and synthesis; 2) development of a catalyst cost estimation tool; and 3) computational physics and chemistry.

Technical Progress

Since its inception in 2016, ChemCatBio has contributed to breakthroughs in process efficiency and catalyst design that have led to a decreased modeled cost for hydrocarbon drop-in fuels. Some sample accomplishments across ChemCatBio are:

- *Reduction of modeled fuel production costs:* Researchers in the core areas identified above have reduced modeled costs from 2015 levels by >$1/gal for pathways through syngas derived intermediates and by $0.85/gal for pathways utilizing catalytic fast pyrolysis.[1,2]
- *Improvements to catalyst lifetime:* Computational modeling capabilities have led to a better understanding of reaction mechanisms and increased catalyst stability.[3]
- *Increased product yields:* Research on ethanol upgrading has led to the development of an ethanol-to-butadiene catalyst with 70% yield (patent pending), and development of an ethanol-to-BTX catalyst that doubles the BTX yield compared to H-ZSM-5.[4]
- *Identification of novel catalysts:* Researchers focusing on catalytically upgrading intermediates from biochemical deconstruction processes have identified a Ru-Sn bimetallic catalyst that achieved 71% yield to 1,4-butanediol.[5]

Future Plans

Moving forward, ChemCatBio plans to pursue research related to increasing catalyst selectivity, extending catalyst lifetime, and maximizing carbon yields in the core topic areas identified above. The consortium also plans to expand work to address additional challenges previously identified by stakeholders subject to available appropriations.

Data Management and Open Access

ChemCatBio is building a Data Hub to provide centralized data/model storage capability for various ChemCatBio generated information in three different categories: 1) Codes/models; 2) Experimental/simulated data; and 3) Journal publications/presentations. The ChemCatBio Data Hub (https://datahub.chemcatbio.org/) will utilize a flexible security system to accommodate access and use by different classes of projects and data. The Data Hub will provide keyword-based searching capability and publish curated metadata to commercial search engines as well as access from data science and discovery organizations. This approach will allow users to employ a variety of ad-hoc and pre-defined queries to search for related data. The ChemCatBio Data Hub will also provide virtual linkages to other relevant materials databases, to enable data leveraging and data sharing.

Advancing Along the Materials Development Continuum

To rapidly develop and improve novel catalytic processes related to biomass conversion, ChemCatBio draws on a diverse knowledge base from across the DOE national lab system. Utilizing the MGI consortium approach allows for efficient collaboration between multiple lab partners which increases the likelihood for significant breakthroughs. ChemCatBio also provides a structure for outside stakeholders to access national lab research and advance the state of the art. In late 2017, ChemCatBio initiated nine projects that allow specific industrial partners to access national lab capabilities. These projects allow industry to address challenges related to catalyst characterization, synthesis, performance evaluation, and technoeconomic analysis through partnerships with experts at the national labs.

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Publications

See https://www.chemcatbio.org/publications.html for an indexed list of publications by ChemCatBio PIs.

High-Throughput Simulations and Experiments to Develop Metallic Glasses

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Website: http://www.materialsatlasproject.org/, http://aflow.org/

Keywords: Metallic glasses; nanocalorimetry; high-throughput; data-mining; AFLOW.

Project Scope

This project aims to develop new bulk metallic glasses (BMGs) by combining calculated materials data from the AFLOW repository with combinatorial materials synthesis and characterization. A new physical mechanism is proposed for glass formation, based on the thermodynamic competition between ordered phases. Advanced experimental techniques are being developed and tailored to rapidly determine the glass forming ability (GFA) of compositions identified by automatically screening the AFLOW database. This project is yielding improved understanding of the physics underlying glass formation, generating publically available theoretical and experimental data, and leading to the development of novel BMGs.

Relevance to MGI

The development of new bulk metallic glasses is hindered by the time and resources required to investigate all possible alloy compositions. This project integrates the physical insight that the thermodynamic competition between ordered phases promotes glass formation, with the pre-existing AFLOW computational data resources and experimental testing and results, to formulate new theoretical models to predict novel glass forming compositions for synthesis. Experimental testing is used to validate and refine the model. This approach creates a synergy between theory, computation and experiment to expand the understanding of the physical mechanisms that underpin the synthesizability of BMGs, accelerating the process of materials discovery.

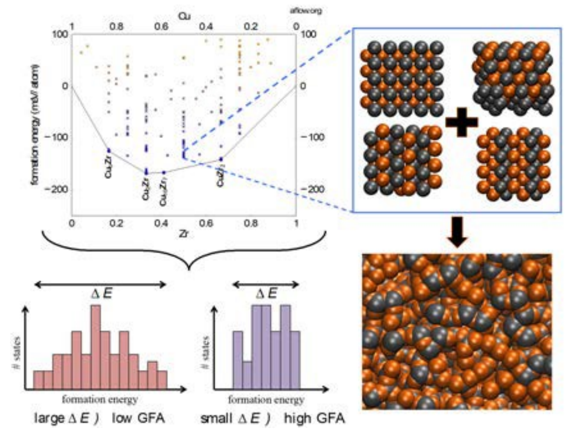

Figure. Metallic glass formation is predicted based on the thermodynamic competition between ordered phases frustrating crystallization and promoting glass formation.

Combinatorial co-sputtering provides a valuable tool for studying a wide range of compositions in a single experiment, validating the predictions and providing feedback to improve the theoretical methods. In order to properly characterize the produced samples, nanocalorimetry techniques are being used, providing data on their thermophysical properties. This data is essential in assessing the technological impact of and the potential industrial interest in these novel BMGs. The most promising

BMGs will be tested for mass production and developed into industrial products.

Technical Progress

The new physical model for glass formation developed in this project is based on the concept that if there are a large number of ordered phases that are very similar to each other in energy, but very different from each other structurally, they will compete against each other during solidification, frustrating the crystallization process and thus promoting glass formation. This model is implemented within the AFLOW framework, and has been applied to the calculated structures in the AFLOW database. The energetic similarity of the different phases is determined from their Boltzmann distribution, while the structural dissimilarity is quantified by comparing their atomic environments. Experimental data, both extracted from the literature and newly generated as part of this project, is used to calibrate and validate the model, and it successfully predicts 73% of the glass forming compositions for a set of 16 experimentally well-characterized systems. The model also predicts that over 17% of the 1400 binary alloy systems in the AFLOW repository should be capable of glass formation.

A major bottleneck in the discovery of new BMGs is the laborious process of analyzing X-ray diffraction measurements to determine whether a particular sample is crystalline or amorphous. The lack of consistent and complete experimental data also hinders the development and validation of theoretical models for glass formation. Therefore, work is underway to develop automated data analysis tools using machine-learning approaches to classify spectra as crystalline or amorphous. These tools will be made available through the AFLOW-ML API. Work is also underway to develop new, high-throughput approaches based on electrical resistivity measurements to characterize the structure of synthesized alloy samples and determine if they form glasses.

Future Plans

The glass formation model implemented in AFLOW is currently being extended and applied to investigate ternary alloy systems. The AFLOW repository contains calculated data for over 30,000 ternary alloy systems, with of the order of 1.4 million ternary entries. Comparison with experimental data indicates that additional effects need to be taken into account as the number of elemental components in the material is increased, particularly the competition between ordered phases with different stoichiometries. Once the model has been fully generalized and validated, it will be incorporated into the main branch of the AFLOW framework for distribution. Work is also underway to leverage machine-learning methods to enhance our glass formation descriptors.

Broader impact (Only required for NSF projects)

This project has been supporting two postdocs and two graduate students across the three different teams, providing them with extensive training in experimental and computational materials science techniques. This process is also leading to the development and/or refinement of computational and experimental tools, which may have broader impact in other projects. Most of the data produced in this project is being made freely available in the AFLOW and Materials Atlas Project databases. Codes written to make the theoretical predictions are being incorporated into the AFLOW framework. Ultimately, we aim on producing novel BMGs with promising properties, which can become available to the broader society for aerospace, biomedical, and other commercial and industrial applications.

Data Management and Open Access

All calculated AFLOW data is freely available online at http://www.aflow.org/, and is retrievable via the AFLOW REST-API and the AFLUX Search-API. The glass formation model is currently being generalized work reliably for multi-component systems, and is being prepared for incorporation into the main branch of the AFLOW framework, the source code of which is now freely available under the GNU license at http://materials.duke.edu/AFLOW/. Machine-learning models, such as those developed to analyze x-ray diffraction spectra, are being made available through the AFLOW-ML API, and models trained on AFLOW data are also available at http://www.aflow.org/aflow-ml/. Experimental data is available at http://www.materialsatlasproject.org/.

Advancing Along the Materials Development Continuum

One of the main limitations to the commercial viability of BMGs is the production cost due to very expensive constituents. The discovery of BMGs based on cheap materials, such as aluminum, would greatly increase the number of viable commercial applications. The new GFA model introduced in this project is enabling high-throughput computational screening, which will facilitate the rapid identification of new glass forming compositions without the need for expensive, time-consuming trial and error synthesis experiments. The new high-throughput synthesis and characterization techniques will facilitate the validation of the computational predictions, leading to the accelerated discovery of novel, cheap, technologically promising BMGs.

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Improving the Accuracy of Electrochemical Capacitance and Solvation Energetics in First-Principles Calculations

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Keywords: electrochemistry, continuum solvation, capacitance, *ab initio* electronic structure.

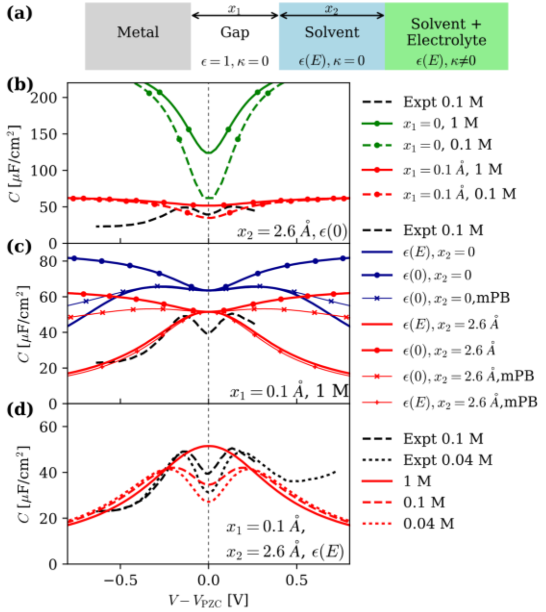
Project Scope

This project aims to develop and benchmark continuum models of the electrochemical double-layer. We implement the most promising models as continuum solvation models for *ab initio* calculations, available in our open-source and freely accessible software package, JDFTx. These models are then applied to probe adsorption and chemical reactions on aqueous, electrified surfaces.

Success for the continuum solvation model development is a single solvation model that both has an MAE (mean absolute error) of solvation free energy below 2 kcal/mol (using a large molecular and ionic benchmark dataset), and also captures the correct features and magnitude of the capacitance of Ag(100).

Relevance to MGI

The project integrates benchmarking against experiment, model development, and computation to develop improved solvation models. While this project does not support an experimental component, the experimental inputs include a large benchmark dataset of solvation free energies of neutral molecules, anions, and cations, and also the capacitance of Ag(100) as a function of electrolyte concentration. Other experimental data provided by our collaborators have included the capacitance of Pt-CO and the potential of hydrogen deposition on Pt step-edges.



Figure[4]: Experimental capacitance of Ag(100)[1] compared against the toy model shown in (a). (b) Effect of x_1 on model capacitance for a linear dielectric ε(0), where x_1= 0 is GCS[2] theory. (c) Effect of x_2 and nonlinearity (ε(E)) on model capacitance; ion packing as described by the modified Poisson-Boltzmann (mPB) theory. (d) Electrolyte concentration dependence of the capacitance: nonlinear toy model with x_1 and x_2

Technical Progress

We have recently demonstrated[3] that the solvation models currently implemented in density functional theory (DFT) codes such as VASP perform poorly for computational electrocatalysis and cannot simultaneously correctly predict solvation energies of metal surfaces, ions, and molecules. We have found that parameterization of the solvation models can improve their accuracy in predicting the total charge with potential, but that the capacitance of these models is still fundamentally incorrect.

To better identify the properties of the solvation model needed to capture the capacitance features observed experimentally, we have developed a numerical toy model for the metal and electrolyte[4]. We have used this model to identify the necessary features of a continuum model that quantitatively correctly captures the double layer capacitance of an aqueous electrified metal surface. With this framework, we have demonstrated that none of the existing models simultaneously contain all of the necessary features, explaining their failure in capturing the capacitance correctly. We have now built a model which captures the correct features of the capacitance, but still has numerical challenges that must be addressed before we reach full success (Discussed in detail in Ref. 4.) These models are all available in our open source software, JDFTx[5,6].

Applying our understanding of the strengths and limitations of our solvation models, we have carefully applied them to study the capacitance of the Pt-CO system[7], and hydrogen adsorption on platinum step-edges[8], through collaborations with our experimental colleagues.

Future Plans

We plan to create a solvation model which builds on our most recent solvation model and addresses the remaining numerical challenges, through a hybrid solvation cavity which we proposed but have not yet created[4].

Data Management and Open Access

The software with the implemented models is available through our website, jdftx.org. The website also includes tutorials, a user's guide, and a developer's guide. Additional information is included in our publication in Elsevier's open access software journal, SoftwareX.

Advancing Along the Materials Development Continuum

As we develop new solvation models, we publish theory and implementation details so that they can be implemented in other codes. Additionally, the code itself is open-source and freely available to everyone, providing the research infrastructure for others to develop new models and apply our models to promote more rapid catalyst materials discovery. In the future, our models may also be implemented in commercial software packages.

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Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: Synergy of Electronic Structure Theory, Molecular Simulation, Machine Learning, and Experiment

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Keywords: Porous Materials • High-throughput screening • Electronic structure methods • Molecular simulation • Validation experiments

Project Summary

The Nanoporous Materials Genome Center (NMGC) will develop computational/theoretical chemistry methods and data-driven science approaches with the aims of (i) de-novo design of novel functional nanoporous materials, (ii) discovery and selection of the most promising functional nanoporous materials from databases of synthesized and hypothetical framework structures, and (iii) microscopic-level understanding of the fundamental interactions underlying the function of nanoporous materials. A pivotal part of the proposed work is a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups that allows for iterative feedback. This cooperative research effort may start either with computational modeling that prompts discovery of materials with optimal properties for subsequent synthesis or with experimental observations on specific nanoporous materials

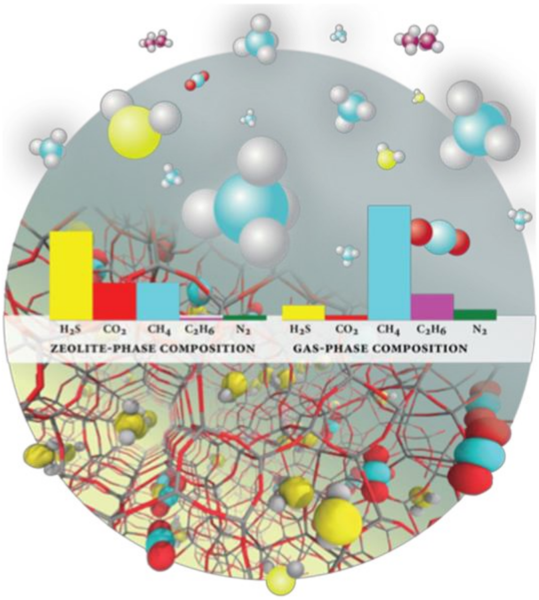

Figure. Illustration of an adsorption-based process for the removal of H_2S and CO_2 from sour gas.

leading to detailed mechanistic questions, which then in turn lead to new computational or experimental efforts to drive the research to completion. Data management and computing will primarily use current petascale and future exascale capabilities at the Argonne Leadership Computing Facility, as well as NERSC.

Building upon prior NMGC research focused mostly on gas capture, separation and catalysis in crystalline nanoporous materials, the team will work on the development and application of a predictive hierarchical chemical modeling toolbox that can tackle increasingly complex chemical separations and transformations in complex nanoporous materials, including metal-organic frameworks, zeolites, and polymers with intrinsic microporosity. Research will be directed toward liquid-phase adsorption and catalysis in multi-component mixtures. The nanoporous materials will include hierarchical architectures, responsive frameworks that may undergo phase transitions or post-synthetic modifications, and may contain defects, partial disorder, interfaces or be a composite material. Tunable electronic properties of nanoporous materials, including luminescence and magnetic coupling and anisotropy, will be addressed Another major aspect of the proposed research is the development and application of data-driven science approaches that will lead to advances in machine learning for the discovery of optimally-performing materials, in genetic algorithms for the tailored design of nanoporous materials, and in computational methods to systematically identify and to characterize metal-organic frameworks and other nanoporous materials.

The team will also work on the development of data repositories for nanoporous materials that add value by providing structures optimized via electronic structure calculations, along with their energetics for solvent removal, pore characteristics, and their adsorption and transport properties. The collaborative NMGC activities will also contribute to the training of postdoctoral associates and graduate students with broad expertise in data-driven science approaches and computational chemistry methods, in addition to the skills to thrive in an integrated experimental and computational research environment.

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DMREF: Dynamic Control of 3-D Printed Hierarchical Soft Materials via Computation-Guided Molecular Design.

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Website: None.
Keywords: Bottlebrush polymers, molecular design, rheology, simulation coarse-graining, 3-D printing.

Project Scope

This project will establish the tools and fundamental science needed to develop process-directed, 3-D printed bottlebrush block copolymer materials. We target materials optimally suited for on-the-fly manipulation of nanoscale morphology, focusing on polymer functionality and bottlebrush architecture. To guide design at this molecular level, we are developing a screening infrastructure based on both coarse-grained simulation and bulk rheology, guiding the appropriate synthesis to achieve nanoscale structures controlled by 3-D printing processes. Our goal is to apply this infrastructure to rapidly optimize a candidate, proof-of-principle material capable of exhibiting on-the-fly 3-D manipulation of photonic properties.

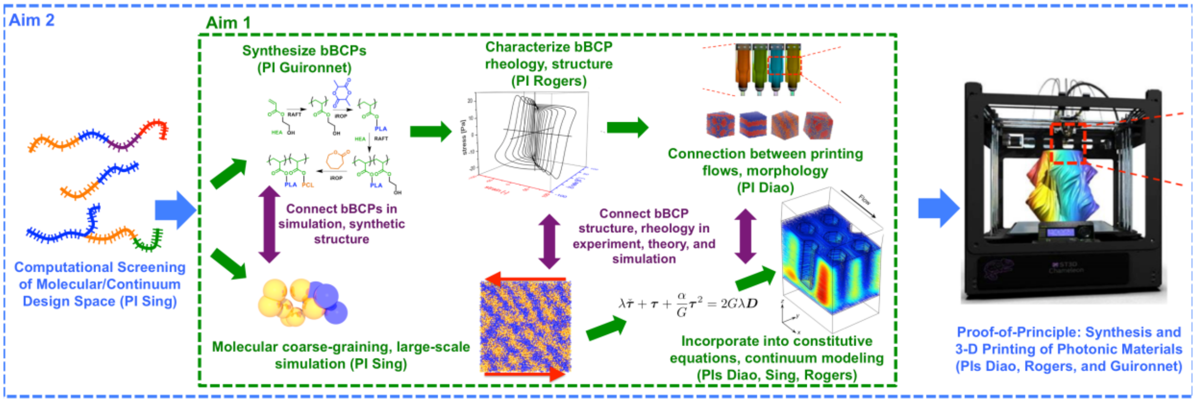
Relevance to MGI

We are structured into a highly coordinated team of researchers, suited to integrate experiment, computation, and theory in line with the goals of MGI. Our strategy is to combine versatile, synthetic polymer chemistry (Guironnet) with advanced rheological characterization (Rogers) and practical implementation of 3-D printing of the final material (Diao). This effort will be guided by multi-scale computation (Sing and Diao) that is capable of rapidly assessing materials over a vast molecular parameter space. Research interactions will arise at all levels: the molecular structures to be synthesized are directly rendered in simulation, and both synthesized polymers and molecular models can be compared to rheological data. Continuum simulations can use molecular simulation as input and predict flow and structures in 3-D printing processes. The parallel tracks of computation and synthesis/rheology/printing are synergistic, with simulation guiding the synthesis, and molecular characterization informing simulation parameterization. This approach will culminate in a procedure to use both simulation and rheology data to screen over a large parameter space, greatly accelerating an otherwise Edisonian search for polymer materials that self-assemble specifically and on-the-fly in 3-D printing processing flows.

Technical Progress

The first six months of the project have been focused on the initial establishment of parameterization between synthesis, computation, characterization, and printing. Sing has developed a coarse-grained model of dilute bottlebrush polymers that is directly influenced by the chemistry of homopolymer bottlebrushes synthesized by Guironnet. This model is capable of directly calculating the rheological properties (hydrodynamic radius and intrinsic viscosity) and structural properties (radius of gyration, sphericity) accessible to characterization from Rogers. A broad exploration of parameters such as backbone length and brush length has revealed a connection between synthesized bottlebrushes and a wormlike-cylinder model. An early version of the dissipative particle dynamics code, which will be used in melt simulations, has been developed. This has been in concert with the development of computational flow simulation from Diao, needed to determine realistic processing conditions.

Guironnet has developed new approaches to making bottlebrush block copolymers, synthesizing over 40 samples of bottlebrush homopolymers (PLA side chains with norbornene backbones) that have been characterized by light scattering, spectroscopy, and GPC. Rogers has been measuring the intrinsic viscosity of dilute solutions of dilute solutions of these bottlebrush homopolymers synthesized by Guironnet using Cannon-Fenske glass viscometers. Diao has begun to develop the morphological characterization necessary for investigating the critical processing-morphology-structure relationships.



Project Approach: We want to screen a molecular design space, using multiscale computation and rheology, to synthesize molecules tuned to exhibit 3D-printed structures with on-the-fly control over nano-scale structure.

Diao has developed a customized 3D printing platform capable of supporting on-the-fly variation of processing parameters for directed flow and morphology control. This includes design of a printhead capable of pneumatic extrusion of polymer in melt or solution phase over a wide range of accessible shear and extension rates. Custom control software has been written to allow synchronized motion and pressure control for precise spatial patterning of geometrically and optically complex structures. Guironnet has successfully synthesized initial bottlebrush block copolymers (PLA and PDMS side chains), which has been extruded through the 3D printing device developed by Diao.

Future Plans

Guironnet will continue to expand the palette of bottlebrush chemistries available to the team, addressing current limitations in dispersity at large molecular weights and elucidating new synthesis routes toward a variety of macromonomers (i.e. branch chemistries). In particular, there is a concern that we are observing bottlebrush 'dimers' in some synthetic schemes, due to the presence of two norbornene groups in the same macromonomer. Diao will test the versatility and performance of the 3D printing setup by printing rheologically both bottlebrush homopolymer analogs, as well as newly synthesized bottlebrush block copolymers. There are upcoming challenges in determining optimal printing temperatures, to avoid polymer degradation at elevated temperatures while still obtaining melt flow printability. The prospect for structural color in bottlebrush block copolymers will be evaluated.

Sing will study the systematic coarse-graining of bottlebrush models using single-bottlebrush simulations parameterized with experimental data. Initial efforts will focus on matching in dilute solution, to be followed by incorporation into melt simulations. Equilibrium and out-of-equilibrium mechanical properties will be compared to melt rheology from Rogers of molecules synthesized by Guironnet, first with bottlebrush homopolymers and then with block copolymer bottlebrushes. Included in this rheology scheme, will be novel recoverable strain techniques developed by Rogers to decouple and identify the relaxation and retardation spectrum, which can be directly tied to molecular simulations by Sing. Conditions similar to those found in the 3D printer, determined by Diao, will be directly probed.

Broader impact (Only required for NSF projects)

The DMREF team is committed to training the next generation of students to work in a collaborative team, where experiment and computation are integrated to accelerate materials design. We promote this MGI philosophy by coordinating biweekly meetings of the entire team, and our current initiative at this early stage is to promote an initial fluency with the breadth of research carried out by the team via biweekly 'review' talks. In the future, we will build on efforts by the Sing, Guironnet, and Diao labs in outreach activities such as the summer GAMES camp, where we design hands-on experiments that go hand-in-hand with computation. With the combined resources of the DMREF team, we envision growing this to encompass more thorough integration of this research effort. We are specifically planning on incorporating our focus on 3D printing, using both demos of real printing equipment along with hands-on simulations of polymer extrusion and molding.

Data Management and Open Access

At the early stage of this process, we have not addressed open access of our data. We are currently compiling all results in a shared *Box* folder, and this data will be made accessible concomitant with publications.

Advancing Along the Materials Development Continuum

This project seeks to leverage information from both experiment and simulation in a synergistic fashion. The cost and time associated with synthesis will be minimized by relying on computational exploration, which will still be closely tied to experimental characterization to continuously validate simulation tools. The key hurdles to commercial development, beyond the initial proof-of-principle that is a goal of this proposal, is the scalable synthesis of the bottlebrush polymers and development of easy-to-use software for the multiscale computation.

Publications

No publications at this time.

Theory-Enabled Development of 2D Metal Dichalcogenides as Active Elements of on-chip Silicon-Integrated Optical Communication

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Keywords: Transition metal dichalcogenides, phase transitions & control, growth, optoelectronic devices

Project Scope

This project explores the underlying phenomena, properties and manufacturability of 2-Dimensional (2D) layered materials. Theoretical investigations around bandgap, phase, stability, strain and doping control are explored (Reed). Synthesis methods include various forms of CVD and target the group of stabile transition metal Dichalcogenides (TMD) such as MoS_2, $MoSe_2$, $MoTe_2$, WSe_2, and WS_2 as well as several of their alloys. Here the aim is for growth control, homogeneity, photoluminescence (PL) quality, and integration- and manufacturability. Towards device fabrication the aim is to utilize 2D materials as active elements in integrated opto-electronic devices on-chip. These include PL enhancements using dimer and monomer antenna structures, waveguide-2D material co-integration, and nanocavities for enhanced light-matter-interaction (Fig. 1)

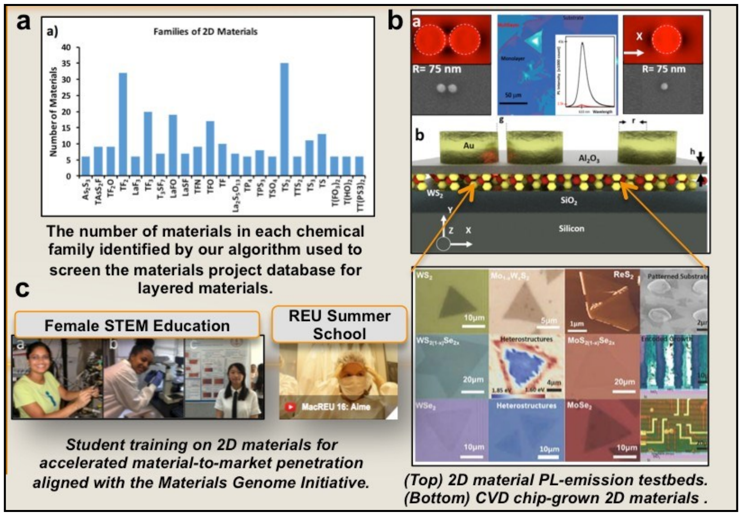

Figure 1. Project overview consisting of theoretical 2D material modeling (a), synthesis and device integration (b), and STEM education (c).

Relevance to MGI

The collaboration between the PI's was highly integrated. Throughout the entire project we held annual team meetings in person at Stanford University where students and PIs alike attended, discussed and shared their respective research. We shared and exchanged students across all campuses up to two weeks at a time. These close collaborations resulted in joint publications across 3 different topical fields and departments. This is actually somewhat uncommon, but signifies that the MGI-vision of vertically-integrated teaming to execute a joint project is indeed fruitful. The team produced multiple joint publications with scope spanning from theory to synthesis to device integration and characterization.

Technical Progress

We developed a database of over 1000 layered materials by data mining the Materials Project[i] database of 70,000 bulk materials that have been mostly either synthesized or mined. We discovered that there are approximately 100 materials that have either been mined or synthesized that are layered, but consist of more than one type of layer. These are essentially bulk 3D analogs to the vertical heterostructures that many researchers are attempting to create mechanically in the lab. We found that the PL emission enhancement of plasmon cavities depend critically on the relative position of the TMD WRT the field enhancement of the cavity. We further found that the often reported E-field field enhancement in the center of a bow-tie or dimer plasmon cavity in fact vanishes when the TMD is placed some in a quenching-save distance away from the cavity. We developed new CVD growth capabilities for directly growing 2D on-chip. We studied phases of 2D materials to in-situ control their properties. Computational screening of the ability of adsorbates to stabilize phases was conducted. Experimentally, we validated the growth of the 1T phase of MoTe2 in the presence of CO2 in the process gas highlighting the viability of the computationally predicted approach. Variation of the growth method allows the formation of hybrid films of mixed phases that exhibit susceptibility to gating and significantly increased conductivity. We demonstrated 2D material interactions with surface acoustic waves on-chip. We developed a new method to integrate CVD-grown TMDs with plasmonic cavities. We found that the TMD PL obtained from the sample is indeed an average of the relative E-field enhancement across not only the cavity's spatially different field enhancement, but more importantly a convolution between the Gaussian pump-profile, the cavity spatial resonances, and the TMD. We found that the exciton, trion, and bi-excitons contribute non-linearly to the PL with changing pump power of the TMD. We designed and deployed a TMD PL-testbed to benchmark a variety of TMD materials. We developed a novel 2D material transfer setup that improves both accurately and cross-contamination compared to all other transfer setups, allowing for on-demand printing of 2D Materials. We filed a patent on this invention with the USPTO. We predicted and then subsequently observed in the lab a new mechanism for structural phase changes using electrostatic gating in a 2D material with large optical contrast between phases. We were granted a US Patent on this technology. We taught a NUE summer course on hands-on nanotechnology using GWU's new clean room facilities.

Future Plans

Our proposed research objective is to identify, catalogue, categorize, synthesize, characterize and validate a broad range of van der Waals (vdW) layered materials as candidates for optical and photonic applications towards accelerating the time frame from material conception to application-near deployment. We will utilize advanced computation methods to screen hundreds of thousands of crystalline systems for the potential to form 2-dimensional (2D) materials including unexplored and yet unidentified material systems. Leveraging results from current funding, we will design and employ lithographically-prepared photonic testbeds for rapid screening and characterization of computationally-identified target materials. We will collaborate with LBL (Materials Project), NIST (Materials Genome Initiative - MGI) and the private sector (IBM, Omega Optics).

Broader impact

This project was able to integrate Hispanic students from an Hispanic Serving Institution (UC Riverside) with research efforts at Stanford and George Washington University. For instance, the first author of the ACS Nano publication on phase control in $MoTe_2$ growth, Thomas Empante, is a Hispanic first-generation individual and he was supported by Sepedeh Naghibi Alvillar, a Hispanic community college student, whose participations in this project allowed her to transfer to UCI this fall. Other Hispanic co-authors on that study were Velveth Klee (a community college faculty originating from the Bartels lab where she received DMR AGEP support), Michael Valentin, Edwin Preciado (an NSF GRFP fellow), Adam Berges (who received an Honorable Mentioning in the latest NSF GRFP competition), Cindy Merida, Michael Gomez, & Miguel Isarraraz (an NSF GRFP fellow). 6 of 13 non-PI co-authors are female and all but one US citizen. Reed's data-mining efforts are the fundament towards establishing an open source platform of 2D material datasets. Moreover the PI has disclosed two patents to the USPTO thus fuelling the venture creating and high-tech sector in the United States. Furthermore, the growth techniques developed by Bartels pave a way for large-scale TMD growth for the chemical industry and semiconductor sector. Co-PI Bartels is the director of an REU site that is based on thin-film growth projects just like this. Leveraging NSF funding from industrial sources, that site was able to support 35 students in Summer of 2017 alone, of whom ¼ worked in the PIs lab on various aspects of this DMREF project. More than 1/3 of the students originate from community colleges and more than ½ from underrepresented minorities.

Data Management and Open Access

We shared our findings from the layered materials databased in the supporting information section in the publication and via our group website (http://web.stanford.edu/group/evanreed/Cheon_NanoLett_2017_SI2.xlsx). These 1000 layered materials found by data mining the Materials Project database of 70,000 bulk materials focuses the community to engage in targeted future research efforts, thus enabling both time and funding to be utilized in a more efficient manner, such as already demonstrated by our team. Such public access allows everyone with an internet connection to access our results free of charge. Moving ahead, we have already started integrating our data mining algorithm into the publicly available and widely used Materials Project database. Here, we are interacting with the Materials Project team, including Kristin Persson at Berkeley to conduct the integration. We will add a data flag to the Materials Project database entries to enable users to search for low dimensional materials. Integration of this database of 2D materials into the Materials Project is perhaps the most useful way to distribute the information given the vast array of other tools available at the Materials Project and the large community of other researchers. The value of integrating into the Materials Project cannot be understated, as this will bring data regarding 2D materials to researchers outside of the 2D community, fertilizing new applications of 2D materials in other communities. Most users of the Materials Project database are a mix of industry and academia, and are engaged in a wide spectrum of activities from batteries to structural materials. We have shared our work in numerous publications, seminars, and conference presentations throughout the nation, and across the world. For the latter, we engaged with students, scholars, and industry and national lab researchers alike to accelerate disseminating our results and findings. Unique this this project and in the spirit to the MGI was that we shared our work outside our own regular field. For instance PI Sorger presented work in materials-related conference session, while he typically addresses the photonics or opto-electronic related community.

Accelerating Materials Discovery & Development

Our team has invested large efforts in integrating our data mining results describing over 1000 layered materials into public databases where they will be accessed and used by not only other 2D material researchers, but the broader materials community, as well, who may not be aware of the features of 2D materials. We expect the availability of the information in these databases to provide exposure for 2D materials in the battery, composites, structural materials communities and potentially others, including industrial researchers who commonly use these databases. This transfer of knowledge to other communities in a format that they are familiar with is an essential ingredient for accelerating the adoption of these materials in practical applications and will undoubtedly increase the development of these materials by a factor of 2 or more. This style of research has not historically been common, and is a unique feature of this MGI-funded project. Our database is already enabling new types of material searches that were previously impossible, via the machine learning approaches we have been using to identify new 2D materials. Such machine learning approaches are impossible without the availability of large databases provided by this MGI-themed project. These approaches are orders of magnitude faster than physics-based methods for predicting materials. It also helped us to recognize technological limitations and hence intellectual property opportunities, otherwise hidden from sight. We for instance submitted the patents mentioned above to the USPTO that used insights from all materials, chemistry and device-related demands concurrently. It goes without saying that patents help securing the national technological competitiveness.

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Developing design rules for enhancing mobility in conjugated polymers

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Website: none.
Keywords: Conjugated polymers, Polarons, Coherence, Microstructure.

Project Scope

Conjugated polymers are a promising family of materials for low-cost, solution-processed electronic devices. High-performance polymers have highly connected aggregates where carrier mobility is ultimately dictated by nanoscopic charge transport in the aggregates. In this project well-controlled model materials and novel donor-acceptor polymers are synthesized. A new theory allows us to determine carrier delocalization from the IR absorption spectrum of charges, which we link to the materials' microstructure. Ultimately, our goal is to determine what molecular structures give rise to best-performing materials.

Relevance to MGI

The iterative feedback loop between theory, characterization and synthesis is clearly operative in our work: An accurate theory which describes the lower energy regions (< 1000 cm-1) of the IR (or Charge Modulated) spectrum (Spano) inspired improvements in the experimental CMS measurements (Salleo). The initial spectral fitting (Spano) of different molecular weight polymers with varying degrees of doping inspired the synthesis (Luscombe) of additional molecular weight materials of varying regioregularity in order to confirm experimental trends and further refine and confirm theory. The very latest measurements (Salleo) on a class of conjugated co-polymers synthesized by Luscombe is providing insight into the next generation of modelling (Spano) which, in turn, will inspire modifications to the polymers and so on. Moreover, the possibility of deconvoluting in-chain and across-chain spectral components using theory (Spano) is the main driver behind the development of polarized CMS measurements (Salleo). Overall, the iterative loop is instrumental in helping us attain a better understanding of the role of disorder in polaron localization along and across polymer chains, information which is indispensable in acquiring a more complete theory for polaron conductivity in conjugated polymer films.

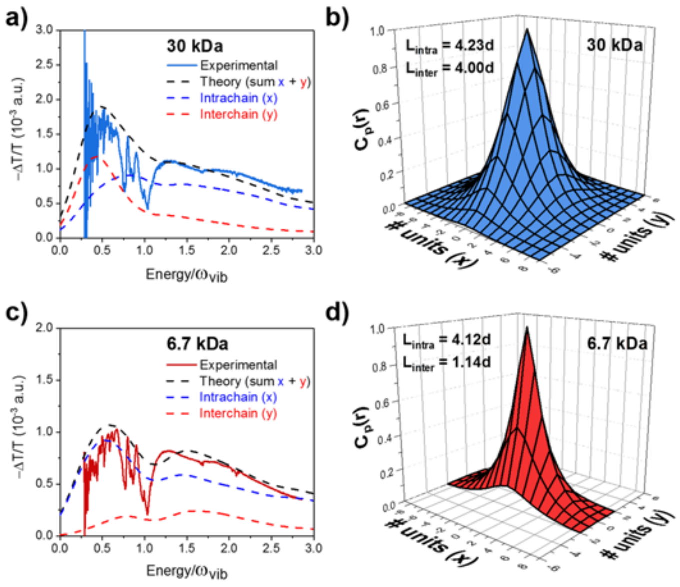

Figure. CMS spectrum of a high-Mw P3HT film (a) and polaron coherence function calculated from the spectrum (b) showing a delocalization on 4 chains and 4 monomers per chain. CMS spectrum of low-Mw P3HT (c) and its associated polaron coherence area (d) suggesting localization of the polaron on a single chain.

Technical Progress

Further computational modelling of positively charged polarons in polymer n-stacks based on the disordered Holstein Hamiltonian by the Spano group extends the size of the polymer assemblies amenable for analysis by a factor of three – to about 100 thiophene units. We have so far achieved excellent agreement with the measured mid-IR spectra obtained by Salleo's group using polymers synthesized *ad hoc* by the Luscombe group. The Salleo group is studying the deposition of 100% RR P3HT -as prepared by the Luscombe group - onto a bare silica surface vs. a surface coated with a self-assembled monolayer (SAM) of octadecyl-trichlorosilane (ODTS). These surface treatments are known to be instrumental for obtaining high mobilities in transistors. Knowing how they affect polaron delocalization in homopolymers is important in order to understand whether these treatments affect the polaron delocalization in donor-acceptor copolymers in a similar fashion. By combining CM spectroscopy measurements with theoretical simulations, the delocalization lengths of gate-induced polarons in these P3HT films were quantified: the presence of a SAM strongly increased the ability of polarons to delocalize across chains. We note that the changes in polymer order that will be studied here are on a scale that is difficult to be captured using other spectroscopies or scattering techniques.

The same combination of materials, IR spectroscopy and theory provided insights into the doping process. The mid-IR spectrum of sequentially-doped P3HT films reveals a broad peak centered at approximately 0.5 eV, independent of dopant concentration. Such films are about three times more conductive than films prepared by the more conventional solution-mixed films, motivating us to look more deeply into the IR line shape especially with regards to hints about polaron delocalization. The IR line shape is characteristic of a hole localized over approximately four thiophene units along a single chain, due mainly to the binding influence of the ionized dopant anion. Our analysis debunks the hypothesis that sequential doping - which preferentially occurs in the amorphous regions of the polymer film - causes hole migration back into the crystalline domains.

Experimental CM studies of DPP-based donor-acceptor copolymers revealed a significant increase in polaron absorption and more clearly resolved peaks for shear-coated samples as compared to spin-coated ones. Our results show that the DPP with the more planar aryl group and reduced torsion due to the shorter alkyl chain is able to form a more ordered morphology, enabling greater delocalization of charges. A new series of donor-acceptor copolymers PIDTBPD, PIDTTPD, and PIDTBTD has been synthesized. PIDTBPD has been characterized in greater detail indicating that this is a disordered polymer and yet possessed a moderate charge carrier mobility of $2 . 10^{-3}$ $cm^2 V^{-1} s^{-1}$. The amorphous nature of the polymer led to beneficial properties for stretchable organic electronics.

Future Plans

We plan on expanding our studies to polarized CMS of aligned films to disentangle experimentally interchain vs. intrachain components. These will be the first mid-IR polarized CMS measurements. Furthermore, we will expand our studies of donor-acceptor copolymers in order to understand the role of segregated vs. mixed donor/acceptor stacks.

Broader impact (Only required for NSF projects)

Thus far a graduate student in the Spano group has been developing Fortran code for analysis of the disordered Holstein Hamiltonian and vectorizing the code to take advantage of the high performance computing cluster (HPCC) at Temple University's College of Science. A graduate student in the Salleo group has developed reproducible protocols for CMS measurements and is developing polarized measurements. A graduate student in the Luscombe group has gained experience in performing air and water sensitive reactions to synthesize semiconducting polymers, and is developing equipment to create aligned polymer films. Once design rules for high mobility conjugated polymers have been identified, they will assist the materials engineering community in the fabrication of the next generation of plastic electronic devices such as solar cells, field effect transistors and light emitting diodes. Initial investigations (Luscombe) into the amorphous nature of the donor-acceptor copolymer PIDTBPD arising from its twisted backbone conformation has uncovered promising mechanical properties for stretchable organic electronics opening new avenues for applications. Overall, the regular meetings and constant communication between the groups has ensured that every participant has a good understanding of all the parts of the project.

The MGI philosophy of the project and the tight loop between theory, characterization and synthesis has been emphasized by PIs in conference presentations.

Data Management and Open Access

All data is stored locally in the PI's universities and periodically backed up through automated services. All data is currently available upon personal request to the PIs, whether it's computer code output, raw spectral data or materials synthesis/characterization data. An efficient computer algorithm which evaluates polaron properties, and in particular, the IR spectrum, for a variety of disordered Holstein Hamiltonians, is in the process of being made generally available. We are in the process of uploading information about our computational code to GitHub, a web-based version control repository. We plan to include not only the fortran source code for evaluating the IR spectrum and coherence function for holes in conjugated polymer lattices but also related material concerning the code vectorization and general information about how the code is organized.

Advancing Along the Materials Development Continuum

Our initial work on D-A copolymers has the potential to establish structure-property relationships between molecular structure and charge delocalization, which we now have identified as a crucial aspect for achieving high mobility. The molecular structure parameter space is virtually endless therefore being able to take advantage of systematic design rules drastically reduces such space and accelerates materials discovery. A promising molecule is the first step towards commercialization, further hurdles are scale-up, purification and synthesis yield.

Publications

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DMREF/GOALI: Novel 3D Experiments, Simulations, and Optimization for Accelerated Design of Metallic Foams

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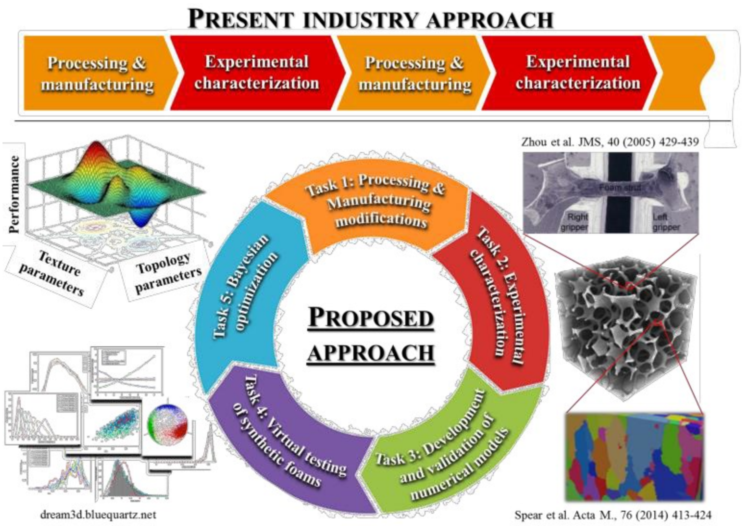
Website: none

Keywords: X-ray diffraction, tomography, crystal-plasticity modeling, Bayesian optimization, cellular metal

Project Scope

The goal of this research is to enable accelerated and performance-based design of open-cell aluminum foams manufactured by investment casting. Specific research objectives are to: 1) manufacture foam variants; 2) perform synchrotron-based measurements and in-situ mechanical tests to characterize 3D structure and deformation mechanisms of the foams; 3) use high-fidelity, multi-scale modeling to predict performance of the as-manufactured foams; 4) conduct virtual tests on synthetic-foam variants to further populate the design space; and 5) use Bayesian optimization to tailor the foam based on specific performance metrics. These tasks are carried out iteratively with our industrial partner. Success will be measured based on the ability of the optimization algorithm to predict performance of physically realized foams.



Zhou et al. JMS, 40 (2005) 429-439

dream3d.bluequartz.net

Spear et al. Acta M., 76 (2014) 413-424

Figure 1. A comparison between the current industry approach for manufacturing open-cell foams and the MGI-inspired approach described here. The five tasks are described at left.

Relevance to MGI

In line with the MGI Strategic Plan, the research tasks underway in this project form a closed, iterative feedback loop, as shown in Figure 1 above. The iterative nature of the work is made possible through a close collaboration with our industrial partner, who is invested in the success of the project and who is able to provide foam samples and (in the future) will be able to implement the optimized-design parameters. The tight coupling among the foam synthesis, characterization/testing, and simulation tasks is necessary because each task, on its own, is insufficient to realize a new design paradigm for investment-cast foams. Task 1 (manufacturing the foam) provides a foundation upon which the design space is developed. In subsequent iterations of the design loop, this task will also serve to test and update the design algorithm by manufacturing new foam samples. Task 2 (experimental characterization) provides necessary measurements of foam deformation and structure across length scales, including the grain scale, which has not been well characterized in the past. The experimental data acquired from Task 2 is used directly in Task 3 to develop and validate numerical models of the as-measured foam. The outcomes from Tasks 1-3 limit the foam-design space to only those foams that the manufacturer currently produces. Thus, Task 4 (virtual testing of synthetic foams) is intended to help expand and further populate the design space of foams. Finally, Task 5 (design optimization) utilizes the results from numerical simulations of as-manufactured and synthetic foams to tailor the design of the foams to meet specific performance metrics, as guided by our industrial partner. This information will then be passed on to our industrial partner to produce the new foam samples, which will provide measurable and tangible outcomes of the research.

Technical Progress

In the first 1.5 years of the project, significant progress has been made in Tasks 2-4. In Task 2, notable progress included the development of a new and portable load frame to enable in-situ characterization of 3D deformation of the foam during crushing. The load frame has been used within an X-ray computed tomography system at the University of Utah [1,2] and will soon be used at the Advanced Photon Source (APS) at Argonne National Laboratory. Additionally, a beamtime allocation at the APS in Year 1 of the project resulted in the first ever grain-mapped volume of open-cell metallic foam [3], shown in Figure 2 below. A new methodology was developed to map the grain structure in the foam by integrating experimental data from high-energy X-ray diffraction microscopy with synthetic data generated using the software, DREAM.3D [4]. Those results are described in a manuscript that is currently under review [3]. Significant progress on Task 3 included the first numerical simulation of a 3D, grain-resolved, aluminum foam. The simulation was carried out using the Material Point Method (MPM) framework, Uintah [5]. To accomplish this, a crystal-plasticity model was first implemented into the Uintah framework. Subsequently, the measurements described above and shown in Figure 2 were then digitally reproduced to simulate the crush response of the foam. Finally, significant progress was made on Task 4 by our external collaborator, Dr. Joseph Tucker (Exponent), who implemented a new plug-in for DREAM.3D [4] that enables the instantiation of synthetic-foam structures. The plug-in enables users to modify grain size and crystallographic texture, pore density, ligament thickness and cross-sectional geometry, and more. The plug-in is robust and produces synthetic-foam instantiations that, so far, appear to be very realistic. A manuscript describing the new plug-in and the algorithms underpinning it is in progress.

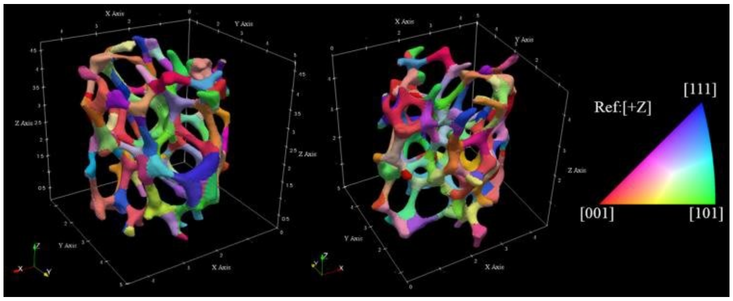


Figure 2. Results from 3D grain mapping of open-cell aluminum foam, generated under Task 2 of this DMREF/GOALI project [3].

Future Plans

Future work will focus on populating the foam-design space and implementing a Bayesian optimization framework. To populate the design space, additional measurements must be made at the University of Utah and the APS to characterize more foam samples provided by our industrial partner. The measurements will be digitally reconstructed to enable numerical simulations of multi-scale mechanical response. Additionally, an initial population of synthetic-foam samples will be generated using the new DREAM.3D plug-in. Simulation results from both the as-measured and synthetic-foam instantiations will be used in the Bayesian optimization framework. Ultimately, output from the optimization framework will be used to help guide physical realizations of the foam.

Broader impact (Only required for NSF projects)

This project has provided research opportunities for seven different students ranging from undergraduate sophomore to Ph.D. level. Through the project, one of the undergraduate students has developed a significant set of skills that has led to an internship at Lawrence Livermore National Laboratory. As a result of his work on the project, the student has also decided to pursue a PhD degree once he completes his BS degree, which will open up a new career path for him. Three of the graduate students have also developed skill sets in computer programming and in data archival and sharing. One of the students produced data files from his research to accompany a journal paper that was published recently [1,2]. The files and metadata have been made available to readers so that they have access to the data described in the accompanying journal article.

The project has also exposed approximately 15 middle school students (who are primarily Latina females) to X-ray computed tomography, 3D printing, and technical writing as part of a semester-long outreach program supported by this DMREF/GOALI award. Surveys were administered at the end of the outreach program to gauge impact. Of 12 student respondents, 6 indicated that no one in their family had ever been to college; 2 indicated that they had never been to a college campus before (until visiting the University of Utah for the final outreach event); 2 indicated that they were not previously interested in engineering but were interested in pursuing engineering after the outreach program; 3 indicated that they were interested in pursuing engineering both before and after the outreach program. Future efforts will be placed on improving the number of students who are interested in pursuing a career in engineering.

Data Management and Open Access

Digital outputs from this DMREF/GOALI project have so far been made (or will soon be made) available via two venues: 1) the NIST Materials Data Repository and 2) DREAM.3D. X-ray computed tomography reconstructions from in-situ mechanical tests of open-cell aluminum foams are publicly available on the NIST Materials Data Repository (http://hdl.handle.net/11256/949). Additionally, the DREAM.3D plug-in described above will soon be made available for public release.

Advancing Along the Materials Development Continuum

This DMREF/GOALI research is firmly grounded by the needs of our industrial partner. The current approach for manufacturing open-cell metallic foams is quite linear and lacks any element of feedback-based design, as shown in Figure 1. This is largely due to a lack of fundamental understanding of process-(micro)structure-property relationships arising from the investment-casting process. Consequently, it is currently not possible for our industrial partner to optimize or tailor the design of their foams to meet specific performance metrics. This research will enable a paradigm shift in the manufacturing process used by industry, which will accelerate the design and development process of new foams based on desired performance outcomes.

References

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2. (see [2] in Publications below)
3. (see [3] in Publications below)
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Metallic-type transport in polymers: Establishing materials design criteria and predicting structure/property interrelations

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Website: none.
Keywords: conducting polymers, dopant, polaron coherence, polaron dynamics

Project Scope

The research addresses fundamental questions of how charge-carrier coherence length and transport properties correlate with specific structural features in doped organic materials. The objective is to gain the capability to predict relevant structure/property interrelations by developing novel experimental, synthetic, computational and theoretical methods for the design of organic materials with metallic-type transport. For this, we exploit optical spectroscopies (absorption, photo-induced absorption, photo-luminescence, two-dimensional excitation spectroscopy) and first-principle calculations with atomistic approaches, nonadiabatic molecular dynamics simulations, and parameterized Holstein lattice models to extract information on the spatial coherence of electrical charge carriers in doped polymers and oligomers with controlled molecular arrangement.

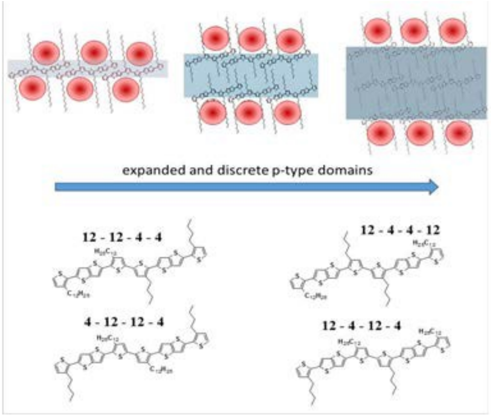

Fig. 1. Isolating the homogeneous excitation linewidth from the total spectral lineshapes in non-linear spectroscopies provide a very sensitive probe of spatial coherence, allowing us to establish structure/property interrelations based on OBTTT model systems.

Relevance to MGI

A close feedback loop between theory and experiment is needed to succeed in our vision to realize a materials design framework that (i) can deliver quantitative insights into what determines charge transport properties in organic semi-conductors, and (ii) provides verifiable hypotheses towards accelerated materials discovery. The motivation is that critical properties of organic conductors can depend subtly on chemical structure and processing conditions and, often, changes in properties and processing parameters are intertwined in non-obvious ways. This creates a daunting task to establish comprehensive structure/processing/property interrelations, often reducing materials discovery to heuristic time-consuming, expensive studies. Here, we use experimental data from optical spectroscopies, thermal analysis and X-ray diffraction to construct a database on doped polymers, oligomers and small molecules, utilizing a variety of dopants. Key spectral observables will be modeled using first-principle calculations with atomistic approaches, non-adiabatic molecular dynamics simulations, and parameterized Holstein lattice models to simulate quantum dynamics of charges. Ultimate goal is to relate spatial coherence lengths of charge carriers in materials with structure.

Technical Progress

In this initial part of the program, we have focused on developing experimental protocols that will provide a platform to deliver the feedback relevant to predicting the necessary criteria for achieving coherent charge transport in doped organic semiconductors. We have developed processing and doping protocols for poly(2,5-bis(3-alkyl)thieno[3,2-b]thiophene)s (PBTTT) and its oligomers (OBTTT). We have set up 2-D spectroscopies that will permit us to measure the homogeneous excitation linewidth of charge carriers in these systems, as a function of carrier density and host solid-state microstructure. This information will be needed to model the measured homogeneous excitation spectra and thereby correlate the two-dimensional carrier coherence length with charge transport and microstructural properties. In addition, initial structural characterization of doped thin-films of PBTTT and OBTTT has been performed, using grazing-angle X-ray diffraction, thermal analysis and optical microscopy. Striking differences between the structural features of doped polymers compared to doped oligomers have been found. In addition, we have begun to establish an international network (Sebastian Beck, Innovation Lab, Germany, dopant diffusion; Henk Bolink, University of Valencia, Spain, small-molecule doping; Colin Nuckolls, Columbia University, perylene diimide materials; Jian Pei, Peking University, China, n-dopable polymers; Jun Takeya, University of Tokyo, Japan, p-dopable polymers; and Elizabeth von Hauff, Free University Amsterdam, The Netherlands, polymer doping) that will enable us to create a database on a broad range of materials, structural characteristics and electronic properties.

Future Plans

With the spectroscopic setups now functional in the Silva lab, we will focus on performing the linear and linear spectroctroscopic measurements described above on the samples provided by our international collaboration network. David Valverde, the postdoc that will take charge of the two-dimensional spectroscopy measurements, joined the team in March 2018, and will begin formalities required to carry out the proposed visits to LANL. Hongmo Li, the PhD student involved in materials processing and spectroscopy, will Join Dr. Valverde in carrying linear and nonlinear optical measurements.

Broader impact (Only required for NSF projects)

One key impact of the program is the delivery of understanding of fundamental structure/property/processing inter-relationships that so far were elusive due to the complex and high-dimensional parameter space organic matter provides. These interrelationships are highly important in a broad range of applications of organic semiconductors, e.g., light-emitting diodes, thermoelectrics, and bioelectronics devices. At the end of the program, we will have developed a unique set of tools and an internet platform that will benefit the broad soft-materials science and industry sector as it will provide an extensive data library and theory tools that will enable a predictive and highly accelerated materials design framework.

Data Management and Open Access

We will create a database that is searchable by the public via a web interface and that includes the following spectroscopic data in compressed binary format: absorption, photoluminescence, photoluminescence excitation, photoinduced absorption, and two-dimensional coherence excitation spectra, differential scanning calorimetry, and X-ray diffraction data. Metadata with each data set will contain information on the solution-processing methods and processing parameters used to produce films, information about the source of the materials and materials properties (molecular weight, dispersity thermal properties, source of the material and links to the synthetic methods, spectroscopic experimental methods description and parameters, etc.). We will also include, cross-linked to the experimental data, output data from computation and simulation tools, along with metadata explaining input parameters to the models as well as thorough description of the models. We also will make available relevant modeling and theoretical code.

Advancing Along the Materials Development Continuum

The sought outcome of our program is to answer the fundamental question of how charge-carrier spatial extent (coherence length) and transport properties are correlated with specific structural features in organic material. For this, we aim at creating an extensive database that is unique in combining structural information (such as crystal lattice constants) with detailed spectroscopic data (linear and non-linear), charge-transport details, and thermal phase behavior, and the necessary theory programs alongside relevant parameters deduced from theory. Such a database can then be exploited to deliver experimental and theoretical models, that will be rigorously validated in our project and that will permit predicting molecular and microstructural criteria that can be fed into materials discovery activities.

IPR and JARVIS databases: Classical Force Fields, Density Functional Theory & Machine Learning to aid Materials Discovery

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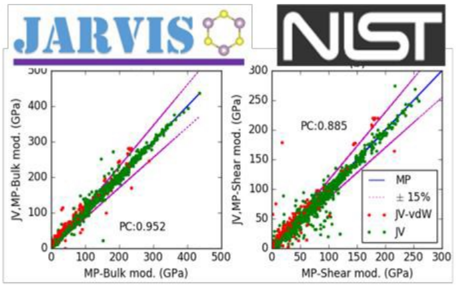
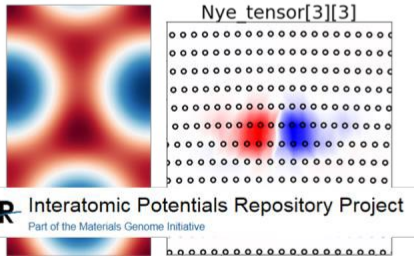
Co-Principal Investigator: Lucas Hale, MSED, NIST, lucas.hale@nist.gov
Co-Principal Investigator: Chandler Becker, MSED, NIST, chandler.becker@nist.gov
Co-Principal Investigator: Zachary Trautt, MSED, NIST, zachary.trautt@nist.gov

Website: https://www.ctcms.nist.gov/~knc6/JVASP.html, https://www.ctcms.nist.gov/~knc6/periodic.html, http://cavendish.nist.gov/jarvisml, https://www.ctcms.nist.gov/potentials/

Keywords: Interatomic Potentials, Density Functional Theory, Machine Learning, Mechanical Properties, Electronic Properties



Comparison of bulk and shear modulus from JARVIS-OptB88vdW and materials project (MP) PBE data. Red dots = modula for predicted low-dimensional bulk materials, while green dots are for the remaining materials (not vdW-bonded ones)



Project Scope

Atomistic computational approaches are widely used to model material behavior at quantum and classical levels. NIST recognizes the need for easy-to-use repositories at both levels, to provide users with systematic evaluations of material properties computed using density functional theory (DFT) as well as classical interatomic potentials. In addition to properties, all our repositories contain downloadable scripts to enable users to reproduce our data or compute similar on their own, as well as various tools to perform data analysis.

Relevance to MGI

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The Interatomic Potential Repository (IPR) website (https://www.ctcms.nist.gov/potentials) serves as host to the parameter files of over 150 interatomic potentials as well as to property calculations and property calculations tools. The potentials are widely downloaded and used in other projects, both inside and outside of NIST. They also have been incorporated into openKIM, JARVIS-FF and other applications. A listing of known external resources supportive of classical atomistics is also provided on the website for researchers to easily find and discover. This includes other potentials repositories, simulation codes, analysis tools, and reference databases. The focus is on tools and information to support appropriate evaluation and selection of models and calculation methods.

The JARVIS-FF database (http://www.ctcms.nist.gov/~knc6/periodic.html) provides a user-friendly web interface for comparing basic properties of metallic and ceramic materials to density functional theory (DFT) and experimental reference data. The data are presented in a user-friendly web interface to enable further material design and discovery. For instance, the interface shows at a glance the corresponding elastic constants predicted with all the potentials available for all materials of a given composition, so that the users can easily judge which force field best suits their needs. The JARVIS-DFT provides structural, mechanical, optical and electronic properties computed using DFT and an exchange-correlation choice that is suitable for standard 3D materials but also for exfoliable ones (0D, 1D and 2D). Such coherent data repository allows for high-throughput search of new materials, which is at the code of the Material Genome Initiative.

Technical Progress

The Interatomic Potential Repository (IPR) serves as host to over 150 interatomic potentials, providing both reference information and developer-verified parameter files. Such potentials can be used to perform atomistic simulations like Molecular Dynamics and Monte Carlo. Selected materials properties for the hosted potentials are being computed and displayed, allowing for users to compare the different models and intelligently select the best for their study of interest. A focus is placed on complex properties, such as dislocation core structures, generalized stacking fault energy surfaces, and temperature-dependent bulk properties. The scripts and algorithms are made available for users. The JARVIS-FF database currently contains a systematic computation of bulk and un-reconstructed surface energetics, elastic properties, point-defect energies and phonon calculations, using all the empirical potentials that are publicly available through LAMMPS and the NIST Interatomic Potentials Repository. The Jarvis-DFT database currently contains more than 20000 materials, adding about 10000 every year. For each material, complete convergence in k-point and cutoff energy is conducted, before computing properties. All calculations are done using VASP and the OptB88 exchange-correlation functional. Some HSE06 calculations are performed as well, to better understand band gap behavior. In addition to band gaps, the database contains elastic properties, band-structures, density of states, refractive indices. For some of the materials that are identified as possibly exfoliable, exfoliation energy is computed as well.

Future Plans

JARVIS-ML on the fly prediction: using our JARVIS-DFT data our ML tool will be able to predict properties like formation energies, band gaps, elastic modula, refractive indices. JARVIS-DFT: adding more single layer materials properties calculations, single layer band gaps. JARVIS-FF: surface energies for different termination surfaces, diffusion coefficients. IPR: the infrastructure for storing interatomic potentials is being updated to provide search capabilities. More material properties will be added to IPR repository, as well as newly developed classical potentials, as they become available. Further development of tools to help users run more reproducible and meaningful simulations is also planned.

Data Management and Open Access

All data for the JARVIS databases are available for download (links on the web pages). The source codes are publicly available on github. Using the tools provided at https://github.com/JARVIS-Unifies/JARVIS-FF, the user can compute the classical convex hull for the material under examination using the interatomic potential of choice, as well as compare it with the corresponding DFT convex hull obtained from energetic data from the Materials Project (https://www.materialsproject.org/).

The iprPy computational framework (https://github.com/usnistgov/iprPy) is the open source collection of calculation scripts and tools used to obtain the potential-dependent materials properties listed on the website. An emphasis is placed on designing the calculations to be easily sharable, have transparent and teachable methodology, have the capability of being performed in a high-throughput manner, and to produce structured and complete results records.

Advancing Along the Materials Development Continuum

Machine Learning (ML) approaches have been around for more than one decade, but, so far, have failed to substantially improve material science. The lack of data availability is one important reason for such underachievement. The NIST databases provide a substantial contribution to solve this problem, as well as to facilitate high-throughput search for new materials and material properties. As an example, we are current in contact with both Citrine and Google, as they are interested in our data capability. As a second example, the “atomman” Python package part of IPR (https://github.com/usnistgov/atomman) provides a simple, yet powerful, representation of atomic systems in Python. The focus of atomman is in performing and analyzing complex, large-scale atomistic simulations containing crystalline defects. It has built-in tools allowing for it to be a wrapper around the LAMMPS MD simulation software, as well as converters to other known Python atomistic representations.

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Kamal Choudhary, Faical Yannick P. Congo, Tao Liang, Chandler Becker, Richard G. Hennig & Francesca Tavazza, “Evaluation and comparison of classical interatomic potentials through a user-friendly interactive web-interface”, Scientific Data volume 4, Article number: 160125 (2017)

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Computationally Driven Targeting of Advanced Thermoelectric Materials

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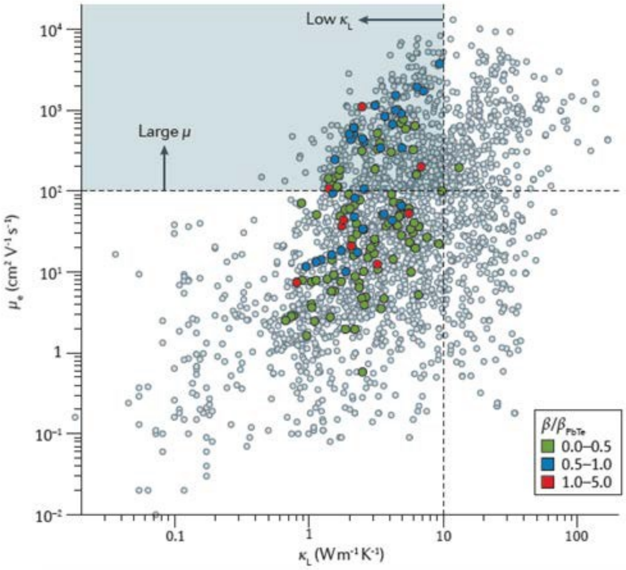
Website: www.tedesignlab.org
Keywords: thermoelectrics, transport properties, electronic structure, thermoelectric performance descriptor

Project Scope

This project seeks to accelerate the discovery and optimization of new *classes* of thermoelectric (TE) materials and guide their subsequent optimization by combining theory, experiments and high-throughput computations. To this end, we have: (i) developed a computational infrastructure for TE materials search, (ii) validated this approach through experiments, and (iii) applied this approach in a high-throughput framework to identify candidate TE material classes. The computational results from this project are publicly shared through our open-access, interactive database to further enable the discovery of promising TE materials.

Relevance to MGI

Development of TE search strategies requires an iterative feedback loop between computations on one end and synthesis and characterization on the other. Historically, the non-trivial nature of electron and phonon transport calculations has limited their ability to be used for TE search. In the first two years of this project, we overcame this challenge by adopting a strategy where empirical data and first-principles calculations were integrated into semi-empirical transport models. Unlike the traditional approach, these models are computationally tractable. We applied this approach to 10,000s of compounds and identified candidate TE materials. In the next two years, we adopted a two-pronged approach to close the feedback loop: (i) the transport models were refined based on an expanded literature survey and in-house experimental measurements, and (ii) the identified candidate materials were synthesized, optimized, and characterized leading to the discovery of new classes of TE materials.



Computational search for good thermoelectric performance, ie high mobility and low lattice thermal conductivity, identifies n-type Zintl compounds (colored) as particularly attractive class of materials. Other semiconductors are shown in grey and the color scheme is referenced with respect to the performance of the classic thermoelectric material PbTe.

Technical Progress

In the first year, our efforts focused on developing and validating a robust and computationally tractable descriptor (13) of TE performance. The semi-empirical models for carrier mobility (μ) and lattice thermal conductivity (K_L) enabled the development of the descriptor. The reliability of the descriptor was validated by correctly identifying known TE materials. In subsequent years, several independent discoveries of TE materials with high *zT* further confirmed the fidelity of the descriptor *13*. Most notably, n-type SnSe and n-type Mg_3Sb_2 were experimentally found to exhibit zT>2, consistent with our predictions based on *13*.

In the second year, we evaluated *13* for 10000s of materials from the Inorganic Crystal Structure Database. The resultant repository of computational data (materials with finite band gap) was made publicly available through www.tedesignlab.org. We also initiated experimental verification of the predictions for specific promising classes of materials. This included, main group oxides, transition metal sulfides, quasi-2D materials, and Zintls.

In the third year, we initiated the "closing of the loop" by using experimental measurements from the second year as well as an expanded literature survey to improve the semi-empirical transport models. These efforts led to a marked prediction improvement of the lattice thermal conductivity model (predictions within an avg. factor of 1.5 of measurements). Simultaneously, we refined our computational methodologies to: (1) improve predictions for quasi-2D materials, and (2) model the paramagnetic behavior of transition metal compounds that are magnetic in the ground state. During this phase, we also recognized the challenge of material dopability as a limiting factor in realizing the predicted TE performance. First-principles defect calculations can provide doping guidance; however, these calculations are computationally expensive and the computational infrastructure to automate these calculations were missing. To address this need, we developed a software package for automation of defect calculations that seamlessly integrated with the high-throughput infrastructure we used for calculating *13*.

In the final year, we intently focused on realizing novel thermoelectric materials. We employed the improved models and methodologies as well defect calculations as a guidance for doping to realize several TE materials. Most notably, n-type Zintls $KAlSb_4$ and $KGaSb_4$ (Fig. 1), oxides (SnO), quasi-2D materials ($ZrTe_5$), and diamond-like quaternaries. The defect automation software enabled us to start using defect calculations as a practical tool for guiding experimental doping decisions. We successfully used defect calculations to explain n-type dopability of Mg_3Sb_2; ongoing work focuses on exploring extrinsic dopants for n-type Mg_3Sb_2 as well as simple empirical rules for realizing n-type Zintls, in general. To disseminate these and related efforts, we published a review in 2017 in Nature Review Materials concerning the computationally driven discovery of thermoelectric materials.

Future Plans

We have come to appreciate that dopability (ability to dope n- or p-type to the desired carrier concentration) is a critical requirement for realizing the computationally-predicted candidate materials. There is a need to develop a computational strategy to allow rapid assessment of dopability. Our current DMREF project "Accelerating Thermoelectric Materials Discovery via Dopability Prediction" seeks to develop such a computational strategy, which will have far-flung applications beyond thermoelectrics.

Broader Impacts

The team is engaged in a suite of activities to promote the MGI approach. In the last 4 years, we have given over 50 invited talks at conferences and universities on our discovery philosophy. We organized a thermoelectrics summer school on the CSM campus to engage the experimental and theoretical communities in MGI-driven materials discovery as well as three conference-based tutorials. Beyond thermoelectrics, electronic and thermal transport properties are important in power electronics, transparent conductors, PV absorbers, microelectronics etc. The semi-empirical transport models will find broad application in the discovery of new materials for these applications. We have integrated material science and data mining into courses within Physics, Material Science and Computer Science at CSM, Northwestern and CU Boulder, respectively. To foster an appreciation at the undergraduate level of the MGI approach, we have had several undergraduate students work on MGI related topics.

Data Management and Open Access

As part of this project, we have made our computational data, codes, and data analysis tools open access and publicly available through our database, www.tedesignlab.org. Users can either use the interactive web-based tools on the website to explore the high-dimensional data space or export the entire repository and perform their own data analysis offline. In doing so, we have strived to empower the users to unearth new structure-property relations as well as materials for other applications. We continue to expand the data repository and functionalities; as part of the new DMREF project on dopability, we plan to add a new module to the website focused on doping.

Advancing Along the Materials Development Continuum

In the absence of an MGI approach, the traditional process for TE discovery is based on chemical intuition and empirical rules. Such an approach takes ~3-6 graduate student months per material and has a low success rate. As such, the discovery of new material classes with high *zT* happens only a few times per decade. The methods developed have attracted significant attention to bring the discoveries to fruition. These include: (1) ARPA-E funding to develop diamond-like semiconductors identified by this DMREF, (2) co-authored paper with Panasonic (Japan) and invited talk at Panasonic headquarters, (3) project from JPL to develop Mg_3Sb_2-based TE for space applications, (4) funded collaboration with IMRA-Europe (France) to develop sulfide-based TE materials, (5) ongoing collaboration with Citrine Informatics to use data mine TEDL and develop a platform for defect calculations.

Publications

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2. P. Gorai, D. Gao, B. Ortiz, S. Miller, S. Barnett, T. Mason, Q. Lv, V. Stevanovic, and E. S. Toberer, *TEDesignLab: A virtual laboratory for thermoelectric material design*, Comp. Mat. Sci. **112**, 368 (2016).

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DMREF: Collaborative Research: Self-assembled peptide-pi-electron supramolecular polymers for bioinspired energy harvesting, transport and management.

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Co-Principal Investigator: Howard E. Katz, Department of Materials Science and Engineering, Johns Hopkins University, hekatz@jhu.edu.
Website: none.
Keywords: peptide, pi-conjugation, organic electronics, self-assembly, nanomaterials.

Project Scope

This project is concerned with the development of pi-conjugated organic semiconductors that can self-assemble into 1-D fibrillar nanostructures due to peptide-driven association, whereby subtle variations in peptide hydrogen bonding geometries can impact optoelectronic outcomes. This project will develop these functional molecular superstructures in a collaboration encompassing molecular synthesis, self-assembly analogous to biological systems, modeling of the structures and electrical properties of the assemblies, and utilizing the assemblies to manage interactions between light and electricity. We hypothesize that an integrated understanding of these assembly processes will enable optimization of energy transport processes within biologically relevant materials.

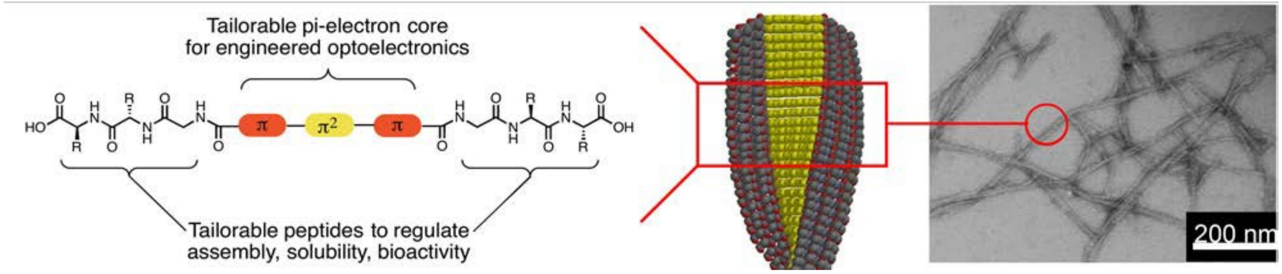

Figure 1. Peptide-pi-electron conjugates studied in this effort (left) yield sheet-like aggregates (middle) that ultimately produce fibrillar nanomaterials (right) with distinct optoelectronic properties.

Relevance to MGI

The optoelectronic properties of pi-conjugated supramolecular systems depend critically on the explicit nature of the intermolecular electronic interactions. These interactions are governed by the molecular structure and the emergent supramolecular arrangements. We developed a peptide construct that offers a pathway to exert such control over emergent supramolecular structure through tailoring of steric bulk and variable hydrophobicity of the component sequences to influence intermolecular orientations, higher-order fibrilization, and specific electronic outcomes. We initially used an Edisonian approach to uncover these variations, but the goals of this project are to wield explicit engineered control through tightly integrated atomistic simulations and electronic structure calculations. The research activities entail (i) the development of sophisticated peptidic semiconductor materials with advanced optoelectronic functionality and (ii) the development of new assembly paradigms leading to heterogeneous peptidic nanomaterials with chemical and electronic gradients and localized electric fields. The execution of this work entails interconnected efforts by the research team in the (i) synthesis of new pi-electron units and new self-assembling peptides, (ii) molecular and data-driven modeling of the nanomaterial aggregates and their higher-order assemblies, and (iii) characterization of electrical transport within the nanomaterials.

Technical Progress

As a new first-year project, we are beginning to achieve the project's specific aims with respect to four points that tie in the goals to integrate synthesic, computational and characterization activities. First, we developed new chemistry that allows for the inclusion of "high-performance" organic semiconductors that are electronically decoupled from the peptidic amide backbone. Photophysical data have been collected to reveal the nature of the pi-electon interactions in the resulting nanomaterials. Second, we are exploring a series of fluorinated peptide derivatives attached to benchmark pi-electron cores as a new way to tune the nature of the interactions within the resulting supramolecular materials. Third, we conducted molecular dynamics simulations to probe the thermodynamics and morphologies of these molecules and computed representative dimerization and trimerization free energies. Fourth, training of a quantitative structure-property relationship (QSPR) model over the molecular simulation data revealed key physicochemical determinants of the observed oligomerization free energies and produced a quantitative predictive model for the oligomerization thermodynamics.

Future Plans

Based on our preliminary progress, we have several lines of anticipated inquiry for the coming year. We will characterize nanomaterial morphologies that result from the assembly of molecules prepared as described above to understand how pi-core variation coupled with alkyl spacers influences the nanostructure assembly. We will also explore how unnatural amino acid variants with pronounced dipole character can further influence the self-assembly and electronic coupling of pi-electron segments. These assessments will be conducted via TEM in addition to standard electronic spectroscopies (UV-vis, circular dichroism, photoluminescence) traditionally employed to understand the electronic interactions within the nanomaterial structures. Those molecules that form fibrillar structures will be used as active layers for field-effect transistors in order to understand their charge transporting properties. At the same time, promising fibrillar structures will be subject to molecular dynamics simulations in order to capture local intermolecular pi-electron geometries. These geometries will be subject to time-dependent DFT calculations that will predict the anticipated spectral reponses. Thus, there will be a strong feedback loop between the experimental activities involved with peptide assembly characterization and the computational activities associated with understanding probable molecular geometries with in the assembled structures and their anticipated electronic spectral signatures. Vice versa, peptide sequences identified in simulations that lead to specific electronic couplings will be used as targets for synthesis to inform on the efficacy of the computational methods used to generate ensemble structures and their associated electronic couplings in silico.

Broader impact (Only required for NSF projects)

This research will provide new opportunities to create self-assembled materials with novel properties that could be engineered to interface living cells into hybrid materials systems which could be transformative in efforts to engineer interfaces with neuronal cells towards repair of nervous system injuries, to image amyloids and other protein deposits, and to couple with photosynthetic machineries or the energy production capabilities of cells. The PIs are committed to workforce training and development within this project, guiding the next generation of materials and data scientists of diverse socio-economic background in state-of-the-art tools and exposing them to an integrated interdisciplinary mode of work that will define future research. This project will make special provision for research opportunities for undergraduate students, women, and underrepresented minorities. The PIs will train and mentor researchers in state-of-the-art experimental and computational tools and expose them to an integrated interdisciplinary mode of work. K-12 outreach activities will inspire excitement and awareness of materials science and encourage students to pursue higher education in science, technology, engineering, and math (STEM) fields.

Data Management and Open Access

The integrated computational and experimental outcomes of this work are expected to be of interest to researchers in diverse fields including synthetic chemistry, biomaterials, polymers, organic electronics, data-driven materials discovery, biomolecular simulation, and post-density functional theory. At this early stage of the project, we anticipate to share the data promptly via publication as peer-reviewed journal articles. Output data sets will be hosted on the Illinois Data Bank maintained by Research Data Services at UIUC that serves as a publically available searchable data repository with permanent DOIs. We will make the codes for data-driven modeling tools publically available as a user-friendly software package hosted on the public code sharing site GitHub with clear documentation and sample input and output.

Advancing Along the Materials Development Continuum

Given the multitude of molecular design possibilities for pi-electron based peptides (hundreds of possible pi-electron units, random oligopeptide sequences comprised of the natural amino acids and unnatural variants), it is essential that experimental programs incorporate molecular modeling and data-driven screening to guide the choice of synthesis targets. Tight integration and mutually reinforcing feedback between computation and experiment can reveal fundamental design rules for molecular assembly, and accelerate the discovery and development of supramolecular assemblies with tailored structure and function. Pi-functional materials in biotically-inspired superstructures remain relatively undeveloped relative to the innovations for organic electronics in abiotic applications. Such mesoscopic structures can combine charge and energy transfer activities with capabilities for assembly in biological media, and compatibility with biological structures. Three patents have been issued previously based on this peptide nanomaterial platform, internal funding has been secured for in vivo studies, and nascent biomedical explorations are underway.

Publications

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DMREF: Collaborative Research: Accelerated discovery of chalcogenides for enhanced functionality in magnetotransport, multiorbital superconductivity, and topological applications

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Website: none
Keywords: Transition Metal Dichalcogenide, Metal-Insulator Transition, Disorder, Luttinger Liquid, Pseudogap

Project Scope

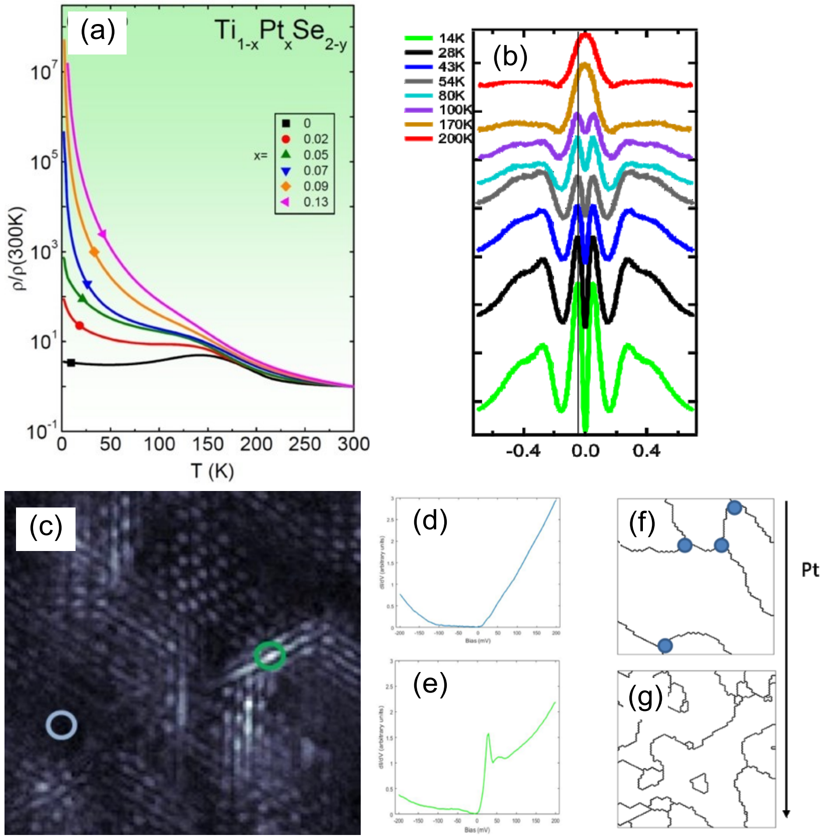
The main objective of this proposal is to establish new paradigms for multi-band systems with moderate correlations and spin-orbit coupling. Some of the expected outcomes of this proposal are: (1) Discovery and optimization of novel electronic phases with unusual magneto-transport properties; (2) Discovery of topologically protected surface states in the background of textured magnetic phases; and (3) Emergence of unconventional superconductivity in insulators or multi-band low density transition metal dichalcogenides (TMDs). In order to achieve these, this project will undertake a multipronged investigation, involving transport, Angle Resolved Photoemission Spectroscopy (ARPES) and Scanning Tunneling Spectroscopy (STS) measurements in close synergy with theoretical modeling.

Relevance to MGI

Our team of four faculty members bring to bear complementary skills and expertise, specifically, material-synthesis of bulk single crystals (EM, Rice) and Molecular Beam Epitaxy (MBE) of thin films (VM, UIUC); complementary expertise in advanced spectroscopy in momentum space via ARPES (UC, UVA) and real space via STS (VM, UIUC); and theory and computation (NT, OSU), including hierarchical theoretical modeling from ab-initio electronic structure to down folded effective electronic and magnetic Hamiltonians and quantum Monte Carlo simulations of these effective Hamiltonians. Each of these, working in a tight feedback loop, is critical for identifying new functional materials as well as advancing the functionalities of the existing ones. The core objective of our project is to take advantage of the above described array of expertise such that both materials- and computation-inspired routes can be adopted towards accelerated discovery of novel materials with desired optimized functionalities. The modeling tools, robust algorithms, and software for computer-aided materials design developed in this project will impact the wider community. The PIs outreach efforts will impact the participation of underrepresented minorities in physics. All these are perfectly tuned to the MGI strategic plan.

Technical Progress in a Nutshell

We have conducted detailed temperature (T)-dependent ARPES, STS and transport studies of pristine and a series of Cu-intercalated and Pt-doped $1T$-$TiSe_2$ single crystal samples. In this structure, $TiSe_6$ form edge sharing octahedra. What first caught our attention was the temperature-dependent electrical transport behavior that, on cooling, showed an increase by eight orders of magnitude for a small amount of Pt substitution in $1T$-$Pt_xTi_{1-x}Se_2$ [Ref. 1]. Our DFT studies indicated that Pt does not dope the system but adds potential disorder. Various attempts to fit the data using Anderson localization and Mott variable range hopping did not prove successful. ARPES clearly showed a CDW gap in the pristine ($x = 0$) sample opening up at the L point of ~50 meV. Upon Pt substitution, a new gap structure developed at the chemical potential at the L point. What is the origin of this pseudogap with sharp pile up in the DOS? The main clue was provided from the spatially resolved STS images that show the formation of domains separated by domain walls (DW) with qualitatively different spectra in these two regions.



(a) Transport data (from Morosan group) on $Pt_xTi_{1-x}Se_2$ showing the dramatic increase in resistivity with Pt doping. (b) ARPES data (from Chatterjee group) as a function of energy at L point showing formation of a pseudogap as a function of temperature. (c-e) STS spectra (from Madhavan group) on doped sample taken within a domain (~100 meV gap) and on the domain wall (an asymmetric pseudogap). (f) Theory proposal (Trivedi group) of emergence of Luttinger liquid rivers in the domain walls separated by insulator within domains leading to power laws in STS and transport.

The domains show a suppressed local density of states (LDOS) with a gap of ~100 meV.

In contrast, the LDOS *on* the DWs show a highly asymmetric spectrum with suppressed LDOS described by a power law. These experimental studies have informed the theoretical modeling. Our understanding is that Pt shatters the pristine CDW material and creates domains separated by DWs, similar to the impact of a stone on a glass sheet. Charge gets sucked into the DWs leaving the domains with a large gap. This observation is also consistent with ARPES measurements at low temperature, that find no energy gap around Fermi momentum in the pristine sample but clear signatures of pseudogap behavior in the doped samples. The narrow DWs harbor rivers of Luttinger liquids that intersect and scatter at connection points. Since the carriers in the DWs are fractionalized fermions, tunneling of electrons into these regions produces a strong suppression because of the orthogonality catastrophe [Ref. 2]. This picture is able to qualitatively explain the *T*-dependence of the electrical transport data that is well fit by a power law and arises due to strong scattering of the Luttinger liquid excitations at the interconnects between DWs.

In the related material *1T*-Cu_xTiSe_2 we have used low-temperature scanning tunneling microscopy to probe the real-space characteristics of the CDW order. Our data show that the incommensuration due to Cu intercalation proceeds through domain formation. Within each domain, the CDW order is commensurate with the sharp DWs showing an enhanced DOS. We conclude that the incommensurate CDW phase and associated DWs should be a common element of *1T*-$TiSe_2$ samples that exhibit superconductivity through doping, gating, or pressure. The enhancement of the DOS in the DW may help the emergence of superconductivity. This paper was published in Phys. Rev. Lett. **118**, 106405 (2017).

Future Plans:

(1) We will further substantiate the Luttinger liquid domain wall (LLDW) mechanism to explain the unusual transport in Pt doped *1T*-$TiSe_2$ by comparing the power laws in LDOS from STS and ARPES both of which measure properties of the single particle Green function versus the power laws from transport that measures a

two-particle green function with vertex corrections. (2) We will conduct experiments in a magnetic field both for transport and STS to see if the LLDW mechanism is corroborated. (3) We will explore other materials in the TMD class to understand the universality of the LLDW mechanism. (4) We will explore other dopants in $TiSe_2$ such as Cu that is known to create superconductivity, however the nature of the superconductor remains unexplored. (4) We will explore the interplay of magnetic dopants in TMDs such as Fe:TaS_2 or Fe:TiS_2.

Broader impact (Only required for NSF projects)

Our collaborative project has been beneficial to the participants (the PIs and junior collaborators) who have interacted weekly through skype meetings and face-to-face at the 2018 APS March meeting. It has given a unique perspective in how problems are identified, how different probes unravel the mysteries, the iterative procedure as we zero in on specific reasons behind interesting phenomena and the final integration of ideas. Participating students and postdocs have been exposed to high impact research areas, hands on training on scientific research, training for future career in academia and/or industry by developing skills for critical thinking and opportunities to exchange ideas with and learn from leading experts and academic peers in the research field. The participating undergraduate student Andreas Butler in UC's group has acquired hands on experience in handling ultra-high vacuum instruments. He has also learned how to analyze ARPES data using Igor Pro, Mathematica and Matlab. UC has worked closely with him to prepare his application package for graduate school. The postdoc Dr. Junqiang Li, who recently joined UC group has been instrumental in mentoring graduate and undergraduate students in the lab. The postdoc Kyungmin Lee in NT's group has developed codes for fitting transport data based on different theoretical models. These could be developed into a standard analysis package.

Data Management and Open Access

Our first collaborative project is currently underway. As it nears completion we will set up a publicly accessible website where we will make the following available: (a) information on available samples; (b) digitized data from transport, STS and ARPES; (c) Mathematica and python codes on data analysis.

Advancing Along the Materials Development Continuum

It is abundantly clear that we could not have zeroed in on the LLDW mechanism, which we believe is relevant to many materials, if we did not simultaneously have transport and spectroscopy. This greatly accelerated our modeling of the unusual phenomenon. We have now gone to the third round of materials synthesis from powder to single crystals with a range of Pt dopants to a more refined range of dopants. Both STS and ARPES are being conducted on the same sample to remove variables. The rapid progression of samples and the sharing of information from different probes could not have happened without the MGI platform. Typically, Luttinger liquids have been observed in narrow wires specifically constructed to observe 1D transport. In this materials platform Luttinger liquids are an emergent phenomenon in the domain walls formed by shattering the CDW pristine state in a TMD with a dopant. The huge change in response of the TMD to a dopant and the asymmetry of the response for forward vs reverse bias suggests possible applications as switches in nano-circuits.

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Publications

1. S. Yan, D. Iaia, E. Morosan, E. Fradkin, P. Abbamonte, and V. Madhavan, *Influence of Domain Walls in the Incommensurate Charge Density Wave State of* Cu *Intercalated* $1T$−$TiSe_2$, Phys. Rev. Lett. **118**, 106405 (2017).

Discovery of Design Rules for High Hydroxide Transport in Polymer Architecture

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Co-Principal Investigator: Michael A. Hickner, Department of Materials Science and Engineering, Pennsylvania State University, mah49@psu.edu.
Co-Principal Investigator: Stephen J. Paddison, Department of Chemical and Biomolecular Engineering, University of Tennessee Knoxville, spaddiso@utk.edu.

Keywords: Hydroxide ion transport, Membrane, Ab initio molecular dynamics, Dissipative-particle dynamics, Morphology

Project Scope

Anion exchange membrane (AEM) fuel cells, in which hydroxide ions are transported from the cathode to the anode under basic conditions, can offer a number of significant advantages compared to proton exchange membrane-based fuel cells under acidic conditions. However, there is little understanding about relationships of polymer structures and hydroxide ion transport until now. A team of skilled researchers made of computational modeling experts and polymer membrane scientists has investigated molecular level understanding of polymer structure and mechanisms of hydroxide solvation and transport in different chemical environments and has elucidated a set of design principles for promoting high hydroxide transport.

Relevance to MGI

The experimental protocol consists of synthesis and characterization of polymer structures with different backbones, tethering groups, terminal ionic groups and study of their effects on morphology, water distribution, and hydroxide diffusivity. The theory and simulation protocol consists of first principles molecular dynamics study of hydroxide solvation and diffusion and coarse-grained simulations to elucidate the connections between backbone composition and morphology. The computational tools provide a molecular level understanding of experimental data and guide new materials design while experimental feedback help refine the theoretical and computational models. Using this protocol, we have developed design rules of next generation AEMs and identified several optimal AEM polymer architectures that possess good chemical stability and high hydroxide conductivity by (i) studying the correlations among polymer structures, morphology, water distribution, and ion transport property via iterative cycles of theory, synthesis, and characterization in this study and (ii) analyzing AEM property data in the existing literature.

Technical Progress

As the first phase of materials synthesis, precursor polymers for AEMs in which polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene) (SEBS) is functionalized with alkyl bromide of different tether lengths have been prepared. The side chains are cations having varying chemical compositions and tethers/tails. The synthesized polymeric membranes, being either random, block, or graft copolymers, were then rendered into a coarse-grained model and simulated using dissipative-particle dynamics in order to elucidate the morphology as a function of water content, tether an tail length, and cation chemical composition. These studies revealed that at low water content, a lamellar structure emerges, but as the water content is increased, pore-like structures develop. These are shown in

Figure 3. The morphologies produced in the dissipative-particle dynamics simulations are compared and confirmed using small-angle x-ray scattering. Although dissipative-particle dynamics simulations include hydroxide ions, they are unable to account for the structural diffusion of the hydroxide ion, a process that is known to be an important component in hydroxide transport. Structural diffusion is a chemical process in which a proton transfer event to the hydroxide ion from one of the water molecules that coordinates it at the oxygen site changes the identity (and orientation) of the hydroxide ion, giving rise to large jumps in the hydroxide ion's position, thereby increasing the diffusion constant it would have under purely a hydrodynamic or vehicular diffusion mechanism. Morphologies produced in the dissipative-particle dynamics simulations and revealed via small-angle x-ray scattering are then rendered into idealized models amenable to study using ab initio molecular dynamics, which are able to capture chemical processes. Ab initio molecular dynamics simulations achieve this by following the classical dynamics of the atoms in a system using forces obtained from electronic structure calculations performed "on the fly" over the course of the simulation. Such calculations can capture both vehicular and structural diffusion of hydroxide, however, the high computational cost requires the use of simplified models that, nevertheless, allow us to identify changes in the hydroxide diffusion mechanism as a function of water content, temperature, cation composition, cation spacing, and size of the lamellae or pore. The simplified models we have employed are hydrogenated graphene sheets in a "sandwich" structure, representing lamellar geometries, or hydrogenated carbon nanotubes, representing cylindrical pores, functionalized with the cation group at specific carbon sites and filled with water up to the desired water/cation ratio (Figure 1). These simulations reveal that the following design protocols yield the highest hydroxide conductivity: Sufficiently close spacing of the cations to prevent water buildup between them, a sufficiently large intersheet spacing or pore radius to allow water to occupy a water layer above the cations, a sufficiently high water content to fully solvate the hydroxide ions, and a sufficiently high temperature to accelerate the hydrogen-bond dynamics associated with structural diffusion.

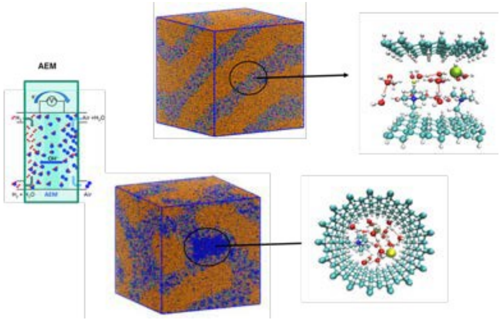

Figure 1. Morphologies generated using dissipative-particle dynamics; sandwich and nanotube idealized structures.

Future Plans

- The beads used in the coarse-grained models used in the dissipative-particle dynamics simulations, which represent clusters of water molecules and hydroxide ions with its first solvation-shell water molecules, will be refined to reflect differences in water content. In particular, a low water contents, both water molecules and hydroxide ions have lower coordination numbers, which requires smaller beads.
- An investigation of the role of nuclear quantum effects in specific chosen models that show high hydroxide diffusion will be investigated using state-of-the-art ab initio path integral molecular dynamics approaches.
- An in-depth survey of the existing anion exchange membrane literature will be carried out, and the correlations and design rules obtained in this project will be applied in order to rationalize previous observations in different polymeric systems and to place them into corresponding design categories.

Broader impact (Optional for DOE grants/FWPs)

After thorough investigation of the structure-property relationships of AEMs, we have begun to classify the experimental and computational results as variations in ionic functional group, tether chain length, and backbone structure and sort out the major factors using an analysis of variance approach. Because most AEM research has been an experimental endeavor with scattered results from various research groups, there is no general consensus on material design. We are applying our structure-property correlations to the available AEM literature data, classify them according to our derived material design rules. We are preparing to write a comprehensive review or account articles addressing the correlation between polymer architectures and ion transport properties, which will benefit to the research community of electrochemical energy society. Dissemination of the project outcomes have been and are being shared at a AEM symposia at professional society meetings, e.g., Electrochemical Society Meetings, and all software tools used in this project are being made available as open source packages. Cross-training of students through close collaboration within the team and their research progress is highlighted via publications and presentations at scientific meetings. In addition, students working on this project have had the opportunity to work with researchers at the national labs and gain a broad sense of sustainable energy conversion technology via internships.

Data Management and Open Access

The Tuckerman group currently runs a GitHub repository (https://github.com/TuckermanGroup) where the main simulation package used by his group is maintained and distributed. This repository will be expanded in such a way as to serve as an archive and public access point for final data sets (theoretical and experimental) and codes generated in this project. Very large raw data sets from molecular dynamics simulations will be stored on local hard drives in the Tuckerman group and provided to community members upon request. The project will also generate new methods and algorithms, which will be disseminated via peer-reviewed publications.

Accelerating Materials Discovery & Development

Although major use of alkaline fuel cells can be traced back to the 1960s, AEM fuel cell technology using solid polymer membranes is a relatively new field (the concept evolved around 2010), and most AEM studies comprise scattered examples of different materials with, thus far, little fundamental understanding. Due to the multitude of possible structural variations in AEM design (e.g., cation head group, polymer backbone, etc.), random synthesis and characterization of AEM materials in hopes of discovering a chemically stable and highly conductive AEM is not feasible. So far, there have been many reports of AEMs in the literature, with no clear path foward. A rational design approach, utilizing theoretical, computational, and experimental tools in a tight feedback loop (following the vision of the MGI), it has been possible to derive a set of design rules for optimal AEM materials and to develop these materials more efficiently. AEMs previously developed by the PIs (**1-2,** patents filed from **Bae**) are currently being tested at national laboratories for commercial and technical viability in AEM fuel cells. Lessons learned from this fundamental research project are helping to develop better performing AEMs in the future and guide the community to develop common descriptors for characterizing high-performance membranes.

Publications

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3. J. Pan, J. J. Han, L. Zhu, and M. A. Hickner, "Cationic side-chain attachment to poly(phenylene oxide) backbones for chemically stable and conductive anion exchange membranes", *Chem. Mater*. **29**, 5321-5330 (2017).
4. J. L. Yan, L. Zhu, B. L. Chaloux, and M. A. Hickner, "Anion exchange membranes by bromination of tetramethylbiphenol-based poly(sulfone)s", *Polymer Chem*. **8**, 2442-2449 (2017).
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Collaborative Research: Emergent functionalities in 3d/5d multinary chalcogenides and oxides

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Keywords: 5d compounds, layered chalcogenides, transition-metal oxides, spin-orbit coupling, topology.

Project Scope

The physics and chemistry of 3d/5d transition-metal compounds is distinguished by strong correlations and large spin-orbit coupling (SOC), which can have a dramatic effect on materials properties. The major goal of this DMREF collaborative research program is to conduct a concerted theoretical, computational and experimental exploration of the physics and chemistry of materials containing heavy elements, aimed at the directed discovery of new functional materials in the class of 3d/5d transition metal multinary compounds.

Relevance to MGI

The project is a joint theoretical, computational, and experimental research effort built upon a materials discovery paradigm in which first-principles calculations are used to scan through candidate materials, identifying promising candidates for directed synthesis and in-depth experimental study. Comparisons between theory and experiment provide feedback to refocus the theoretical and computational effort. We seek a transformative acceleration of progress in our understanding of these materials, in particular (i) investigate competing interactions and resulting phase behavior in strongly spin-orbit-coupled materials; (ii) improve our understanding of how SOC can enhance functionality through SOC strength, d-shell filling, dimensionality, and structural distortions; (iii) use computational design approaches to identify potentially new materials with improved properties and interesting phases, such as topological-insulators, Weyl-semimetals, and other topological phases; (iv) theoretically explore a new paradigm for understanding strongly-correlated "bad metals" in the Hunds/selective-Mott class.

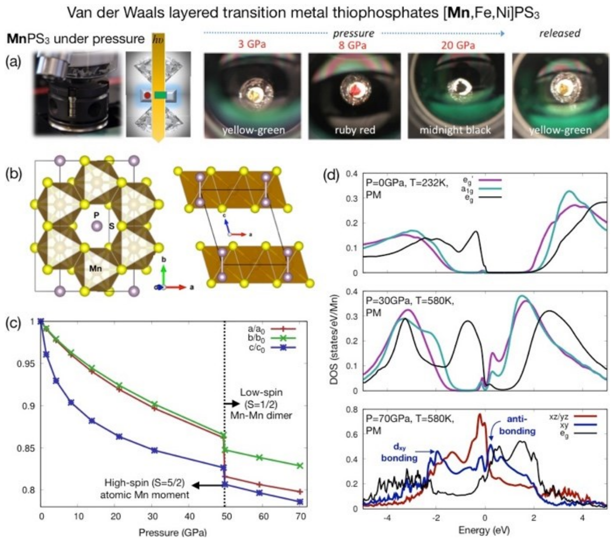

Figure. (a) Reversible color change of $MnPS_3$ single crystal with pressure up to 20 GPa. (b) Top and side views of crystal structure. (c) Theoretical prediction of lattice parameters vs. pressure. (d) Calculated spectral functions A(ω) at P=0, 30, and 70 GPa, showing gap closure at 30 GPa and Mn dimer formation at 70 GPa.

Technical Progress

The correlated van der Waals layered compounds [Mn,Fe,Ni]PS_3 are candidates for tunable Mott-transitions with strong electron-phonon coupling and 2D magnetism. Our theory predicted the collapse of the Mott gap under pressure, as confirmed by optics experiment in $MnPS_3$. It also predicts a spin-state and structural transition at higher pressure, which is a novel example of spin-orbital-lattice interplay.

Recently, our DMREF team discovered colossal magnetoelectricity in the collinear antiferromagnetic insulator Ni_3TeO_6 that derives from the near degeneracy of the two magnetic states in the vicinity of the spin flop transition. Ni_3TeO_6 supports the largest linear magnetoelectric coupling constant in a single phase material known to date (α = 1,300 ps/m), and for its understanding we are combining high field optical spectroscopy, a symmetry analysis, and first principles calculations to analyze the electronic structure of Ni_3TeO_6 across the 9 and 53 T spin-flop magnetic transition.

3D topological insulators (TIs) are materials with 2D chiral surface states, possessing essential properties for future applications in spintronics. 2D chiral states in non-topological materials with strong SOC have been predicted, but not observed, to support novel collective spin modes (chiral spin waves) even in nonmagnetic systems. Recently, members of our team explored collective spin excitations of the chiral surface states of the TI Bi_2Se_3 using polarization-resolved resonant Raman spectroscopy. By comparing with the theoretical calculations, a sharp peak at 150 meV in the pseudovector symmetry channel was identified as the transverse collective spin mode of the surface fermions. This mode is analogous to a magnon that is "peeled off" from the continuum of non-interacting particle-hole excitations by the exchange interaction.

At low temperature the charge-density-wave (CDW) state in $TaTe_2$ is commensurate, but our DMREF team found that it becomes partially incommensurate around 100-200K. By employing STM topography, LEED, and DFT calculations, it was shown that there are multiple nesting vectors incommensurate to the lattice periodicity, which explains the coexistence of different CDW phases, and is a rare example of a CDW with very weak lattice distortions.

The deficient spinels GaV_4S_8, GeV_4S_8, and GaV_4Se_8 form a series of ternary chalcogenide compounds that become ferroelectric and multiferroic at low temperature. The tetrahedral molecular V_4S_4 clusters play the role of basic building blocks for the electronic structure, which was simulated by a four site cluster-DMFT theoretical approach that obtains the correct Mott gap in the paramagnetic state. Surprisingly, the non-local Hund's coupling between molecular-orbital states is found to substantially renormalize the charge gap, a factor that was found to be crucial for stability of the experimental molecular-crystal structure.

Future Plans

We will investigate 3d-5d mixed compounds $A_3BB'O_6$ (A=Ca, Sr; B=Co, Ni, Cu, Zn; and B, B'=Ir, Rh), which consist of in a triangular lattice of ferrimagnetic chains. These materials are promising candidates for large magnetic anisotropies, as they have strong magnetic moments coupled ferromagnetically in-chain but weak and switchable interchain interactions. We will complete our joint theoretical and experimental study of colossal magnetoelectric behavior, giant optical activity, and dichroic effects in Ni_3TeO_6. We will extend our theory of deficient spinels to the symmetry-breaking structural and magnetic transitions at low temperature, in combination with growth and optical spectroscopy capabilities of the team. We will carry out optical spectroscopy of $MoTe_2$ as a type-II Weyl semimetal, and study polar transitions and domains in (Mo,W)Te_2. We will investigate monolayers (such as K, Bi, Pb) on cleaved single-crystal surfaces of layered transition-metal chalcogenides such as 1T-TaS_2, $CrGeTe_3$, Fe_3GeTe_2, and $CrTe_2$. We will investigate behavior of iridates under pressure, especially chain compounds (e.g.,Sr_3NiIrO_6) and pyrochlores (e.g., $R_2Ir_2O_7$). We will attempt synthesis or exfoliation of ultrathin (single- or few-layer) 5d transition-metal dichalcogenides, and study their behavior theoretically and experimentally. We will initiate exploratory spectroscopic work to uncover the properties of the novel improper ferroelectric $Fe_2Mo_3O_8$. In collaboration with two other DMREF teams, we will design, populate, and disseminate a database of spectral functions obtained from a variety of methodologies including DFT, DFT+U, DFT+DMFT, and GW, and from experiment.

Broader Impacts

We will continue to provide research experience for high school students during summers through the Partners in Science Program of the NJ Liberty Science Center, and for undergraduate students though the Rutgers REU (Research Experience for Undergraduates) program and the Aresty program. We arranged significant participation of graduate students and young researchers in workshops/conference that we have organized. In particular, we organized 2013 and 2015 *Telluride Workshops on Spin-Orbit Coupling in 4- and 5d-Containing Materials*, and are now organizing a 2018 meeting in the same series. We also organized the *2014 Gordon Research Conference on Multiferroic and Magnetoelectric Materials,* and initiated a Focus Topic session on "Strongly spin-orbit coupled materials" beginning with or the 2015 March APS Meeting.

Data Management and Open Access

Our full publication list reprints, and other materials are posted on our DMREF project webpage http://dmref.physics.rutgers.edu. General data are stored at http://hauleweb.rutgers.edu/database_w2k/, and codes are available at http://hauleweb.rutgers.edu/tutorials/.

Advancing Along the Materials Development Continuum

The MGI approach of our DMREF project allowed us to swiftly identify the fundamental mechanism of tunable Mott transition, dimerization, and emergent complexity of forming stripes in layered heavy chalcogenides. This understanding opens up a material design paradigm for novel functionalities such as periodic structures for nano-templates or giant Rashba splitting for spintronics. Our results will accelerate materials discovery in layered chalcogenides and related functional materials. In addition, our theoretical DMREF efforts help clarify both the strengths and limitations of current state-of-the-art computational approaches, and our software developments will prove useful to the community at large.

Selected Publications

[1] "*Heat transport study of the spin liquid candidate 1T−*TaS_2", Y. J. Yu, Y. Xu, L. P. He, M. Kratochvilova, Y. Y. Huang, J. M. Ni, L. Wang, S.-W. Cheong, J.-G. Park, and S. Y. Li., *Phys. Rev. B* 96, 081111 (2017).

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[4] "*Electronic chirality in the metallic ferromagnet* $Fe_{1/3}TaS_2$", S. Fan, I. Manuel, A. al Wahish, K. R. O'Neal, K. A. Smith, C. J. Won, J. W. Kim, S.-W. Cheong, J. T. Haraldsen, and J. L. Musfeldt, *Phys. Rev. B* 96, 205119 (2017).

[5] "*A nanoscale-inhomogenious topological phase transition without band gap closure in* $(Bi_{1-x}In_x)_2Se_3$", W. Zhang, M. Chen, J. Dai, X. Wang, Z. Zhong, S.-W. Cheong, and W. Wu. Submitted.

MAterials Genome Innovation for Computational Software (MAGICS)

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Website: https://magics.usc.edu
Keywords: Layered materials genome, ultrafast X-ray laser experiments, exascale computing, chemical vapor deposition, exfoliation.

Project Scope

Development of next-generation methods and software to predict and control materials processes at the level of electrons for computational synthesis, intercalation and exfoliation of stacked, two dimensional, functional layered materials (LMs) with energy-related application to electronics and catalysis. Validation of materials specific predictions includes ultrafast X-ray laser and electron diffraction experiments at SLAC, which are directly mirrored by peta-to-exascale supercomputing resources at the Argonne Leadership Computing Facility under Aurora/A21 ESP and INCITE programs. Data management integrates the Materials Project at Lawrence Berkeley National Laboratory and uses computing capabilities at NERSC.

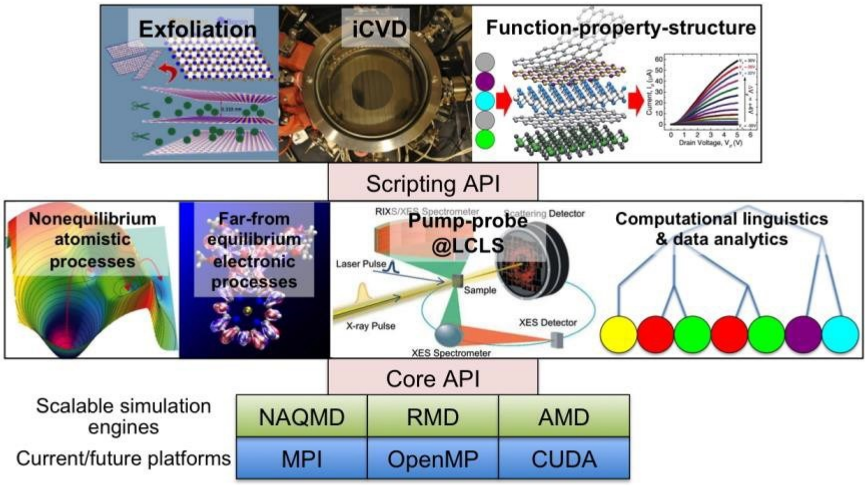

Figure 1. Layered materials genome: Computational software for the synthesis and characterizations of stacked functional LMs. **iCVD**–initiated CVD; API–application programming interface; **NAQMD**–nonadiabatic quantum molecular dynamics; **RMD**–reactive molecular dynamics; **AMD**–accelerated molecular dynamics; **MPI**–message passing interface; **OpenMP**–open multi-processing; **CUDA**–compute unified device architecture.

Relevance to MGI

Functional layered material (LM) architectures will dominate materials science in this century. We are developing theory, modeling, simulation, and software and data tools that enhance understanding and guide synthesis, enable characterization of complex structures, and improve capabilities in the predictive design and growth of LMs.

Technical Progress

***Computational Synthesis of LMs*:** Quantum molecular dynamics (QMD) and Reactive Molecular Dynamics (RMD) simulations were carried out to determine chemical and atomistic processes in the CVD growth of LMs. We found that alloying $MoSe_2$ monolayer with Re atoms not only transforms it from semiconducting to semimetallic crystalline phases but also makes them magnetic (Fig. 2). Our MD simulations to study liquid-phase exfoliation of bulk MoS_2, which reveals that collapsing bubbles give rise to high-speed nanojets in the solvent. The impact of nanojets on bulk MoS_2 generates large shear stresses which exfoliate bulk MoS_2 into nanosheets.

***Novel Synthesis of Tellurene and 2D Alloys*:** We have synthesized tellurene — a monolayer of tellurium — using physical vapor deposition. We have also succeeded in the controlled CVD growth of a monolayer transition metal dichalcogenide alloy ($MoSe_2$/WSe_2) and discovered a structural phase tranformation in this system under mechanical straining.

***Nonadiabatic quantum molecular dynamics (NAQMD) Validation by Ultrafast Electron Diffraction (UED)*:** Experimental validation involves the study of electron-phonon coupling in LMs under intense optical excitation and probing of light-induced structural phase transitions using UED at Stanford. NAQMD simulations explained UED-observed ultrafast electron-to-lattice energy transfer in CVD grown $MoSe_2$ via photo-induced phonon softening. The joint Stanford-Rice-USC work was published in Nature Communications (Fig. 3).

New Polarizable reactive force-field (ReaxPQ) approach for reactive molecular dynamics (RMD) has been developed, incorporating a novel Pareto-front approach for uncertainty quantification (UQ).

Thermal-conductivity Software has been developed to compute thermal conductivity of LMs with quantum correction and isotope effects.

***Scalable Software Development*:** To develop and deploy scalable simulation engines for layered materials genome (LMG), we won two DOE supercomputing resource awards — Aurora/A21 Supercomputer ESP (Early Science Program) award, *"Metascalable layered materials genome"* and INCITE (Innovative and Novel Computational Impact on Theory and Experiment) award, *"Petascale simulations for layered materials genome."* Under Aurora/A21 ESP, we are one of the 10 exclusive users of the Nation's first exaflop/s supercomputer when it is introduced in 2021 [featured in *Science* **359**, 617 (2018)].

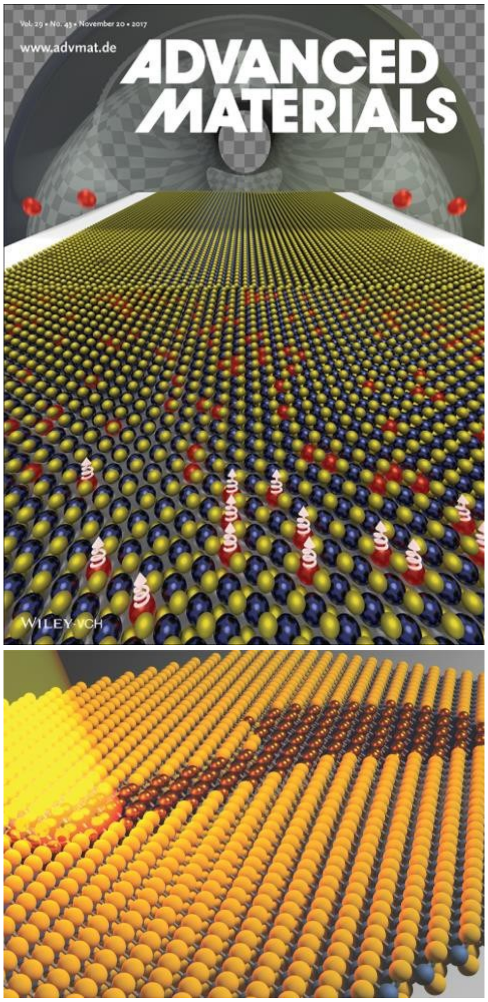

Figure 2. MAGICS journal cover images. (Top) Atomically thin $Re_xMo_{1-x}Se_2$ magnet [*Advanced Materials*, Nov. 20, 2017 issue]. (Bottom) Optical control of semiconductor-to-metal transition in$MoTe_2$ [*Nanoscale*, Feb. 14, 2018 issue].

Future Plans

We continue to design novel LMs using MAGICS computational-synthesis software. We will explore synergy between our Aurora/A21 ESP for exascale computing and next-generation free-electron X-ray laser experiments at Stanford's Linac Coherent Light Source (LCLS-II). The goal is to do full-machine simulations and develop time-to-solution approaches to do a 10-20 μs simulation within a day.

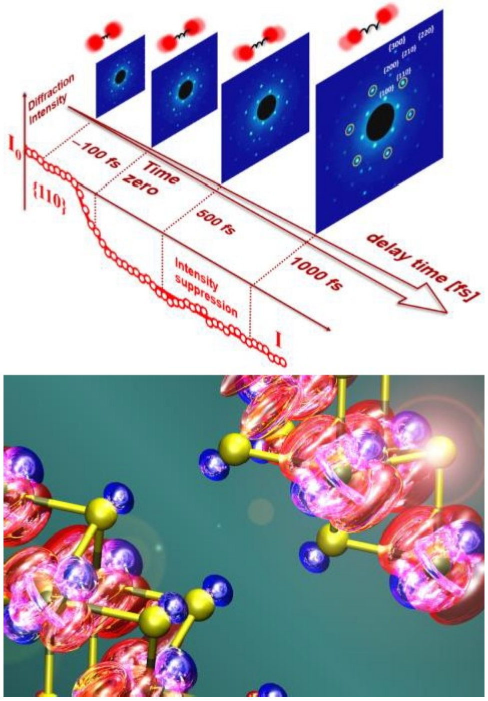

Figure 3. UED experiment (top) and NAQMD simulation (right).

Data Management and Open Access

***Materials Project (MP)*:** We have started sharing MAGICS simulation data [https://magics.usc.edu/data] on LM heterostructures *via* the Materials Project (MP) framework [https://materialsproject.org]. This new project is supported by two main codebases that the LBL team is developing: *MPComplete* and *MPContribs*.

***MAGICS Workshop*:** We have organized workshops in November 2017 and March 2018 to train users in Center software and data (Fig. 4).

Advancing Along the Materials Development Continuum

MAGICS develops software for computational synthesis, available to the materials-genome community, which is available at the MAGICS Web site:

- ***QXMD*** code for NAQMD to study far-from-equilibrium dynamics.
- ***RXMD*** for RMD with a new ReaxPQ model.
- ***ThermoSoft*** thermal-conductivity calculation plug-in.
- ***GEARS*** simulation framework in virtual reality (Fig. 5).

A number of novel materials have been developed using the MAGICS software. For example, the novel 2D magnetic alloy we have discovered may find applications in spintronic devices.

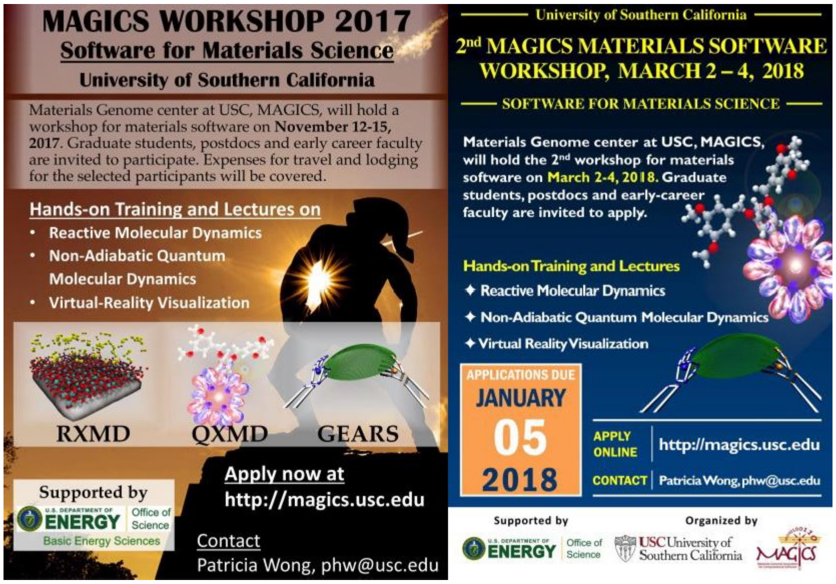
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Fig. 4: Posters of MAGICS workshops for software and data training (November 12-15, 2017 and March 2-4, 2018).

Publications

1. M.-F. Lin, V. Kochat, A. Krishnamoorthy, L. Bassman, C. Weninger, Q. Zheng, X. Zhang, A. Apte, C. S. Tiwary, R. Li, R. K. Kalia, P. M. Ajayan, A. Nakano, P. Vashishta, F. Shimojo, X. Wang, D. M. Fritz, and U. Bergmann, *Ultrafast non-radiative dynamics of atomically thin* $MoSe_2$, Nature Communications, **8**, 1745 (2017).
2. V. Kochat, A. Apte, J. A. Hachtel, H. Kumazoe, A. Krishnamoorthy, S. Susarla, J. C. Idrobo, F. Shimojo, P. Vashishta, R. Kalia, A. Nakano, C. S. Tiwary and P. M Ajayan, *Re-doping in 2D transition metal dichalcogenides as a new route to tailor structural phases and induced magnetism*, Advanced Materials **29**, 1703754 (2017).
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Fig. 5: GEARS allows interactively performing simulations in virtual reality.

Poster

Title: Functional Layered Materials – Computational Synthesis and Validation by Ultrafast Experiments

Presenter: Dr. Aravind Krishnamoorthy, Post-doctoral researcher, CACS, University of Southern California

DMREF: Collaborative Research: A Blueprint for Photocatalytic Water Splitting: Mapping Multidimensional Compositional Space to Simultaneously Optimize Thermodynamics and Kinetics

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Website: none
Keywords: Heterostructures, mid-gap states, charge transfer, photocatalysis, machine learning.

Project Scope

This project involves the theory-guided design, synthesis, and characterization of semiconductor heterostructures with programmable light harvesting and charge transfer for photocatalysis. Heterostructures comprise single-crystalline $M_xV_2O_5$ nanowires (NWs), where M is an intercalated metal cation, functionalized with quantum-dots (QDs). Photocatalysis arises from the transfer of excited-state holes from QDs into mid-gap states of NWs (Fig. 1). Given the vast array of compositional possibilities, an iterative approach involving theory, diversified synthesis guided by machine learning, high-throughput characterization, and associated analytics, along with spectroscopic studies of electronic structure and dynamics, is being implemented to design, synthesize, and characterize heterostructures demonstrating exceptional photocatalytic performance.

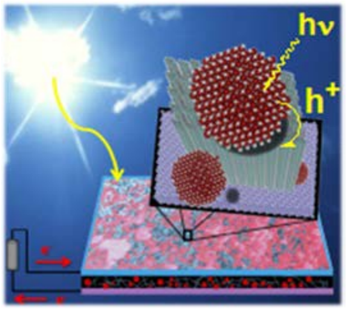

Figure 1. Transfer of photo-generated holes from a quantum dot to an $M_xV_2O_5$ nanowire, a central step in redox photocatalysis.

Relevance to MGI

We hypothesize that the iterative integration of theory, guided synthesis, high-throughput screening, and analytics will enable the rapid development of photocatalysts. Calculations have identified $M_xV_2O_5$ compositions characterized by mid-gap states and have revealed interfacial electronic structure as a function of composition and interconnectivity. Spectroscopy (*e.g.,* X-ray photoemission and absorption, transient absorption) has revealed structure-property-reactivity relationships for charge-transfer and photocatalysis, and has informed the refinement of computational methods. Statistical analysis of hyperspectral X-ray imaging data has allowed for elucidation of signatures of specific intercalated $M_xV_2O_5$ phases. High-throughput synthesis and characterization in conjunction with machine learning are enabling rapid screening of material compositions and guiding synthetic conditions.

Our recent development of second-generation [3-$Sn_xV_2O_5$@CdTe heterostructures illustrates the power of this approach. Calculations predicted that mid-gap states of [3-$Sn_xV_2O_5$ are higher in energy than those of [3-$Pb_xV_2O_5$, rendering them more effective as acceptors of photogenerated holes. X-ray photoemission spectra confirmed this prediction, provided detailed insight into energetics, and revealed that narrow-bandgap CdTe QDs, absorbing into the near-IR, could be interfaced with the NWs while preserving the charge-transfer driving force. Time-resolved spectra confirmed that the [3-$Sn_xV_2O_5$@CdTe heterostructures indeed promote rapid and efficient charge separation.

Technical Progress

We have demonstrated a heterostructure with viable energetic offsets and charge-transfer and photocatalytic reactivity, used data analytics to define syntheses of QDs, developed theoretical tools for calculating electronic structures of interfaces, and elaborated the mid-gap state concept to multiple $M_xV_2O_5$ structures.

Generalizability of Mid-Gap States in $M_xV_2O_5$: A primary hypothesis of our DMREF project is that the distinctive electronic states derived from Pb $6s^2$ lone pairs in $Pb_{0.33}V_2O_5$ can be tuned by substitution with different post-transition-metal cations. A major finding was the preparation of P-$Sn_{0.33}V_2O_5$ by topochemical cation insertion and the observation that mid-gap state energetics can thus be modulated by ca. 1 eV. The topochemical intercalation reaction was designed based on elucidating mechanisms for intercalation using Li-ions as model systems.

Machine-Learning-Driven Design of Quantum Dots: A training set of synthetic conditions has been developed for $CsPbBr_3$ QDs, and a remarkable correlation was established, using statistical learning, between the free energy of aggregation in the ligand shell and the dimensional confinement of QDs (Fig. 2a).[1] This result reveals that machine-learning methods can be applied to refine and precisely modulate colloidal synthesis.

Theory-Driven Design of Interfaces: Calculations are addressing the electronic structure of P-$Pb_{0.33}V_2O_5$/CdX (X: S, Se, Te) interfaces, focusing particularly on how interfacial properties modify the electronic structure of the interface. The surface workfunctions of P-$Pb_{0.33}V_2O_5$ have been found to vary considerably with surface orientation.

Rapid GW Calculations: Fast, high-level electronic-structure calculations are required for theory-driven material design. We accelerated, by nearly two orders of magnitude, GW calculations of large systems.[2] Our method exploits the resemblance of densities of states of materials to that of the free electron gas at high energies (Fig. 2b).

Solving Anodic Corrosion: The targeted and observed rapid transfer of holes from photoexcited QDs to mid- gap states of NWs[3] prevents anodic corrosion, a massive impediment to using QDs in energy-related photocatalysts. We demonstrated that hole transfer, within heterostructures with well-designed energetic offsets, happens at sub-picosecond timescales and is much faster than electron transfer, facilitating charge separation and redox catalysis.

Reductive Photocatalysis: We have measured reductive photocurrents and the evolution of hydrogen gas upon illumination of P-$Pb_{0.33}V_2O_5$@CdSe heterostructures. The ultrafast extraction of holes from CdSe QDs to mid-gap states of NWs promotes photocatalysis. Thus, catalytic functionality is directly attributable to the mid-gap states.

Future Plans

Next-Generation Heterostructures: We will continue to explore compositional space, using theory and experiment, to design and synthesize heterostructures with optimal light harvesting and thermodynamics and kinetics for excited-state charge transfer and photocatalysis. Themes currently being explored include the crystallinity of NWs, the identity of intercalating cations and the corresponding nature, energy, and density of mid-gap states, and the mode by which QDs and NWs are interfaced. Promising heterostructures will be incorporated into photocatalyst architectures and interfaced with earth-abundant redox catalysts to split water.

Refinement and Application of Tools: Statistical learning has enabled the rational optimization of synthetic conditions to yield perovskite QDs with programmable properties. We will develop and release a statistical model in which 3D linear discriminant analysis enables classification of reaction conditions yielding materials that exhibit particular properties and fall within or outside the quantum-confined regime. Such a tool sets the stage for fully automated syntheses of QDs. Additionally, we will apply machine learning tools to large sets of spectroscopic data for our intercalated phases leveraging a promising hyperspectral singular variable decomposition framework we have developed that has allowed for the first observational of compositional stripes in X-ray imaging data of $Li_xV_2O_5$. Our development of fully-converged GW calculations for large oxide systems has opened the door to GW calculations for

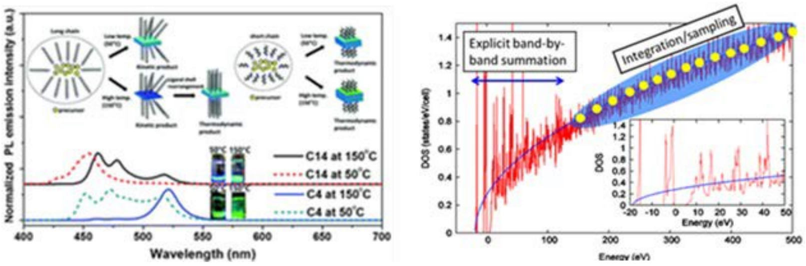

Figure 2. (a) The free energy of ligand aggregation is a clear correlator that allows for tuning of perovskite QDs' dimensions; (b) calculated density of states of MgO showing free-electron-like behavior at high energies.

nanostructures, complex multinary compounds, surfaces and interfaces, and defects in solids. These are the subject of ongoing research.

Broader impact

Broader impacts are derived from several avenues. As described above, statistical learning tools have been developed and applied to materials synthesis and spectroscopy. In collaboration with the RISE program at the University of Puerto Rico Cayey, a 10-week summer internship program for students from underrepresented groups has been implemented and will continue. In summer 2017, interns performed research at the University at Buffalo and at Texas A&M. A workshop was held in Buffalo, New York, in spring 2017 focusing on informatics-driven materials design for energy. The workshop attracted an audience of about 150 and provided faculty, students (graduate and undergraduate), and postdocs with opportunities to interact with experts, to foster collaborations among leading researchers in the field, and to promote science and higher education.

Data Management and Open Access

We have adapted a sample- and data-management system using a MySQL database with an HTML/PHP/Javascript front end. The database (http://piperlab.binghamton.edu/DMREF_database/) is currently an internal system within our DMREF project to track samples, experiments and calculations. A future version of the database will allow open read-only access to search for spectra and calculations generated from our DMREF project. Software for automated synthesis of QDs is expected to be shared through this database within the next 6 months after further cross-site validation.

Advancing Along the Materials Development Continuum

Iterative theoretical modeling and spectroscopy measurements are informing the choice of synthetic targets and bringing about a much-accelerated evolution of photocatalytic architectures. The demonstration of machine learning to colloidal crystal growth represents a potentially transformative advance for the community and has enabled rational, instead of empirical, determination of reaction parameters, greatly eliminating the need for resource-intensive screening of reaction variables. Similarly, Bayesian-PCA methods are providing important insight into the utility of topochemical intercalation methods to prepare phase-pure $M_xV_2O_5$ phases. The iterative interplay of statistical learning has thus greatly advanced design and synthetic control of both the QD and $M_xV_2O_5$ NW components of our proposed architectures. Accelerated GW calculations facilitated by advances in this project period are being applied to interfaces and will inform interfacial design in subsequent project periods.

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PFHub: Phase Field Community Hub

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Website: https://pages.nist.gov/pfhub/

Keywords: jekyll-website, phase-field, benchmarks, quality-assurance, web-platform

Project Scope

PFHub is a web platform directed at the phase field community. The primary goal is to provide a set of benchmark problem specifications for phase field codes alongside a platform that facilitates uploading, curating and sharing of benchmark results for comparison based on performance and accuracy. A secondary goal is to increase the adoption of phase field methods in engineering and academic applications by developing practical documentation for implementing phase field problems. By achieving these goals, PFHub aims to foster a more engaged and integrated phase field community.

Relevance to the Materials Genome Initiative

As phase field modeling has gained popularity, a variety of codes have emerged. Some of them are community-based codes, such as MOOSE, FEnICs, and FiPy, and some are proprietary or in-house. Currently, there is no easy way to determine the accuracy, efficiency and applicability of each of these codes in a timely manner. PFHub aims to address this need by providing a set of benchmark problems for the phase field community to test and validate their codes. Furthermore, PFHub provides a web infrastructure for uploading and comparing results from these benchmark problems and, thus, provides valuable feedback to code developers and users. This work directly addresses the needs of the Materials Genome Initiative by providing a testing and validation platform for the wider phase field community improving phase field code development at multiple stages. An important aspect of this project is the community building effort centered around developing the website and designing the benchmark problems. The community effort includes hosting hackathons, workshops and regular online meetings as well as developing the tool chain in an open and inclusive manner so that a wide range of phase field practitioners can influence the direction of PFHub.

Technical Progress

Example of a code comparison page for one of the benchmark problems. Includes two figures demonstrating code accuracy and a table of relevant uploads.

The PFHub benchmark effort has been heavily developed over the last few years and includes contributions from 10 developers and has at present 1,316 commits. The website currently hosts 55 uploaded benchmark results from different users and code bases and has had 1.7K unique views in the last year (up 411% from the previous year). The community has developed 7 separate benchmark specifications, which are all hosted on the website in Jupyter notebooks. The design of the benchmarks has resulted in arecent journal publication [1].

The core group that both develops the benchmark specifications and the website platform consists of members from NIST, Northwestern University, Argonne National Laboratory, Idaho National Laboratory, University of Michigan and Penn State University. The group has hosted 6 workshops and 3 hackathons to support both the development of the benchmark specifications and the website. Each workshop consists of 20 to 30 participants that represent many of the community-code development efforts including lead scientists, post-docs, and graduate students). The workshops are used to help determine the relevance of the benchmarks as both a tool to assess code quality and as instructional material for teaching the phase field method.

Development of the website platform began in 2014 and has subsequently undergone many development cycles. The original notion for the website was to have a custom representation of cross comparison between the uploaded benchmark results based solely on static website generation without a content management system. Dynamic components of the website are enabled by using third-party apps supplemented with external APIs where necessary and, thus, minimizing the development and maintenance overhead. The users are currently asked to store their data at any archival data service (such as Figshare, Backblaze or S3) that they choose and then provide the links to the website via a web form. This mode of operation minimizes the overall development required for the website, allowing the developers to focus on the frontend user experience rather than hosting and deploying backend infrastructure. The frontend is built around Materialize CSS providing a familiar look and feel. All data processing occurs in the browser using high-level, maintainable CoffeeScript (a high-level programming language that compiles to JavaScript).

Future Plans

In the future PFHub will likely be used as a model template for hosting frontend portals for other small scientific projects. To enable this, deployment and development of the website needs to be made seamless and modular. In the future, it will be beneficial for users to not have to archive their own data, but unify data archiving as part of the metadata upload. To achieve this PFHub will use the Materials Data Facility (https://www.materialsdatafacility.org) as a backend service. Long term goals include implementing features to enable uploading and running executable container implementations of the benchmarks.

Data Management and Open Access

All data and code is stored in publicly available archives. Code is tested via Travis CI at each push to the website repository. The simulation code along with the result data for uploaded benchmark simulations must be in a publicly available archive. Users are encouraged, but not required, to containerize benchmark simulations. Containerizing simulations will become mandatory in the future. The website code repository includes development documentation to encourage external developers. The developers hold monthly chat meetings to try to encourage external developers.

Advancing Along the Materials Development Continuum

This project accelerates the development and usage of phase field codes, a fundamental tool for understanding mesoscale materials and creating linkages with meta-models for integrating into integrated computational materials engineering workflows.

Publications

1. A. M. Jokisaari, P. W. Voorhees, J. E. Guyer, J. Warren and O. G. Heinonen, *Benchmark problems for numerical implementations of phase field models*, Computational Materials Science **126**, 139 (2017).

Disclaimer

Accelerated Soft Magnetic Alloy Design and Synthesis Guided by Theory and Simulation

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Website: None.

Keywords: Magnetic alloys, Nanostructured, Micromagnetics, thermodynamics modeling, .

Project Scope

The collaborative project reinvents the design of new nanocomposite soft magnetic alloys using hierarchical, multi-scale, magneto-structural modeling with input from density functional theory (DFT) calculations of structural and magnetic properties for single-crystals. Micromagnetic theory provides the constitutive law for the continuum-level model for optimization of realistic microstructures consisting of an amorphous matrix surrounding nanocrystals. Structural considerations are evaluated by continuum thermodynamics modeling and magnetic performance characteristics are evaluated by micromagnetics modeling. Successful validation of this framework (by nanocomposite soft magnetic alloy fabrication) will result in new alloy compositions thwarting conventional alloy design principles and have excellent magnetic softness (coercivity <10 A/m).

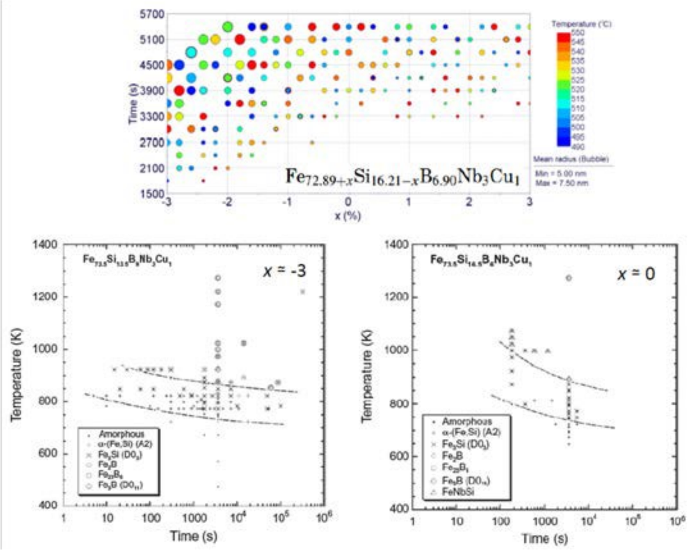

Figure 1: (top) Combined CALPHAD and machine learning predicts the microstructure evolution in complex (Fe,Si)-based nanocomposite alloys;[1] as compared to experimental (bottom) time-temperature-transformation (TTT) diagrams for two compositions of (Fe,Si)-based nanocomposite magnets.[2]

Relevance to MGI

There are two key directions in which this project is evolving that are directly relevant to MGI. First (in incipient stage) is the computational search for new soft magnetic phases based on high-throughput DFT calculations; this search will result in a database of mostly new and still-hypothetical crystalline magnetic phases. Since the DFT calculations cannot be exhaustive (all combinations of elements and space groups), machine learning techniques will guide the course of the high-throughput DFT calculations towards soft magnetic materials developing correlations and predicting what set of DFT calculations should run next. The second direction pertains to modeling nanocrystalline phases precipitated from amorphous matrix. This work is well underway at CWRU/CSM and has produced valuable processing-structure relationships [1]. As shown in the figure, the present application of the computational design methodology accurately predicts characteristics of phase transformations and microstructure evolution in well-known (Fe,Si)-based nanocrystalline soft magnets. Based on this success, we will begin investigation of nanocomposite alloys of compositions that have been rarely explored – especially (Fe,Co,Ni)-based nanocomposite soft magnets. In the spirit of MGI, we will use the CALPHAD and precipitation modeling for determination of processing parameters and compositional ranges to guide synthesis of these new magnets with optimal properties.

Technical Progress

- Coupled CALPHAD and machine learning approaches to optimize structural characteristics as functions of processing parameters and composition for (Fe,Si)-based nanocomposite soft magnets (a.k.a. Finemet)
    - Developed accurate metamodels for radius and volume fraction of the nanocrystalline phase in Finemet, which are responsible for desirable soft magnetic properties of the alloy
- Development of metastable phase diagrams (CALPHAD) and precipitation model for simulating nucleation and growth of metastable a"-(Fe, Si) nanocrystals from an amorphous precursor for Finemet
    - Developed precipitation model for a set of compositions and isothermal annealing temperatures.
- Developed analytical model for the coupling of crystal structures, textures, and numbers of grains interacting within a magnetic domain.
    - Verified ability to match the random anisotropy model[3] when using the same assumptions, but model expands more generally to exploring new crystal structures and textures, and considering any arbitrary 2D or 3D isotropy.
- Produced (Co,Ni)-based nanocomposite soft magnetic alloys with compositions determined considering compositionally dependent magnetic anisotropy and magnetoelastic effects (an extension of conventional alloy design methodologies)
    - Observed a discrepancy between the predicted and experimental minimum coercivities, thus motivating the micromagnetics modeling in this project (which will enable greater prediction accuracy)

Future Plans

- High-throughput framework for density functional theory calculations is under development: in this framework, known space groups will be populated with select elements, and magnetostriction and magnetic anisotropy will be calculated using DFT. Results will lead to a database of crystalline magnetic materials, which will be made available as a database.
- Machine learning techniques will be applied to the created database of crystalline compounds to determine correlations between space-groups and soft magnetic properties; formal collaboration with CITRINE Informatics on data management and machine-learning approaches to predicting future soft magnetic phases
- A continuum-level description of the amorphous-crystalline composite microstructures is being developed in a Differential Geometry framework, free of constraints of Cartesian coordinate systems that limit ability to model amorphous structures.
- Validation of computationally designed alloys by structural and magnetic characterization will support this methodology as a viable tool for down-selecting compositions in complex alloy systems

Broader impact (Only required for NSF projects)

Three full-time graduate students, one full-time postdoc, and one (in part) graduate student are being trained under this project. NASA Glenn offered an internship over the summer to one of the grad students (David Grimmer), and Colorado School of Mines hosted an expert in machine learning techniques (Prof Nirupam Chakraborti from Indian Institute of Technology, Kharagpur) during the summer. Two invited talks and two student-delivered contributed talks (all at CWRU) have been to the scientific community regarding the methodology and outcomes of this work. In these ways, we are training the next generation of students for the necessary skills to perform meaningful computational materials science.

Data Management and Open Access

CSM has developed a formal collaboration with CITRINE Informatics for data repositories, data management, and open access. As such, for the data-intensive publications from this project, we make publicly available all data leading to those publications, at the time of manuscript submission and regardless of the institutional access to the respective journal(s). In the near future, CITRINE will also host a database of magnetic properties for calculated alloys and compounds. In addition, CSM maintains another materials database website https://materialsmine.mines.edu/ which can also host some of the results if necessary.

Advancing Along the Materials Development Continuum

We have established a Technical Advisory Board (TAB) consisting of partners from Federal research labs (AFRL, NASA GRC, NETL) and industry (Tesla). As we progress through the program, we will engage the TAB during our team meetings to make use that the direction of the research continues to be a commercially relevant technology. Related SBIR work has been proposed (by Willard, CWRU) through the Department of Energy. State of Ohio funds for research on high temperature nanocomposite soft magnets emphasize the commercialization of this technology. The present computational design efforts will enable greater convergence on relevant materials for these efforts.

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NIST data resource for curated thermophysical property data of metal systems

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Co-Principal Investigator: Chris Muzny, Thermodynamics Research Center, NIST, chris.muzny@nist.gov
Website: https://trc.nist.gov/metals_data
Keywords: thermophysical properties, metals, alloys, experimental data, metadata, uncertainty

Project Scope

The scope of our work is to make original experimental thermophysical property data of metal systems electronically available in a well-structured, machine readable data format. We specifically target property data for unary, binary, and ternary systems in support of the CALPHAD approach to computational material development. Properties captured and represented in our online resource include, but are not limited to: Enthalpy, specific heat capacity, thermal expansion, thermal conductivity and other transport properties, phase transition temperatures and extensive phase information.


The NIST Alloy Data web application provides access to thermophysical property data with a focus on unary, binary, and ternary metal systems. All data is from original experimental publications including full provenance and uncertainty.

Figure 1: Screenshot of the search page of the free online data resource for experimental, thermophysical property data for metal systems: https://trc.nist.gov/metals_data

Relevance to MGI

The output of TRCs (Thermodynamics Research Center) effort addresses multiple academic and industrial needs within the MGI community. With many projects focused on computational tools for Integrated Computational Materials Engineering (ICME), the electronic availability of curated, reliable experimental thermophysical property data is crucial to inform simulation algorithms, prediction tools or high throughput scanning for specific property characteristics. In materials development the CALPHAD community can take advantage of the data repository to aid the development of new or optimized alloys for specific applications.

A vast improvement compared to other, limited data resources which consistently lack metadata, our approach includes curation of metadata, such as processing information, which can be key to correct interpretation and data evaluation. Equally important is the provenance of the data and a clear statement regarding their quality quantified in statements of uncertainty – all this is embedded in the core of our data capture process.

Technical Progress

The many challenges in characterizing metal-based systems required substantial augmentation of data structures and processes within the NIST/TRC Data Archival System to address additional data types and complexities with phase characterizations necessary to describe metal systems. New and substantially modified features developed for capturing data for metal and alloy systems include capabilities for additional metadata: from heat treatments and other processing of samples to metadata for temperature scales and representation of phase information. All this is in addition to information on the chemical compounds involved, the bibliographic information and numerical data values themselves, where each data record includes comprehensive methodological metadata, including pointwise uncertainties assigned via expert review within TRC. The inclusion of evaluated uncertainties is essential, as uncertainties represent the only quantitative metric of quality for an individual datum, and these are essential for any subsequent critical evaluation.

After the initial development of a custom guided data capture software the efforts to actually capture experimental data from primary, publicly available sources is a continuous, long-term, and ongoing effort. So far, about 272,000 data points have been captured, see Figure 2, about half of them for pure elements, the other half for binary and ternary alloy systems.

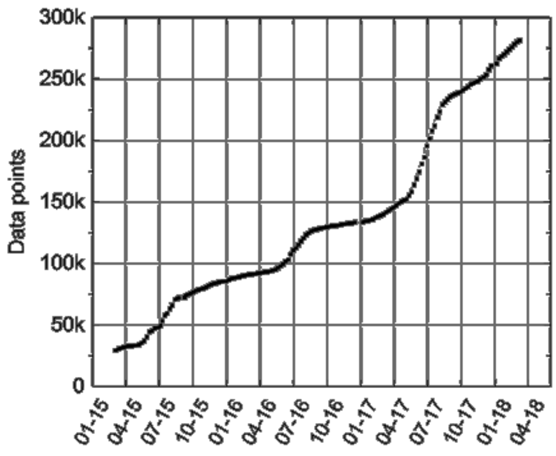

Figure 2: Number of data points captured for thermophysical property data of metal systems.

Future Plans

To add even more value to the readily available data we continue to improve our analysis tools to include a data normalization and advanced curation layer. A simple example is the normalization of the various temperature scales used over time to report data. Other features will focus on increasing the automation of already implemented processes to optimize the data capture process and curation of data for properties of interest. Adding more relevant data to our repository is, of course, a high priority for each project year.

Broader impact

As part of its mission to provide data reliably to a broad range of interested parties, TRC also maintains an IUPAC-standard XML format for dissemination of thermophysical and thermochemical property data, ThermoML. ThermoML is presently an active project with the International Union of Pure and Applied Chemistry to extend support to metal-based systems. This format allows for consistent data representation, spanning industrial and academic needs with one data structure. (https://iupac.org/projects/project-details/?project_nr=2017-016-3-100)

Data Management and Open Access

TRCs online data resource for thermophysical property data of metal systems meets the MGI objective for making results publicly accessible and useful to the community by presenting all the captured original experimental data in an interactive online resource (https://trc.nist.gov/metals_data). In addition to plots and tables of the data we also list important meta data, bibliographic provenance and uncertainty estimates. A more computer-oriented (API) interface is available for automated data consumption and collaborative efforts of interested parties.

Publications

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Collaborative Research: Interface-promoted Assembly and Disassembly Processes for Rapid Manufacture and Transport of Complex Hybrid Nanomaterials (IpAD)

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Website: none

Keywords: interface-promoted assembly, block polymers, inorganic nanoparticles, particle transport, polymer reference interaction site model (PRISM) theory, molecular dynamics simulations

Project Scope

This work aims to develop approaches to rapidly discover and manufacture hybrid inorganic-organic nanostructured objects (HIONs) possessing complex compositions, structures, properties and functions. By leveraging interface-driven synthesis and dynamic assembly/disassembly of organic polymers and inorganic nanoparticles under flow (**Figure 1a**), our goal is to expedite and drive intermolecular and interparticle assembly that is inefficient or impossible in the absence of such interfacial interactions.

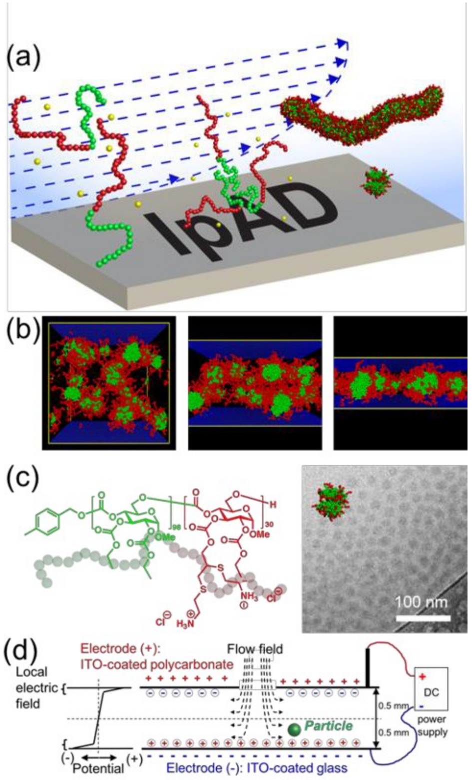

Figure 1. (a) Interface-promoted assembly and disassembly (IpAD) of complex hybrid nanostructures comprised of organic polymers and inorganic nanoparticles. (b) Simulation of block polymer assembly near surfaces and under confinement. (c) Transmission electron micrograph and coarse-grained simulation of glucose-based block polymer assembly. (d) Experimental imaging of particle transport under flow.

Relevance to MGI

Team exchanges, integrated work activities, and communication by e-mail, data sharing, monthly meetings *via* Webex and an in-person meeting of all four teams has integrated the development and optimization of synthetic procedures, characterization techniques, theory and simulations for the relevant materials systems, identified new targets and inspired new directions, and facilitated cross-disciplinary education and training of the next-generation workforce. Based on specific synthetic polymer chemistries in the Wooley lab, coarse-grained models, liquid-state theory and high performance molecular simulations in the Jayaraman lab have yielded a large library of predictions of hybrid nanostructures formed from assembly of a variety of polymers and nanoparticles in solution and at surfaces (**Figure 1b,c**). Preliminary hybrid nanostructures synthesized in the Wooley lab have been employed by the Johnson lab to establish computational and experimental methods for investigation of assembly and transport at surfaces under flow (**Figure 1d**), and by the Pochan lab for the optimization of *in-situ* transmission electron microscopy, which will complement solution-state atomic force and optical microscopy in the Wooley and Johnson labs. Toward increasingly-sophisticated hybrid nanomaterials, the Wooley lab has embarked on the synthesis of advanced polymer architectures, with compositions, and sequences guided by Jayaraman group predictions.

Technical Progress

Stemming from the iterative loop established between the four teams, major technical achievements include the development and validation of computational and experimental methods that guide and enable: 1) assembly of naturally-derived, glucose-based polymers into well-defined nanostructures; 2) investigation of charge-selective surface adsorption of polymer particles; 3) implementation of liquid state integral equation theory to focus the use of computationally-intensive molecular simulations, and, thus, accelerate predictive materials discovery and manufacture; and 4) evaluation of particle transport near and on surfaces under flow.

Integrating synthesis, assembly, characterization, and modeling techniques across our four teams has yielded a library of diverse nanomaterials and facilitated preliminary investigation of charge-selective surface adsorption towards interface-promoted assembly and disassembly. Degradable glucose-based polymers in linear and bottlebrush architectures have been synthesized by the Wooley lab, and afforded spherical, cylindrical, and vesicular nanostructures upon assembly in solution. Advanced transmission electron microscopy, atomic force microscopy, and small angle neutron scattering studies by the Pochan lab have provided insight into the morphology and size of the resulting nanostructures in solution. In the Jayaraman lab, coarse-grained models of the glucose-based polymers have enabled computational prediction of these assemblies as a function of polymer composition and architecture, both in solution and near surfaces, at experimentally relevant length and time scales. These predictions are informing future syntheses and surface-mediated assembly experiments. Towards surface-mediated assembly, adsorption of anionic polymer particles to charged surfaces have been investigated by the Johnson lab using fluorescence microscopy and simulations, and by the Wooley lab using solution-state atomic force microscopy.

Advancements in methods that will accelerate the discovery and manufacture of complex hybrid nanomaterials include an integrated approach of Polymer Reference Interaction Site Model (PRISM) theory and molecular dynamics simulations by the Jayaraman group, and a combination of fluorescence microscopy and simulations by the Johnson lab for characterization of particle transport under flow near surfaces. Jayaraman and coworkers have demonstrated that PRISM theory can predict assembly of copolymers over a wide range of design parameters and, thus, focus the use of computationally-intensive molecular dynamics (MD) simulations on a smaller set of design parameters. The selective use of MD simulations enabled by the theoretical predictions substantially reduces time and computational expenses associated with purely simulation-based prediction of polymer assembly. In conjunction with simulations based on DLVO theory, the Johnson group has implemented total internal reflection fluorescence microscopy to investigate the transport of polymeric particles near and on surfaces under an impinging jet flow field. These techniques are amenable to a variety of surfaces and particles, and, as such, will be instrumental in advancing understanding of interface-promoted assembly and disassembly processes throughout this project.

Future Plans

Having established an iterative feedback loop and commenced development of methods for theoretically and experimentally understanding and enabling interface-promoted assembly of organic polymers and inorganic nanoparticles into complex hybrid nanomaterials, we will continue to advance and implement these approaches. The objectives are to: 1) advance the theoretical and experimental understanding of assembly/disassembly of polymers, nanoparticles and HIONs; 2) develop *in situ* HION production in a complex column environment during flow that takes advantage of solution- and substrate-mediated interactions; 3) produce complex morphologies, compositions and properties; 4) engineer-in dynamic morphology-shifting character, disassembly mechanisms and/or degradable switches to provide diverse, adaptive behavior; 5) demonstrate preliminary HION utilization as hosts for complex mixtures of guest species.

Broader impact

Longstanding benefits to society will come from education and training through integration of theory, simulation and experiment across multiple length and time scales and the disciplines of chemistry, geosciences and materials science and engineering, from community outreach, and from the design of pathways for rapid access to data and translation of materials. In April 2017, PI Wooley and her research group organized a Science Night at a local elementary school, with researchers across multiple disciplines at Texas A&M, the University of Utah, and local companies to provide *ca.* 15 engaging activities that were enjoyed by hundreds of students and their families. In June 2017, PI Johnson and graduate student Cesar Ron taught a short course on Particle Transport in Porous Media to 60 chemical engineering students at the Escuela Politecnica Nacional in Quito, Ecuador. In July 2017, PI Wooley and her research group led a week-long Nanotechnology Youth Adventure Program (YAP) with the Batteas group at Texas A&M for middle-to-high school students that incorporated the preparation and characterization of magnetic polymer nanoparticle composites designed for oil recovery, while PI Jayaraman and her group contributed simulations that were presented as an interactive lecture. Substantial mentoring and outreach efforts have engaged a diverse population with interdisciplinary training, professional development, and hands-on activities related to polymer- and materials-based research to enable and inspire the field's future leaders.

Data Management and Open Access

Project outputs have been provided to the scientific community and to the general public through publications, scientific lectures, a laboratory manual for YAP and the PIs' websites. The supporting information files accompanying the Jayaraman group publications include details of the model, simulation protocols, analyses procedures and all of the analyzed data from the theory and simulations. The Johnson group has developed detailed descriptions of calculations describing transport of polymer-nanoparticle composites near and on surfaces, which will be optimized and provided online. We are piloting electronic notebooks for data sharing between the collaborator laboratories, which will then facilitate broader sharing with the public *via* creation of experimental DOIs that will be shared on the PIs' websites. Efforts continue toward enhanced data sharing *via* publishers.

Advancing Along the Materials Development Continuum

Hybrid inorganic-organic materials are of significant fundamental and technological interest in solution-, thin-film or bulk states, and this project addresses complex challenges with the assembly of discrete hybrid nanoparticle systems by utilizing a combination of solution- and interface-promoted interactions to access unique morphologies rapidly. The theory, processes and materials in this project have potential to impact many fields, such as environmental remediation, biomedicine and energy. The magnetically-active hybrid nanostructures used in this research have already been discussed with Flotek Industries, ExxonMobil and Dow Chemical Company. While scale-up of these materials presents a hurdle to commercialization, the theoretical and computational guidance is expected to accelerate the down-selection of targets to pursue the scalability of the synthetic methods and assembly processes. Integration of experiments with theory and simulations that capture and predict polymer-particle-solvent-substrate interactions under flow is central to enabling, disseminating, and translating these technologies.

Publications

1. Y. Song, Y. Chen, L. Su, R. Li, R. A. Letteri, K. L. Wooley, *Crystallization-driven Assembly of Fully Degradable, Natural Product-based Poly(L-lactide)-block-poly(α-D-glucose carbonate)s in Aqueous Solution*, Polymer **122**, 270 (2017).
2. I. Lyubimov, D. J. Beltran-Villegas, A. Jayaraman, *PRISM theory study of amphiphilic block copolymer solutions with varying copolymer sequence and composition*, Macromolecules **50**, 7419 (2017).
3. D. J. Beltran-Villegas, I. Lyubimov, A. Jayaraman, *Molecular dynamics simulations and PRISM theory study of solutions of nanoparticles and triblock copolymers with solvophobic end blocks*, Molecular Systems Design & Engineering, Special Issue on Machine Learning and Data Science in Materials Design, DOI: 10.1039/C7ME00128B
4. D. J. Beltran-Villegas, A. Jayaraman, *Assembly of amphiphilic block copolymers and nanoparticles in solution: Coarse-grained molecular simulation study*, J. Chem & Eng. Data, DOI: 10.1021/acs.jced.7b00925.

SPEC: Center for Scalable Predictive methods for Excitations and Correlated phenomena

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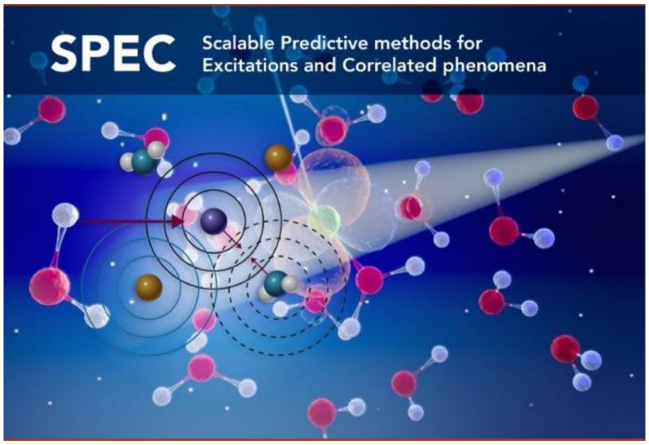
Co-Principal Investigators: Karol Kowalski, Niranjan (Niri) Govind, Edoardo Apra, Sriram Krishnamoorthy, Anne Chaka, Chris Mundy (PNNL), John Rehr, Thom Dunning, Xiaosong Li (University of Washington), So Hirata (University of Illinois, Urbana-Champaign), Dominika Zgid (University of Michigan), Wibe de Jong, Chao Yang (LBNL)
Website: None
Keywords: correlation, spectroscopy, Green’s function, multireference, embedding

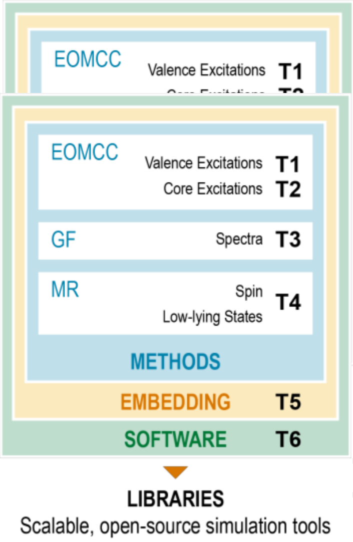
Project Scope

The overarching goals of the SPEC project are (1) to provide scalable open-source software with implementations of state-of-the art, many-body electronic structure methodologies required to address challenges in excited- state and correlated phenomena in complex chemical systems; and (2) to apply the developed software to tackle spectroscopic challenges needed to support research at DOE light source facilities. The implementation of these methodologies will be performed using novel scalable programming models and libraries to enable their efficient performance on existing peta- and forthcoming extreme- scale computer architectures. The focus will be on the development of accurate *ab initio* methodologies such as equation-of-motion coupled cluster methods, relativistic methods, Green’s function approaches, multi-reference formulations, and self-energy embedding methods.



Relevance to MGI

The planned methodologies in the SPEC project will be applicable to a broad range of science domain areas including light-harvesting systems, artificial photosynthesis, correlated molecular and materials systems, carbon- based materials, solvation chemistry, catalysis, geochemistry, and novel ultrafast femtosecond techniques.



Future Plans

The SPEC center will achieve the theoretical, methodological, and computational scientific research goals through a comprehensive and integrated six-task research program:

T1: Accurate Equation-of-Motion Coupled Cluster Formalisms for Valence Excited States
T2: Accurate Equation-of-Motion Coupled Cluster Formalisms for Core Excited States
T3: Hierarchical Green’s Function Formulations
T4 Scalable Multi-Configurational and Multi-Reference Methods for Quasi-Degenerate Molecular Systems
T5: Self-Energy Embedding Approaches
T6: Programming Models, Computer Science Tools, and Optimization for Many Body Methods

Materials Genome Initiative Principal Investigator's Meeting

Poster List

March 26-27, 2018

1 **Nicholas L. Abbott** University of Wisconsin-Madison
Collaborative Research: Chemoresponsive Liquid Crystals Based on Metal Ion-Ligand Coordination

2 **Douglas H. Adamson** University of Connecticut
Polymeric Composites and Foams Based on Two Dimensional Surfactants

3 **Rakesh Agrawal** University of Connecticut
Rapid Design of Earth Abundant Inorganic Materials for Future PVs

4 **Mark D. Allendorf** Sandial National Lab
HyMARC Consortium on Breakthrough Materials for Hydrogen Storage

5 **John Anthony** University of Kentucky
Organic Semiconductors by Computationally Accelerated Refinement (OSCAR).

6 **Raymundo Arróyave** Texas A&M University
Accelerating the Development Of Phase Transforming Heterogenous Materials: Application To High Temperature Shape Memory Alloys

7 **David Baker** University of Washington
Integrating theory, computation and experiment to robustly design complex protein-based nanomaterials

8 **Leonid Berlyand** Pennsylvania State University
Design of active ink for 3D printing: integrating modeling and experiments

9 **Mark Bathe** Massachusetts Institute of Technology
Computational Design of Next-generation Nanoscale DNA-based Materials

10 **Katia Bertoldi** Harvard University
Biologically Inspired Optimized Materials And Technologies Transformed by Evolutionary Rules

11 **Irene J. Beyerlein** University of California Santa Barbara
Collaborative Research: Multiscale alloy design of HCP alloys via twin mesh engineering.

12 **Kaushik Bhattacharya** California Institute of Technology
Designing Microstructure for Engineering Toughness

13 **Simon J. L. Billinge** Columbia University
Towards more robust models for nanostructure

14 **Volker Blum** Duke University
HybriD3: Discovery, Design, Dissemination of Organic-Inorganic Hybrid Semiconductor Materials for Optoelectronic Applications

15 **Geoff Brennecka** Colorado School of Mines
Computation Of Undiscovered Piezoelectrics and Linked Experiments for Design

16 **D.W. Brenner** NC State
Development of Fundamental Design Rules for Material-Liquid- Nanoparticulate Interfaces that Optimize Control of Friction, Adhesion and Wear.

17 **L C Brinson** Duke University
A Data-Centric Approach for Accelerating the Design of Future Nanostructured Polymer and Composite Systems

18 **M.Carme Calderer** University of Minnesota
Materials engineering of columnar and living liquid crystals via experimental characterization, mathematical modeling and simulations

19 **Michael Chabinyc** University of California Santa Barbara
Collaborative Research: Controlling Hierarchical Nanostructures in Conjugated Polymers

20	**K. S. Ravi Chandran**	University of Utah	Computational Design, Rapid Processing, and Characterization of Multiclass Materials in Ti-B-X Platform
21	**Hai-Ping Cheng**	University of Florida	Exploring Multi-functional Molecular Electronic Materials
22	**Ashutosh Chilkoti**	Duke University	High Throughput Exploration of Sequence Space of Peptide Polymers that Exhibit Aqueous Demixing Phase Behavior
23	**Kamal Choudhary**	MSED NIST	JARVIS: Understanding Fundamental Material Interactions and Properties with Classical Physics, Quantum Physics and Machine Learning
24	**Vincent P. Conticello**	Emory University	Collaborative Research: Helical Protein Assemblies by Design
25	**Ismaila Dabo**	The Pennsylvania State University	Photocatalysts by Design: Computational Screening of Reconstructed Perovskite Semiconductor Electrodes for Efficient Solar-to-Fuel Conversion
26	**Michael Demkowicz**	Texas A&M University	Designing and synthesizing nano-metallic materials with superior properties
34	**Michael Donahue**	NIST	μMAG: Micromagnetic Modeling Activity Group
27	**Kevin D. Dorfman**	University of Minnesota	Computationally-driven design of advanced block polymer nanomaterials
28	**R. Engel-Herbert**	The Pennsylvania State University	Collaborative Research: Materials design of correlated metals as novel transparent conductors
29	**C.B. Eom**	University of Wisconsin-Madison	Antiperovskite interfaces for materials design
30	**Zahra Fakhraai**	University of Pennsylvania	Engineering Stable Glass Films Using Molecular Design and Surface-Mediated Equilibration
31	**Gregory A. Fiete**	University of Texas at Austin	Collaborative Research: Design and synthesis of novel materials for spin caloritronic devices
32	**Amar H. Flood**	Indiana University	Multiscale Theory for Designing Hierarchical Organic Materials formed by Self-assembly
33	**Ian Foster**	University of Chicago	Polymer Property Predictor and Database
35	**Seth Fraden**	Brandeis University	Programmable Chemomechanical Materials
36	**Laura Gagliardi**	University of Minnesota	Inorganometallic Catalyst Design Center
37	**Giulia Galli**	UoC&ANL	Interoperability of advanced sampling and electronic structure codes and data reproducibility
38	**William A. Goddard III**	California Institute of Technology	Shear driven formation of nano-diamonds at 0.6 GPa and 300 K
39	**Enrique Gomez**	The Pennsylvania State University	Design Rules for Flexible Conductors: Predicting Chain Conformations, Entanglements, and Liquid Crystalline Phases of Conjugated Polymers
40	**Jeffrey Greeley**	The Pennsylvania State University	Design of Multifunctional Catalytic Interfaces from First Principles
41	**Martin Green**	NIST	Building a High-Throughput Experimental Materials Collaboratory (HTE-MC)
42	**Michael Groeber**	USAF	Challenges in the Digital Materials Enterprise: Structural Materials Examples

43	**Timothy Grotjohn**	Michigan State University	Doping and Defects in Diamond for Electronics
44	**Jason Hattrick-Simpers**	NIST	Iterative Machine Learning – High Throughput Experimental Platform for the Discovery of Novel Amorphous Alloys
45	**Hendrik Heinz**	University of Colorado at Boulder	Design and Testing of Nanoalloy Catalysts in 3D Atomic Resolution
46	**Matthew E. Helgeson**	University of California Santa Barbara	Programming mesostructured colloidal soft matter through complex quenching and annealing
47	**Graeme Henkelman**	University of Texas at Austin	Toolkit to Characterize and Design Bi-functional Nanoparticle Catalysts
48	**Andreas Heyden**	University of South Carolina	Collaborative Research: Design and Discovery of Multimetallic Heterogeneous Catalysts for a Future Biorefining Industry
49	**Kai-Ming Ho**	Iowa State University	Collaborative Research: Design and Synthesis of Novel Magnetic Materials
50	**Kai-Ming Ho**	Iowa State University	Control Phase Selection in Liquid Solidification for Materials Discovery and Synthesis
51	**Robert Hull**	Rensselaer Polytechnic Institute	Adaptive Control of Microstructure from the Microscale to the Macroscale; In-Situ Thermomechanical Processing and Measurement in the SEM
52	**Koblar Jackson**	Central Michigan University	FLOSIC: efficient density functional calculations without self- interaction
53	**Anubhav Jain**	Lawrence Berkeley National Laboratory	Software tools for data-driven research and their application to thermoelectrics materials discovery
54	**Michael Janik**	Pennsylvania State University	Computationally guided design of multicomponent materials for catalytic reactions
55	**Debdeep Jena**	Cornell University	Extreme Bandgap Semiconductors
56	**Jeremiah A. Johnson**	Massachusetts Institute of Technology	Analysis and Optimization of Polymer Networks for Emerging Applications
57	**Yung Joon Jung**	Northeastern University	Accelerated Design of Strong, Highly Conductive Carbon Nanotube-based Fibers via Electrical Fusion
58	**Kathleen Kash**	Case Western Reserve University	The heterovalent nitride semiconductors and mixed binary-ternary heterostructures
59	**Paul Kent**	Oak Ridge National Laboratory	Center for Predictive Simulation of Functional Materials
60	**Sanjay V. Khare**	Rensselaer Polytechnic Institute	Nitride Discovery – Creating the Knowledge Base for Hard Coating Synthesis
61	**John Kieffer**	University of Michigan	SusChEM: Simulation-Based Predictive Design of All- Organic Phosphorescent Light-Emitting Molecular Materials
62	**R. Joseph Kline**	NIST	Extracting thermodynamic parameters of nanoscale structures by integrating physics-based modeling with X- ray scattering
63	**Robert V. Kohn**	New York University	Adaptive fine-scale structure design: from theory to fabrication

64 **Sanat Kumar** Columbia University
Collaborative Research: Designing Optimal Nanoparticle Shapes and Ligand Parameters for Polymer- Grafted Nanoparticle Membranes

65 **A. Gilad Kusne** NIST
Autonomous Materials Research Laboratory: Phase Mapping

66 **A. Gilad Kusne** NIST
Autonomous materials characterization systems: XRD and electrochemical prototypes

67 **Igor Levin** NIST
Deriving atomistic structural models of materials with correlated disorder from experimental data

68 **Shengyen Li** MSED/NIST
Material Design Toolkit: towards a computational framework for materials design

69 **Sheng Lin-Gibson** NIST
Computational Design of Topological Disorder and Emergent Properties of Polymers using Stochastic Reaction-Diffusion Simulation

70 **Steven G. Louie** University of California at Berkeley
Ab initio Theory and Computation of Multiple-Particle Correlated Excitations in Materials at C2SEPEM: Trions and Biexcitons

71 **Peter Ludovice** Georgia Institute of Technology
Rapid Design and Engineering of Materials Systems for Nanomanufacturing via Directed Self-Assembly

72 **Tyler B. Martin** MSED/NIST
pyPRISM: A Computational Tool for Liquid-State Theory Calculations of Macromolecular Materials

73 **David J. Masiello** University of Washington
Nanoscale Temperature Manipulation via Plasmonic Fano Interferences

74 **Paul McEuen** LASSP Cornell
Graphene based Origami and Kirigami Metamaterials

75 **Julia E. Medvedeva** Missouri University of Science and Technology
Collaborative Research: Synthesis, Characterization, and Modeling of Complex Amorphous Semiconductors for Future Device Applications

76 **Eric Miller** DOE
HydroGEN Consortium on Advanced Water Splitting Materials

77 **Matthew P. Miller** Cornell High Energy Synchrotron Source
Extracting real time material evolution information at a synchrotron using machine learning methods

78 **Michael J. Mills** The Ohio State University
Mechanistic and Microstructure-Based Design Approach for Rapid Prototyping of Superalloys

79 **Jin Kim Montclare** New York University
Computationally Driven-Genetically Engineereed Materials

80 **Dane Morgan** University of Wisconsin-Madison
High Throughput Design of Metallic Glasses with Physically Motivated Descriptors

81 **Tim Mueller** Johns Hopkins University
Design of Nanoscale Alloy Catalysts from First Principles

82 **Deborah J. Myers** Argonne National Laboratory
Electrocatalysis Consortium (ElectroCat) - A DOE Energy Efficiency and Renewable Energy Energy Materials Network Consortium

83 **Sankar Nair** Georgia Institute of Technology
Accelerating the Discovery and Development of Nanoporous 2D Materials (N2DMs) and Membranes for Advanced Separations

84	**Thao D. Nguyen**	Johns Hopkins University	Predictive Multiscale Modeling of the Mechanical Properties of Polymers 3D Printed Using Fused Filament Fabrication
85	**Christopher Ober**	Cornell University	Paired Ionic-Electronic Conductors in Spatially Confined Self- Assembling Rod-Coil Block Copolymers and Bolaamphiphiles
86	**Elsa Olivetti**	Massachusetts Institute of Technology	Collaborative Research: The Synthesis Genome, Data Mining for Synthesis of New Materials.
87	**Jeremy C. Palmer**	University of Houston	Integration of computation and experiments to design a versatile platform for crystal engineering
88	**Paul Patrone**	NIST	Uncertainty Quantification for Molecular Dynamics
89	**Gregory F. Payne**	University of Maryland	Thin Film Biofabrication for Integrated Bio-Electronics
90	**John P. Perdew**	Temple University	SCAN Meta-GGA: An Accurate, Efficient and Physically Sound Density Functional for Wide Classes of Materials
91	**John H. Perepezko**	University of Wisconsin-Madison	A Combined Experiment and Simulation Approach to the Design of New Bulk Metallic Glasses
92	**Warren Pickett**	University of California Davis	Designing Insulating Topological Insulators
93	**Raymond Plante**	NIST	Data Discovery with The Materials Resource Registry
94	**Viktor A Podolskiy**	University Massachusetts Lowell	Collaborative Research: Semiconductor Heterostructure Platform for Active Nonlocal Plasmonic and Hyperbolic Materials
95	**Tresa Pollock**	University of California Santa Barbara	Accelerating the Design and Synthesis of Multicomponent, Multiphase Metallic Single Crystals
96	**Eran Rabani**	University of California Berkeley	Tackling Disorder and Ensemble Broadening in Materials Made of Semiconductor Nanostructures.
97	**Miladin Radovic**	Texas A&M University	Collaborative Research: Accelerated Development of Damage Tolerant and Oxidation Resistant Alumina- Forming MAX Phases
98	**Joan Redwing**	Pennsylvania State University	Materials Innovation Platform: 2D Crystal Consortium (2DCC)
99	**Andrew Reid**	NIST	Microstructure-sensitive Crystal Plasticity in the OOF Finite Element Modeling tool
100	**Gregory S. Rohrer**	Carnegie Mellon University	Grain Growth Beyond Isotropic Models: Microstructure Evolution with Experimentally Derived Interface Properties
101	**A. H. Romero**	West Virginia University	Search for Magneto-Electronic Complex Fluoride-based Interfaces with Novel Properties
102	**Paul Rulis**	University of Missouri – Kansas City	Predictive Modeling of Polymer-Derived Ceramics: Discovering Methods for the Design and Fabrication of Complex Disordered Solids
103	**Gregory C. Rutledge**	Massachusetts Institute of Technology	Discovery and Design of Additives for Novel Polymer Morphology and Performance
104	**Amin Salehi-Khojin**	University of Illinois at Chicago	Operation of Lithium-Oxygen Batteries with Long Cycle Life in a Realistic Air Atmosphere
105	**Mehmet Sarikaya**	University of Washington, Seattle	Biologically-Interfaced Single Layer Devices

106 **Sapna Sarupria** Clemson University
Collaborative Research: An integrated multiscale modeling and experimental approach to design fouling- resistant membranes

107 **Josh Schaidle** NREL
ChemCatBio Consortium on Chemical Catalysis for Bioenergy

108 **Jan Schroers** Yale University
High-Throughput Simulations and Experiments to Develop Metallic Glasses

109 **Kathleen Schwarz** NIST
Improving the Accuracy of Electrochemical Capacitance and Solvation Energetics in First-Principles Calculations

110 **J. Ilja Siepmann** University of Minnesota
Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: Synergy of Electronic Structure Theory, Molecular Simulation, Machine Learning, and Experiment

111 **Charles E. Sing** University of Illinois at Urbana- Champaign
Dynamic Control of 3-D Printed Hierarchical Soft Materials via Computation-Guided Molecular Design.

112 **Volker Sorger** The George Washington University
Theory-Enabled Development of 2D Metal Dichalcogenides as Active Elements of on-chip Silicon-Integrated Optical Communication

113 **Frank Spano** Temple University
Developing design rules for enhancing mobility in conjugated polymers

114 **Ashley Spear** University of Utah
Novel 3D Experiments, Simulations, and Optimization for Accelerated Design of Metallic Foams

115 **Natalie Stingelin** Georgia Institute of Technology
Metallic-type transport in polymers: Establishing materials design criteria and predicting structure/property interrelations

116 **Francesca Tavazza** NIST
IPR and JARVIS databases: Classical Force Fields, Density Functional Theory & Machine Learning to aid Materials Discovery

117 **Eric S. Toberer** Georgia Institute of Technology
Computationally Driven Targeting of Advanced Thermoelectric Materials

118 **John D. Tovar** Johns Hopkins University
Collaborative Research: Self-assembled peptide-pi-electron supramolecular polymers for bioinspired energy harvesting, transport and management

119 **Nandini Trivedi** The Ohio State University
Collaborative Research: Accelerated discovery of chalcogenides for enhanced functionality in magnetotransport, multiorbital superconductivity, and topological applications

120 **Mark E. Tuckerman** New York University
Discovery of Design Rules for High Hydroxide Transport in Polymer Architecture

121 **David Vanderbilt** Rutgers University
Collaborative Research: Emergent functionalities in 3d/5d multinary chalcogenides and oxides

122 **Priya Vashishta** University of Southern California
MAterials Genome Innovation for Computational Software (MAGICS)

123 **David Watson** University at Buffalo
Collaborative Research: A Blueprint for Photocatalytic Water Splitting: Mapping Multidimensional Compositional Space to Simultaneously Optimize Thermodynamics and Kinetics

124 **Daniel Wheeler** NIST
PFHub: Phase Field Community Hub

125 **Matthew A. Willard** Case Western Reserve University
Accelerated Soft Magnetic Alloy Design and Synthesis Guided by Theory and Simulation

126 **Boris Wilthan** NIST
NIST data resource for curated thermophysical property data of metal systems
127 **Karen L. Wooley** Texas A&M University
Collaborative Research: Interface-promoted Assembly and Disassembly Processes for Rapid Manufacture and Transport of Complex Hybrid Nanomaterials (IpAD)
128 **Sotiris Xantheas** Pacific Northwest National Laboratory
129 SPEC: Center for Scalable Predictive methods for Excitations and Correlated phenomena
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131 Consortium on Hydrogen Materials Compatibility
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Interagency Collaborative Opportunities

MGI PI Meeting

March 26-27, 2018

AIR FORCE RESEARCH LABORATORY ARL DEPARTMENT OF ENERGY UNITED STATES OF AMERICA NIST NSF

DOE Computational Science Centers

C2SEPEM:
Center for Computational Study of Excited-state Phenomena in Energy Materials
Director: Steven G. Louie
Lawrence Berkeley National Laboratory and University of California Berkeley

Methodological development of many-body theory software for single-particle and optical excitations as well as higher-order correlated processes in functional materials, with the objective to deliver state-of-the-art excited states calculations by advancing the GW-Bethe-Salpeter-Equation approach and beyond. The emphasis is on semiconducting, transition metal oxide, halide perovskite, graphene and two-dimensional transition metal dichalcogenide quantum materials. Excited-state phenomena, such as charge transport and optical response, are central to a variety of applications including electronics, photovoltaics, light-emitting diodes, information storage, energy storage, and electro- and photo-chemistry. Validation of materials-specific predictions includes experiments at the Advanced Light Source and the Molecular Foundry. Data management and computing will primarily use current petascale capabilities and future exascale capabilities at NERSC and the Leadership Computing Facilities. Access to the Materials Project and the emerging CAMERA center will be leveraged.

COMSCOPE**: Center for Computational Materials Science and Design**
Director: Gabriel Kotliar, Brookhaven National Laboratory and Rutgers University

Development of next-generation methods and software to accurately describe electronic correlations in oxides and complex materials and a companion database to predict targeted properties with energy-related application to thermoelectric materials. Validation of materials specific predictions includes experiments at the National Synchrotron Light Source II. The project will use capabilities at the National Energy Research Scientific Computing Center (NERSC), and the Argonne and Oak Ridge Leadership Computing Facilities.

CPSFM: **Center for Predictive Simulation of Functional Materials**
Director: Paul Kent, Oak Ridge National Laboratory

Methodological development of Quantum Monte Carlo software for functional materials, with the objective to deliver accurate and robust determination of electronic eigenstates, perform calculations beyond ground state properties, and improve valence Hamiltonians. The emphasis is on doped correlated oxides for electronic and spin-dependent functionalities, vacancy and strain control of metal-insulator transitions, and heterostructured transition metal oxides. Such quantum materials exhibit novel magnetism, optical properties, metal-insulator transitions, and exotic quantum phases that make them well-suited to energy applications. In many cases, small changes in composition, structure, doping, applied strain, or applied field yield substantially altered physical properties. Validation of materials specific predictions includes experiments at the Advanced Photon Source, Spallation Neutron Source, and the Nanoscale Science Research

Centers. Data management and computing will primarily use current petascale and future exascale capabilities at the Argonne and Oak Ridge Leadership Computing Facilities, as well as NERSC.

ECC: Center for Exascale Computational Catalysis
Director: Judit Zádor, Sandia National Laboratories

Development of theoretical strategies and computational tools that accelerate the discovery and characterization of coupled heterogeneous/gas-phase reactions and reaction mechanisms with relevance to catalytic conversion of hydrocarbons, oxygenates, and other small molecules. The computational tools to be created will automatically characterize elementary reactions using advanced machine learning algorithms coupled to quantum chemistry codes suitable for heterogeneous exascale architectures. These reactions are then incorporated into automatically generated reaction mechanisms coupled to efficient solvers and analysis tools for heterogeneous catalysis to predict macroscopic observables. Effort also creates a related modern, intelligent, user-friendly and accurate thermodynamic database that is self-consistent and can be grown by the broader scientific community and the team. Data management and computing will primarily use current petascale and future exascale capabilities.

FLOSIC: Efficient density functional theory calculations without self-interaction
Director: Koblar Jackson, Central Michigan University

Fundamental development of new theoretical and computational approaches to enable efficient density functional theory calculations that are exactly corrected for the electronic self-interaction error. Team will develop, test, and validate a user-friendly, open source software package, scalable over the number of electrons, that implements the Fermi-Löwdin-orbital-based self-interaction-correction (FLOSIC) to DFT. The code development effort will be integrated with theoretical research investigating the use of FLOSIC with sophisticated semi-local density functionals such as the new "strongly constrained and appropriately normed" SCAN functional for both ground-state and time-dependent applications. Additionally, the FLOSIC code will be tested and validated through research involving heterogeneous, transition-metal-based catalysts and molecular magnets. Work is accomplished on the NERSC computers.

MAGICS: **Materials Genome Innovation for Computational Software**
Director: Priya Vashishta, University of Southern California

Development of next-generation methods and software to predict and control materials processes at the level of electrons for computational synthesis, intercalation and exfoliation of stacked, two dimensional, functional layered materials with energy-related application to electronics and catalysis. Validation of materials specific predictions includes ultrafast free electron laser and electron diffraction experiments at the Linac Coherent Light Source at SLAC, which are directly mirrored by peta-to-exascale supercomputing at the Argonne Leadership Computing Facility under Auro/A21 ESP and INCITE. Data management integrates the Materials Project at Lawrence Berkeley National Laboratory and uses NERSC and uses computing capabilities at NERSC and the Argonne Leadership Computing Facility. MAGICS develops software for computational synthesis, including the QXMD code for nonadiabatic quantum molecular dynamics, RXMD for reactive molecular dynamics, ThermoSoft thermal-conductivity calculation plug-in, and GEARS simulation framework in virtual reality.

Materials_Project**: The Materials Project**
Director: Kristin Persson
Lawrence Berkeley National Laboratory and University of California Berkeley

Harnessing the power of supercomputing and state of the art electronic structure methods, the Materials Project provides open web-based access to computed information on known and predicted materials as well as powerful analysis tools to inspire and design novel materials. By computing properties for a large data base of known and unknown materials, the Materials Project aims to remove guesswork from materials design in a variety of applications. Experimental research can be targeted to the most promising compounds from computational data sets. Researchers are able to data-mine scientific trends in materials properties. Supercomputing clusters at national laboratories provide the infrastructure that enables Materials Projects computations, data, and algorithms. These include the Lawrence Berkeley National Laboratory's NERSC Scientific Computing Center, Oak Ridge's OLCF, Argonne's ALCF, and San Diego's SDSC. Computational materials science is now powerful enough that it can predict many properties of materials before those materials are synthesized in the lab. The Project has predicted several new battery materials which were made and tested in the lab and identified new transparent conducting oxides and thermoelectric materials using this approach.

MICCoM: **Midwest Integrated Center for Computational Materials**
Director: Giulia Galli, Argonne National Laboratory and University of Chicago

Development of interoperable quantum, classical and particle-continuum software, enabling the simulation and prediction of functional materials for energy conversion processes, with an emphasis on interfaces, the transport across them, and the manipulation of matter under conditions far from equilibrium. Validation of materials specific predictions includes experiments at the Advanced Photon Source and the Center for Nanoscale Materials. Data management and computing will primarily use capabilities at the Argonne Leadership Computing Facility.

NMGC:
Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials
Director: J. Ilja Siepmann, University of Minnesota

Development of computational/theoretical chemistry methods and data-driven science approaches enabling *de-novo* design of functional nanoporous materials, discovery and selection of the most promising functional nanoporous materials from databases of synthesized and hypothetical framework structures, and microscopic-level understanding of the fundamental interactions underlying the function of nanoporous materials. NMGC's predictive hierarchical modeling toolbox will be applied to increasingly complex chemical separations and transformations in increasingly complex nanoporous materials. Research will be directed toward liquid-phase adsorption and catalysis, multi-component mixtures, flexible framework structures that may undergo phase transitions or post-synthetic modifications and may contain defects, partial disorder, interfaces or be a composite material, and tunable electronic properties of nanoporous materials allowing for luminescence and desirable magnetic coupling and anisotropy. Validation of predictions for specific separations and transformations is accomplished through collaboration with leading experimental groups. Data management and computing will primarily use current petascale and future exascale capabilities at the Argonne Leadership Computing Facility, as well as NERSC.

PRISMS: Predictive Integrated Structural Materials Science
Director: John Allison, University of Michigan

The overarching goal of the PRISMS Center is to establish a unique scientific platform that will enable accelerated predictive materials science for structural metals. The vision is that the PRISMS tools and protocols will become a community-developed, extensible scientific core for accelerating the development of new materials. The Center has three primary thrusts that work together to support each other. They are (1) Integrated Science – focuses experimental and computational approaches on important demonstration problems. (2) Computational Tools - an integrated framework of open-source multi-scale simulation software. (3) Materials Commons – a unique repository that enables collaboration, seamless capture of important findings and community building. The open source computational tools that have been developed and updated annually are CASM (Cluster Approach to Statistical Mechanics), PRISMS-PF (an advanced phase field code), PRISMS-Plasticity (an advanced crystal plasticity code) and DFT-FE (a new real space DFT code). The Materials Commons is designed to be a general repository and collaboration platform for the metals community in the areas of microstructural evolution and mechanical properties by becoming a continuous, seamless part of the scientific workflow. Researchers will upload their results of experiments and computations as they are performed, automatically where possible, along with the provenance information describing the experimental and computational processes. It will provide a common site to store, share, curate, analyze and reuse materials data, linking experiments and computations

SPEC: Center for Scalable Predictive methods for Excitations and Correlated phenomena
Director:
Sotiris S. Xantheas, Pacific Northwest National Laboratory and University of Washington

The Center for Scalable, Predictive methods for Excitation and Correlated phenomena (SPEC) enables scientists to simulate excited states and excited-state processes with unprecedented predictive power and orders-of-magnitude greater computational performance than current methods. Examples of high level electronic structure methods that are being currently developed include: formulations and the parallel implementation of Coupled Cluster (CC) formalisms for core and valence excited states, hierarchical Green's Function (GF), multi-configurational (MC) and multi-reference (MR) methods and self-energy embedding approaches. These methods will be used to explore valence and X-ray spectroscopies in large molecular and nano systems. Effort aspires to remove a major barrier to realizing discoveries from next-generation experiments at BES light sources and accelerate progress on Grand Challenges in fields such as solar energy capture, catalysis, and energy storage. Multidisciplinary team consists of domain scientists, computer scientists and applied mathematicians who are working towards coupling theoretical and computational breakthroughs to deliver scalable, open-source software libraries suitable for simulating realistic systems on extreme-scale leadership computing facilities.

TIMES: Theory Institute for Materials and Energy Spectroscopies
Director: Thomas Devereaux, SLAC National Accelerator Laboratory and Stanford University

The goal of TIMES is to provide leadership in the theoretical and computational study of x-ray-based spectroscopy and imaging. The Institute fosters the development of advanced theories, numerical algorithms, and the associated simulations required for addressing cutting-edge problems in materials and energy sciences investigated at current and next-generation photon facilities. While focused primarily on the capabilities of LCLS and SSRL at SLAC National Accelerator Laboratory, TIMES impacts the photon sciences community more broadly, initially in those areas with the greatest need and where one can exploit the infrastructure of existing computational methods. The activity provides a strong link between the facilities, photon sciences, and advanced mathematics and computation, with a goal of moving from comparative to predictive simulation. The computational tools, and the scientists who use them, can build on the natural synergy between theory and experimentation to increase scientific interaction among the various stakeholders and enhance scientific productivity of these facilities.

DOE Energy Materials Network

CaloriCool™: Caloric Cooling Consortium - focuses on development of caloric materials for cooling applications.

ChemCatBio: Chemical Catalysis for Bioenergy Consortium - dedicated to identifying and overcoming catalysis challenges for biomass conversion processes.

DuraMat: Durable Module Materials Consortium - focuses on durable photovoltaic (PV) module materials to further optimize reliability and capacity of low-cost PV modules.

ElectroCat: Electrocatalysis Consortium - dedicated to finding new ways to replace the platinum group metals currently used in hydrogen fuel cells with inexpensive and more abundant substitutes, such as iron and cobalt.

HydroGEN: focuses on advanced water splitting materials, initially for the photoelectrochemical, solar thermochemical, and advanced electrolytic hydrogen production pathways.

HyMARC: Hydrogen Materials – Advanced Research Consortium. .Focuses on the thermodynamic and kinetic limitations of storage materials, to create an entirely new capability that will enable accelerated materials development to improve energy storage.

LightMat: Lightweight Materials Consortium - focuses on materials that can lightweight vehicles to increase fuel efficiency, such as specialized alloys and carbon fiber-reinforced polymer composites that can be manufactured on a large scale.

2018 Digitization of the Materials Enterprise:

Representative efforts within AFRL's Materials and Manufacturing Directorate that cross the boundaries of Data – Decision Making – Analytics – Modeling – Informatics – Automation

Discovery (Science / Low TRL)

Characterization of Crack Initiation in Crystalline Materials using High-Energy X-rays

AFRL/RX: T J Tuner <todd.turner.5@us.af.mil>

This project focuses on in-situ measurements of crack initiation in crystalline materials, coupled with simulations to use the experimental data to validate the modeling effort. Joel Bernier at LLNL has developed a software suite (HEXRD) to reduce high-energy diffraction microscopy (HEDM) datasets, allowing novel experiments to determine the crystal level-stress leading up to and past crack initiation. This is a coupled effort funded with AFRL/RXCM. In addition, Nathan Barton continues development on the crystal level finite element code (inside ALE3D), which is used to validate the models using the HEDM datasets. Jon Almer at APS 1ID beamline is conducting experiments. Together, the team is attempting to validate materials models and ICMSE techniques to predict failure in engineering materials. At AFRL this also involves data-analytics (Paul Shade and Bill Musinski) to reduce the HEDM datasets to obtain crystal-level stresses at crack initiation and propagation. The objective is to make HEXRD a scalable and publically available code for the community to use for high-pedigree datasets. (Collaborators: Joel Bernier (LLNL), Nathan Barton (LLNL), Jon Almer (APS))

3D Characterization, Automated Identification, and Quantification of Anomalies and Rare Events in Polycrystalline Ensembles

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Understanding the behavior of anomalies and rare events in polycrystalline aggregates is important for predicting macroscale behavior in many materials systems. Statistical analysis of such outlier features usually lacks predictive merit due to small experimentally-generated characterization volumes coupled with the rarity of interesting events. Recent advances in computationally-controlled polarized light microscopy and serial sectioning systems allow for the automated characterization of large-volume 3D data sets in optically anisotropic materials. Current experimental collection and post-processing workflows can produce 3D data sets with more than 100,000 unbiased grains in a single phase alpha titanium alloy, offering unique opportunities for exploring outlier features in a polycrystalline structure. Areas for data exploration and discovery include statistical techniques from extreme value theory for quantifying outliers in microstructure feature distributions (e.g., grain size and morphology), and the use of sub-sampling for cross-validation of statistical models.

Automation of Phase Diagram Development for Alloy Discovery:

AFRL/RX: Dan Miracle, daniel.miracle@us.af.mil

Inverse Design of Meta-Surfaces:

AFRL/RX Matt Mills, matthew.mills.25@us.af.mil

Single-layer, submicron thick metasurfaces consisting of periodic arrays of silicon nanopillars on SiO2 substrates have recently demonstrated near-perfect reflection (> 99.5%) and low absorption (<10-3) over narrow wavelength regimes across the electromagnetic spectrum – making them an attractive alternative to conventional optical coatings, and potentially offering a paradigm shift in approach to transmissive/reflective optics. These structures have shown considerable pulsed laser damage resistance, and are expected to withstand irradiances 10x-100x that required to damage silver mirrors. In our recent work, experimentally verified in-house developed Rigorous Coupled Wave Analysis (RCWA) simulations have shown that by altering the geometry, size, and orientation of such periodic structures, one can shift the perfect reflection/minimal spectral absorptance to a prescribed wavelength of interest. The primary focus of this work is to explore various dielectric material sets and designs that provide multiple perfect reflection bands within a single submicron layer. In order to navigate such an expansive parameter space, we intend to utilize machine learning algorithms in order to identify and optimize metasurface design to achieve desired/prescribed optical properties and draw out relationships between design and performance.

MIrACLE: MachIne And Computational Learning Exploration:

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Ever-increasing Air Force materials requirements, combined with the advent of machine learning, data analysis, and availability of materials databases, pose a need to understand and exploit these methods and concepts for acceleration of the materials/manufacturing life-cycle. The recently established MIrACLE (MachIne And Computational Learning Exploration) AFRL/RX forum aims to address this challenge by (i) providing a forum for discussion and collaboration on using machine learning for materials research; (ii) building a community in the machine learning cross-cutting area, sharing information/training, and (iii) developing a broader collaborative base for materials problem solving through machine learning. The goal is to enable discovery of materials having a required functionality, improvement of experimental/computational data analysis, moving towards autonomous systems.

Photonics of 2D Systems: High throughput computation & discovery:

AFRL/RX: Ruth Pachter ruth.pachter@us.af.mil

Two-dimensional (2D) nanostructures have drawn much interest for photonics, e.g. 2D transition metal dichalcogenides or 2D hybrid organic-inorganic perovskites, which may provide an improved optical response due to unique excitonic effects. However, although much progress was made in high throughput computation and discovery of bulk materials, and also for chemical systems, there has been less emphasis on emerging 2D materials. 2D materials databases based on prediction of the exfoliation energy were recently developed, but the type of materials considered is still rather limited. To enable 2D materials discovery and address Air Force requirements, the goal is to further develop high throughput computed 2D materials databases, also including engineered 2D nanostructures, e.g. by defects or heterostructures, combined with the use of machine learning and experimental validation.

Autonomous Research Systems for Materials Development

AFRL/RX: Benji Maruyama, Benji.Maruyama@us.af.mil

Closed-loop data flow, from acquisition to analysis to decision on next acquisition has been a long term goal of MGI which has been demonstrated for the first time using ARES (AFRL's Autonomous Research system). The first application of ARES was to carbon nanotube synthesis, where it autonomously learned to grow carbon nanotubes using AI/Machine learning. We are broadening the application of ARES to include Additive Manufacturing (Additive ARES) and Synthetic Biology (SynBio ARES). We plan to further expand ARES to include dynamic, targeted microstructure acquisition, in-line materials property understanding/improvement and closed-loop simulation for development of broad materials categories including structural, catalytic, and electronic.

Topology Optimization of Percolating Structures using Graph-Based Algorithms

AFRL/RX: Phil Buskohl, philip.buskohl.1@us.af.mil

Numerous condensed matter structures are composed of percolating elements, a critical requirement for achieving targeted behavior such as maximum stiffness in porous microstructures and conductivity in conductive inks. Moreover, additive manufacturing techniques currently allow for manufacturing these complex morphological features. We propose to design optimal morphologies using topology optimization techniques that strictly enforce a percolating network. Expanding on basic graph theories described in literature, e.g. weighted edge creation of a minimum spanning tree with heuristics for pruning, we will extend these techniques to three-dimensional structures and develop heuristics for topologies of interest. This toolset will enable efficient design of complex morphologies that can directly lead to manufacturing and testing.

Design-Build-Test for Biosynthetically Produced Materials

AFRL/RX: Maneesh Gupta, maneesh.gupta.2@us.af.mil

Numerous efforts aim to expand exisiting bio-infomatic and high throughput microbiology practices with evolving innovations in Data, Decision Making, Analytics, Modeling, Informatics, and Automation. Example material development activities include:

- Protein Biopolymers: Focused on development of protein biopolymers for applications in biomimetic cellular scaffolds for organ-on-chip devices, matrices for biomolecule stabilization/cold-chain remediation, and substrates for implantable/wearable biosensors and drug delivery platforms. Key research interests include use of synthetic biology approaches to increase protein design space, bioinformatics approaches to evaluate structural proteins, materials characterization techniques to evaluate protein biopolymers in a high-throughput manner, and machine learning techniques to iterate and optimize protein design.
- Antifouling/Antimicrobial Materials: Interested in material coating and decontamination strategies to prevent and mitigate biofouling and corrosion. Approaches and research areas of interest include materials and surface topographies with intrinsic anti-fouling properties, antimicrobial/antifungal materials and biomolecules, and methods to characterize material corrosion caused by the microbiome.
- Chemical/Biological Sensors: Research is focused on the development of peptide and aptamer based biological recognition elements (BREs) for development of chemical/biological sensors with applications in biomarker detection for human performance monitoring, detection of non-CBRNE microbial contamination, and small molecule chemical sensing. Key areas of interest are *in silico* optimization of mined BREs, fundamental understanding of BRE interactions with abiotic sensor surfaces and novel strategies for BRE functionalization, and optimization of BRE density and sensor architecture to maximize analyte transport, binding, and signal transduction.
- Nanomaterial Templating/Assembly: Research is focused on identification and optimization of biomolecules (proteins and lipids) capable of nucleating and templating the growth of a wide range of nano/micro-scale crystalline materials (metallic/semiconducting nanoparticles, metal-organic-frameworks, and organic crystals) with precise size and shape control. Additional work is focused on the use of biomolecular interactions for precision assembly of nanomaterials and design of biomolecules to increase processibility of nanomaterial dispersions.

Development (Engineering / Mid TRL)

Digital Mfg and Design Innovation Institute (MPDD)

AFRL/RX: Brent Boden <brenchley.boden@us.af.mil>

Defense weapon systems are complex and manufacturing trade-offs are often disregarded until product design is complete. The minimal assessment accomplished today tends to be human-in-the-loop, followed by thousands of Engineering Changes (ECs). Mfg Process Driven Design (MPDD) addresses the "moving mfg left" problem: analytical evaluation of producibility issues as part of the design tradespace. In this case MPDD is focused at the detailed design stage. "Producibility" is (still) not a well-defined term, but should include material properties where relevant to the tradespace, i.e., analytical representation of the interactions between material, process, design feature, performance, and initial requirement. Objectives include: Evaluation of designs using objective techniques; Linkage of CAD-CAM-CAE + and in-house producibility tools and information to support trade studies; Commercialization & technology transition for at least two DoD/AF programs including ROI results when deployed.

NextFlex Materials & Process Database

AFRL/RX: Ben Leever <benjamin.leever@us.af.mil; Scott Miller, smiller@nextflex.us

The objective is the launch of a Flexible Hybrid Electronics (FHE) database for process and property data via web interface. The goal is to support existing and future digital design, modeling, and simulation tools to accelerate and standardize FHE device design. NextFlex members and government partners can enter data and access data in the database. NextFlex, in partnership with NIST, established the initial data schema, which has pre-defined properties & processes but that can accept new properties in the future

Flexible Hybrid Electronics Foundational Engineering Problem

AFRL/RX: Lt Carl Thrasher, carl.thrasher.1@us.af.mil

The objective is to demonstrate potential for accelerated Air Force relevant FHE device design through the use of digital design tools supported by process/property data. The current team includes NextFlex, UMass Lowell, SUNY Binghamton, SI2 Technologies. The objective is to print antennas and carefully characterizing performance against established data schema to populate NextFlex database. If successful, follow efforts will continue to demonstrating accelerated design by combining use of database with NextFlex PDK and other digital design tools.

Robust GaN Device Design using Failure Models (Foundational Engineering Problem)

AFRL/RX: Eric Heller, eric.heller.2@us.af.mil; Joe Bruns joseph.burns.9@us.af.mil

Holistic Multi-Layer Optical Filter Design (Performance-Processing-Environment): (Foundational Engineering Problem)

AFRL/RX: Matt Mills, matthew.mills.25@us.af.mil; Jen DeCerbo, jennifer.decerbo@us.af.mil

HyperThought

AFRL/RX: Matt Jacobsen matthew.jacobsen.1@us.af.mil

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NSF Materials Innovation Platforms

2DCC: **2D Crystal Consortium**

Director: Joan Redwing, Pennsylvania State University

The 2DCC is focused on advancing the state of the art in the crystal growth of bulk chalcogenides and two-dimensional (2D) thin film chalcogenides through transformational research and mid-scale investments in bulk crystal and thin film growth instrumentation. 2DCC's in-house research team focuses on advancing our knowledge and understanding of synthetic routes and approaches that are aimed at applications of 2D chalcogenide thin film systems in current electronic devices and next generation electronic architectures. Researchers from across the U.S. working on next-generation electronic materials and devices can access the 2DCC's growth facilities at Pennsylvania State University and its expertise in synthesis, characterization, and theoretical modeling, or request "standard" characterized samples via the 2DCC external user program.

PARADIM

Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials

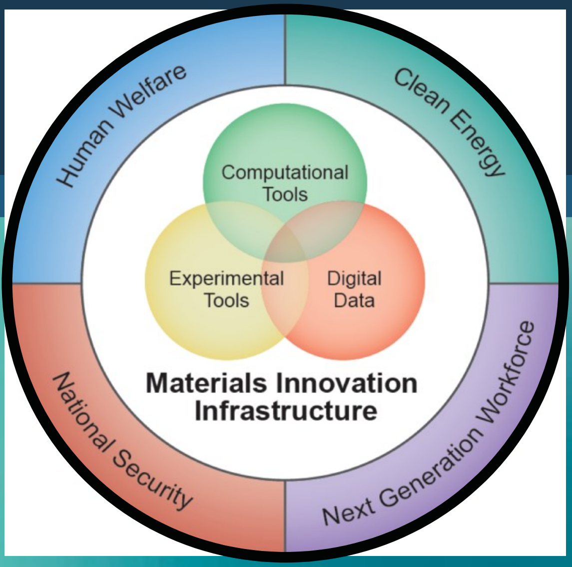
Director: Darrell Schlom, Cornell University

PARADIM's mission is to empower practitioners to accelerate the discovery of atomically engineered, inorganic materials that revolutionize electronics. Discovering electronic materials—by design rather than by serendipity—is accomplished at PARADIM through a synergistic set of state-of-the-art user facilities dedicated to theory, synthesis, and characterization. These include PARADIM's bulk crystal growth user facility at Johns Hopkins, which is the only location within the United States where all major optical floating-zone techniques are available at a single site, and the only location in the world where floating zone growths in supercritical fluids, in the fluid regime, are possible. In PARADIM's thin film facility users can select between a record 62 elements in the periodic table to synthesize the materials they envision by MBE. To this fully automated MBE, ARPES and MOCVD are being added to increase the diversity of heterostructures and enable users to determine the electronic structure of the materials they create. PARADIM's electron microscopy user facility at Cornell has enabled PARADIM users to investigate 2D materials by scanning transmission electron microscopy with the highest spatial resolution (0.39 Å) ever achieved on this class of materials. Users access PARADIM facilities by submitting two-page proposals online. These are reviewed by well-known materials innovators who are external to the universities that constitute PARADIM.

Materials Genome Initiative

BUILDING THE MATERIALS INNOVATION INFRASTRUCTURE

The Materials Genome Initiative (MGI) seeks to accelerate the discovery, design, development, and deployment of new materials for insertion in manufactured products. To realize the vision of the MGI, NIST and its partners are developing elements of the materials innovation infrastructure. This document details a number of the tools and data resources NIST has created to achieve this goal.



NIST

Materials Data Resources

GENERAL

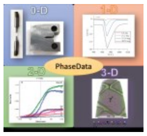
Materials Resource Registry allows for the registration of materials resources, bridging the gap between existing resources, software and repositories and end users. The Materials Resource Registry functions as a federated service, making the registered information from multiple institutions available for research to the materials community. https://materials.registry.nist.gov/

NIST MaterialsData Repository is an effort to establish data exchange protocols and mechanisms to foster data sharing and reuse across a wide community of researchers, with the goal of enhancing the quality of materials data and models. Data present on this system are varied and may originate from within NIST or from the worldwide materials community and may or may not be critically reviewed. https://materialsdata.nist.gov/

NIST Schema Repository and Registry is a service operated to improve discovery, access and reuse of materials-related schemas, data models, ontologies and more. https://schemas.nist.gov/

PHASE-BASED

TRC Alloy Data is a collection of published experimental thermophysical and thermochemical property data, including full provenance and critically evaluated uncertainties. Data collection efforts focus on unary, binary, and ternary metallic systems. API access is available upon request. http://trc.nist.gov/metals_data



PhaseData Repository contains a variety of zero-, one-, two-, and three-dimensional computational and experimental data. The current focus is on diffusion data and multicomponent experimental data. Data can be both downloaded and contributed. https://phasedata.nist.gov

Interactive Diffusion Data is a collection of experimental and computational self and impurity diffusion data. http://www.ctcms.nist.gov/~gkl/selfdiffusion.html

High-Throughput Experimental Materials Collaboratory aims to make high-throughput experimentation (HTE) available to those who currently have no access to it, and further expand the availability of experimental datasets. https://mgi.nist.gov/htemc

ATOMISTICS

Interatomic Potential Repository provides interatomic potentials (force fields), related files, and evaluation tools to help researchers obtain interatomic models and judge their quality and applicability. http://www.ctcms.nist.gov/potentials/

JARVIS-FF provides data to evaluate classical force-fields for various applications. It contains elastic constants, vacacy formation energies, surface energies and phonon evaluations for many different force-field types and all classes of materials. https://www.ctcms.nist.gov/~knc6/periodic.html.

DFT

DFT Bench Marking is a that resource provides high-throughput density functional (DFT) calculations and data analytics tools to examine precision of DFT computed data for multiple materials and DFT codes. https://materialsweb.org/nist_pages

JARVIS-DFT contains density functional theory data for pure elements, 2-D, solar cell and thermoelectric materials. For 2-D materials, bulk and single layer material properties are compared. http://www.ctcms.nist.gov/~knc6/JVASP.html

Materials Modeling Software and Tools

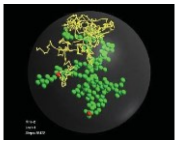
Materials Data Curation System provides a means for capturing, sharing, and transforming materials data into a structured format that is XML-based and amenable to transformation to other formats. https://github.com/usnistgov/MDCS; https://github.com/MDCS-community

Materials Resource Registry software provides an open source registry tool that makes content available via both a web-based user interface and a RESTful API. Metadata harvesting between data providers and service providers is made possible using the OAI-PMH version 2.0 protocol. https://github.com/usnistgov/MaterialsResourceRegistry

Roots and Rules provides a strategy for extensible, evolving terminology for the MGI by creating meaningful machine generated snippets to index and search documents. The meaningful snippets are generated with novel Natural Language Processing techniques integrated with the root and rule-based linguistic concepts of some Indo-European languages. https://randr.nist.gov/mgi/Default.aspx

Cloud of Reproducible Records (CoRR) is a cloud infrastructure for storing, disseminating, federating and collaborating on reproducible record atoms. It is composed of two Python Flask REST web services (Cloud and API), a cloud storage space, a MongoDB database and a Material Design AJAX web front-end. https://mgi.nist.gov/cloud-reproducible-records

OOF (Object-Oriented Finite Element Analysis) helps materials scientists calculate macroscopic properties from images of real or simulated microstructures. It reads an image, assigns material properties to features in the image, and conducts virtual experiments to determine the macroscopic properties of the microstructure. http://www.ctcms.nist.gov/oof/



ZENO calculates basic properties required in the characterization of polymer and nanoparticles such as the electric polarizability tensor, intrinsic conductivity, self-capacitance, intrinsic viscosity, radius of gyration and radius of gyration tensor to characterize polymer and nanoparticle shape, hydrodynamic radius (and thus the diffusion coefficient and sedimentation coefficient), Smoluchowki rate constant, and more. https://github.com/usnistgov/ZENO

FiPy is an object oriented, partial differential equation solver, written in Python based on a standard finite volume approach. https://www.ctcms.nist.gov/fipy/index.html

The **Materials Knowledge Materials (MKS) in Python (PyMKS)** framework is an object-oriented set of tools and examples, that provide high-level access to the MKS framework for rapid creation and analysis of structure-property-processing relationships. http://pymks.org/en/latest/rst/README.html

Open Calphad (OC) is an open source tool for performing thermodynamic calculations using the CALPHAD method. OC enables the calculation of phase equilibria and thermodynamic properties using the general compound energy formalism for the description of the composition dependence of the phase properties. http://www.opencalphad.org/

Materials Design Toolkit provides a generic framework for materials design linking CALPHAD tools with mechanistic property models and a genetic algorithm for design optimization. https://mgi.nist.gov/materials-design-toolkit

CHiMaD
Center for
Hierarchical
Materials Design
chimad.northwestern.edu

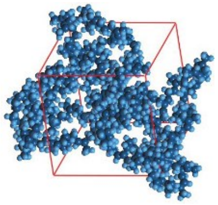
NIST Center of Excellence

The **Materials Data Facility** (MDF) is a set of data publication and data discovery services to support materials science researchers. The production-ready data publication service offers a scalable repository where materials scientists can publish, preserve, and share research data. The repository provides a focal point for the materials community, enabling publication and discovery of materials data of all sizes. https://materialsdatafacility.org/

The **Open Quantum Materials Database** (OQMD) is a high-throughput computational database containing thermodynamic and structural properties of materials calculated using density functional theory (DFT). It has an online interface at http://oqmd.org for convenient, small-scale access. The entire database is available for download from the website, and the python-based API, qmpy, that enables a more powerful interaction with the data can be accessed on GitHub at https://github.com/wolverton-research-group/qmpy. The OQMD currently contains calculations of more than ~470,000 unique, experimentally reported and hypothetical compounds, and is constantly growing.

Magpie, the Materials Agnostic Platform for Informatics and Exploration, is a tool designed to simplify the creation of machine learning models from materials data. The main features of Magpie are a rich library of methods for transforming raw materials data (e.g., crystal structures) into a form compatible with machine learning, and methods to easily employ models to search for new materials. Magpie is available under an open-source license from https://bitbucket.org/wolverton/magpie.

CHiMaD Phase Field is a community-based effort to improve phase-field codes with resources to compare and contrast phase field codes and libraries. https://pages.nist.gov/chimad-phase-field/



The **Polymer Property Predictor and Database** includes both a database of polymer interaction parameters (χ), glass transition temperatures, as well as tools to predict polymer properties and phase diagrams. Phase diagrams for both neutral polymers (Flory- Huggins and Lattice Cluster Theory) and charged polymers (Voorn-Overbeek) can be generated given either molecular information or data from the database. Additionally, one of the tools calculates the structure factor (RPA), which is useful for analyzing experimental scattering data to extract polymer interaction parameters. http://pppdb.uchicago.edu/

DMREF PI (Lead)	Institution (Lead)	Project #	Partner (Lead)	Agency	Title	Amount ($)
Arroyave, Raymundo	TX A&M	1534534	Pachter, Ruth	AFRL	AI in Materials Science: Toward Autonomous Computational Materials Discovery Frameworks	100,000
Mills, Michael Pollock, Tresa	OH St. U. UCSB	1534826 1534264	Payton, Eric	AFRL	Superalloy Performance Cooperative	99,999
Montclare, Jin	NYU	1728858	Gupta, Maneesh	AFRL	High-throughput Assessment of Mechanical Properties of Protein Engineered Biomaterials	100,000
Helgeson, Matthew	UCSB	1729108	Gupta, Maneesh	AFRL	Software for Accelerated and Automated Micro-rheology Analysis to Enable Rapid Soft Material Development	100,000
Chelikowsky, James	U. TX	1729202	Targut, Zafer	AFRL	Magnetic Materials Database for Informatics and Artificial Intelligence Design	150,000
Billinge, Simon	Columbia U.	1524910	Pouchard, Line	DOE	Materials Structure in the Cloud	100,000
Spear, Ashley	U. UT	1629660	Allison, John	DOE-CMS	Enabling Data-driven Materials Deign via Rapid Processing, Integration, and Analysis of Three-dimensional Image Data	97,600
Blum, Volker	Duke U.	1729297	Galli, Giulia	DOE-CMS	Data Reproducibility and Traceability for a Community Materials Database: Qresp for HybriD3	99,999
Snyder, Jeffrey	Northwestern U.	1729487	Jain, Anubhav	DOE-CMS	Investigating Low-dimensional Electronic Structures in Three-dimensional Materials	99,999
Janik, Michael	PA St. U.	1436206	Myers, Deborah	DOE-EMN	Elucidating Active Site Properties of Platinum Group Metal-free Oxygen Reduction Electrocatalysis through Computation and Experiment	99,999
Piper, Louis	Binghampton U.	1627583	Prendergast, David	DOE-EMN	A Blueprint for Photocatalytic Water Splitting: Mapping Multidimensional Compositional Space to Simultaneously Optimize Thermodynamics and Kinetics	100,000
Toberer, Eric	CO School of Mines	1729594	Ginley, David	DOE-EMN	High Temperature Defects: Linking Solar Thermochemical and Thermoelectric Materials	100,000
Greeley, Jeffrey	Purdue U.	1437251	Farberow, Carrie	DOE-EMN	Automating Prediction of Catalyst Structures at Metal/oxide and Metal/Carbide Interfaces	100,000
Dabo, Ismaila	PA St. U.	1729338	Deutsch, Todd	DOE-EMN	Experimental Validation of Designed Photocatalysts for Solar Water Splitting	75,000
Hickner, Michael	PA St. U.	1534326 1534289	Dinh, Huyen Audus, Debra	DOE-EMN	Membrane Databases - New Schema and Dissemination	100,000
Abbott, Nick	U. WI	1435195	Bedolla, Marco	GOALI	Accelerated Design of Chemoresponsive Liquid Crystals using Metal Alloy Surfaces for Next Generation Sensors for Personal Monitoring	100,000

Adamson, Doug	U. CT	1535412	Smith, Alex	GOALI	Graphene Surfactant Based Foams for Microwave Absorption	100,000
Faber, Kathy	Caltech	1535083	Schaedler, Tobias	GOALI	Designing Microstructure for Engineering Toughness	100,000
Arroyave, Raymundo	TX A&M	1534534	Benafan, Othmane	NASA	Machine Learning-based Predictive Models to Accelerate the Discovery of High-temperature Shape Memory Alloys	100,000
Anthony, John	U. KY	1627428	Trautt, Zachary	NIST	A DMREF-NIST Collaboration to Design and Build the OSCAR Data Curation Platform	100,000
Brinson, Cate	Duke U.	1729743	Phelan, Fred	NIST	Connecting NanoMine with MRR/MDF/MDCS for Nanostructured Polymer Design	100,000
Rohrer, Gregory	Carnegie Mellon U.	1628994	Kusne, Aaron DeCost, Brian	NIST	Development of a Gaussian Process Model to accelerate the Acquisition of Three-dimensional Orientation Data	99,012
Nguyen, Vicky	Johns Hopkins U.	1628974	Seppala, Jonathan	NIST	Connecting Polymer Alignment, Diffusion and Print Strength	100,000
Gomez, Enrique	PA St. U.	1629006	Snyder, Chad	NIST	Linking Theory and Experiment to Describe Chain Stiffness of Conjugated Polymers	100,000
Medvedeva, Julie	MS&T	1729779	Trautt, Zachary	NIST	Complex Amorphous Semiconductors: Repository, Tools, and E-Collaboration Platform	94,000
Berlyand, Leonid Bertoldi, Katia	PA St. Harvard U.	1628411 1533985	Youssef, Sharief	NIST	Magnetic Dumbell Lens Composites for Micro-optics	100,000
Rondinelli, James Trivedi, Nandini	Northwestern U. Ohio State	1729303 1629382	*none*	*none*	A Transport Classifier to Predict Electrical Responses in Metal-insulator Transition Compounds	79,999