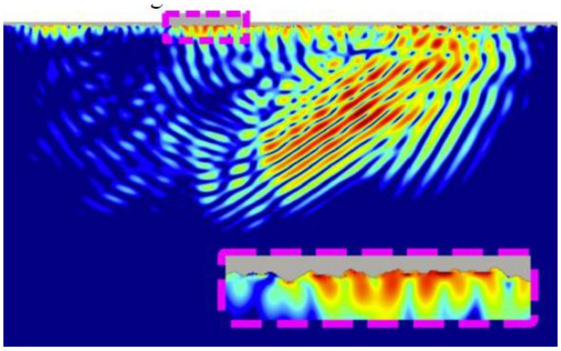
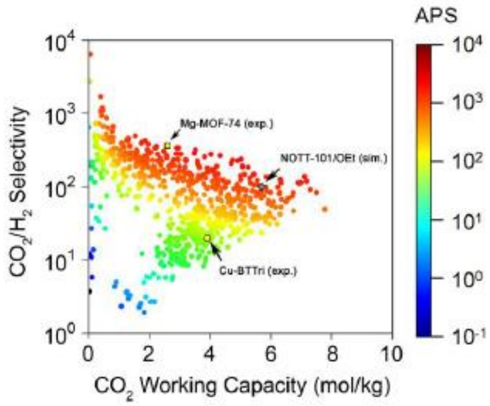
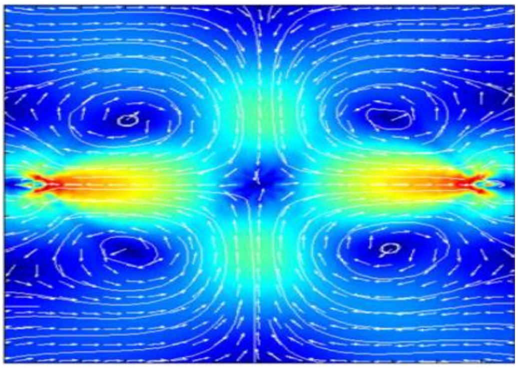
Materials Genome Initiative

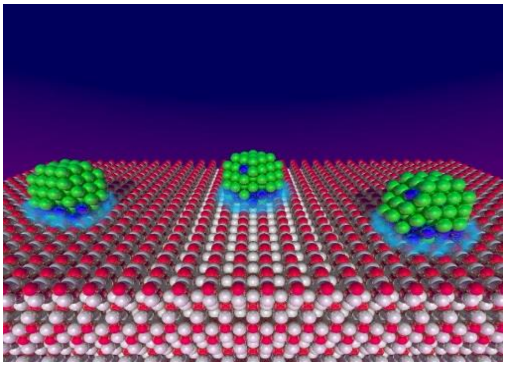
Accelerating Materials Research

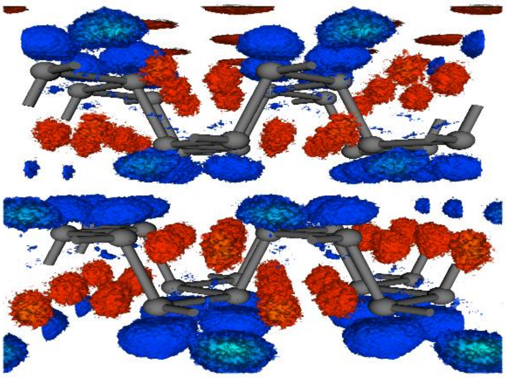
Third Principal Investigator Meeting











NIST

January 11-12, 2016 – Bethesda, MD

On the Cover

Top left: Colorized energy-density profile after a longitudinal acoustic wave scattered from a rough surface, converting partially into a localized Rayleigh Wave. (Maurer and Knezevic)

Top right: 3D structure of complex DNA objects predicted through use of CanDo. (Bathe)

Center left: A generic algorithm for efficiently identifying top-performing MOFs was developed and applied to pre-combustion CO_2/CH_2 separations (APS = Adsorbent Performance Score). Available experimental data points and a target MOF in the optical region for selectivity and working capacity are labeled. Validation experiments support the computational prediction. (Siepmann)

Center right: Numerical simulation of the electroosmotic flows in a liquid crystal electrolyte with two point singularities. (Lavrentovich)

Bottom left: Highly stable AuIr/TiO_2 catalyst: Strong adhesion and high stability of AuIr nanoparticles due to the segregation of iridium atoms toward the TiO_2 surface. (Greely)

Bottom right: The nature of the binding between layers of black phosphorous. Charge reorganization induced by the interaction of black phosphorus layers based on diffusion quantum Monte Carlo predictions. (Shulenburger)

Foreword

This volume documents the proceedings of the joint National Science Foundation (NSF), Department of Energy (DOE), and National Institute of Science and Technology (NIST) Materials Genome Initiative (MGI) Principal Investigator (PI) Meeting held January 11–12, 2016, in Bethesda, Maryland. The meeting was co-chaired by Tresa Pollock (University of California - Santa Barbara) and Kristin Persson (University of California - Berkeley).

The Materials Genome Initiative (MGI) is an interagency program 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 data, and targeted synthesis. Further information on MGI is available at www.whitehouse.gov/MGI including the MGI Strategic Plan released in December 2014.

The meeting brought together principal investigators from NSF's DMREF (Designing Materials to Revolutionize and Engineer our Future) Program, the DOE's Predictive Theory and Modeling Program funded by the Office of Basic Energy Sciences (BES), and NIST. Additional BES PIs were included from selected Energy Frontier Research Centers (EFRCs). The meeting provided a venue for scientists to present and exchange information about their research activities, to foster new ideas and establish collaborations and to discuss future research directions. It also aided NSF, DOE, and NIST in assessing the needs of this research community and in charting future programmatic directions.

Principal Investigators were asked to submit an abstract and to prepare a poster. Several projects were selected for oral presentation. NSF, DOE, NIST, ONR, and AFRL program managers provided overviews of MGI and related research opportunities in their agencies. The meeting emphasized the importance of contributions from the Mathematical and Computer Sciences, with featured talks in these areas. Two talks from the White House Office of Science and Technology Policy (OSTP) highlighted the current status of MGI and Advanced Manufacturing. Breakout sessions focused on the accomplishments of MGI in various material classes and methods for accelerating materials research.

DMREF supports activities that accelerate materials discovery and development by building the fundamental knowledge base needed to design and make materials with specific and desired functions or properties from first principles. This is accomplished by understanding the interrelationships of composition, structure, properties, processing, and performance. Achieving this goal will involve modeling, analysis, and simulation, validated through sample preparation, characterization, and device demonstration. It will require new data analytic tools and statistical algorithms; advanced simulations of material properties, advances in predictive modeling and a data infrastructure that is accessible, extensible, scalable, and sustainable.

BES supports fundamental research to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels and fundamental research that provides the foundations for new energy technologies relevant to DOE's missions in energy, environment and national security. BES participants in the MGI have contributed fundamental advances in algorithms and codes, large public searchable databases, and applications to materials research in areas such as light alloys for transportation.

We thank all the meeting participants for their active contributions in sharing their ideas and research accomplishments. We wish to thank Tammy Click and Verda Adkins-Ferber at the Oak Ridge Institute for Science and Education (ORISE) for their outstanding work in all aspects of the meeting organization.

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AGENDA

NSF/DOE Materials Genome Initiative Principal Investigators' Meeting

Monday, January 11, 2016

8:00 – 8:30am	*******Registration and Continental Breakfast*******
8:30 – 8:40am	**Welcome and Introductions from Co-chairs:** Meeting Chairs: **Tresa Pollock and Kristin Persson** UC–Santa Barbara / UC–Berkeley
8:40 – 9:00am	**MGI at NSF** **Linda Sapochak and John Schlueter**
9:00 – 9:20am	**MGI at DOE** **Linda Horton and Jim Davenport**
9:20 – 9:35am	**MGI at NIST** **Jim Warren**
9:35 – 9:50am	**MGI at ONR** **Julie Christodoulou**
9:50 – 10:00am	**MGI at AFRL** **Chuck Ward and Ali Sayir**
10:00 – 10:30am	*******Break*******
10:30 – 10:50am	**NSF Material Innovation Platforms** **Sean Jones**, NSF
10:50 – 11:20am	**MGI and Applied Mathematics** **Robert V. Kohn**, New York University
11:20 – 11:50am	**MGI and Computer Science** **Jim Belak**, Lawrence Livermore National Laboratory
11:50 – 12:00pm	**Introduction to Breakouts**
12:00pm	**Breakout Session #1 with Working Lunch** *What is MGI accomplishing across Material Classes?*

1) Metals, Alloys, and Ceramic Materials, **Srinivasan Srivilliputhur (UNT)** and **Martin Green (NIST**)

2) Magnetic and Electronic Materials, **Warren Pickett (UC Davis), Hai Ping Cheng (UF),** and **Paul McEuen (Cornell)**

3) Molecular, Polymer, and Biomaterials, **Mike Toney (Stanford)** and **Mark Bathe (MIT)**

4) Materials for Catalysis & Chemical Transformations, **Jeff Greeley (Purdue)** and **Randall Snurr (Northwestern)**

5) Photonic and Thermoelectric Materials, **Chris Van de Walle (UCSB)** and **Irena Knezevic (Wisconsin)**

1:45 – 2:10pm **Preparation of Reports**

2:10 – 3:00pm **Presentation of Breakout Sessions (5 x 10 minutes)**

3:00 – 5:00pm **Poster Session with Refreshments**

5:00pm *****Adjourn for the Day*****

Tuesday, January 12, 2016

8:00 – 8:30am *****Continental Breakfast*****

8:30 – 8:50am **MGI in Perspective**
Lloyd Whitman (OSTP)

8:50 – 9:10am **MGI in Advanced Manufacturing**
Megan Brewster (OSTP)

9:10am *****Breakout for Parallel Sessions*****

Session A: **Hard Materials**
Chair: **Alexis Lewis**

9:20 – 9:30am **Stathis Meletis**, University of Texas
Multiscale Design of Hard and High Temperature Resistant Coatings by Computation and Experiment

9:30 – 9:40am **Patrick LeClair**, University of Alabama
First-principles Based Design of Spintronic Materials and Devices

9:40 – 9:50am **Robert Hull**, Rensselaer Polytechnic Institute
Real Time Control of Grain Growth in Metals

9:50 – 10:00am **Chang-Beom Eom**, University of Wisconsin
Multifunctional Interface Materials by Design

10:00 – 10:10am	**Maarten de Boer**, Carnegie Mellon University *High-Throughput Discovery, Development and Demonstration of Materials Systems to Enable Low-power NEMS-based Computation*
Session B:	**Soft Materials** Chair: **Mark Pederson**
9:20 – 9:40am	**Ilja Siepmann**, University of Minnesota *Nanoporous Materials Genome: Methods and Software to Optimize Gas Storage, Separation, and Catalysis*
9:40 – 9:50am	**Randy Snurr**, Northwestern University *Simulation-Driven Design of Highly Efficient MOF/Nanoparticle Hybrid Catalyst Materials*
9:50 – 10:00am	**Lian Yu**, University of Wisconsin *Engineering Organic Glasses*
10:00 – 10:10am	**Mohammad Islam**, Carnegie Mellon University *Mechanics of Three-Dimensional Carbon Nanotube Aerogels with Tunable Junctions*
10:10 – 10:40am	*******Refreshment Break and Poster Setup*******
Session C:	**Hard Materials** Chair: **Matthias Graf**
10:40 – 11:00am	**Kristin Persson**, University of California – Berkeley *Materials Project*
11:00 – 11:20am	**John Perdew**, Temple University *SCAN Meta-GGA: An Accurate, Efficient, and Soundly Based Density Functional for MGI?*
11:20 – 11:30am	**Kristjan Haule**, Rutgers University *Enhanced Functionalities in 5d Transition-Metal Compounds from Large Spin Orbit Coupling*
11:30 – 11:40am	**Lian Li**, University of Wisconsin – Milwaukee *Emergent Functionalities at the Epitaxial Interfaces of Correlated and Spin-Orbit Materials*
11:40 – 11:50am	**Alex Zunger**, University of Colorado *Theory-Guided Experiments in Search of Designed Topological Insulators and Band-Inverted Insulators*
Session D:	**Soft Materials** Chair: **David LaVan**
10:40 – 10:50am	**Darrin Pochan**, University of Delaware *Materials with Predetermined Nanostructures via the Computational Design and Solution Assembly of Peptides*

10:50 – 11:00am	**Todd Yeates**, University of California – Los Angeles *Integrating Theory, Computation, and Experiment to Robustly Design Complex Protein-Based Nanomaterials*
11:00 – 11:10am	**Kris Delaney**, University of California – Santa Barbara *Computationally Driven Discovery and Engineering of Multi-block Polymer Nanostructures using Genetic Algorithms*
11:10 – 11:20am	**H. Jerry Qi**, Georgia Institute of Technology *Laminated Elastomer Composites with Anisotropic Shape Memory*
11:20 – 11:30am	**Ronald Hedden**, Texas Tech University *Combinatorial Methods to Enable Rapid Prototyping of Polymeric Pervaporation Membranes for Biofuels*
11:30 – 11:40am	**Brad Olsen**, Massachusetts Institute of Technology *Analysis and Optimization of Polymer Networks for Engineering Applications*
11:40 – 11:50am	**Hamish Fraser**, The Ohio State University *Design Knowledge Base of Low-Modulus Titanium Alloys for Biomedical Applications*

11:50 – 12:00pm **Introduction to Breakouts**

12:00pm **Breakout Session #2 with Working Lunch**
Accelerating Materials Research

1) Data Repositories, **Carrie Campbell (NIST)** and **Stefano Curtarolo (Duke**)
2) Mathematics, Software and Cyberinfrastructure, **Elsa Olivetti (MIT)** and **John Allison (Michigan)**
3) Advanced Manufacturing, **Peter Collins (Iowa State)** and **Cliff Henderson (Georgia Tech**)
4) Transitioning Fundamental Science to Technology and Applications, **Volker Sorger (GWU)** and **Bill Tumas (NREL)**
5) Equipping and Educating the Next Generation, **Kathlene Kash (Case Western),** and **Richard LeSar (Iowa State)**

1:45 – 2:10pm	**Preparation of Reports**
2:10 – 3:00pm	**Presentation of Breakout Sessions (5 x 10 minutes)**
3:00 – 5:00pm	**Poster Session with Refreshments**
5:00pm	*******Adjourn*******

Breakout Session Reports

Metals, Alloys, and Ceramic Materials

Moderators: Raj Banerjee (UNT), Srinivasan Srivilliputhur (UNT) and Martin Green (NIST)

Around fifty researchers attended the Metals, Alloys, and Ceramic Materials break out session. The discussions focused on identifying: (i) Examples of how MGI is accelerating materials discovery and development in metals, alloys, and ceramics. (ii) How data, software, samples, etc. are being shared with community? (iii) Knowledge-gaps that need filling – needed data, software, samples, sharing. (iv) Challenges we face in applying MGI principles. (v) What does the MGI community needs to flourish?

The participating researchers came from industry and academia, and their interests spanned a wide-range of materials, properties, and applications. While they were unanimous in agreeing that the MGI approach is helping understand many phenomena at the molecular scale, it was also felt that much more need to be done over a longer timescale. We summarize some main ideas related to above mentioned focus areas below.

(i) Examples of how MGI is accelerating materials discovery and development in metals, alloys, and ceramics

- Collaboration with industrial partners help us compare and sort out academically useful data from industrially useful data and examine if a new material that is being developed is patentable.
- Development of a Materials Commons for Mg alloys – a unique collaborative environment – integrating computational and experimental results under one platform. A robust scheme that links microstructural features such as precipitate evolution, recrystallization and grain growth, and fatigue behavior to alloy design has been developed. This provides a template for other technologically relevant alloys.
- Discussions of ceramics encompassed the eternal question of how to make ductile, lightweight, and hard ceramics. A novel experimental-computational approach was introduced wherein quantum-mechanical simulations provided potential directions to larger scale simulations, material synthesis, and experiments.

(ii) How data, software, samples, etc. are being shared with community?

- This was identified as a weak link. Participants were concerned that the many, fragmented efforts need to be better linked and made visible to the researchers. This would avoid effort duplication and wastage of resources.
- Researchers pointed to nascent efforts at NIST and other institutions to create web links such as Code Catalog to important MGI efforts worldwide.

(iii)Knowledge-gaps that need filling – needed data, software, samples, sharing.

- A need to monitor the processing of a material efficiently in real-time was broadly accepted. This raised a question of whether we need to change of way of thinking about the modeling paradigm.
- Modeling was recognized as necessary to predict how changing the parameter space, such as temperature gradient, changes the microstructure gradient that will develop. Mapping the landscape of the microstructures would not succeed without achieving fidelity in modeling tools.

- Optimal experimental design was identified as a challenge. This involved design of experiments scanning large parameter space and using of national user facilities.
- Real-time analysis of experimental data to identify the parameters of space of interest, and to refocus experiments in the critical parameter space.
- Importance of data versus models was discussed extensively. Importance of Error and Uncertainty in predictions was stressed and addressed as a critical gap. The need for rules-based and fundamental models for data generation for complicated systems was highlighted. Participants also emphasized that models that are developed should be compatible for integration into existing industrially relevant, commercial software platforms.

(iv) Challenges we face in applying MGI principles.

- Concerns were expressed on the sustainability of current MGI developed resources once their project funding expires.
- Some participants also warned against the current emphasis on generating data and databases by arguing that we dissociate models from data. They also exhorted the participants to pay heed not only to the data but also the methodology used to generate the data.
- Data generated using proprietary software related to instruments, and making the data available easily and in an open source format, was emphasized as a very critical need.

(v) What does the MGI community needs to flourish?

- A need to identify different kinds of materials data and an Application Programming Interface (API) based approach to navigate between various data was proposed. The refrain from many participants was, “Can we go from abstraction to broad contours, and eventually to APIs?”
- Input from other disciplines and active collaborations with Applied Mathematicians, Computer Scientists, and experts outside MSE was encouraged for MGI to flourish
- Cooperation with software industry, and especially with developers of popular current materials databases, was advocated.

Magnetic and Electronic Materials

Moderators:
Warren Pickett (UC Davis), Hai-Ping Cheng (UF), Paul McEuen (Cornell)

Prologue: In 2014 a Chinese computational physics group predicted superconductivity at 200K in a cubic structure H_3S material at pressures in the 200 GPa range. This audacious prediction was based on a broad search for low enthalpy compounds in the H-S system at high pressure, thus identifying the compound of interest, followed by calculation of T_c based on strong coupling Eliashberg theory. One month after this prediction was published, a German high pressure group posted their finding of superconductivity up to 200K in the H-S system, at pressures in the 200 GPa range. The structure (at least the S sublattice) was determined to be the same as predicted. There is no evidence that there was communication between the theoretical and experimental groups, hence it is not an example of MGI principles *per se*, but this recent breakthrough, for theoretical prediction as well as for high temperature superconductivity, is a provocative example of the capabilities of computational science.

Our breakout team was tasked to address three topics, which we summarize in turn.

1. Identify examples of how MGI is accelerating materials discovery and development within this specific material class.

Several examples were discussed. Names of teams (available upon request) are not included because there are likely several more examples that were not conveyed to us. [Certain parts of the work related below were performed "pre-MGI" but the actual success is MGI-related and supported.]

- Solid state Li ion conductors. Numerous crystal structures and compositions of quaternary systems were simulated. Specific compounds with distinctive structural motifs were identified as most promising. Certain of these predictions have been confirmed by experiment.
- Atomic layer by layer deposition enables synthesis of designed new materials that are metastable, hence unobtainable by other synthesis routes. Three successes were discussed. (i) A "polar metal" was obtained in the $LaAlO_3/NdNiO_3(111)$ system: a low density metal retains local aspects of a polar (insulating) background. Feedback with theory and TEM characterization were central to this success. (ii) Multiferroics with high ordering temperatures were designed, then grown and characterized (TEM, magnetization), establishing FE-FM and FE-ferrimagnetic behavior. (iii) MBE growth in the STO-LMO system was used to engineer new optical absorption bands in the near-IR range, feedback from electronic structure studies was central in obtaining desired characteristics.
- A theoretical proposal of a new Fe pnictide compound was followed by its synthesis and by characterization of its superconducting and magnetic behavior. This team reported high visibility theory-experiment successes on transition metal oxide materials.
- Calculations of the stability of two new compounds in the Ce-Ir-In system was followed by synthesis and substantial characterization of $CeIr_4In$. Though not superconducting as hoped (with no viable theory to predict or test), this establishes some predictive capability for rare earth compounds. The publication was first-authored by an undergraduate researcher.
- Adaptive genetic algorithms applied to the Co-N system predicted a few promising rare-earth free strong magnets. The theoretical work has stimulated synthesis and characterization of Co_4N (in progress).

- High entropy replaced low enthalpy as the descriptor to identify entropy-stabilized oxides. While quaternaries (four cations + O) were found to be unpromising, study of quintenary systems led to promising materials where random site occupations are predicted, and certain of the predicted materials have been synthesized.
- Predictions in the ABX system with cubic LiAlSi structure of 54 stable new compounds was followed by accelerated synthesis of 18 of them. Predicted properties include transparent conductors, thermoelectric materials, and topological semimetals.
- Two theoretical developments may accelerate materials discovery. (i) A new library of accurate, standardized pseudopotentials has been obtained from optimization on a 600-compound training set; this should enhance the reliability and uniformity of computational results. (ii) A new density functional that satisfies all 17 known exact constraints has been constructed, with preliminary tests indicating it performs better than known functionals for most materials (covalent, ionic, metallic, van der Waals).

2. **How are products (data, software, samples, etc.) being shared with community? What are the gaps we need to fill, either in terms of needed products or needed sharing?**

There are some strong developments in this area, although data curation and sharing remain items of active discussion. In the area of computational data there are a few strong players. The Materials Project (MP) was recognized rather early on as the "first of its kind search engine for materials research," and it has gained thousands of users as it expands its capabilities. Its ability to make use of users results may fulfill some aspects of the "wiki" capability that was discussed in the session (without any specific suggestions, however). NIST has placed emphasis in this area, with its *Materials Data Curation* and *Standard Reference Materials* systems being mentioned during this workshop or discussed on the web. European scientists are publicizing a recent AiiDA project. MIT sports a Python-based Computational Materials Design Facility that is an example of more local efforts in materials design and data management.

On the sample curation and sharing side, the UCSC-hosted Materials Advancement Portal provides a platform for experimentalists to post descriptions of materials they are retaining on their shelves and cabinets, with the objective of promoting collaborations and bypassing inefficiency of synthesizing materials that exist and are available.
Synopsis: impressive efforts on data management have been made, with results so far being extremely useful for some purposes. Efforts must continue, as surely will be expounded in more detail in the report of the Data Repositories breakout group.

3. Identify challenges for this community in applying MGI principles. What does the community need to flourish?

Data management: "materials" together with both theory & simulation and broad experimentation is an extremely broad field from which to collect, curate, and share data. However, surely the Data Repositories breakout session will far outstrip the brief interchanges our breakout group had on this topic.

Refining procedures for "closing the MGI loop." The loop is vulnerable at nearly every angle.

- High among the topics discussed under this heading is the need for 'cleaner' samples by several teams. Single crystal synthesis in particular has received less emphasis and support in the U.S. in recent decades than in Japan and perhaps Europe. Quantitative simulation of point and extended defects that is being addressed by very few groups, but it is a daunting task often requiring very precise methods for success.

- Lack of sufficient accuracy of computational methods thwarts some efforts. Energetics (viz. cohesive energies) are the most basic need. Recent developments in the DFT exchange-correlation functional and in pseudopotentials that reproduce all-electron predictions provide two positive developments. Beyond energetics lie numerous properties obtained from DFT calculations, many of which need to be improved to facilitate smooth operation within the loop.
- More broadly, it may be time to discuss the various types of feedback within the loop, what seems to work and what needs attention. Constraints need to be recognized: a step in the loop may take one or even a few months, whereas other steps may be an order of magnitude shorter.
- Also more broadly: the veracity of data may be an issue. “Bad data is worse than no data,” applying to both computational and experimental data. The originator may (or may not) understand the (relative) reliability of her data, but a user who pulls it off a repository surely will not. At the least, standards for a class of data should be constructed and made available with the data.
- Finally, interest was expressed in developing an experimentally-verified set of “standard” materials and their properties for benchmarking new codes. Such standards for molecules were very valuable in the development of accurate quantum chemistry codes.

Forward-looking materials properties. “Far from equilibrium” drew some discussion, revealing that it has a continuum of meanings, ranging from synthesis under conditions well away from equilibrium (but low energy) to ultrafast, pump-probe types of dynamic processes on a short time scale. For the former, an array of computational techniques have been undergoing extension in recent years, ranging from advanced force field simulations to Monte-Carlo accelerated DFT methods. At the ultrafast end, theory and computational methods remain near their infancy, with work done at the model Hamiltonian level and some pioneering studies at the “DFT and beyond” level.

Molecular, Polymer and Biomaterials

Moderators: Mark Bathe (MIT) and Michael F Toney (SLAC)

Approximately 40 faculty, postdocs and graduate students participated in the breakout session focused on the broad topic of soft matter MGI. The goals were to identify: (1) examples of how MGI is accelerating materials discovery and development, (2) how products are being shared with the community, and (3) challenges and needs for the community to flourish.

1) Identify examples of how MGI is accelerating materials discovery and development within this specific material class.

Several examples were shared in which *in silico* design of structured soft materials with target 3D structure and mechanical properties have been enabled, including programmed protein and DNA assemblies, as well as polymeric network materials.

In the protein domain, rules of symmetry have been applied to produce highly structured, well-defined nanometer-scale objects including icosahedral protein cages consisting of 120 protein subunits each, which are some of the largest programmed protein assemblies achieved to date. These protein assemblies can be conjugated to other chemical moieties to engineer functional materials for catalysis, therapeutic delivery, and sensing applications. In the nucleic acid domain, top-down geometric specification or ‘printing’ of arbitrary programmed DNA assemblies has been achieved, together with the synthesis of diverse classes of both symmetric and asymmetric polyhedral nanoscale structures. Synthesis of these assemblies that are designed fully in *silico* demonstrates high yield and structural fidelity on the nanometer-scale, and they can similarly be functionalized with nearly arbitrary chemical moieties to engineer diverse functional materials. Together, these examples demonstrate profound control over our ability to rationally design and synthesize highly structured synthetic biological materials at the nanometer-scale.

In the polymer domain, network models have been developed to predict *in silico* the number of defects present in these materials, as well as their resulting mechanical properties, by accounting for the number of loops present in the network. Quantitative prediction of the mechanical properties of these networks is enabled using a computationally efficient algorithm that offers rapid feedback on this broad class of functional materials. Highly predictive models have also been developed to predict the shape memory response of hybrid polymeric materials synthesized using electrospinning. These models have been used to predict not only structural properties but also complex response to environmental cues including temperature and water, and have also been implemented using 3D printing. Together, these examples demonstrate predictive *in silico* modeling of functional network properties that inform next-generation polymeric materials design and synthesis for diverse applications.

2) How are products (data, software, samples, etc.) being shared with community? What are the gaps we need to fill, either in terms of needed products or needed sharing?

Theories and computational models are being distributed online via various servers and databases, as well as incorporated into commercial and open source software packages. Hierarchical protein design algorithms are being distributed as part of the ROSETTA software suite, and structured DNA assembly design algorithms are being distributed as part of CanDo.

Polymer network models as well as the preceding packages run efficiently on workstations using distributed computing.

A number of important gaps were identified including major challenges associated with relating multi-scale modeling and simulation to experiment, with regards to data/model sharing. In particular, how can multi-scale experimental assays be developed and applied to better test and validate computational models, theories, and simulation results across laboratories? Even when models are successful on longer time-scales or larger length-scales, often researchers still utilize first principles models to interpret results mechanistically or structurally. Can feedback from data to models be more effectively shared across laboratories to speed the testing and validation process? Comparison of results across distinct experimental platforms and assays also poses a major challenge, both for reproducibility of results but also development and validation of models. Organic photovoltaics provide a classic example in which energy transfer needs to be probed from the nanometer- to the micron-scale, offering major challenges that are faced for numerous laboratories for model validation. Nevertheless, despite these challenges and the gaps present in both our understanding and ability to share information/data/models across our community, it is clear that the tightly integrated computational-experimental approach to materials research that is supported by the MGI and DMREF offers a highly effective route to overcoming these challenges. Additional sponsored workshops and competitions for predictive models offer additional opportunities to speed development and validation timescales.

3) Identify challenges for this community in applying MGI principles. What does the community need to flourish?

There was much discussion on the topics of challenges and community needs and the breakout identified several common themes emerged related to multiscale modeling and validation, the development and maintenance of sustainable software, the incorporation of processing in MGI and accessible databases.

The breakout put a high priority on the development of multi length-scale (nm to > µm) modeling tools and measurement technologies in order to probe soft materials across many time- and length-scales at high resolution. This is very important for soft matter (compared to hard materials) where this large range of length and time scales is inherent to the materials. A major challenge is how to merge experiment and computational results from molecular scale to the mesoscale scale. Notably, without the multi-scale measurement abilities, the community does not have the ability to test multi-scale models.

Soft materials structure and function are often dictated by their processing conditions. This is true at the local (<nm) length scale and especially on the mesoscale and presents a large challenge for MGI of soft matter. For example, small molecule force-fields with a solvent do not predict the structure or properties of a film cast from the solvent. The development of coarse-grained models is needed for this prediction along with appropriate experimental validation. This should explicitly capture non-equilibrium properties and features of polymeric and other materials. In addition, this multiscale problem is time-consuming because multiple theoretical iterations are needed to make predictions with tandem experimental validation. After which these models are used to predict larger-scale polymeric material properties. There is thus a significant opportunity for MGI approaches to develop predictive capacity, including the effects of processing on materials structure, especially at the mesoscale.

Another major challenge is how to sustain software developed with MGI funds such that it is usable beyond the life of the funded program. Major resources are needed to take a highly specialized program, code and/or software into something that is more generalized and ultimately useful to the community. It was suggested that, perhaps, a separate funding mechanism is needed to take the code to another level of use. Within this community, there was also a perceived/real conflict between open source code and free distribution of methods/software relative to patenting for commercialization purposes. There was no clear consensus on which approach was ultimately more useful. Another major challenge is the student training that is needed for proper code writing and distribution, which is at a very different level than in computer science.

Databases are needed to store structure/property information from the MGI for soft materials and there was much discussion on how to effectively accomplish this in a way that enabled data mining. The Protein Data Bank was mentioned as a good example of data that are stored and minable. One significant issue that was identified related to metadata, which is important beyond this community. For example, how do you define the process, the material, or even the molecule so that it's unique; an atomic definition is often inadequate. It was suggested that NIST could play a central role here in helping to define the metrics and data standards.

Materials for Catalysis and Chemical Transformations

Moderators: Jeff Greeley (Purdue) and Randall Snurr (Northwestern)

Abstract: The breakout panel on Materials for Catalysis and Chemical Transformations highlighted the challenges posed by the existence of multiple phases and interfaces, in many catalytic systems, for the adoption of a comprehensive MGI-related design paradigm for heterogeneous and homogeneous catalysis. The presence of these disparate elements in successful catalysts necessitates an integrated use of multiple "puzzle pieces," including computation, synthesis, characterization, and reactivity testing, to accelerate catalyst design. Through improved use of these essential tools, MGI-inspired efforts have recently resulted in several breakthroughs: the discovery of novel heterogeneous catalysts and catalytic structures, the identification of fundamental physico-chemical principles to inspire catalyst design efforts, the development of communal databases of catalytic information, and the development of numerous outreach programs for catalysis science. To further enhance these efforts, the panel identified several crucial needs, including development of experimental and theoretical tools that provide enhanced atomistic information, the development and efficient exploitation of combined experimental/theoretical databases of high quality kinetic and computational data, and direct incorporation of *in-situ* information into catalyst design strategies.

Discussion summary: The breakout panel highlighted the issue of complexity in heterogeneous and homogeneous catalytic phenomena as an important overall challenge in the development and deployment of MGI-related strategies to design new catalytic materials. The presence of multiple phases and interfaces was identified as a particular source of complexity that is central to catalytic science. To address this and related challenges, the integrated development and use of four "puzzle pieces" of catalysis, including computation, synthesis, characterization, and reactivity testing, is imperative. In each of these areas, faster approaches for data gathering and analysis are needed, and higher accuracy/resolution methods are also required.

By adoption of the above strategies, MGI-based approaches to catalysis have begun to facilitate crucial advances in four key areas of catalyst science: the discovery of improved catalytic materials for specific chemical reactions, the identification of fundamental catalytic principles that will facilitate future catalyst design efforts, the development of new communal databases and methods for catalytic studies, and the enhancement of outreach efforts to promote catalysis science among students and the general public. Although still limited in number, MGI-inspired approaches to catalyst screening and discovery are becoming increasingly common, and exciting examples of the design of improved catalytic materials include, among others, the use of high throughput computational screening to find optimal zeolites for hydrocarbon iso-dewaxing[1] and the identification of a NiGa alloy for enhanced methanol synthesis through descriptor-based catalytic screening methods[2]. Recent advances in the understanding of fundamental principles governing heterogeneous and homogeneous catalysis are also poised to accelerate the identification of improved catalysts by facilitating refinements to traditional catalyst design methods. Important developments in this area include the use of computational methods to elucidate active site structures for a growing number of catalyst surfaces, the development of strategies to probe the *in-situ* stability of catalysts with first principles computational techniques, the atomic-level simulation of catalyst synthesis processes, the understanding of reactivity limits of heterogeneous catalysts derived from scaling relationships, and the tighter coupling of theory and experiment at the quantitative level to evaluate reaction rates and catalytic mechanisms with unprecedented accuracy. A further example of a recently developed experimental tool that will permit significant enhancement of atomic-level structural understanding of heterogeneous catalysts is dynamic nuclear polarization solid-state NMR[3]. New catalyst databases and analytical tools are also accelerating the adoption of MGI science in catalysis, including the CatApp database of calculated surface adsorption energies from the Nørskov group at Stanford, the Materials Project of simulated bulk crystal structures and properties, and the development of a growing number of experimental and computational databases that currently reside within individual research groups. Finally, the proliferation of outstanding summer schools related to computational- and chacterization-based techniques for catalyst studies has recently begun to enhance the visibility of catalyst science in the public domain and to accelerate training of the next generation of catalytic scientists.

Without minimizing the successes that have emerged in the past few years, it is important to recognize that the catalysis community has struggled to adopt MGI approaches in some areas. Analysis and mining of emerging catalytic databases is one area in which progress has been limited. Since catalysis is not a classically "big data" science, limited availability of information makes the efficient extraction of physico-chemical trends and fundamental understanding difficult, and more efficient machine learning algorithms will be critical to surmounting this problem. A related need includes the measurement and incorporation of high quality experimental kinetic data, taken using differential reaction conditions and titrated active sites, into publicly available databases. In the computational space, simulation methodologies have not yet succeeded in seamlessly integrating electronic structure calculations with higher length and timescale methods, and electronic structure calculations themselves suffer from limitations in accuracy and in the difficulty of extending ab-initio molecular dynamics simulations to long times. Incorporation of environmental effects into ab-initio methods is also a critical goal, and combining such calculations with enhanced *operando* probes of catalyst structure and degradation modes is potentially of great interest.

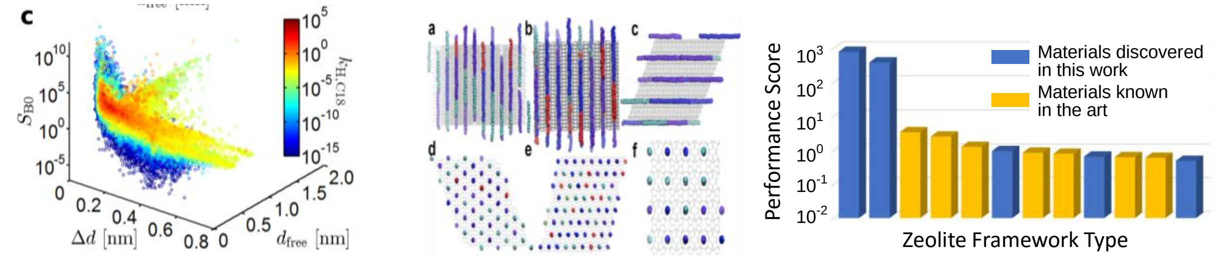


Figure 1. Computational Screening to Find Optimal Zeolitic Scaffolds for Hydrocarbon Iso-Dewaxing. Bai et al., Nature Communications **6**, 5912 (2015).

As a final, overarching need, the imperative to more seamlessly integrate computational and experimental data and analysis is particularly noteworthy. Such integration will accelerate methods to identify reactivity descriptors that will, in turn, facilitate catalyst screening, will improve the accuracy and resolution of existing methods for catalyst synthesis, characterization, testing, and theory, will expand existing databases of catalytic information, and will enhance outreach efforts on behalf of the catalyst community. By systematic exploitation of these opportunities, MGI-based approaches will play an increasingly central and productive role in catalytic science.

[1] Computational Screening to Find Optimal Zeolitic Scaffolds for Hydrocarbon Iso-Dewaxing. Bai et al., Nat. Commun. **6**, 5912 (2015).

[2] Discovery of a NiGa Catalyst for Carbon Dioxide Reduction to Methanol. Studt et al., Nat. Chem. **6**, 320 (2014).

[3] Dynanic Nuclear Polarization Solid-State NMR in Heterogeneous Catalysis Research. Kobayashi et al., ACS Catal. **5**, 7055 (2015).

Photonic and Thermoelectric Materials

Moderators: Irena Knezevic (U Wisc.-Madison) and Chris Van de Walle (UC Santa Barbara)

1) Identify examples of how MGI is accelerating materials discovery and development within this specific material class.

The participants found it **challenging to identify all MGI-backed projects** (outside of NSF/DMREF). We recommend **creating a registry** of all MGI-affiliated projects.

Success stories:

- EFRC/BES Center for Inverse Design: Trimetallics
- EFRC/BES Center for Next Generation Materials by Design: New metal oxides (Zn-Co-O) as hole transport layers for Organic PV
- Rapid development of PV devices (NREL)
- Disseminating high-throughput calculations for thermoelectrics (CSM)

DMREFs: Photonics

- Debdeep Jena/Emmanouil Kioupakis/Eric Pop: DMREF Extreme Bandgap Semiconductors
- Zhenan Bao, Vijay Pande, Michael Toney: DMREF High-Throughput Morphology Prediction for Organic Solar Cells
- John Kieffer/insang Kim: DMREF/SusChEM: Simulation-Based Predictive Design of All-Organic Phosphorescent Light-Emitting Molecular Materials
- Rakesh Agrawal: DMREF/SusChEM: Collaborative Research: Rapid Design of Earth Abundant Inorganic Materials for Future PVs
- Kathleen Kash/Walter Lambrecht/Hongping Zhao: DMREF/SusChEM: Heterovalent Ternary Nitride Semiconductors and Mixed Ternary-Binary Heterostructures
- Chris Van de Walle/James Speck/Steven Ringel: DMREF Design and Fabrication of Wide-Band-Gap Nitride-Based Alloys
- Volker Sorger, Ludwig Bartels, Evan Reed, NSF DMREF, Collaborative Research: Theory-Enabled Development of 2D Metal Dichalcogenides as Active Elements of On-Chip Silicon-Integrated Optical Communication

DMREFs: Thermoelectrics

- Chris Wolverton/Scott Barnett/Thomas Mason:
    - http://www.mccormick.northwestern.edu/news/articles/2015/11/doping-powers-new-thermoelectric-material.html?utm_source=internal-newsletter-12-09-15&utm_medium=email&utm_content=email-position3&utm_campaign=internal-newsletter

- Eric Toberer/ Qin Lv: DMREF: Computationally Driven Targeting of Advanced Thermoelectric Materials
    - TE Design Lab: A virtual laboratory for thermoelectric material design, Gorai et al., Comput. Mater. Sci. A 112, 368 (2016).
- Ram Seshadri: Data-Driven Review of Thermoelectric Materials: Performance and Resource Considerations, M. Gaultois et al., Chem. Mater. 25 (2013).

2) How are products (data, software, samples, etc.) being shared with community? What are the gaps we need to fill, either in terms of needed products or needed sharing?

a) During the breakout session, it became clear that the community favors **decentralized maintenance of repositories**, each catering to a different community, but with a **common, well-maintained registry**. The participants felt that www.mgi.gov (NIST) would serve that purpose well, as it is the one that comes up prominently in online searches for Materials Genome Initiative, just after the White House link.

b) On the experimental side, there is a need for an **open-access equivalent to ICSD** (Inorganic Crystal Structure Database).

c) Another issue that was brought up was the **incentive to share raw data**, especially in the context of junior faculty and difficult-to-obtain experimental results. Researchers, especially assistant professors, should be allowed enough time to be done publishing on a given set of data/samples before being required to share.

Notable databases/repositories:

- Databases: Materials Project: https://www.materialsproject.org/
- OQMD: http://oqmd.org/
- ESTEST http://eslab.ucdavis.edu/software/estest/index.htm
- NoMaD: http://NoMaD-Repository.eu/
- University of California Digital Library: http://www.cdlib.org/uc3/merritt/

3) Identify challenges for this community in applying MGI principles. What does the community need to flourish?

a) There was a consensus that MGI is **accelerating the acquisition of knowledge** and understanding of the properties of materials; unclear if we were accomplishing better materials faster.

b) A need to broaden the scope of materials to possibly **include biomaterials** was brought up.

c) Some participants urged more interaction with **statisticians and applied mathematicians** to aid with both experiment and theory.

d) The issue of **bridging scales** – from atomistic to experimentally accessible – was identified as extremely important, along with the associated need to balance between full **computational rigor vs. faster phenomenological models**, and accurate benchmarking for the latter.
e) An important problem was to identify ways in which computation and experiment can be reliably compared (**benchmarking, validation, calibration**). Several participants raised the issue that there is **insufficient funding for benchmarking**, yet it is critical. It is important to identify the ways in which computation and experiment can be reliably compared, and the associated cost.
f) Issues for high throughput computation: The issue of benchmarking was also raised from the standpoint of high-throughput computations, in that it is important to identify **reliable property predictors** and **avoid false negatives** (which could erroneously eliminate whole material groups). The participants felt considerable attention and funds were needed for validation and benchmarking of calculations. How can we ensure that computational data is of high quality? We need to share enough details about the computation-generated data as well as the approximations under which they were obtained to speak of **data reliability**.

3.1 Technical challenges in photonic materials

- Linear response: Static dielectric tensor; Dynamical screening and high-frequency dielectric response; The role of dissipation (phonons, impurities, properties of the surrounding media)
- Nonlinear optical response of bulk materials
- Electron-phonon interactions in general (transport, also loss mechanisms such as Auger, defect-assisted recombination, hot-electron relaxation, etc.)
- Excited states calculation and connection to transport

3.2 Technical challenges for thermoelectric materials

- Power-factor engineering: the critical role of doping (identifying dopants for novel materials, nanostructuring to engineer density of states), dealing with interfaces and point disorder
- Thermal transport engineering: dealing with interfaces and point disorder, nanostructuring (nanoporous structures and meshes). What are the limitations of popular semi-classical transport models relying on the relaxation-time approximation and some broadly available codes; relationship with first principles and molecular dynamics
- Treating defects in a high-throughput mode in atomistic calculations

3.3 Overarching technical challenges

- Benchmarking and widespread implementation of new methods (e.g., for van der Waals-bonded systems)

- Description of phenomena far from equilibrium and connection between first principles techniques and transport
- Extracting quantities such as electronic, phononic, and spin lifetimes that could be used in semi-phenomenological or semi-classical transport techniques
- Experiment would like guidance from theory as to what to measure to best test certain hypotheses or probe for specific materials properties. In general, there is a need for more and better comparison between computation and experiment, and the funds are often insufficient for experimental benchmarking
- Property-centric design on new materials: developing the abilities to create materials with specific desired performance. This is a great challenge for functional materials, such as photonic and thermoelectric ones, where the properties are tied to nonequilibrium behavior

Data Repositories

Moderators: Carrie Campbell (NIST) and Stefano Curtarolo (Duke)

Databases being used:

Materials data are diverse and semi-structured, ranging from melting temperatures to 3D atom probe data. There are a variety of materials data repositories, which the Materials Accelerator Project has attempted to summarize (http://acceleratornetwork.org/mse-challenge/). In the USA, three of the large DFT data repositories contain results generated through automated high-throughput computational materials design frameworks:

- AFLOWLIB (aflowlib.org),
- Materials Project (www.materialsproject.org), and
- Open Quantum Materials Database (oqmd.org).

Other computational data repositories include the NIST Interatomic potential repository (http://www.ctcms.nist.gov/potentials/), Knowledgebase of Interatomic Models (https://openkim.org/), and the Harvard Clean Energy Database. International resources for computational data include the NoMaD repository (nomad-repository.eu), which contains computational data collated from different sources. A variety of experimental data repositories are also available, including:

- International Crystal Structure Database (icsd.fiz-karlsruhe.de) which contains experimental crystal structures,
- MatWeb: http://www.matweb.com/
- ASM International: http://www.asminternational.org/materials-resources/online-databases
- MatNavi : http://mits.nims.go.jp/index_en.html
- MaterialsData : https://materialsdata.nist.gov/dspace/xmlui/
- Citrine : http://www.citrination.com/
- Materials Data Facility: https://materialsdatafacility.org/

Communities which are benefitting most and what is needed to engage other communities:

Computational materials scientists find it relative easy to pipe high-throughput first principles data results into curated databases. The curation of experimental results is more problematic. One solution that experimental scientists would find helpful is if data curation software was directly installed on their instrumentation so that data is tagged as it is being generated. Both NIST and the University of Michigan are working on developing data curation tools, Materials Data Curation System and Materials Commons respectively. Granta Design provides a commercial tool for data curation. Citrine Informatics also provides a open platform for data curation and storage. There is also a need for sample provenance tracking for experimental work, so that there is a record of what was done to a sample. The Materials Commons software focuses on tracking sample provenance. Raymundo Arróyave from Texas A&M commented that tracking the sample provenance is important for reproducibility.

Ideally, graduate students and scientists will use electronic notebooks and data curation software in place of traditional lab notebooks to enable the rapid tagging and dissemination of data (Thomas Proffen, James Warren). This will also help solve the problem of when a student or researcher leaves the group and their data is insufficiently annotated, and thus prevent data from getting lost (Raymundo Arróyave). It was suggested that beamlines and light sources at large national laboratories would be a good place to start the process of automated data curation, and they should start investing in good data infrastructure (James Warren).

An umbrella registry is being created by NIST (Materials Resource Registry) to list all of the available data repositories in one place to facilitate the easy location of useful data resources (Carrie Campbell, James Warren).

There was discussion over whether specific data repositories were needed, or if it would be easier to just tag the data and make it available online, for web crawlers and search engines to sort and organize (Hannas Schniepp). There needs to be incentives for researchers to tag their data appropriately, and workshops on data curators (Zach Trautt). Incentives could be similar to citation indices (Hannas Schiepp), and could also be tied to funding (James Warren). Incentives are also needed at the institutional level, such as taking into account a researcher's record of data sharing when making promotion decisions (Raymundo Arróyave). Demand for tracking data citations will arise naturally if the infrastructure is there (James Warren). There is a need to avoid incompatible standards, and to ensure that the data formats are interoperable to allow for data collation (Hannas Schniepp). If there is a common standard, then the data tagging and curation will spread across more research groups.

More effort should be made to bring data scientists into materials science (Chandler Becker). Part of the problem is that the quantity of materials science data available in data repositories is insufficient for them to work with (Kristin Persson). This might be solved if the automated data curation for experimental work is adopted more widely, as the quantity of unpublished data is sizable (Thomas Proffen). Data scientists also tend to be very frustrated with materials science data as it is high dimensional (Eric Toberer). A solution to this is to restrict the data space being examined to a few key properties (Kristin Persson).

Data scientists are interested by the problem of how make different data repositories interact (Kristin Persson). For data infrastructure creation, materials scientists should try to leverage the existing knowledge of information technology companies who already work with big data, such as Google, etc. This could take the form of mid-career internships for materials scientists at these companies in order to learn their techniques (Thomas Proffen).

Obstacles preventing data repositories from reaching their full potential:

As described above, more work is required to make it easier for experimentalists to curate and tag their data. Having data curation software installed directly on the instrumentation would assist greatly (Carrie Campbell). A potential obstacle to this is that instrument manufacturers see software as a profit source, and tend to use proprietary formats to force researchers to purchase their own analysis software. This also obstructs the creation of interoperable data formats.

More work is also needed to improve data verification and experimental validation of predicted materials, as it is far too easy to generate large quantities of bad data (Eric Toberer).

Another obstacle is the lack of training that junior researchers and graduate students receive in data science. More could be done to incorporate data science and data management courses into the graduate student materials science programs. Summer schools and workshops on data science and data curation could be set up (Carrie Campbell). Web-based tutorials on data science would also be useful (Raymundo Arróyave).

Sustaining databases in the long term, and making them robust against the turnover of key personnel was also discussed. One suggestion was to have university libraries start to take responsibility for data curation and management (Raymundo Arróyave). Libraries are starting to move from managing physical books to managing information, and are used to being rated by the content of their collections, which in the future could also include data repositories. It was also suggested that as long as data is appropriately tagged and available on the internet, web search engines should be able to find it and categorize it (Hannas Schniepp). Addtionally, if the data repositories are useful and being used, then researchers will demand that they continue to be funded, and funding will continue to be there to sustain them (Thomas Proffen). It is also important that data repositories evolve, which means some of them will die out and this should be regarded as a necessary and useful part of the process (Eric Toberer).

Mathematics, Software and Cyber Infrastructure

Moderators: J. Allison (U. Michigan) and E. Olivetti (MIT)

This breakout session was attended by approximately 25 individuals from a broad set of backgrounds. The format of the discussion involved going around the room so that each attendee could contribute his/her thoughts on a set of four questions. Notes were taken on the computer and on flip chart paper. The remainder of the session was divided between the questions such that participants spoke in more detail and clarified points made going around the room. This document provides a summary of the input received and follows the format of the out-brief presentation given by the moderators during the MGI PI meeting.

Summary of take home messages:

There have been significant advances benefitting the materials community within mathematics and computer science. The group felt there were a few key challenges to continued advancement at the desired pace for realizing MGI goals. One key obstacle raised by the group was the lack of sustained funding (and interest) along a software pipeline, similar to what the field discusses around technology transition, from early prototype through a community coding phase and potential commercialization. The community needs well-crafted curriculum and summer school opportunities so that we train domain experts in how to develop robust algorithms and code. One tension this raises, however, stems from the lack of sustained career paths (and reward structures) for individuals who cross train in this way.

1) How are advances in mathematics, software, and cyberinfrastructure benefitting the materials community?

At the outset the group felt that development of improved algorithms can be an enabling technology (many examples were provided by Robert Kohn's introductory talk, such as evolution of grain structure, phase field crystal methodology. It was clear that the availability of commercial and open source software are widely used in developing new scientific understanding and ICME tools for industry for developing new materials, manufacturing processes and products. Some examples include DFT, Molecular Dynamics, Dislocation Dynamics, CALPHAD, Crystal Plasticity capabilities as well as process simulation codes. Furthermore community code project development via GitHub, for example, is becoming more usual in the field (SciPy was cited as an example). Many mathematical tools that are considered "standard capabilities" are now widely used (e.g. FFT). Image science, data science, computational imaging are coming together to provide new capabilities, which means we can extract new and useful information from "noisy" data. In addition, the availability of large scale computational resources (such as NERSC, XSEDE) has been essential for computationally intensive problems and education.

There were a few examples of success in other fields and domains cited such as computational scientists working with chemists and biologists have worked well for code transferability. These may be an exemplar for the materials community. The group also cited use of existing libraries from other domains being brought into materials domain (e.g. DEAL ii FEA Libraries).

A more indirect example of these advances becoming more wide spread was the interest and implementation of jointly sponsored conferences between mathematicians, computer scientists and domain experts such as an upcoming SIAM and MRS conference, among others.

2) How can mathematicians and computer scientists most effectively connect with material scientists (others) to accelerate discovery and deployment of materials? What are keys to beneficial collaboration?

The main point discussed around this question was the need to foster long term relationships between materials scientist and computer scientist (CS)/mathematicians. These relationships have to be mutually interesting and beneficial. The key to being mutual beneficial was to engage early and define research questions where the contributions for both domain experts and CS/mathematicians experts are clear. The goal is to get to the science as fast as possible, so we need to have mathematicians on board early to know what is feasible and what has been done already. Successful project should also disseminate knowledge of best practices and leverage the successful work of others. This perhaps is a point that goes without saying, but many felt that there was not enough crosstalk across disciplines and projects where collaborations were effective. Effective collaboration was found in places where there had been significant curriculum development (making use of summer schools on high performance computing, “Software Carpentry”, e.g. LLNL- CCMS program).

The community should make use of new government programs including leveraging joint opportunities that encourage collaboration among the various expertises under one fully integrated project. Some examples were provided including NSF Mathematical Sciences Innovation Incubator (MSII) program, the SCIDAC program and MIMEX (Large centers to develop math for domain side).

3) What obstacles exist for maximizing the impact of mathematics, software, and cyberinfrastructure on the materials/chemistry community?

Where appropriate, there is need for sustained long term support (and incentives) for community and major open source software development, including maintenance of codes for the long term. The group discussed the level of resource need between community codes, production codes, and prototype codes and the need for sustained funding along the entire code pipeline. One key obstacle was the lack of stable career paths for software experts (e.g. the soft money issue for non-tenure track faculty and scientific staff in academia) therefore qualified individuals are often lost to other fields. We need to improve the ability to reward deep engagement and training. For example, we need improved reward schemes – e.g. What is the “exchange rate” between code development and publications? or How do we reward for publications outside domain (e.g. CS in Materials Science etc.)?- Some cited difficulty in recruiting computer-savy students into materials science stating that we should promoting Computational Materials Science as important and exciting approach to attract students who are capable and interested in both. One issue may be that some important problems may be considered “engineering” by computational scientist and the CS community may need to revisit this.

4) Are there major software needs/gaps in advancing MGI? What is your wish list?

While some specifics were mentioned, the general gaps to advance MGI were “standardization” of code interfaces that would lead to robust approaches for code linking, including well designed

& specified inputs/outputs; more emphasis on transferability of code and ease of use; and dissemination of best practices. A few other specifics were:

- Opportunities to leverage existing and new approaches including:
    - Optimization approaches and algorithms
    - Existing signal processing software that should help a lot with image analysis.
    - Real Space Image Analysis and 3D imaging analysis
- Approaches to solve ‘the inverse problem” – e.g. property goals driving materials design”

Advanced Manufacturing

Moderators: Peter Collins (Iowa State) and Cliff Henderson (Georgia Tech)

Prior to initiating the Advanced Manufacturing breakout session, a brief survey was conducted of the attendees in order to: (1) determine their primary materials interest areas and (2) some of the manufacturing topics represented in the room.

36.4% of the room were in the area of metals, 36.4% in the area of functional materials, 18.1% in the area of polymers/soft materials, and 9.1% in the area of other ceramic materials. The room included individuals working on additive manufacturing, extrusion, roll-to-roll printing, powder bed fusion, solid-state joining, powder synthesis, and sensing/modeling/theory.

Given this diversity, we also started with some guiding thoughts on a broad topic. These were:

1. Advanced Manufacturing represents a very broad spectrum of industries, materials, and processing techniques.
2. MGI integrates theory, modeling/simulation, synthesis, and measurements.
3. This session has a <u>challenge</u> to discuss a broad subject, while being informed by our own experiences.
4. Impact of processing method and its interaction with in-use material morphology/structure/properties is important in many areas but is it captured well in modeling?

The breakout session addressed the following questions:

1. How is MGI contributing to Advanced Manufacturing
2. What fundamental research is needed to maximize the effectiveness of Advanced Manufacturing?
3. What obstacles exist for maximizing the impact of Advanced Manufacturing?

These are discussed below.

How is MGI contributing to Advanced Manufacturing?

The breakout session provided examples of where MGI has made significant contributions to advanced manufacturing, including broadly direct contributions and more rapid discoveries. With respect to direct contributions, the panel identified: more effective cure models for stereolithography; tools for topology optimization to design new architectures to be produced using 3D printing; design and production of new digital materials; and more mature ICME tools. Indirect contributions included materials and techniques that were enabled by MGI that will lead to discoveries, including: access to controlled materials enabling new functions of materials to be enabled; combinatorial materials discovery; and some breakthroughs in the area of self-assembly.

The panel was probed on how MGI can impact advanced manufacturing. It was quickly pointed out that the panel should consider not only advanced manufacturing (i.e., new manufacturing), but also on *advancing* existing, legacy manufacturing techniques. In general, the following was identified as ways that MGI could impact both.

- New materials tailored to benefit from new manufacturing approaches

- Enhancing local properties
- Identifying ways to create local stability (thermodynamic, kinetic, mechanical, etc)
- Identifying ways to control microstructure, texture, and chemistry
- Establish data-driven process-structure-property models, as community integration is enabled/encouraged under MGI

In addition to these topics, the breakout session also discussed the fact that MGI is enabling a new cohort of scientists and engineers to be trained in MGI strategies. This is important for multiple reasons, including the fact that it helps to stem the losses of scientific and technical workforces faced by industry to retirements, and the fact that the new cohort can bring MGI strategies *into* the workplace, resulting in paradigm changes from within. This will help companies overcome barriers to adoption. The MGI is also perceived as helping to reinvigorate materials modeling in both universities and industry.

What fundamental research is needed to maximize the effectiveness of Advanced Manufacturing?

These are general topics identified by the breakout session attendees. Some are singular broad topics, while others have second tier research identified.

Topics

- Apply MGI to roll-to-roll flex printing
- New ways to integrate multiple manufacturing techniques *across scales*
    - Requires that MGI models be developed for each scale/technique
- Predicting properties in metals remains a key difficulty
- Closed-loop control
    - Need to integrate sensors
    - Need *new* sensors, algorithms, and modeling
    - Rapidly seek solutions to the ‘inverse problem’ to refine process parameters
    - Develop continuum temporal modeling techniques whose time scales are equivalent to industrial time scales
- Need to make modeling approaches general so that they can be broadly accepted (like FEM) as opposed to uncurated, specific academic codes.
- Need to attempt to solve the highly non-linear response to modeling various processing techniques involving both time and temperature
- Need to determine ways to more efficiently and accurately model complex (i.e., 8+ component resins, alloys, etc) materials
- Need to implement MGI into the certification process for industrial end users
- MGI can play a significant role in understanding the interaction of energy beams with solids
- MGI can provide “plus research” activities. Specifically, in advanced manufacturing there are many heavy lifts underway between industry, academic, and national labs. The problem is that there are sometimes additional models/methods that fall outside the scope of the heavy lifts but would be truly enabling. These include, for example, modeling of residual stress, porosity, or the evolution of large ‘ala’ grains in additive manufacturing.

What obstacles exist for maximizing the impact of Advanced Manufacturing?
These are general topics identified by the breakout session attendees. Some

Obstacles:

- In the area of semiconductors, the MGI techniques are focused less on industry and more on fundamental science. Thus, there is a potential obstacle owing to the asymmetric resource availability for implementing MGI techniques into industry

- Regarding infrastructure, advanced manufacturing equipment is: very expensive, not research friendly, or heavily burdened with production. It makes it difficult to conduct the research critical to make the significant advances necessary. In addition, research-grade instruments and industrial scale advanced manufacturing are not necessarily the same, and can result in significant differences in the heat loads, unit operation speeds, providing great uncertainty for predictions. A potential solution is the design of new, industrially relevant physical simulators.

- In the area of materials, the following challenges were noted.
    - Changing either the material or process to something "like" the target material or process may lead to very different results.
    - Predicting non-equilibrium structures remains a challenge across material types.
    - Transitioning from simple 'model' materials to materials used by industry is difficult.
    -
- Industrial Culture:
    - How to we encourage industrial acceptance?
    - How can we accelerate the feedback between industry and academics/labs?
    - How to we bridge the valley of death between laboratory and industrial scale? (solution: transition results into companies with the infrastructure/supply chain to handle technology development)
    - IP: Industry does not necessarily want to share their proprietary recipes, so it limits the value of the interactions
    - Students graduating after MGI activities who have conducted extensive modeling will not take jobs with industry if modeling groups do not exist

- Academic Culture:
    - How can we accelerate the feedback between industry and academics/labs?
    - How to we consider the MGI and advanced manufacturing during the tenure/review process? Individuals might not engage in manufacturing/processing because it is not perceived as the same quality of science

Transitioning Fundamental Science to Technology and Applications

Moderators: Bill Tumas (NREL), Ravi Chandran (U. Utah), and Volker Sorger (GWU)

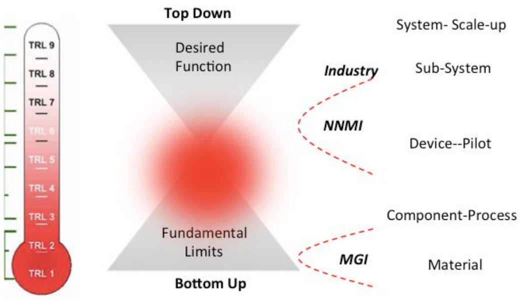
Attendees: Jesse Bond, Maarten de Boer, Cynthia Jenks, Stephan Lany, Oleg Lavrentovich, Alpha Lee, Pete Ludovice, James Morris, Sankar Nair, Luke Roling, Ilja Siepmann, Steve Tait, Chris van de Walle, Dalong Zhang, Hongping Zhao

1. How is MGI accelerating the transition from fundamental research/discovery to deployment?

Tech transfer is a long-standing complex issue, so our breakout group tried to stay focused on MGI-specific aspects. The DOE-BES and NSF MGI programs are focused on accelerating discovery, providing the foundational science and tools, and thereby elucidating the broad search and discovery (e.g. "genomic") aspects of materials and their fundamental properties. Other components of the national MGI initiative focus on manufacturing and deployment of advanced materials. Key outputs from MGI are new understandings of the fundamental limits of materials (properties/functionalities) for a number of promising technology areas including those specifically discussed at the workshop. Many MGI projects are driven by functionality or properties for specific applications and focus on fundamental studies to explore a wide range of materials. MGI also provides important collections of data, capabilities and networks and can play a critical role helping to fill the pipeline with new materials and concepts. There are already a number of examples where MGI approaches have led to the discovery of new materials including battery electrode materials, structural materials, and catalysts. It is recommended that successes in MGI be cataloged and publicized, but it should be done carefully to delineate potential success stories where new materials could have impact from demonstrated cases where their impact has been validated.

2. What routes/indicators (patents, industrial partnerships, entrepreneurial activities, grant applications to applied funding sources, etc.) can be used to demonstrate the transition of fundamental research to applied research to deployment?

The breakout group discussed a number of key elements of "success" for transitioning to deployment. Success eventually involves benchmarking or validation of the performance of discovered materials in components, devices, sub-systems or processes for specific applications. This transition requires connecting bottom-up materials discovery with a top down applications-driven approach (see figure) that necessarily spans various technology readiness levels. Indicators of this success can include intellectual property and patents as well as utilization of MGI-discovered materials for I-corps, GOALI or SBIR projects or applied R&D projects from for example DOE applied energy offices, innovation hubs, ARPA-e or DARPA. These and related projects would lead to prototype or device level of testing or demonstration. Industrial partnerships either with start-ups or with large companies can be an important metric of success. Increased use of MGI tools, databases, and approaches by industry to address specific needs or problems could be another indicator as well as counting the number of academia-industry co-authored patent disclosures, which are initial indicators of innovation within MGI projects. There is also a growing base of companies, including a number of small or start-up companies including those in materials but also in pharmaceutical and biotechnology, providing accelerated discovery services that could provide excellent examples of transition.



It was suggested that university technology transfer offices may not have much experience with the patentability of MGI-derived concepts (e.g. predicted materials vs. demonstrated materials), and communicating precedent in this area would be helpful. Furthermore, it is likely that there are a number of examples such as early work on Freon alternatives with computationally predicted problems (DuPont in 1990s), and someone at the workshop mentioned MOF development from GaTech.

3. What is needed to promote the transition from fundamental science to technology & applications?

Increasing the availability, access, and utilization of MGI approaches, databases, information, best practices, and tools can be a key enabler. Some suggestions also centered on developing a registry of databases, networks, and capabilities. Mechanisms to enable fundamental researchers to have access to applied research laboratories or capabilities that can provide “proof of concept” testing and demonstration are important. Supporting collaborations between academia, industry, and national laboratories could incentivize this. Defining a transition from MGI to, for example, the National Network of Manufacturing Initiative (NNMI) could be an important pathway. There were some discussions on whether a consortia or center approach could essentially provide user facilities for MGI researchers to help with experimental and prototype development necessary for tech transfer. Increasing the connectivity to applied research programs and laboratories for prototype (“device”) development and testing through applied MGI consortia would also span technology readiness levels and even span the gap from fundamental MGI approaches to NNMI and other tech transfer concepts (see Figure). This effort could also help catalog capabilities and laboratories that could efficiently and rapidly test new materials in specific applications or components. It is important to also continue to create and communicate new materials and databases and to continue to advertise existing transition mechanisms including SBIR, I-Corps, GOALI, and DOE Applied energy offices, ARPA-e, DARPA. Technology roadmapping activities in concert with industry in key application or technology areas could get industry and application needs to the MGI community and also increase industry interest in MGI. The group also agreed that most of the current MGI approaches focus on correlating structure and composition with properties but there is a critical need to include and understand the impacts of materials processing (i.e.. processing-structure-properties).

Equipping and Educating the Next Generation

Moderators: Kathleen Kash (Case Western) and Richard LeSar (Iowa State)

Introduction:

The goal of the education activities in the Materials Genome Initiative are quite diverse, but are centered on enabling a change in paradigm in how we do materials discovery and development science by integrating experiments, simulations and advanced data analytics. Reaching this goal is complicated by the very diverse audience for the educational program, which includes general outreach to K-12 students as well as more formal educational programs for undergraduate and graduate students. Education and training opportunities for postdoctoral fellows as well as continuing education for industrial and national laboratory researchers will also be important for reaching the largest possible audience for the MGI philosophy. Finally, we recognize the strong need for engaging the public and, in particular, legislators.

There were seventeen people at the breakout session, with somewhat less than half being from physics departments and the rest from various engineering disciplines, including materials science, chemical engineering, and civil engineering. We had a vigorous discussion, focusing on the following assigned questions:

1. How are students and the public being informed and educated in the MGI philosophy?
2. How can the MGI philosophy best be instilled into the next generation of scientists?
3. How can the impact of MGI research best be related to the public and legislators?

We summarize the discussion of each of these questions in turn.

1. How are students and the public being informed and educated in the MGI philosophy?

There was one essentially unanimous agreement between the participants in this breakout session that while “MGI” is a recognized acronym, there are many misconceptions about what it actually is, with the most common misconception seeming to be that it is (just) computational materials science. The participants also noted that their students and those of their colleagues on MGI projects do have a reasonably good notion of the MGI philosophy; MGI is embraced and taught by the groups involved in the MGI program.

There seem to be a number of ways that MGI projects use to bring together their students and teach them about MGI. One project, for example, uses an immersive annual research workshop for participants, collaborators, and potential collaborators to provide a learning 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.

Given the lack of a general understanding of the philosophy of MGI, it should not be surprising is that one of the big challenges is that there are few MGI-focused courses in the various departments represented at the breakout session. One participant mentioned that their department has their graduate students go to another department for data-science courses, with the opportunity for them to obtain certificates upon completion of four courses in data science from that other department.

A concern is that as graduate students begin to specialize, they lose touch with other parts of their discipline. It was suggested that the MGI provides a motivation for students to broaden their appreciation for their discipline through close collaboration with people with complementary expertise. It was noted, however, that it is often difficult to bring these students together because of the difference in concepts and language of their particular specialities. It was suggested that an effective means to do that is to simplify the language, i.e., to limit the use of jargon and keep ideas straightforward. One way to do that is to bring undergrads and even high school students in to the meetings.

2. How can the MGI philosophy best be instilled into the next generation of scientists?

Our discussion focused on two main areas, education for graduate students and outreach to the public. We had no substantive discussion about what is needed for undergraduates, most likely because we came from so many different disciplines. One suggestion for undergraduates that spanned across all disciplines was that we need to have more “inquiry-based” labs for the students, i.e., labs that are less deterministic and more open to potential failure. Such labs could easily involve MGI activities.

Given the issue of available classes mentioned in Question 1, the education discussion centered primarily on how we can share resources within our teams and between our teams. A number of examples were suggested; for example, starting specialized workshops for graduate students on special topics. There was some consensus that such workshops would be useful, but no substantive discussion on how to make them a reality. Another example focused on online (recorded in real time) lectures by scholars providing detailed introductions to special topics (based on a program in Physics at Columbia, but focused on MGI). These workshops and lectures would be shared between teams. One question was whether NSF would have a mechanism to help support such activities (e.g., an NRT focused on data science?).

3. How can the impact of MGI research best be related to the public and legislators?

The participants agreed that we need a marketing strategy that includes making sure that the public understands the importance of materials in their lives and the roles that computational design can play in enhancing those materials. One part of that strategy is to define a measure of success to which the public can relate. Possible metrics include how MGI-based discoveries may impact society, e.g., new batteries based on materials discovered through MGI. Another possible metric is the degree to which industry adopts and benefits from the MGI strategy. We all agreed that metrics would be more powerful when MGI has clear successes in “save the world and creating jobs”.

We heard about a number of activities that focused on the public, mostly through the interaction with K-12 students. The participants all recognized that younger students have grown up in an age in which interactions with computers is completely natural. Programs such as the one at Ohio State which enables students to interact with MGI-like applications are popular. At Wisconsin, they do extensive outreach with teachers from Puerto Rico, who learn about basic ideas in materials design, synthesis and analysis and then use iPad-based software to develop interactive teaching modules, for both real-time interactive in-class use, and for off-line student use.

A number of the other projects are doing extensive outreach activities. It was mentioned that the MRSEC at UC Santa Barbara has an excellent outreach program (with 4 staff specifically in outreach) that has an excellent assessment component. Projects with outreach activities should be encouraged to examine and learn from the UCSB program.

Finally, to have an impact on legislators, the MGI need successes, specifically the kind that excite the media.

Abstracts

Chemoresponsive Liquid Crystals Based on Metal Ion-Ligand Coordination

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

Project Scope

In this project, we are tightly coupling advances in electronic structure calculations, techniques for synthesis of organic mesogens, and advanced materials characterization methods to accelerate the design of chemically responsive liquid crystals (LCs) capable of detection of a wide range of targeted small chemical species. The approach is based on the formation of coordination complexes between metal cation-decorated surfaces and chemically functionalized mesogens; ligand exchange at the metal centers, which is triggered by targeted chemical species, results in ordering transitions in the LCs. While previous studies have succeeded in demonstrating the concept of chemoresponsive LCs for a narrow class of chemical targets,[1] efforts to generalize the concept have met with limited success due to the slow and laborious nature of the experiments. To accelerate the design of chemoresponsive LCs, we are employing novel synthesis techniques to tailor LC functionality for optimal properties, as predicted by first-principles computation. Experimental characterization of chemoresponsive LCs is being performed to verify their enhanced ability to respond to targeted molecules (e.g., ClO_2, HCN, ClCN, $(CH_3)_2CO$, HCHO) and to validate and/or provide guidance for improved computations, thus closing a cycle of prediction, synthesis, and characterization.

Relevance to MGI

This DMREF project is structured around three *generations* of electronic structure calculations, where each generation is designed to increase our capability to predict key properties of chemoresponsive LCs. For each *generation* of calculations, synthesis and characterization are integrated with computation in tight *cycles* with the goal of (i) providing feedback for improvement of the theoretical models and (ii) evaluating and validating the most promising candidate materials identified by calculations.

Our initial 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 has yielded a simple computational model for design of chemoresponsive liquid 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) that could quickly and efficiently screen candidate LCs and metal cations. This validated model was used to subsequently predict new chemoresponsive LC materials, which demonstrated improved sensitivity and selectivity to targeted chemical compounds. Building from this success, to improve further the accuracy of the *Generation 1* model, we have undertaken a series of more sophisticated *Generation 2*-level calculations that include larger LC-forming molecules and explicit solvent molecules. These predictions hint that solvent used in the experiments can be optimized to enhance the responsiveness of the LCs. Experiments are ongoing to evaluate these predictions. *Generation 3*-level models, which include counter ions, are currently under development. This focus on counter ions is motivated by experimental observations, and the results of *Generation 1 and 2*-level calculations.

Technical Progress

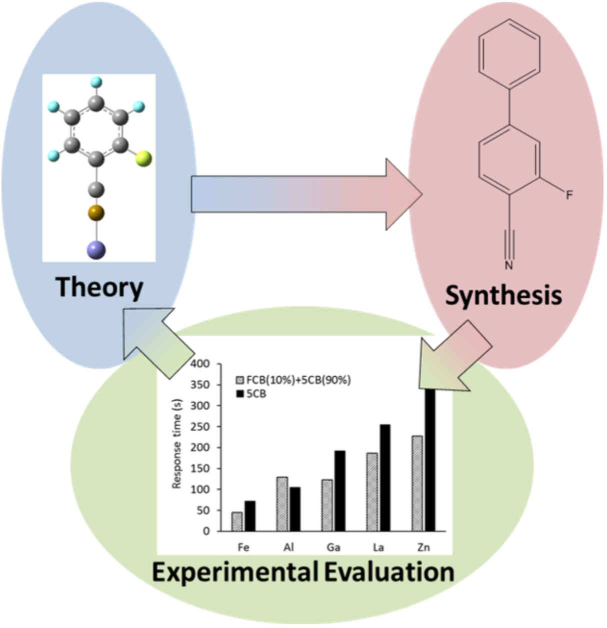

Figure 1. Cycle of calculations, synthesis, and advanced characterization that successfully identified “FCB” as an improved chemoresponsive LC.

Our *Generation 1*-level electronic structure calculations have enabled an accelerated, high-throughput approach to the screening of hundreds of candidate LC materials on the basis of calculated thermochemical binding energies of mesogens to metal cations. Our calculations led to the identification of several classes of mesogen functionalities with desirable properties for chemical responsiveness. For example, one of the most promising candidate LCs incorporated fluorine substitutions into the terminal aromatic rings of the mesogens. The fluorine atoms were predicted to weaken binding of mesogens to metal cations and thereby increase the ease by which they can be displaced from coordination complexes with the metal cations by targeted chemical compounds (as noted above, ligand exchange at the metal ion-decorated surfaces leads to ordering transitions in the LCs, which are readily transduced by changes in optical properties). Based on these predictions, several new molecules were synthesized to incorporate fluorine substitutions into the terminal ring of the mesogen, as shown in Figure 1. Mixtures of these mesogens were used in experiments to test the theoretical predictions that these LCs would exhibit improved chemoresponsiveness when used in combination with some metal cations and reduced performance with others. Experimental evaluation of the “FCB” candidate shown in Figure 1, which maintains the terminal nitrile group characteristic of the reference LC system, demonstrated that *all* materials studied had improved response times, which seemingly contradicted the predictions that only *some* would have improved detection. This motivated an additional *cycle* of computations, which demonstrated that weak interactions between the fluorine substitution and the metal cations were responsible for the improved responsiveness of these mesogens.

Motivated by the above-described result that fluorinated aromatics bind weakly to metal cation-decorated surfaces, we subsequently evaluated the chemoresponsiveness of mesogens in which the nitrile group was removed from the mesogen, and instead replaced by one or more fluorine substitutions. As noted above, as compared to nitrile-containing mesogens, our computations predicted that these mesogens should bind much more weakly to metal cations and thus have significantly improved responsiveness. Following the synthesis of these mesogens, our experiments revealed that mesogens with a single fluorine substitution (“F1”) bound too weakly to the metal cation-decorated surfaces to orient the LCs. In contrast, mesogens with multiple fluorine substitutions (e.g., “F5”) formed multiple bonds to the surface and thus strongly oriented the LCs. These results suggest that multivalent coordination interactions are important in these systems. Such interactions, which are difficult to capture with our simple *Generation 1* model, have informed future computations in *Generations 2 and 3* that are underway.

Future Plans

Over the past 18 months, *Generation 1*-level calculations have yielded a wide range of predictions, and these have been used to guide the synthesis of a number of new mesogens. In the near future, we will invest effort in characterizing the predicted properties of these new mesogens. A significant finding of our project to date is that the rate-limiting step in our cycle of prediction, synthesis and characterization, is characterization. A future goal is, therefore, to explore possible approaches to the “debottlenecking” of the characterization steps. Spectroscopic methods (e.g., FTIR) will be explored in this context. In terms of computation, the next stages of this project will begin the first cycles of *Generation 3*-level calculations, in which the effects of environmental species such as counter ions and solvent are explicitly evaluated. Experimental evaluation will test the predictions of the effect of counter ion identity on responsiveness of the LCs. Some preliminary data obtained with nitrate and perchlorate ions already indicates that the effects are potentially large. In conjunction with the model development, calculations will continue to identify new classes of mesogens for experimental synthesis and evaluation.

Broader Impact

This project is contributing to the training of the next generation workforce by designing new materials through a multidisciplinary approach integrating computational chemistry, organic synthesis, and advanced materials characterization. Additionally, students are enrolling in graduate-level coursework offered by Abbott and Mavrikakis addressing the fundamental principles underlying interfacial phenomena, including the use of computational surface science methods as learning tools. The PIs have participated in a range of outreach activity in 2015, demonstrating the importance of new materials to society, including the 2015 University of Wisconsin Engineering Expo, which was attended by several thousand members of the public. In addition, all senior investigators have hosted undergraduate student researchers in their laboratories over the past year, including during summer of 2015. Finally, Abbott is working closely with Platypus Technologies LLC, a UW-Madison spin-out, to translate advances in the design of chemoresponsive LCs into next generation sensors for occupational health and environmental monitoring applications.

Data Management and Open Access

This project has generated a large volume of raw data (from both thermochemical calculations and experimental synthesis and characterization results) and metadata (from analyses). A web database is currently under construction by our campus Division of Information Technology, which will enable rapid internal sharing of tabulated theoretical and experimental data between the three research groups involved in the project. This web database will also have a public interface; after theoretical and experimental data are considered for IP protection, this website will allow data to be “unlocked” and disseminated in the same form to the larger scientific community.

Accelerating Materials Discovery & Development

A trial-and-error approach to the design of chemoresponsive LCs, as implemented since their discovery,[1] has led to limited progress due to labor-intensive experimental testing of the many design parameters in these systems. This MGI project has enabled high-throughput computational screening of candidate materials and in a short period of time (18 months) has already led to the identification of promising new classes of materials with technological potential. The chemoresponsive materials developed in this project have strong potential for commercialization in a range of fields, including defense, medicine, and general industrial safety applications.

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Publications

We have three manuscripts in advanced stages of preparation (drafts available upon request) that will be submitted in early 2016 for publication.

Polymeric Composites and Foams Based on Two Dimensional Surfactants

Lead Investigators: Douglas Adamson, Department of Chemistry and Polymer Program, the University of Connecticut, Adamson@UConn.edu, and
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Keywords: graphene, surfactants, emulsion, boron nitride, composites

Project Scope

We will develop a multi-scale and unifying theoretical, computational and experimental framework to describe the behavior of two-dimensional materials at the liquid/liquid interface. Using graphene and boron nitride as examples, our work will reveal general selection principles for which the novel concept of using two-dimensional sheets as surfactants can be realized to design 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.

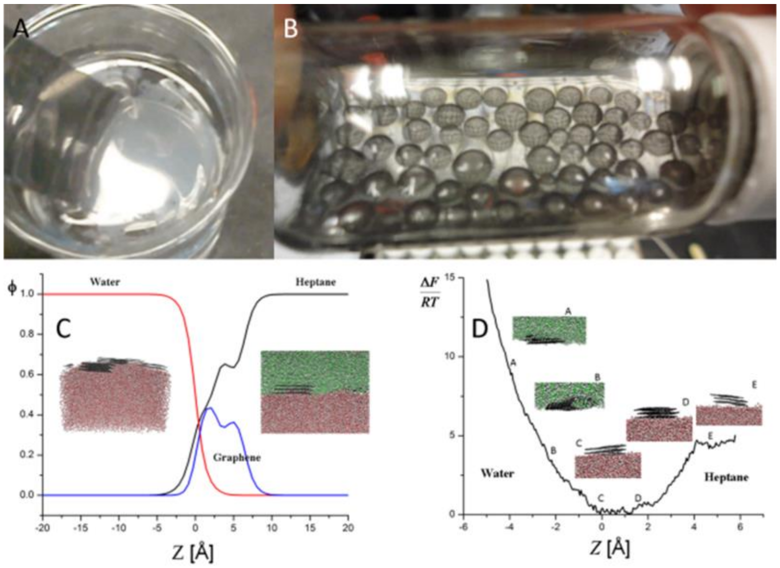

Figure 1. (A) Graphene film formed by climbing a glass slide being floated off the slide onto the surface of water. (B) Droplets of water in heptane stabilized by pristine, natural flake graphene. We have to change fires A and B to ones showing graphene stabilized emulsion A and graphitic skin after emulsion bubbles burst. (C) Number density distribution of water, heptane and graphene along the z-axis, normal to the interface. Insets show snapshots of the simulation box. In left inset heptane is transparent. In figures 1C and 1D, hydrogen atoms are shown in light gray, oxygen atoms are colored in red, carbon atoms belonging to graphene are black and carbon in heptane is green. (D) Potential of the mean force for three-layer graphene flake assembly. Insets show typical configuration of the graphene flakes. The solvent into which the graphene assembly is pulled is transparent.

Relevance to MGI

The high-energy interface between two immiscible solvents causes stacked graphene sheets to exfoliate and spread, driven by lowering the overall free energy of the system,[1] as shown in Figure 1. Forming emulsions stabilized by these sheets, and polymerizing the continuous phase, results in composite materials with superior electrical conductivity, porosity, and strength.[2] The method has been shown to be broadly applicable to other two dimensional materials, such as boron nitride. However, development requires computational guidance as the possible combinations of sheets, monomers and synthesis conditions represents an intractable number of options for a solely trial and error synthetic approach. Since the computational tools in development are carried out at the atomistic level, several length scales have to be bridged in order to correctly describe phenomena observed at the macroscale. To address this challenge, atomic force microscopy (AFM)-based experiments carried out at the nano and meso scale are used to calibrate and verify the models at an intermediate length scale. This approach will greatly accelerate development of this new class of polymeric materials. The developed theoretical and computational models will provide a solid foundation for the development of computational materials design tools for the optimization of mechanical and physical properties of low-density materials.

Technical Progress

A key element of our project is the ability to test interfacial forces at the nano- and meso-scale. We have thus developed scanning probe-based methods using colloidal AFM probes functionalized with two-dimensional sheets to measure their interfacial interactions at the single-sheet level. Our probes are manufactured by first attaching micron-sized silica spheres to blank AFM cantilevers (see Figure 2A–C). In preliminary experiments, we have demonstrated the functionalization of these probes with graphene oxide (GO) by first rendering the silica spheres positively charged by functionalizing them with an amine-terminated silane. GO is then added to the aqueous solution and subsequently attracted to the surface of opposite charge, where it is ultimately attached through a combination of electrostatic and van der Waals forces. Figure 2D shows an image of an uncoated probe, while Figure 2E shows an AFM scan of the GO-functionalized probe after this process, demonstrating that the sphere surface is covered with GO sheets.

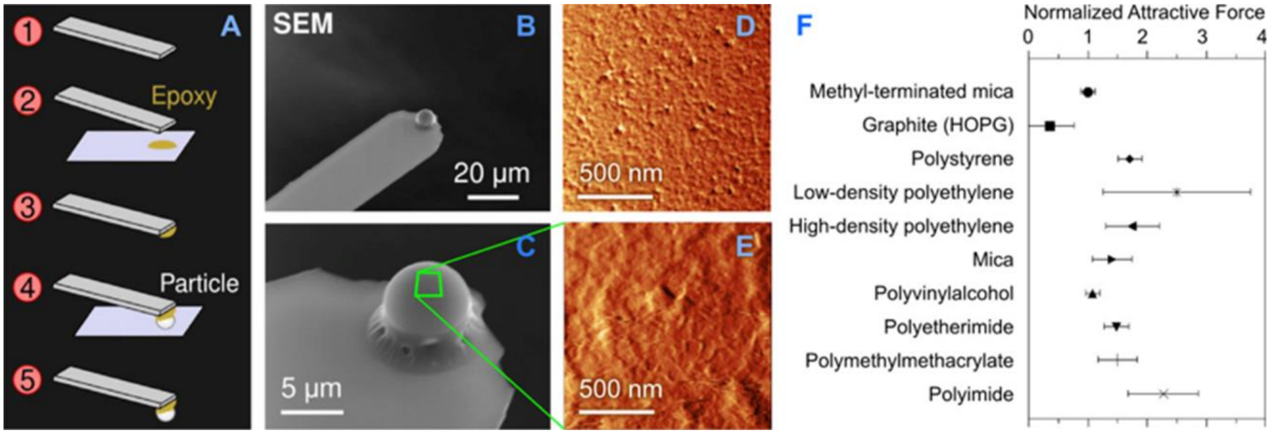

Figure 2. (A–C) Making graphene-functionalized AFM probes: a 7 μm-diameter silica sphere is glued to a tipless cantilever using epoxy. The sphere is then surface-functionalized with an amine group. When immersed into an aqueous GO dispersion, GO sheets are attracted to the amine groups and cover the silica surface. (D) and (E) are AFM scans of the surface of the probe before and after applying the graphene coating. (F) Attractive forces between this graphene-functionalized AFM probe and various polymers reveal systematic differences in attractive forces.

To demonstrate that this custom-made AFM probe can be used to probe interactions between individual graphene sheets and interfaces, we carried out force spectroscopy using the probes on different solid surfaces, focusing on a range of different polymers. To demonstrate reproducibility, the experiments were repeated with three different probes. The results in Figure 2F show that there are significant and reproducible systematic variations for different surface materials. Interactions were weak on surfaces of highly oriented pyrolytic graphite (HOPG), and were strong on polyimide and low-density polyethylene. Other materials, such as poly(vinyl alcohol) or mica, exhibited intermediate forces. These results will be used for a systematic design of graphene–polymer nanocomposites with tailored properties.

Future Plans

This project has three main strategic goals:

1. Understand the governing physical principles of the pristine graphene surface activity and its role in formation of precursor emulsions and apply these principles to both graphite and to other two dimensional materials such as boron nitride (BN);
2. Develop experimental, theoretical, and computational frameworks capable of predicting the physical and mechanical properties of foam-like composites based on the structure and properties of precursor emulsions;
3. Establish the structure-property relationships responsible for composite strength and superior electrical and thermal properties.

To realize these goals, we will use large-scale detailed molecular dynamics simulations for scanning monomer libraries to guide design of materials with the desired electrical and mechanical properties. We will verify our theoretical predictions by (a) characterizing the rheology and structure of precursor emulsions and (b) by measuring the mechanical, electrical and thermal conductivity properties of the resultant foams. This verification will provide a feedback loop for the optimization of the materials properties. We will apply a combination of analytical methods, molecular dynamics simulations and experimental techniques including (but not limited to) XRD, TGA, mercury porosimetry, BET, acoustic spectrometry, rheology, electron microcopy, AFM and force spectroscopy in liquid cell and dry, three and four point bending, thermal conductivity analysis, electrical resistivity, and DMA to develop correlations between interfacial properties and the controlled formation of the composites. We will also study the effect of the formed polymer partially encapsulating the stabilizing graphene films during polymerization, and the effect of increasing viscosity in the oil phase as the polymerization progresses. In addition, we will develop processing approaches with an eye to scaling up the process. In particular, emulsifying techniques and curing approaches will be studied in an effort to create a roadmap for large volume materials manufacturing.

Broader impact (Optional for DOE grants/FWPs)

One barrier to increasing the number of under-represented minorities is stimulating interest at a young age. We will use the current grant to help address this, by continuing and building on our Chemistry Wizards Program started with funds we received from the Camille and Henry Dryfus Foundation. The Wizards program is designed to target middle school children learning about scientific inquiry and chemistry, and aims to spur some of them to pursue post-secondary study and careers in chemistry and other STEM fields. The program is designed to addresses the lack of underrepresented minority students earning degrees and pursuing careers in chemistry and other STEM fields. The Wizards program will send graduate students supported by this proposal, and will conduct engaging hands-on chemistry activities for middle school students who are rarely exposed to these kinds of learning experiences. A similar Chemistry Wizards program will be developed and deployed for the Hampton Roads area in Virginia. Based on the experiences from the program already underway in Connecticut, there will be a great leverage effect for the implementation in Virginia. Through the scientific collaboration in this project the students from the research groups on both campuses will be in frequent and close contact. This will facilitate the exchange of information for this outreach program, so that W&M students can also bring this exciting experience to middle school classrooms.

Data Management and Open Access

This project shares digital data from both experimental and computational work. Working infrastructure for sharing, long-term archiving and backup is in place both at U Conn and William & Mary. We also have policies in place to make sure all data is available in open (rather than proprietary) file formats wherever possible. Our policy is to hold our data in confidence pending publication or patent application. Since this project has only been started about 3 months ago, no data has been released for public sharing, at this moment. After publication, data will be shared at http://128.239.100.218/open/DMREF/, amongst other locations.

Accelerating Materials Discovery & Development

The materials enabled by this project will have potential applications that include structural construction components, flame resistant thermal insulators, electrodes for capacitors and batteries, substrates for flexible electronics, and superabsorbent materials with unique mechanical properties. However, the development of these materials, optimized for specific applications, would prove to be intractable without the guidance of computational studies. By indicating the most promising experimental pathway in terms of components and processing methods, the computational component of this project will not only speed the development of commercially viable materials, it will also decrease development costs by greatly reducing the parameter space that would otherwise need to be explored.

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Rapid Design of Earth Abundant Inorganic Materials for Future PVs

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Keywords: Photovoltaics, Materials Science, Earth abundant semiconducting materials, inorganic compound semiconductors

Project Scope

This project's goal is to identify promising earth-abundant inorganic materials for high performance solar cells through a coupled, computationally guided search; synthesize the identified materials with targeted crystal structure and optoelectronic properties through solution phase processing; assemble the tailored earth-abundant materials into targeted thin film structures through low-cost solution processing; and evaluate and verify the synergy between identified materials and solar cell devices through design, fabrication, characterization, simulation of the finished devices, and feedback to the first principles calculations.

Relevance to MGI

One main reason for the slow progress in the development of earth abundant solar cells has been the lack of close integration between the experiments and the first principles calculations. Critical information regarding possible material properties are not available in a timely manner from the first principles calculations to provide much needed guidance for the experiments. Similarly, the first principles PV screening typically focuses on only a few material properties and does not have simultaneous experimental feedback. While state-of-the-art, first-principles computational methods are now quite advanced, it is still not parameter free, and often there is a need to validate and readjust computational parameters based on experimentally observed material properties for new materials. In the absence of timely experimental feedback, the models do not achieve optimal efficiency, and numerous false positives may be predicted that are not taken seriously by device makers. Given these considerations, as shown in Figure 1, a central aspect of our proposed research is a close coupling among the computational material search, material synthesis, the absorber synthesis, and the device design and fabrication to accelerate the creation of scientific knowledge needed for the design and large-scale use of Earth-Abundant PVs.

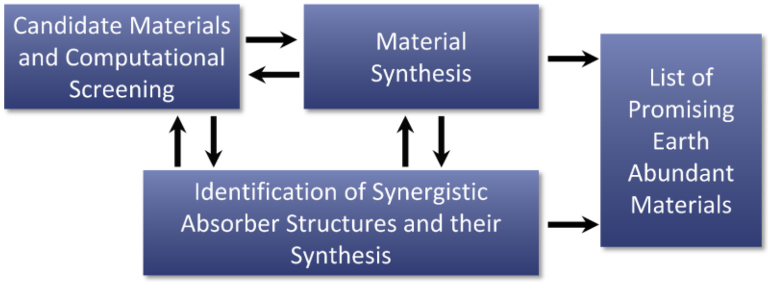

Figure 1. Our strongly coupled approach for screening and identification of promising earth abundant materials will greatly accelerate new material development for PV applications.

Technical Progress

We have just initiated the project by identifying and synthesizing some of the earth- abundant materials based on Cu_3VS_4 class of material. It is based on some initial property estimates (band gaps etc.) using first principles calculations. The liquid phase synthesis of nanoparticles of Cu_3PS_4, Cu_3AsS_4, Cu_3SbS_4 and their alloys is in progress. Preparation of their thin films with proper grain structure has also been initiated. Initial challenge in controlling a particular crystal structure during film growth is being addressed.

Future Plans

The near term plan is to develop methods for the successful liquid phase synthesis of thin films of Cu_3PS_4, Cu_3AsS_4, Cu_3SbS_4 and their alloys, characterize the material properties of these thin films, design and fabricate solar cells from the thin films, characterize performance of these solar cells and provide feedback of all the characterization parameters into the first principle calculation models. We will continue to develop high-throughput computation methods and strategies to identify various compound earth-abundant elements and their alloys based on band gaps, stability of material, optical absorption coefficient and effective mass of the minority carrier. The approach for theoretical study will be mainly based on DFT calculations using the projector augmented wave method and the generalized gradient approximation (GGA-PBE) and screened hybrid Heyd-Scuseria-Ernzerhof (HSE) functionals as implemented in the Vienna ab-initio simulation package (VASP). The possible structures resulting from alloying will be constructed by using the special quasi-random structure (SQS) method to describe the random occupation of cation or anion atoms at the special sites. Similarly, on the experimental front we plan to systematically develop chemistry for the liquid phase synthesis of the identified materials and their thin films.

Broader impact

Electricity is the fastest growing sector in the U.S. and electronic devices are becoming ubiquitous. Identification of new earth-abundant semiconductors along with their properties and low-cost processing technology will influence how future thin-film electronic devices are fabricated. It will also enable widespread use of photovoltaics as an abundant source of electricity for a sustainable energy economy in the U.S. The integrative nature of the research and education will train and co-mentor graduate and undergraduate students in cross-disciplinary skills that are essential for developing innovative solutions as they join the workplace and contribute to the U.S. leadership in the burgeoning field of electronics.

Data Management and Open Access

The proposed research project will result in the generation of numerous electronic records of measurement data from materials and optoelectronic characterization, essential metadata regarding sample preparation/fabrication and specifics regarding measurement conditions, as well as relevant computer coding necessary for modeling and data analysis. Support for data management for this project throughout its lifecycle will occur using the Purdue University Research Repository (PURR), Purdue's institutional data repository (http://purr.purdue.edu). To broaden the educational impact, project research results, presentations, and all the developed tools will be deployed online via the NSF-sponsored nanoHub.org at Purdue.

Accelerating Materials Discovery & Development

The closely integrated research between first principles calculations and experiments for PV will accelerate inorganic material discovery and development for electronic applications by simultaneously achieving several results: (i) many new materials composed of earth-abundant elements will be identified through computational screening; (ii) technology for the liquid phase synthesis of multinary compounds and their thin films consisting of three or more elements with tailored composition will become available; (iii) analysis of material and optoelectronic properties of the nanoparticles, films and solar cells will provide a list of new well characterized materials for numerous electronic applications; (IV) experimental feedback will lead to refinement of the models used in first principles calculations; (V) next generation of high efficiency solar cells composed of earth-abundant elements will become available for commercial development; and (VI) a low-cost roll-to-roll solution-processed thin-film technology based on inorganic semiconducting materials will become available for electronic device manufacturing.

Center for PRedictive Integrated Structural Materials Science (PRISMS)

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Keywords: Integrated Multi-Scale Modeling, Metals, Magnesium, Microstructural Evolution, Mechanical Behavior
PRISMS Center Website: http://prisms-center.org

Project Scope

The primary objective of the PRISMS Center is the development and demonstration of a unique scientific platform for enabling accelerated predictive materials science. We are developing a suite of open-source integrated multi-scale computational tools for predicting the microstructural evolution and mechanical behavior of structural metals. These computational methods are being integrated with quantitative measurements from advanced experimental methods to determine model inputs, fill gaps in theory and validate simulation predictions. This new capability is being demonstrated by providing improvements to the quantitative and predictive understanding of magnesium alloys, in particular precipitate evolution and the influence of microstructure on monotonic and cyclic mechanical behavior. An important component of the PRISMS Center is the development of “The Materials Commons,” a knowledge repository and virtual collaboration space for the broader materials community.

Relevance to MGI

The Materials Genome Initiative necessitates new collaborative and integrated modes of materials research and development. Our vision is that the platform being developed within the PRISMS Center will become an important and extensible contribution to MGI and lead to accelerated development of new materials and new materials science.

Technical Progress

The PRISMS Center supports 11 faculty members, five staff members engaged in science and software development and 15 graduate students/post-doctoral researchers. The integrated multi-scale computational tools the Center is developing include software for statistical mechanics, real-space density functional theory, massively parallelized 3D finite element implementations of phase field, mechano-chemical transformations, crystal plasticity and continuum plasticity analysis methods, as well as software for integrating these codes and results from other advanced computational methods (e.g. dislocation dynamics) into a holistic capability. The computational results are being integrated with the results of advanced experimental methods that include quantitative transmission electron microscopy and atom probe tomography, SEM-based digital image correlation (SEM-DIC) and specialized in-situ fatigue experiments.

To ensure effective integration of PRISMS Center activities, our science objectives are organized around "use cases". These use cases provide a means to establish collaborative communities, advance science and demonstrate linkages and capabilities. The primary use cases are prediction of precipitate evolution, recrystallization and grain growth, tensile properties and cyclic/fatigue properties of Mg and Mg alloys.

Highlights of our progress include:

- Released four new open-source PRISMS Codes on GitHub: CASM (Statistical Mechanics), PRISMS-PF (FEA-based Phase Field Method), PRISMS-Plasticity (FEA-based Continuum Plasticity and Crystal Plasticity), PRISMS-Integration Tools.
- Held annual workshop in September 2015 attended by over 90 people including training for PRISMS Codes and Materials Commons.
- Completed development of The Materials Commons a new collaboration and information repository for materials information (See Data Management below)
- Integrated results of high-resolution TEM imaging and statistical mechanics calculations to define a new approach for understanding the precipitation sequences in Mg-rare earth alloys.
- Used the massively parallel PRISMS-PF (phase field) code with the CASM-determined energetics to predict growth of β' precipitates in Mg-Nd alloys.
- Completed the first use of PARADIS dislocation dynamics simulations to calculate strengthening from precipitates in Mg (hcp) alloy (with LLNL).
- Completed real space DFT calculations that estimated that core-size of edge dislocation in aluminum are three times larger than indicated by conventional estimates.
- Established methodology for modeling mechano-chemical phase transformations.
- Used phase field crystal model to calculate grain boundary structures and energies in 2D and compared with molecular dynamics simulations.
- Developed novel in-situ ultrasonic fatigue instrumentation to examine fatigue crack initiation and small crack growth in Mg alloys.
- Integrated results of experimental SEM-DIC measurements of heterogeneous surface strain distributions with PRISMS-Plasticity (CPFEA) to provide new understanding of deformation mechanisms within grains, at grain boundaries and adjacent to twins in a precipitation hardened Mg alloy.
- Demonstrated capability of PRISMS crystal plasticity code to simulate tensile cracking at grain boundaries and fatigue crack propagation in polycrystals.

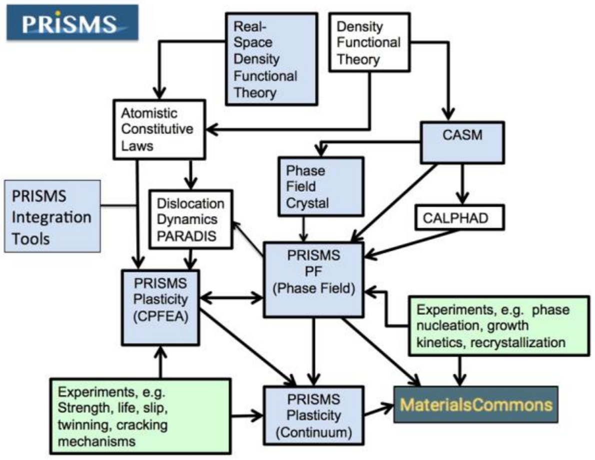

Figure. PRISMS Framework: Integrated computational and experimental capability (blue boxes are PRISMS Center-developed codes)

Future Plans

The PRISMS Center will have another major open-source code release (including Materials Commons) and scientific/training workshop in late summer 2016. We have established collaborations with a number of external research groups and are actively seeking additional collaborations aligned with our use cases and/or our open-source codes. Our future plans include: a comprehensive and systematic capability for integrating these advanced PRISMS codes with experiments; advanced capability for predicting phase stability and thermodynamic and kinetic properties of Mg alloys; advanced, validated capability for predicting precipitate evolution in complex Mg-Nd-X alloys; integration of results of advanced PRISMS precipitate predictions with dislocation dynamics and DFT for calculating tensile and cyclic stress-strain response of Mg alloys; and coupling these results with 3D crystal and continuum plasticity models and traction separation laws for predicting the influence of precipitation on grain boundary tensile fracture, local strain distributions determined by SEM-DIC and local fatigue crack initiation and growth characteristics determined by the new in-situ ultrasonic fatigue capability.

Data Management and Open Access – PRISMS Open Source Codes and The Materials Commons

The PRISMS codes are being developed as open-source codes and initial versions of four codes (described above) have been released via GitHub. A key objective of the PRISMS Center is the development of the Materials Commons, an information repository and collaboration platform for the materials community. Our goal is for the Materials Commons to become a continuous, seamless part of the scientific workflow process in the technical areas being investigated within the PRISMS Center. The Materials Commons website provides an easy-to-use interface for uploading and downloading data and data provenance, searching and sharing data. At its core, the Materials Commons consists of a secure 390 TB data storage cluster, an application for efficiently uploading and downloading large data sets, and an application program interface (API) to access and extend the capabilities of the repository. The Materials Commons is currently being used internally by members of the PRISMS Center with release to the materials community planned for mid-2016.

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Accelerating the Development of Phase Transforming Heterogenous Materials: Application To High Temperature Shape Memory Alloys

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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 high temperatures as a result of reversible phase transformations. Recently, it has been discovered that nanoprecipitation[1] in NiTiHf HTSMAs leads to highly efficient and stable actuation behavior. 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.

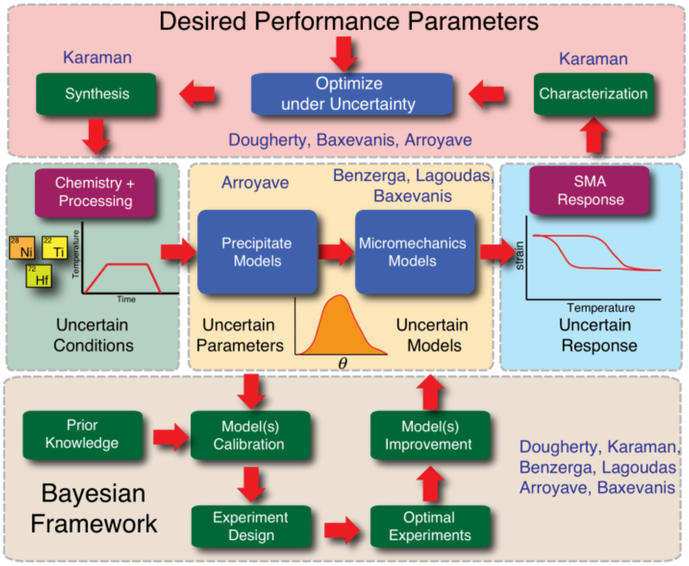

Fig. 1: Proposed approach.

Relevance to MGI

The framework (**Fig. 1**) 1) considers that chemistry and processing determine the microstructure of the HTSMA and its response; 2) takes into account the existence of significant prior work; 3) assumes that physical models responsible for the chemistry-processing-microstructure-performance linkage describe the physics relevant to the problem; and 4) uses a Bayesian paradigm to describe the probability of all models consistent with the data, the physical models and any prior knowledge.

At the core of the framework lies a two-level physical model: (i) a precipitation model is used to predict the precipitate population distribution as a function of initial composition and heat treatment schedule; (ii) the precipitate distribution is used to construct Representative Volume Elements that are in turn used within a micromechanics framework to simulate the shape memory response of HTSMAs. 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. *This step closes the theory-model-data-model loop.* Finally, stochastic optimization is used to identify feasible solutions that connect desired response to chemistry and processing, *closing the chemistry/processing-microstructure-performance-chemistry/processing loop.*

Technical Progress

Over the first three months of the project, we have focused on the following complementary tasks:

Composition Effects on Martensitic Transformation: Available experimental data from the literature as well as generated within this collaboration (Karaman) are being collected to develop models for the effect of composition on the martensitic transformation temperatures as well as on the transformation hysteresis. The data is being used to construct an extensive database. The data is being used by Dougherty's group to design optimal experiments necessary to further refine the composition-transformation models.

Thermodynamic Assessment of the NiTiHf System: A CALPHAD model for the ternary phase diagram of the Ni-Ti-Hf system is also being developed by the Arroyave group. This model is an essential component of the precipitation model. The binary Ni-Ti, Ni-Hf and Ti-Hf binary models have been integrated to predict a preliminary version of the ternary Ni-Ti-Hf phase diagram.

Micromechanical Model: A micromechanical model for the prediction of thermo-mechanical response of the NiTi alloys with precipitates has been developed by the Baxevanis/Lagoudas groups[3]. Precipitate structures are represented in terms of RVEs with matrix composition and precipitate volume fraction inferred from experiments. The effective properties of the alloy is predicted from the FEA responses of RVEs and favorably compared with experiments.

Future Plans

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

- Karaman's group continues to generate data on the transformation behavior of Ni-Ti-Hf over a wide composition range. The samples will be characterized through SEM and DSC to augment knowledge about process-structure connections.
- Using the experimental information generated by the Karaman group, the Dougherty group is working on methods to identify the concentrations of Ni, Ti, and Hf that would satisfy the twin objectives of minimizing transformation hysteresis (A_f-M_s or A_p-M_p) and a desired range of M_s and use this knowledge to have optimal experiment design to identify alloys with the desired properties in fewest experiments.
- 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 micromechanical Ni-Ti model will be extended to the Ni-Ti-Hf system by Baxevanis and Lagoudas' group. Precipitate solubilities will be estimated from the CALPHAD model by Arroyave and the transformation temperatures will be extracted from model developed by Dogherty's group.
- Benzerga's group will begin the incorporation of transformation induced plasticity within shape memory thermodynamically-consistent micromechanical model developed by Lagoudas[4].

Broader impacts

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. One publication[5] has resulted from research partially supported through this award.

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 organized through user-developed templates encoded in XML Schema. The data is saved in the MongoDB non-relational (NoSQL) database system. Prototype repositories with data for High Temperature Shape Memory Alloys are currently being under construction by Karaman and Arroyave's group in collaboration with NIST's MDCS group.

Accelerating Materials Discovery & Development

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 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 cages, self-assembly, co-assembly

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.

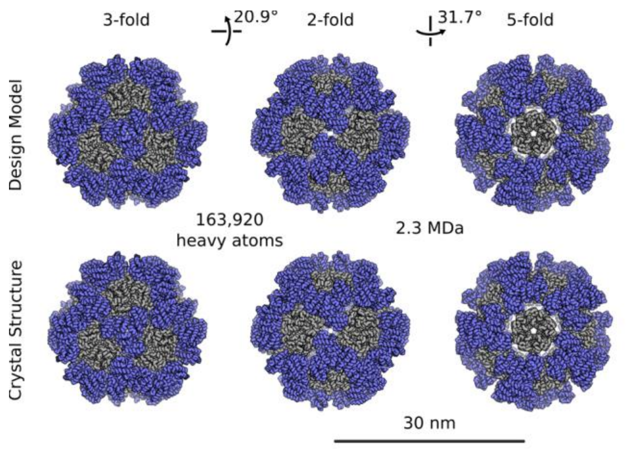
Relevance to MGI

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 dihedral protein complexes, tetrahedral, octahedral, and icosahedral protein nanocages, and two-dimensional layers.

Technical Progress

An underlying hypothesis of the project is that large and highly symmetric self-assembling protein materials can be created by using simpler oligomeric proteins as the building blocks. Multiple strategies are possible for building higher assembly properties into such simpler building blocks. In the most general approach, amino acid sequence design is used to introduce geometrically specific protein-protein interfaces into the building blocks [1]. In another strategic variation, the higher symmetry requirements are met by combining two simpler oligomeric building blocks together by genetic fusion [2]. Both approaches have produced exciting results.

Our recent protein-protein interface design efforts have focused on improving and expanding our initial methods to enable the design of increasingly large and complex materials with atomic-level accuracy. In order to increase the percentage of designs passing our criteria for experimental testing, we modified the score function and search algorithms used during the initial docking stage of our design process to favor protein backbone configurations matching commonly observed interaction motifs found in high-resolution crystal structures in the Protein Data Bank (PDB). In order to increase the throughput and robustness of our protocol, we have developed new algorithms to aid in the final refinement stages of the design process. And in order to improve the solubility of our designed materials, we have tested several approaches involving focused redesign of solvent exposed side chains. As published recently in *Protein Science,* redesign of side chains to increase the net charge on the individual components led to a variant of one of our designed two-component tetrahedra with significantly increased soluble yield. This enabled us to determine the crystal structure of the design, which we were unable to obtain previously due to low yield of soluble protein. The crystal structure was found to match closely with our design model.



Comparison of crystal structure and design model of a two-component icosahedron successful produced during this project. Views of the designed materials are shown down the icosahedral 3-fold, 2-fold, and 5-fold symmetry axes. The material, which has a molecular weight of over 2.3 megadaltons and contains over 160K heavy atoms, is formed through the co-assembly of 60 trimer forming subunits (colored slate) and 60 pentamer forming subunits (colored grey). The crystal structure matches the design model remarkably well, with a root mean square deviation over all backbone atoms of 0.6 Å.

Building off of our initial success with tetrahedra and octahedra, our methods have now been used to successfully design 3 one-component layers, 2 two-component layers, 3 two-component dihedra, 1 one-component icosahedron, and 10 two-component icosahedra. A paper describing the two-dimensional layers was published in June in *Science* and papers describing the icosahedra are currently in preparation. In addition to data from size exclusion chromatography, small angle x-ray scattering, and electron microscopy, crystal structures have been obtained for three of the two-component icosahedra. Comprising 120 subunits each, with molecular weights (1.8 to 2.8 MDa) and dimensions (240 to 400 Å diameter) comparable to those of small viral capsids, these are the largest designed protein materials to be verified by crystallography to date. These results represent a significant advance in the field of computational protein design and protein-based nanomaterials, opening the door to the atomically accurate design of novel protein nanostructures much larger and more complex than previously accessible. Furthermore, following redesign to increase solubility, we have now generated versions of three different two-component icosahedra capable of undergoing assembly *in vitro* from individually expressed and purified components.

We have also continued to explore the second design strategy in which the two oligomeric components are covalently attached by way of an alpha-helical linker. A paper on the design and crystal structure of a 23 nm diameter cube comprised of 24 identical subunits was published in Dec. 2014 in *Nature Chemistry*. Various biophysical studies showed some degree of polymorphisms in assembly in solution, while a low-resolution crystal structure showed the 24-mer cube with a backbone deviation of only 1.2A compared to the design. In further studies on the helix fusion method (published in *Protein Engineering Design and Selection*), through crystal structure analysis of a series of incorrectly assembled crystal structures, we were able to make observations about the range of helical bending one expects to see in the fusion approach. In another paper currently under review we developed and applied new computational tools for visual analysis of large numbers of SAXS data sets and showed their usefulness for exploring the solution behavior of large designed assemblies.

Future Plans

Our primary objectives for the future are to: 1) publish a symmetric architecture rule set, making it freely available to the broader scientific community, 2) continue refining our methods based on experimental feedback in order to increase success rates and enable design of increasingly complex architectures, and 3) to demonstrate successful solid-phase assembly of a subset of our designed two-component materials. The architecture rule set is nearly complete, but each architecture needs to be evaluated in terms of the practicality of realizing the materials using compact globular protein components as building blocks and the rule set needs to be formulated in more a user-friendly manner in terms of the minimal construction steps required. Future method development and design will focus on utilizing recent updates to the Rosetta energy function and the incorporation of new algorithms for designing hydrogen bond networks into the assembly interfaces. These changes to our methods are anticipated to further increase our success rate and the solubility of our future designs. In the meantime, we will seek to demonstrate solid-phase assembly using a subset of our designs capable of assembling from purified components.

Broader impact (Optional for DOE grants/FWPs)

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. See PDB codes 4NWO, 4NWQ, 4NWN, 4NWP, 4NWR, 4QCC, and 4ZK7.

Accelerating Materials Discovery & Development

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. Using our updated methods, we have more than doubled the number of successful design created and confirmed during the previous year, and we expect similar increases in throughput as we continue to iterate our theory-design-test cycle. In anticipation of the broad potential utility of our materials and methods, we have also filed several patent applications related this project.

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Predict Blend Morphology of Organic Photovoltaic Materials

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Keywords: organic photovoltaics; blend morphology; Folding@home; x-ray scattering.

Project Scope

Our work aims to address the biggest challenge that has hampered the development of organic materials for solar cell applications – predicting the nanoscale morphology. The goal is to develop a quick, accessible framework of modeling and characterization techniques through an integrated, multidisciplinary collaboration between experimentalists and theoreticians. It will not only significantly speed-up the discovery of new high-performance organic photovoltaic (OPV) materials, but also the methodology we develop can be applied to other areas of materials research.

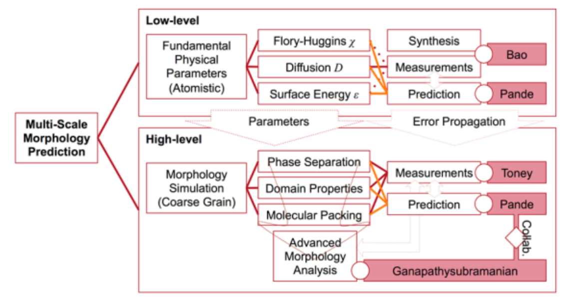

Figure 1. A scheme shows the strategic planning of collaborative efforts on this research project.

Relevance to MGI

Our proposed discovery pipeline will directly link the work of theory (Pande), synthesis (Bao) and morphology characterization (Toney) into a closed linked feedback loop. We will establish theoretical models and a computational framework to rapidly screen candidate compounds at a massive scale, assess their morphology, and identify structures with potential for high-performance OPVs. We will synthesize and model compounds for comparison with theoretically predicted morphology and prepared promising compounds predicted by theory. We will characterize morphology of the most promising compounds and provide feedback for fine tuning the theoretical platform.

Technical Progress

Strategically, we categorize the morphology computational work into two levels: (1) low-level force field simulation of fundamental physical parameters at atomic scale, eg. Flory-Huggins parameter χ, diffusion coefficient D, surface free energy ε.; and (2) high-level continuum simulations of morphology formation over larger length scale and temporal scale. This is shown in Figure 1, which summarizes the collaborative efforts on this research project. Pande's group focused on taking advantage of his tremendous experience in atomic level biology related simulation using the computational power from his Folding@home simulation engine. We carried out simulation of thermodynamic and kinetic properties, specifically the densities of single component systems, atomic radial distribution functions of mixtures, and diffusion coefficients of single oligomer chains in solution. By defining the interactions between atoms in a modeled system, the force field configurations dictate the predicted values of these fundamental physical properties. Therefore, these calculations are essential to verify the force field by comparing to literature reported values and experimental values obtained in this project, which is critical for improved accuracy of high-level continuum simulations of larger scale morphology. We also have initiated collaboration with Prof. Baskar Ganapathysubramanian (Iowa State University), who is also a recipient of the NSF Materials Genome Project and has developed useful methodologies for OPV blend morphology prediction using coarse-grain molecular dynamics (CGMD) and continuum simulation. [1,2] The parameters calculated by Pande group will be feed into these simulations for large-scale morphology prediction.

To verify the modeling tools developed, experiments on related systems have been carried out by Bao and Toney. The ultimate goal of the simulation work is to establish a model that can be used for material screening when relevant parameters changed in material design and bulk heterojunction (BHJ) fabrication, for instance, either chemical structure modifications of molecules, or processing conditions. Two blend systems for OPVs have been selected and prepared as models to obtain comprehensive information of BHJ films as a function of molecular structure and processing conditions: fullerene derivatives are acceptors, with either polymer or small-molecule donor. Comprehensive morphology information involves not only complex phase separation but also molecular ordering within domains (crystallization). Furthermore, because the final morphology of the BHJ is usually not in its thermaldynamic equilibrium state, the temporal evolution information of the morphology during fabrication is extremely valuable as reference for simulation. For the small-molecule donor system, we obtained results on the drying process and morphology development in real time with in-situ grazing incidence wide-angle x-ray scattering (in-situ GIWAXS). Ex-situ GIWAXS measurements and resonant soft x-ray scattering (RSoXS) were performed on both systems to further characterize the crystallization and molecular packing and examine the phase separation scale and domain purity. The effects of blend ratio, solvent additive, and substrate temperature have been investigated and analyzed. Our results correlated well with the effect of drying process and morphology evolution predicted by continuum simulation by Ganapathysubramanian group. Incorporation of more accurate force field calculation by Pande will further improve the accuracy of the modeling. [1]

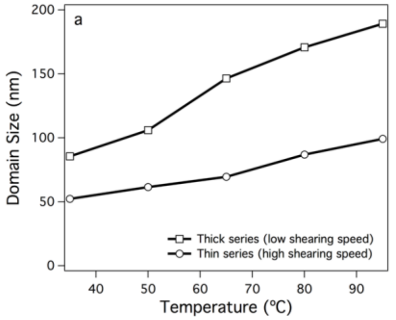

Figure 2. Domain size increases as a function of temperature for two thicknesses. Shearing speed is increased with temperature, but is not expressed on this figure.

Future Plans

We will optimize the current force field and further use it to improve the accuracy of predicted fundamental parameter values (χ, D, ε and density ρ) of the donor and acceptor materials we used in model systems, for example ρ of PCBM and the solvent chlorobenzene, and D of small molecule donor and acceptors in chlorobenzene. Some of these parameters can be verified from reported values or with experimental measurements; for instance, D will be experimentally measured with NMR, which will be used to refine the force field. Further collaboration with Prof. Baskar Ganapathysubramanian will allow us to utilize the physical parameters predicted with force fields to perform high-level continuum simulation methodologies he developed to predict the morphology in larger length scale (>100 nm) in the future. Furthermore, Prof. Pande has developed computational methods to propagate the uncertainties of parameters into simulations, which will be incorporated into this process and is expected to greatly enhance the reliability of the final predictions. These larger scale simulated morphologies will then be correlated to experimentally derived results. In order to provide more complete morphology information for this purpose, we will continue with further data analysis on current experimental data and acquire further data to complete the systematic studies for both model systems. More quantitative analysis will be performed in order to extract crystallization growth information from in-situ solution drying experiment and to derive relative crystallinity information from ex-situ GIWAXS of final films. According to current data collected, more RSoXS data on extended blend ratio range will be extremely beneficial to understand the domain purity as a function of blend ratio. In addition, small-angle x-ray scattering of solutions will be performed to examine the effects of solvent type, additive and temperature on the dispersity of molecules in solution in order to provide evidence to the computational simulation whether molecular aggregation is in presence in the solution and whether (and how) its existence impact the BHJ morphology. It is of great significance to determine the original model parameter configuration of continuum simulation in morphology simulation starting from solution.

Broader impact (Optional for DOE grants/FWPs)

Our work will establish an integrated framework for prediction of morphology of OPV materials. This research will lead to a better understanding of the materials design requirements and the gained insights will shorten the cycle for new material discoveries. Our approach is likely to also have a transformative influence on materials science and engineering in general as morphology prediction is a key challenge for many other research fields while materials properties are often strongly dependent on the morphology. The methodology developed here should be adaptable for other organic materials.

Data Management and Open Access

Optoelectronic, structural and morphological measurements will be performed on all selected model systems. The experimental data – regardless of positive or negative outcome – will be made available to the theory group where it will be added to a collection of empirical data. The latter is utilized in calibration schemes and provides the parameterization for many of the employed models. Extending this data set will improve the related modeling efforts and their predictive capacity. This in turn will lead to a refinement in the development processes. An extensive results and reference database will serve as the hub for the information exchange between the three participating groups. The vast amount of data accumulated in the course of this project will provide the foundation for a better understanding of the molecular structure/morphology correlations, and it will be an openly available resource for the OPV community through the Stanford Data Repository service.

Accelerating Materials Discovery & Development

The traditional experimental development of new materials is predominantly based on empirical intuition, professional inspiration, or experience with certain compound families. This could result in a long, iterative cycle. The prediction model and methodology we are developing is expected to address this issue and significantly speed-up the discovery of new high-performance OPV materials by screening current candidates and providing guidance for synthesizing new chemicals. In the long term, the models established in this research could form part of the in-line smart control when metrology signals collected through advanced sensors during roll-to-roll production of OPV modules and possibly other fields.

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Computational Design Principles for Functional DNA-based Materials

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Keywords: DNA origami, programmable biomaterials, nanotechnology, structure prediction, structured materials

Project Scope

The aim of this project is to accelerate our ability to program functional DNA-based materials with complex nanometer scale structural features that are spatially addressable chemically. These structured nanoscale materials are unique in their ability to host multiple enzymes for chemical synthesis, chromophores for nanoscale energy transport, drug cargo for therapeutics, as well as to synthesize metallic nanoparticles with custom optical properties. Our computational tool CanDo (http://cando-dna-origami.org) that contains our procedures is available online for broad use. We are additionally integrating our procedures into other open source software platforms. Success is measured by our ability to design arbitrary DNA-based nanostructures in silico that are validated experimentally.

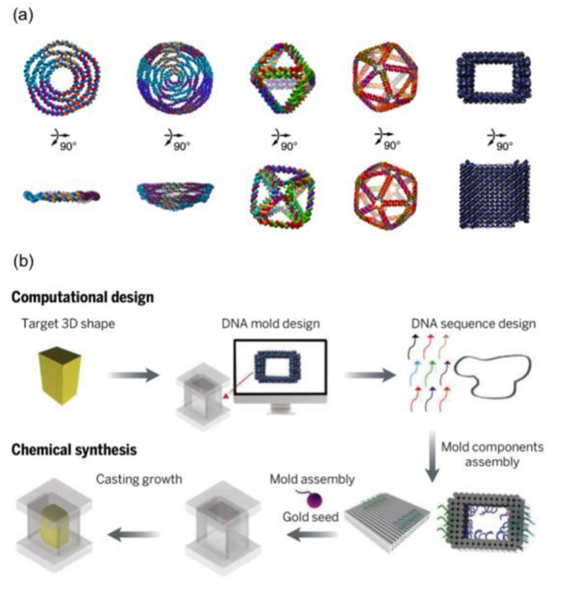

Figure 1. (a) 3D structure of complex DNA objects predicted using CanDo [1] and (b) inorganic nanoparticle design and synthesis framework [2].

Relevance to MGI

The Bathe lab is developing a computational framework for DNA-based materials design and synthesis [1] that includes bottom-up prediction of 1D/2D/3D nanometer-scale structure and self-assembly properties, which are validated experimentally in the Yan and Yin labs. 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. Computational models of programmed inorganic nanoparticles synthesized using DNA molds have also been developed to predict the optical and plasmonic properties of gold and silver nanoparticles produced in the Yin lab [2].

Technical Progress

Our team previously published two articles based on this project, one in *Nature Communications* [1] that represented a major advance in our ability to predict 3D structure of complex DNA-based assemblies in silico (Figure 1a) and the other in *Science* [2] that represented a major advance in our ability to program inorganic nanoparticles in silico using DNA-based molds (Figure 1b). Recently, we followed these works with publications that include the first framework to synthesize single-stranded DNA origami objects that are important to enabling high volume production of structured DNA assemblies [3], experimental characterization of the folding nucleation of structured DNA assemblies [4], and the application of CanDo to the design of large-scale DNA-based plasmonic metamaterials [5]. In prior work, the Bathe lab introduced the computational framework CanDo to predict the 3D structure of DNA origami objects. However, that framework was overly restrictive because it was limited to origami objects designed using square or honeycomb lattice cross-sections. To overcome this limitation we invented the preceding [1] lattice-free computational design and 3D structure prediction framework that treats multi-way junctions as mechanical elements with known ground-state geometry and flexibility. In the past year we have generalized this model to include a large class of off-lattice origami objects and also invented a sequence design algorithm that offers top-down structured DNA-based materials design using Computer-Aided Design [in preparation]. This computational procedure is based on experimental work from the Yan lab in which wireframe objects are programmed using DX-tiles. In related work, the Yin and Yan labs have also implemented a single-stranded DNA origami design procedure that obviates the need for hundreds of synthetic staple oligonucleotides that are conventionally used to fold scaffolded DNA origami objects [3]. The Yin lab has also developed an innovative approach to cast 3D metallic particles using DNA-based containers or molds [2]. This methodology utilizes DNA origami molds that are designed in silico to ensure maximal structural integrity that limits the particle growth during synthesis. Computational 3D structure prediction together with mechanical property analysis has enabled proper mold design by the Bathe lab, which was verified experimentally by the Yin lab [2]. We also used electromagnetism simulations to compute the plasmonic properties of the particles in solution [2], demonstrating their potential for biomolecular sensing. In recent work, the Bathe lab applied 3D structure prediction to aid in the design of plasmonic metamaterials that utilize extended lattices of DNA origami objects to structure plasmonic nanoparticles on the micron-scale [5].

Future Plans

The principal aim of this work is to empower our ability to predict 1D/2D/3D structure and stability of complex programmed nanoscale DNA assemblies, 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 motivated by experimental work from the Yin and Yan labs [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 [4].

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.

Accelerating Materials Discovery & Development

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 inorganic nanoparticle design framework that is fully in silico additionally offers the ability to program custom nanoparticle geometries and optical properties prior to synthesis. The latter framework may be used commercially to design multiplexed electron microscopy imaging probes as well as plasmonic-based biosensors for fluorescence enhancement in single-molecule imaging and detection. Increased volume and purity of production will likely be required to translate these developments to commercial venues. Patents and provisional patents have been filed by the Yin lab on the inorganic nanoparticle and 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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Publications

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The NIST Materials Resource Registry as a Platform to Improve Data Discoverability

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Keywords: resource registry, metadata, repository, data collections.

Project Scope

To help researchers better navigate the new and changing data landscape, NIST is developing a Materials Resource Registry system that will aid in making resources and their contents discoverable. Data providers will be able register their resources to make them easier to find, while researchers will be able to use the registry system to locate resources of interest. The NIST project is part of an international collaborative effort to create a federated network allowing interoperability between many registries. Data will not be deposited with the registries; rather, the registries will index available resources and facilitate the appropriate brokering between the data provider and the researcher looking for resources.

Relevance to MGI

One result of the MGI is the increasing number of projects, websites, repositories, etc., making data, software, and associated information available to materials researchers. Thus it is increasingly difficult for researchers to keep track of what is available, where it is, and how to access it. A major goal of the NIST Registry project is to develop the technical infrastructure and consensus-based metadata and protocols necessary to support a federated, searchable system to enable researchers to more easily locate and use materials data.

Technical Progress

Early work has focused on the development of open-source registry software that will support a federated system and allow for demonstration of the pilot application. Users can search records that are already contained within the system, and further records are being added. Necessary for this, but also crucial for developing international consensus and interoperability, is the development of schemas that support both metadata for describing resources (organization, project title, etc.) and high-level materials-specific metadata to aid in the discovery of relevant materials resources (repositories, data collections, websites, etc.). Prototype versions of the schemas have been created to facilitate further development and refinement. Additionally, a web-based interface has been developed for registering resources and searching, and an API (application programming interface) is under development for additional access.

Future Plans

An early version of the NIST Materials Resource Registry software will be made available in January 2016. This release will support further development of the metadata harvesting protocols, required schema development, and initial population of the system with appropriate resource descriptions. It is intended that institutions will host registry instances as appropriate (supporting a federated network), and that the underlying infrastructure will allow the systems to harvest appropriate metadata and make their own resource descriptions available for discovery.

Data Management and Open Access

The NIST Materials Resource Registry project supports the more effective use of the data, software, and other products being developed as part of the MGI. Additionally, the software, protocols, and schemas will all be made available to support further development and interoperability.

Accelerating Materials Discovery & Development

By improving the discoverability of data and resources as part of the MGI, the Materials Resource Registry will make it easier to find and use data, which will then accelerate materials discovery and development.

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

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Keywords: Biologically Inspired Materials, Multifunctionality, Material Design Rules, Analytical & Computational Algorithms

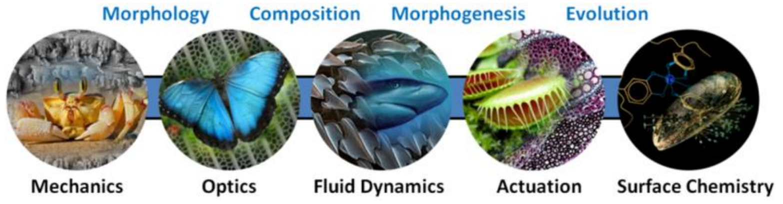

Figure 1. We will study the interplay between material morphologies, composition and morphogenesis and the emerging functionalities in multifunctional biological and bio-inspired materials.

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

Materials that provide solutions to global 21st century challenges in energy efficiency, resource management, technology development, human health, and world security are required to simultaneously exhibit multiple functions. However, most material design efforts focus on single-property optimization and static materials, partly owing to the complexities of dynamic systems and difficulties in multifunctionality optimization in the absence of theoretical guidance. Revolutionary advances in the design and fabrication of multifunctional materials require the establishment of design strategies that originate from a systemic and categorical understanding of fundamental relations between material morphology, morphogenesis, and composition across a wide range of length scales. Consequently, there is a substantial need for mathematical models and computational algorithms that evaluate synergies and trade-offs when optimizing multiple functionalities in novel, adaptive, autonomous and responsive materials. These analytical and computational approaches require careful benchmarking. A great model evaluation platform, and parameter set treasure trove is provided by biological multifunctional materials with superior performance across multiple property classes (Fig. 1). These materials provide advantageous starting points for studying the role of morphology, morphogenesis and composition on emerging material properties, providing crucial information for building and testing novel analytical and computational material design environments.

Technical Progress

Since the initiation of our program in autumn of 2015, we have made progress in the following directions:

(1) We have gained a deeper understanding of biological strategies used by marine organisms for integrating optical sensory elements into protective biomineralized shells and revealed several principles employed in the co-optimization of optical and structural functions. Our work shows that while the integration of lenses in the shell of the West Indian fuzzy chiton weakens the structural stability of the shell, as it requires integration of living signal-transducing tissue, the strategic localization of mechanically weak sensory regions in the valleys created between protruding, robust non-sensory regions, the application of robust shell layers between the weaker optical element, and an in-build redundancy of optical components compensates for the lenses' structural vulnerabilities.

(2) We are working on establishing an initial platform of computational algorithms for co-optimization of optical and mechanical parameters in artificial materials. We have formulated analytical models that will help to make theoretical predictions of the mechanical and optical properties of regularly micro- and nanostructured materials. This analytical framework will be combined with a multi-objective parameter optimization algorithm that should allow a user to design model-type material structures with desired mechanical and optical performance. Structures identified by the analytical framework will then be tested in more computationally intense FEA analysis (ABAQUS, COMSOL) and FDTD modeling (MEEP, COMSOL) to assess their mechanical and optical behavior in greater detail. The computational assessment of preselected material motifs will also allow to test for material aspects that can not easily captured by an analytical framework, such as structural disorder and compositional irregularity.

(3) Inspired by natural origami patterns in insect wings and leaves, we have recently begun to study the question of how to program shape – i.e. control fold number, location and orientation to drape arbitrary surfaces. We couch these results in terms of a geometric optimization framework that allows us to create origami-like quad tessellations that are developable (i.e. can be mapped onto the flat plane) and can drape surfaces of piecewise constant Gauss curvature (0,+,-) or pairwise combinations of these. A natural next step is to build activity into these structures so that they can respond to environmental stimuli.

(4) We started investigating the potential mechanisms by which the sponge spicules are structurally optimized for increased fracture toughness and stiffness. In particular, we developed Finite Element simulations and focused on the mechanical functionality, while in the future we are planning to also extend our investigations to hydrodynamic and optical properties. Preliminary findings using FE analysis based on comparing a traditional diagonally reinforced square grid cell model to the double strut bracing system observed in *Euplectella* spp. suggest that the incorporation of twice as many diagonal components with an offset from the nodes of the underlying quadrate skeletal lattice, results in a significant reduction in node strain accumulation and an overall more diffuse strain field.

Future Plans

BIOMATTER will create a synergistic platform of expertise in mathematics, modeling, materials synthesis and characterization through a collaboration that coalesces research in the field of programmable, multifunctional materials. We propose 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 (Fig. 1). This will enable us to identify a generalized set of rules for guiding the design and fabrication of multifunctional 21st century materials. We focus on emerging synergies and trade-offs between mechanical functionalities, optical properties, actuation behavior, fluidics and surface-chemistry induced effects. 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. In summary, we propose to tackle the challenges of multifunctional material design using a feedback-oriented “evolutionary research algorithm” with focus on the realization of dynamic multifunctional materials capable of fast autonomous or controlled functional morphing stimulated by external influences or user input. BIOMATTER will enable a set of discoveries related to our understanding of the biological strategies involved in the design of high-performance materials, in particular the study of multifunctionality; it will lead to innovations in the integration of these biological strategies into current and future materials technologies; it will develop new algorithms for the optimization of modeling processes for natural and synthetic multifunctional materials, and it will produce new processing technologies to fabricate bio-inspired 21st century materials with optimal structure and properties at multiple length scales. These technologies will leverage advances in mathematics, physics, chemistry, mechanics and nanotechnology.

Broader impact (Optional for DOE grants/FWPs)

The five PIs are taking leadership positions in organizing workshops, symposia, conferences and courses aimed at reaching out to the broader research community and at facilitating multidisciplinary conversations. Findings will be disseminated in regular seminars of the Kavli Institute for Bionano Science & Technology (KIBST) at Harvard. KIBST seeks to develop a deeper understanding of the functioning of life and biology at the nanoscale level bringing together experimental and theoretical researchers across disciplines. At Harvard and MIT, the project will be leveraged to impact many students, including undergraduates involved in the labs and projects of the PIs, women and underrepresented groups. The courses taught by participating researchers will be expanded by incorporation of project results; new courses will be developed as well, with a focus on Biomaterials and Bio-inspired Materials Engineering. Once course content is well established, the PIs plan to contribute to Harvard’s and MIT’s mission to facilitate education worldwide by realizing HarvardX and MITx courses on bio-inspired materials and engineering. The PIs will also collaborate with the Harvard Museum of Natural History to promote science and engineering to a broad audience. For most of the visitors the design and development of new materials is a mysterious process. The PIs will create an exhibition where such design process will be explained using a natural history lens. The lessons learned from the research outlined in this proposal will also be presented during the annual NanoDays event at the Boston Museum of Science.

Data Management and Open Access

Analyzed and metadata will be published in theses, dissertations (both are available through the Harvard and MIT libraries), refereed journal articles and conference proceedings. All data with the exception of computational codes will be available immediately after publication and shared under the Creative Commons Licenses. Protocols and code modules relevant to the scientific community will be published online under the Creative Commons Attributions Share Alike License. □

Accelerating Materials Discovery & Development

The proposed research will aid in the establishment of novel paradigms for the design and fabrication of programmable, dynamic, multifunctional materials, which will have a disruptive effect on current materials development approaches and enable scientific breakthroughs and technological innovation. The material design rules and computational toolboxes resulting from our effort will find application in two reciprocal approaches: (1) Given a specific set of material characteristics, they will aid in the identification of the emerging physical, chemical and biological functions. (2) If a specific set of functions is required, our rules will suggest a subset of material compositions, morphologies and processing strategies to ensure this particular functionality. The proposed research will systematically identify foundational design rules that will guide academic and industrial efforts to create the next generation of innovative materials.

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Designing Microstructure for Engineering Toughness

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Keywords: microstructural design, heterogeneous materials, optimal design, 3D printing, engineered ceramics.

Project Scope

The project brings together an interdisciplinary team motivated by the vision of exploiting digital methods including 3D printing and ink-jet printing to synthesize structural materials with exceptional mechanical properties. Specifically, the project seeks a fundamental understanding of the relation between material microstructure and fracture toughness through mathematical modeling and simulation and to use this understanding to design microstructures for desired toughness subject to the constraints of stiffness, strength and synthesis (Fig. 1). It exploits emerging methods of digital manufacturing to synthesize materials with designed microstructures, and use mechanical characterization to validate the designs.

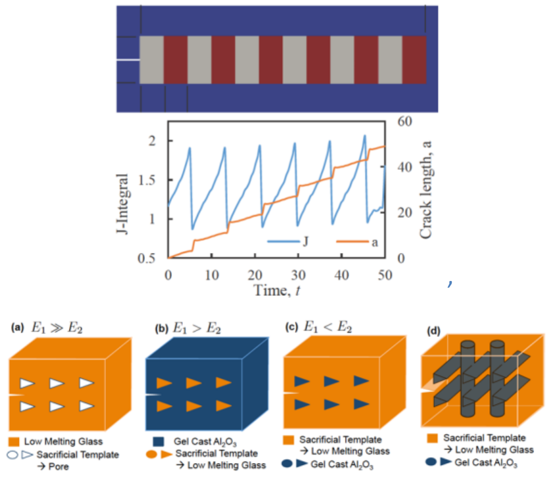

Figure 1. Fracture of layered heterogeneous material with alternating elastic modulus and uniform toughness. The crack gets stuck at each compliant to stiff interface thereby requiring a higher driving force to propagate. (a)-(d) are schematics of engineered ceramic microstructures.

Relevance to MGI

It has long been understood that microstructure can affect mechanical properties, and this has been exploited in both materials processing and in creating composite materials. However, such effort has historically been limited in the range of microstructures it can explore. Our vision is to overcome this limitation by adapting methods of digital and additive manufacturing – that emerged and have largely been used as tools for prototyping – to make structures of arbitrary complexity specifically designed for superior mechanical performance based on modeling and validation. While 3D printing and related methods have gained considerable attention, we propose to use these strategies to synthesize structural ceramics at the appropriate size scales based on rigorous mathematical modeling and validation.

Technical Progress

We have made progress on a number of fronts to advance the project. This includes (i) computing the effective toughness of idealized microstructures, (ii) design and processing of sacrificial polymer templates for ceramic microstructures via stereolithographic 3D printing and gelcasting, (iii) design of heterogeneous microstructures for 3D printing as informed by models, (iv) development of a loading device for applying surfing boundary condition that enables stable crack growth in brittle solids.

Future Plans

We plan to address four intertwined tasks in this project: (i) the forward problem of finding the effective toughness given a microstructure [1], (ii) the inverse problem of defining the microstructure for a desired toughness under constraints of stiffness, strength and manufacturability, (iii) methods of synthesizing materials with prescribed microstructures [2] and (iv) characterizing the microstructure and mechanical properties.

We plan to systematically explore mathematical structure of the set of effective fracture toughness. We will validate the theoretical framework of computing effective toughness of heterogeneous microstructures in 2D and

3D settings using systematic experiments. We will use optimization techniques to design microstructures of desired toughness, which will include topology optimization. We plan to design optimal micro-geometries under a variety of elementary loading (uniaxial tension, hydrostatic loading, pure shear), or a combination of loadings. We will plan to process the optimal microstructures and our focus will be on two-phase ceramic materials, either oxide-void couples or modulus-mismatched oxide pairs. The basic route to synthesis is to use 3D printing and other additive manufacturing techniques to create sacrificial template around which a ceramic matrix is created. The sacrificial layer is then removed and either left as void or infiltrated with a second phase. The geometry, size and spacing of the templates will be an outgrowth of the theoretical models. The resistance to crack propagation (effective toughness) of the newly engineered heterogeneous microstructures will be evaluated using established techniques like the double cleavage drilled compression (DCDC) and wedge opening loaded (WOL) fracture specimens. Full field measurements using optical techniques, such as digital image correlation and the grid method, along with X-ray computed tomography (XCT), will be used to validate the models and predicted optimized microstructures.

Broader impact

The broader impact of this project is many fold. First, fracture is a significant technological challenge, and a new approach to making materials with superior toughness will have a major technological impact. Second, there are a number of physical phenomena in heterogeneous media described by free boundary and free discontinuity problems. Progress in our understanding of fracture will also have a major impact on those fields. Third, the project provides for the training of doctoral students as well as undergraduate researchers in an interdisciplinary setting. Fourth, the results of the proposed research will be broadly disseminated and incorporated into teaching. Finally, the project provides new opportunity of engaging K-12 students in STEM, and for promoting STEM education amongst underrepresented groups.

Data Management and Open Access

Our research efforts generate: (i) mathematical theorems, (ii) experimental data including those from tomography and mechanical tests, (iii) results of numerical simulations, (iv) computer codes and (v) new material designs. Caltech maintains a secure institutional repository that provides access to material that is of long-term value to the academic community, including datasets. The Caltech Collection of Open Digital Archives (CODA) is accessible at http://libguides.caltech.edu/CODA, which conforms to international standards. vDef, a phase-field implementation of the variational approach to fracture is available at http://bitbucket.org/bourdin/mef90-sieve.

Accelerating Materials Discovery & Development

In prior composite technology, reinforcement morphologies have been generally limited to those that can be mass-produced, e.g., fibers and particles. With the advancement of 3D printing, including laser sintering, stereolithography and inkjet printing, constraints imposed by prior reinforcement processing no longer exist. It is anticipated that unique inclusion morphology designed through theory and modeling could lead to novel heterogeneous engineered ceramics and composites.

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Patent Application

1. M. Z. Hussain, C.-J. Hsueh, K. Bhattacharya, G. Ravichandran, and B. A. Bourdin, *Systems and Methods for Determining the Effective Toughness of a Material and for Implementing Materials Possessing Improved Effective Toughness Characteristics*, U.S. Patent Application No. **14/937,634** (2015).

Novel, data validated, nanostructure determination methods for accelerating materials discovery

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Keywords: local structure, nanomaterials, x-ray scattering, uncertainty quantification, machine learning

Project Scope

This project will used advanced applied math and data analytic approaches to obtain robust determinations of the nanoscale structure of materials from scattering data: the nanostructure inverse problem (NIP). Properties of advanced materials depend sensitively on defects and non-periodic structures, but no robust way of determining them exists. The reason is that the NIP is ill-posed: there is not enough information in a single dataset to constrain a unique solution. We will combine machine learning and uncertainty quantification approaches to develop methods to regularize NIPs from quantum dots, noble metal clusters, and other systems, by complexing different data-sources and theoretical inputs.

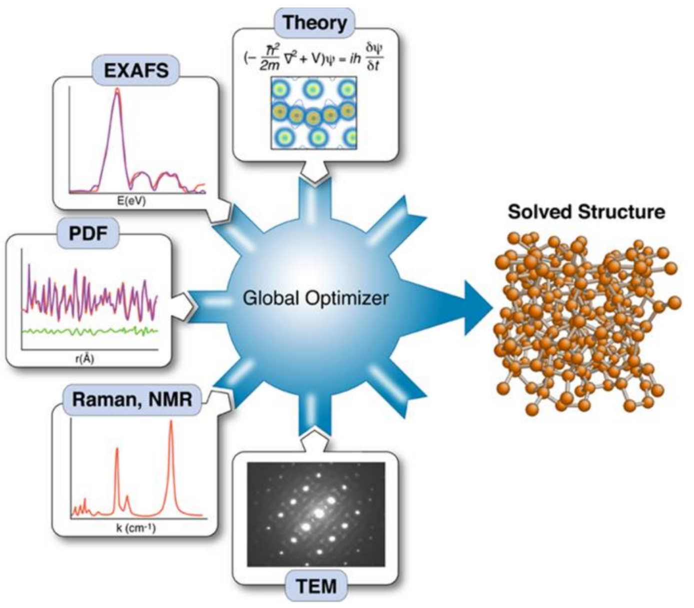

Figure. Complex (multi-modal) Modeling: by combining multiple different information sources as inputs, and using data analytic, uncertainty quantification and advanced stochastic optimization approaches, we will obtain reliable, validated, nanostructure solutions that will allow the structure of real materials to be determined.

Relevance to MGI

The MGI aims to shorten the time from materials discovery to deployment in applications. The keystone of this iterative discovery-development-deployment loop is the knowledge of material structure: Once this is known (or predicted theoretically), material properties may be computed and synthesis iterated to obtain a more desirable structure. The entire loop fails if the material structure is not known with sufficient fidelity. Increasingly, to obtain the best materials performance we seek to engineer materials at the nanoscale and to design and control structural defects. Theoretical calculations are not accurate enough to predict defect structures with certainty. Furthermore, defect structures and nanostructures cannot be solved directly from scattering data because of the nanostructure inverse problem. This presents a major problem for MGI as applied to "real" materials with defects and nanostructure which we will address with this award. Our loop involves synthetic chemists producing nanoparticles and metallic clusters, scattering scientists collecting and analyzing scattering data, physics theorists doing quantum mechanical calculations and applied mathematicians and computer scientists working on the robust NIP solutions.

Technical Progress

New project, nothing to report.

Future Plans

We will develop novel methods, and computer codes, to determine and validate nanostructure of materials made by synthetic chemists and characterized using x-ray, neutron and electron diffraction methods. Uncertainty quantification will be used to assess the robustness of nanostructure solutions. Multiple information inputs such as multiple complementary experiments and inputs from theory will be combined as needed to increase the robustness of the solutions. Directed and undirected machine learning will be utilized for parameter estimation and to cluster multiple solutions and understand the uniqueness of solutions. First we will build libraries of exemplar nanostructure problems as test targets for our methods. These will be systems where it is possible to get high quality samples with unique structures, are tractable for computation, and are scientifically interesting and have potential applications. The first three are: (1) quantized growth CdSe ligand capped quantum dots (2) magic number Au144 gold clusters (3) bulk crystalline PbTe which, nonetheless, exhibits nanoscale lead displacements. These samples will be synthesized and measured using x-ray, neutron and electron scattering data, which will be stored in databases. Software modules for solving the (defective) structures of these materials will be developed and tested against the libraries of data in an iterative fashion, with the sophistication of the analysis increasing over time as needed to obtain robust results. As the project develops, we will add new materials systems to the library, and increase the range of tools available to solve and test the nanostructure models, and make them available to the broader community.

Broader impact

Beyond the societal impacts of accelerated materials discovery flowing from our developments, we will disseminate as widely as possible the software and databases that we generate and make them available to the broad materials community, and we will take measures to train as broad a range of people as possible in data analytic and materials genomics methods. For the latter aspects we will leverage the newly created Center for Materials Discovery Analytics (CMDA) within the Data Science Institute (DSI) at Columbia University. CMDA will host a series of events annually including seminars, workshops, short courses and public lectures. We will use these forums to build community and to attract young students and scholars, in particular, those from under-represented groups. We plan to organize special sessions and public lectures targeting students in undergraduate colleges and high-school in local NYC areas including those from schools with large under-represented minority populations.

Data Management and Open Access

Computer codes that are developed under this grant will be open source and hosted on GitHub in open repositories. The GitHub repository may be cloned by anyone and community development will be encouraged. Code developments made by people outside the group may be incorporated by a process where the contributor makes a pull request. After a period where the code is reviewed, improved and brought up to the group coding standards it may be pulled into the main code base. Low dimensional data (for example, structure files containing atomic coordinates, 1D spectra, etc.) and metadata will be maintained in a mongoDB database that is running on a cloud resource. This will be accessible through a browser to registered members of the website. We also aim to present an interface to the modeling codes running on cloud resources through a web interface and connected to the database.

Accelerating Materials Discovery & Development

Only by understanding and controlling the role of defects in materials properties can we hope to make materials prediction robust and therefore avoid false-trails. Our tools will explicitly focus on this important robustness aspect of the prediction process of “real” materials, including defects and nanostructures.

COUPLED: Computation Of Undiscovered Piezoelectrics and Linked Experiments for Design.

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Keywords: High-throughput, piezoelectric, combinatorial, thin films, active subspaces.

Project Scope

COUPLED incorporates high throughput computational and combinatorial experimental techniques to rapidly explore the extensive white space of piezoelectric nitrides. Guided by knowledge from oxide piezoelectrics, our hypothesis is that piezoelectric properties of interest are enhanced in the vicinity of composition-induced phase transformations due to a flattened energy landscape. Existing codes and capabilities are being significantly extended, and data from this work will expand the open **materials.nrel.gov** database. Our active and growing industrial advisory board (IAB) ensures application relevance, provides supplemental validation and educational opportunities, and accelerates deployment of the new materials developed during this work.

Relevance to MGI

Our process consists of coupled and iterative parallel computational and experimental paths, each of which employs low fidelity screening followed by high-resolution study. Data from each path inform and are guided by the other and a Gaussian regression enabled by dimension reduction. Statistical tools are also crucial for rigorous comparison of seemingly similar but subtly different parameters output from computation vs. those measured via a large suite of complementary chemical, structural, and property techniques.

We began with the (Al,Sc)N pseudobinary system in order to compare our results against existing literature, but are quickly moving to more complex chemistries. Active subspace tools allow us to quantify uncertainties in sparsely populated experimental and computational datasets, a particularly important feature of the open database. Finally, because of the complexity and often divergent materials figures of merit that exist across the vast and varied piezoelectric device landscape, our IAB is helping to craft the way(s) in which the data are organized and results presented to the general public, other researchers, device designers, and end users. The entire project is focused around the rapid discovery, development, and deployment of new materials with the potential for rapid and broad impact on industry.

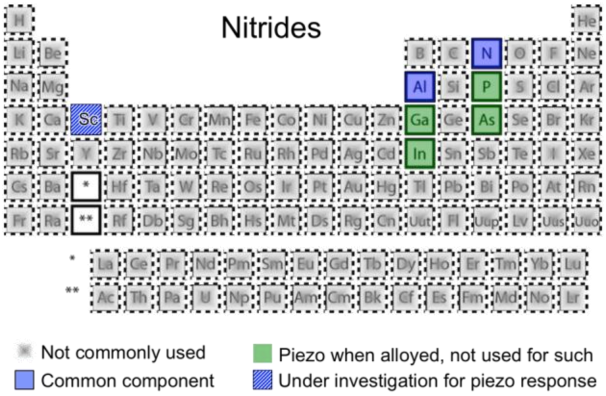

Figure 1. Graphical representation of the compositional opportunities in nitride piezoelectrics based upon the elements currently used in commercial piezoelectrics.

Technical Progress

Three of the 4 students have been identified and are actively engaged in the project, and a post-doc is starting in January, 2016. VASP- based calculations of thermodynamic stability of stoichiometric pseudobinary systems with AlN as one end member (e.g., AlN-MN and AlN-($X_{0.5}Y_{0.5}$)N, respectively, where M is a trivalent ion, X is bivalent, and Y is tetravalent) are ongoing. Existing combinatorial fabrication tools at NREL and high-throughput measurement and characterization capabilities at NREL and Mines were modified for use in this project, and high quality films of AlN and (Al,Sc)N with up to 25% ScN have been grown and characterized. The IAB has grown to seven members, already met once electronically, has an in-person meeting planned for Feb, 2016, and is negotiating the details of a blanket NDA.

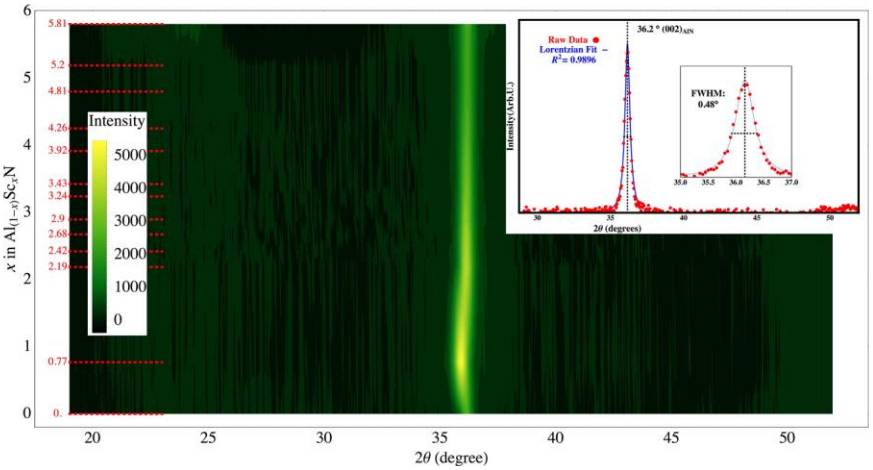

Figure 2. X-ray diffraction from (Al,Sc)N film grown by combinatorial reactive sputtering showing a highly-textured wurtzite structure (inset, AlN end member).

Future Plans

Codes are being developed for the extension of existing DFT-based capabilities to calculate full and accurate electromechanical parameters including intrinsic coupling coefficients. High throughput measurements of electrical and electromechanical properties are being ramped up, data management systems are being expanded to accommodate the increased breadth of relevant parameters and facile transfer between laboratories. and example datasets of a variety of characterization and measurements techniques are being used to develop a Kriging model framework. Through FY16, we will focus on simple stoichiometric AlN-based systems, guided primarily by crystal chemistry and the results of screening by high throughput calculations of thermodynamic stability. During this time, a statistical framework will be created and validated for carrying out Gaussian regression on dimension-reduced experimental and calculated data sets to assist in targeting of future systems. Statistical techniques for comparing the various datasets (and merging when appropriate) for broad uncertainty quantification will also be developed during the summer of 2016. We expect the first complete and fully annotated datasets to populate the publicly-accessible database early in the summer of 2016, and for progress to accelerate significantly from there.

Broader impact

In addition to the 4 students and one post-doc directly engaged in this work, all of the PIs are engaged in significant outreach activities. The technical output of the work will be published in peer reviewed journals, the data (both experimental and computational) will be available to the public at materials.nrel.gov, targeting the materials research community, device designers, and end users alike. The IAB will assist with the utility of this database and accelerate deployment of the new materials developed here.

Data Management and Open Access

Raw data are initially being stored internally; vetted and validated data will be available at materials.nrel.gov. Links to existing codes 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.

Accelerating Materials Discovery & Development

Close ties with a broad cross-section of companies in the piezoelectric device market gives this project a direct and rapid pipeline from development to deployment. Having IAB members actively engaged early in the process and some even committed to providing additional fabrication, testing, and validation of the materials and associated device performance accelerates the process even further. Consolidating the screening process via this project and parallelizing scale-up of the most promising materials massively reduces both time and costs.

Control of colloidal assemblies using dynamic DNA nanostructures

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Keywords: DNA, self-assembly, nanotechnology, origami, responsive materials

Project Scope

This project seeks to develop a fundamental understanding of how (dynamic) DNA nanostructures can control and program colloidal self-assembly, and, by putting this concept on a strong fundamental footing, to exploit it to maximum effect, through the design of DNA reaction networks that solve essential challenges to making colloidal self-assembly a practical materials fabrication platform. We aim to both discover the fundamental principles underlying DNA particle-nanostructure interactions, and create new materials, from plasmonic molecules to metafluids. Success will be measured by how well the structure and response of the experimentally produced assemblies can be predicted by theoretically-derived design rules.

Relevance to MGI

This project involves close work between an expert in colloidal particle physics (Manoharan), an expert in DNA nanostructure fabrication (Shih) and an applied mathematician with expertise in theoretical and computational models of self-assembly (Brenner). Theoretical models from the Brenner group are used to first predict qualitative features (such as geometry) of DNA nanostructures that are suitable for combining with colloidal particles. Shih's lab synthesizes such nanostructures. Manoharan's lab prepares DNA-colloid hybrid systems and measure properties such as assembly dynamics and melting characteristics. Brenner's computational models are with the results of such experiments and predict parameter regimes for the next round of experiments.

Technical Progress

Progress in this period has largely focused on creating new ways for colloidal scale objects to interact using DNA nanotechnology; specifically by (i) creating specific functionalized binding sites on surfaces of particles, breaking down the paradigm of uniformly coated particles; and (ii) creating mechanisms for controllable time dependent interactions.

Localized functionalized binding sites Led by Shih, we are using hierarchically self-assembled DNA nanostructures ("*bead catchers*") with controlled rigidity and well-defined dimensions to create localized binding sites on colloidal particles. The structures consist of repeating monomer units ("plates") that are polymerized into longer, finite structures with the aid of a scaffold unit made of more flexible double-stranded DNA ("molecular ruler"). Despite its rigidity, the *bead catchers* are designed to enable flexible unidirectional bending around the curvature of spherical colloid particles. We have thus far designed the plates using 3D DNA origami, including ssDNA handles for attachments. These have been synthesized and success confirmed using agarose gel electrophoresis, AFM and TEM. The final step and current challenge is to immobilize the constructions on colloidal particles.

Localized binding sites with Viruses Another approach for building programmable interaction sites (led by Manoharan) is to interface DNA nanotechnology with the "natural" RNA nanotechnology of viruses. We have shown that monofunctional virus particles can be synthesized using principles borrowed from DNA nanotechnology. Specifically, we carry out the self assembly of virus-like particles from mixtures of capsid protein and RNA molecules whose 5'-ends have been made "unpackageable" through hybridization with a long enough DNA oligo. Each self-assembled virus-like particle is a monodisperse spherical (icosahedral) shell with a single RNA-DNA duplex extending from it as an addressable "handle".

Time Dependent Interactions would significantly enlarge the structures that can be built with colloidal spheres. Brenner has shown, for example, that this is sufficient to enable self replication reactions. We have investigated theoretically the parameter regime in which these interactions can be effective, and invented new types of reactions that could be carried out were this experimentally realized. Experimentally, we have designed a DNA-mediated colloidal bond in which a free "linker" strand bridges grafted strands on two different particles. A detailed characterization of this interaction strength as a function of linker length and linker concentration is currently underway. By changing the concentration of a particular linker strand over time, the strength of the interaction mediated by that linker can be increased or decreased without affecting the strength of the interactions between other species.

Colloidal Walkers are a simple realization of a dynamic colloidal system. The first realization of this type of system consists of a track of DNA coated particles with another DNA coated particle (the dancer) placed on top, which can be made to move through any arbitrary set of steps along the track in response to temperature cycling. Using a combination of simulation, theory and experiment, we were able to design and realize a set of three different sets of DNA interactions, allowing the dancer to bind to each distinct pair of track particles at different temperatures using DNA strand displacement reactions. By changing the temperature of the system we realized motion of the dancer processively through the three distinct states along the track.

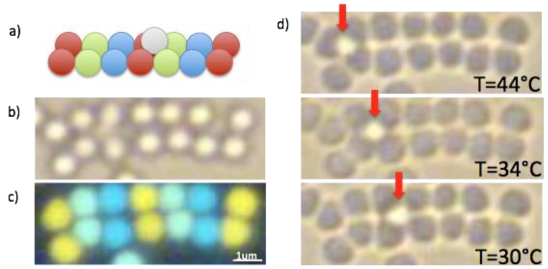

Figure. a) A schematic of the track with dancer particle on top (in grey). Different colors represent different DNA coating. b-c) Experimental images of a track of DNA coated particles assembled using optical tweezers in b) bright field and c) fluorescence. d) A dancer is added to the track and as the temperature of the system is lowered the dancer (indicated with the red arrow) accesses the three distinct states on the track (red/green, green/blue, and blue/red) processively.

Future Plans will use and extend the concepts outlined above to create new types of materials. The free energy provided by DNA strand displacement reactions can be used to power novel structural transformations common in natural systems but not typically seen in synthetic constructs. We plan to investigate two such possibilities – self-replication and autonomous error correction in structures. Self-replication in colloidal assemblies can allow for selection-amplification cycles that lead to discovery of novel functionalities that cannot be realized easily otherwise. We plan to realize such self-replicating cycles using DNA dynamic nanostructures and colloidal assembly, guided by published and ongoing simulation work from the Brenner group. The central ingredients needed are time-dependent specific interactions between colloidal particles, something that we are well on our way to creating in the laboratory. These interactions allow a parent structure to induce the assembly of a new child structure that can then separate from it. We will create theoretical framework for quantitative analysis of these experimentally realized interactions, so that they can be used as engineering tools.

We are also studying the use of free energy stored in DNA nanostructures to correct errors in assembly, mimicking analogous proofreading processes seen in biology such in the ribosome during protein synthesis. We are presently focused on `proofreading' errors in the hybridization of almost complementary DNA strands, a central problem of biomedical significance. We are studying the sequence design problem for DNA strand displacement reactions that can disrupt and undo erroneous hybridization.

Once perfected, the localized binding sites on colloidal scale objects will open up a new set of possible materials and dynamic structures that can be created in the laboratory. We plan on continuing to develop this technology and then using it to create new materials.

Broader impact (Optional for DOE grants/FWPs)

The broader impacts of the project include the training of graduate students and postdocs from experimental physics, biology, physics and mathematics in an interdisciplinary environment, as well as a program developing a design curriculum for inner city middle schools in Cambridge, MA. Last summer we hosted a team of four undergraduate students, developing computational tools for the project through a summer program run through Harvard's Institute for Applied Computational Science. This fall we offered a course, Engineering Sciences 110, in which Harvard students worked together with 80 inner-city 8th grade science students on an engineering design project.

Data Management and Open Access All computational frameworks developed in this project will be made widely available, with source code, on github.com, a site that allows multiple users to contribute code, report bugs, and suggest enhancements to open-source software projects. DNA sequences and protocols used in the experiments will be made publically available through the world-wide web.

Accelerating Materials Discovery & Development

The coupling of the three different expertise (theory, colloidal experiments and DNA nanotechnology experiments) are critical to make and the materials we are aiming for. This is especially important given the enormity of the potential design space.

Publications

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4. A. Murugan, J. Zou and M.P. Brenner, Undesired usage and the robust self-assembly of heterogeneous structures, Nature Communications, 6, (2015).

Design of Material-Liquid-Nanoparticle Interfaces for Tribological Control

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Keywords: Nanotribology, nanoparticles, complex interfaces

Project Scope

There is a pressing need for revolutionary new materials to reduce friction and wear, and to eliminate the harsh environmental impact of the ones currently in use. To meet this need, we are developing a new approach toward rational design of material-liquid-nanoparticle systems to achieve superior tribology performance that combines multi-physics simulation, statistics, friction characterization at nano- and macroscopic scales, and fabrication and chemical functionalization of nanostructured materials. This work is leading toward a web portal that will predict tribological performance based on physical properties of the system constituents.

Relevance to MGI

Our approach is motivated by the challenge of identifying correlations between combinations of highly heterogeneous properties of nanoparticulates and surfaces with their tribological performance. This capability will enable predictions of new lubricants designed for particular applications. The first part of the statistical analysis involves collecting non-tribological features for a large pool of material-liquid-nanoparticulate components, and a factor analysis to uncover a subset of essential factors that account for variability in non-tribological features. In the second stage, tribological experiments are carried out for a subset of the materials considered in the first stage. Using these experimental results, a statistical model is built to predict the measures of tribological performance as a function of non-tribological factors. The science that underlies these purely statistical correlations is then explored using multi-physics modeling. These results feed back into the search for statistical correlations and to the design of additional experiments, hence closing the loop between statistical analysis, experiment and computation.

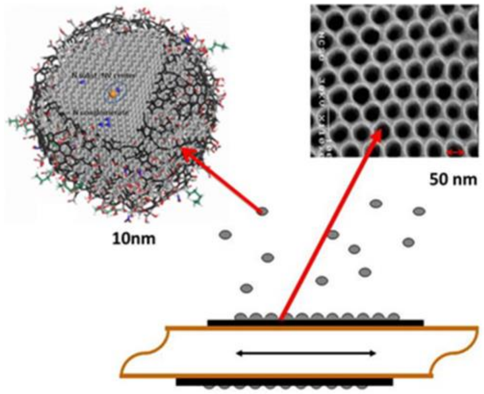

Figure. Illustration of a quart crystal microbalance (QCM) showing the horizontal oscillation. Also shown are a nanoporous anodic aluminum oxide on the QCM electrode and a functionalized nanodiamond particle. A unique aspect of our research is the range of materials and the ability to vary nanoparticulate sizes relative to the substrate. features.

Technical Progress

This effort is only a few months old, and therefore the technical progress is restricted to preliminary experiments, work toward a new atomic modeling tool, and coordination among experimental, statistical and computational groups. In experiments that helped motivate this study, the tribological properties of nano-diamonds with different surface functional groups were evaluated using liquid QCM. It was discovered that nano-particulate net charge can have a profound effect on both nanometer-scale and macroscopic tribological performance in water. In our multi-physics modeling it was determined that the qEq charge equilibration method can reproduce the classical electrostatic field for a point charge above a metal, and that the field penetration into the metal is limited to the first 2-3 atomic layers. This result is enabling our multi-physics modeling of charged nanoparticles to discern between substrate dielectric properties and particulate charge state, which is an important step for the simulation-statistics-experimental feedback loop that is central to our design strategy.

Future Plans

QCM measurements of interfacial friction and wear rates are being carried out for solid-liquid interfaces in the absence and upon introduction of nanoparticulates to the liquid, as well as in the presence of external magnetic and electric fields. Our setups are capable of applying normal and perpendicular magnetic fields with strengths of 0 – 0.5 T, and we operate wide-bore solenoid magnets capable of 12 T. Electrical bias of the electrode up to 100 V is a standard feature. Sliding friction of the QCM with macroscopic contacts as well as AFM measurements of sliding friction under similar conditions are being implemented. AFM characterization of topography before and after the friction measurements will be used to assess wear of the sliding interface. Commercial suppliers are being used for the initial set of nanoparticulates. An internal chemical synthesis effort is creating water-soluble surface functionalized cationic gold nanoparticulates as well as substrates with nanoporous anodic aluminum oxide (AAO) and nanotubes/nanorods prepared using the AAO templates. These materials provide well-characterized system charge and size control, which is critical to statistics and multi-physics modeling.

Our statistical effort is working with idealized datasets to develop the statistics infrastructure, and the simulation tools like that described above are being developed and will be deployed in the next few months. These studies will begin with functionalized nanodiamonds interacting with a gold substrate, and will progress to the gold nanoparticulates being created in our synthesis efforts.

Broader impact (Optional for DOE grants/FWPs)

Our effort is training a new generation of workforce by having graduate and undergraduate (NC State and REU) students work within an interdisciplinary research team. Initial meetings have created opportunities for the physical science, engineering and statistics students to appreciate tools and approaches of each field. These efforts will be expanded through middle school job shadowing. Our outreach will build on prior efforts by our team members that have introduced principles of friction (“granular stability via stacked fruit”) and statistics (“visual analyses of regional dialects”) to create a web-based citizen science portal in which data related to friction (e.g., stability of fruit pile configures) from the general public can be uploaded to the website, and statistical outcomes predicted to illustrate the benefits of large-scale data collection and statistical/machine learning algorithms.

Data Management and Open Access

In addition to publication in the open literature, our team will be developing web-based portals and modeling tools that provide access to our results for multiple communities. We envision access to both the details of the statistical factor analysis, which attempts to correlate tribological performance across a diverse set of materials properties, as well as results of specific experiments. Our multi-physics modeling tools will be distributed through the LAMMPS code. All of these activities will be of interest to the basic research community. We also plan a web-portal aimed at lubricant design technology that will use the basic science and statistics to design lubricant combinations for specific applications.

Accelerating Materials Discovery & Development

Our project is focused on identifying structure-property relations for material-liquid-nanoparticle systems that correlate with tribological performance. These relations will enable rapid identification of materials combinations based on the properties of the individual constituents for a given application related to friction and wear. This design of individual components is a stark departure from traditional lubrication technology that assumes a limited number of lubricants that work over a broad range of conditions.

Publications

None yet.

Materials Engineering of Chromonic and Colloidal Liquid Crystals *via* Mathematical Modeling and Simulation.

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Keywords: Liquid Crystals, Electrokinetics, Photo-patterning, Micro-pumping, Micro-mixing

Project Scope

Transport of fluids and particles at the microscale is an important theme in fundamental and applied science. One of the most successful approaches is to use an electric field [1]. We develop a versatile approach to generate electrokinetic flows by using a liquid crystal (LC) with spatially varying molecular orientation as an electrolyte. In the presence of an electric field, the spatially varying orientation induces space charges that trigger flows of the LC, Fig.1. We construct a mathematical model of LC electrokinetics (LCEK) based on the Leslie-Ericksen approach that succesfuly describes the electrokinetic flows in complex director patterns, Fig.2.

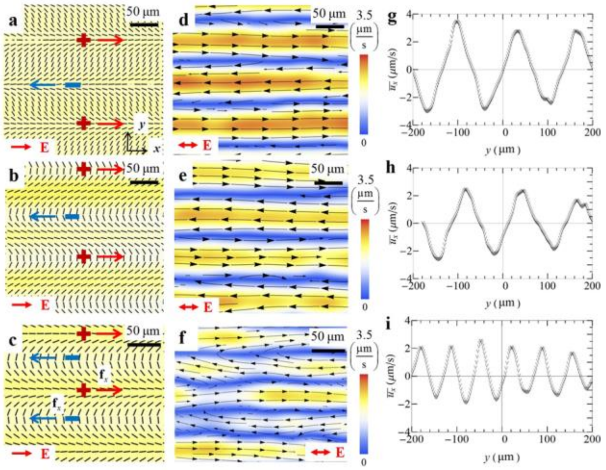

Figure 1. Electrokinetic flows in an LC electrolyte with periodic director patterns.

Relevance to MGI

Liquid crystals enable a new concept of electrokinetics through a mechanism of charge separation that occurs because of director distortions. To progress in the field, the project combines efforts within the discipline of materials science (creation of director distortions through photopatterned substrates), physics (experimental determination of the electrokinetic flow velocity maps, theoretical understanding of how the electrokinetic velocities depend on material parameters such as conductivity and dielectric anbisotropy and director patterns) and mathematics (analytical and numerical description of how the complex director pattern generates charges in presence of an electric field and how these charges trigger flow of the material). The progress is anabled by cooperation among the specialists within these three disciplines and by development of the analytical models that demonstrate how the electrokinetic phenomena are shaped by the materials parameters. In its turn, this fundamental understanding accelerates the development of new liquid crystal electrolytic materials. The collaborative nature of the project already resulted in successful demonstration of the directed transport in microfluidic chambers.

Technical Progress

We describe a versatile approach to generate electrokinetic effects by using a liquid crystal (LC) with surface-patterned molecular orientation as an electrolyte. In the past, the LCs were demonstrated to enable electrophoresis od spheres with a particular director field around the inclusion [2-4]. The new challenge is to make any particle dispersed in a LC to show electrophoretic activity. We achieve it by forming predesigned director patterns in the LC. The patterned molecular orientation (described by the spatial variations of the so-called director) is achieved by photo-alignment of the substrates bounding the LC cell. The substrate-imposed pattern imposes director distortions in the entire LC bulk, because of the elastic nature of the LC orientational order. In the presence of a uniform alternating current (AC) electric field, the spatially varying molecular orientation produces space charge that triggers streaming liquid crystal-enabled electrokinetic (LCEK) flows of practically any complexity and vorticity. The flows are persistent, as their velocities are proportional to the square of the applied field, so that the driving field can be of an AC type. The transport of LC and particles dispersed in it is easily controlled by the predesigned director gradients; no mechanical parts and no external pressure gradients are needed. The flow polarity can be changed either by changing the director patterns or the electric field direction. Since the charges are separated in the bulk of electrolytic LC medium rather than at the solid-liquid interfaces, the proposed approach eliminates the need for polarizable/charged interfaces. For example, we demonstrate that LCEK created by surface patterns can carry inclusions such as solid colloids, droplets of water and air bubbles even if these inclusions have no electrophoretic activity (zero charge or zero polarizability) on their own. The patterned LC electrolyte induces persistent vortices of controllable rotation speed and direction that are quintessential for micro- and nanoscale mixing applications. The cross-sections of the patterned LC microfluidic chambers are not obstructed by any barriers (such as ridges, electrode posts or colloidal particles, needed in other electrokinetic devices), thus combining efficiency of flows with simplicity of design. The approach might find applications in lab-on-the-chip and microfluidic devices of a new type. From the fundamental point of view, the described patterned LC electrolyte represents a new type of active matter in which the energy input that drives the system out of equilibrium occurs locally through orientation distortions of the medium rather than at the particles dispersed in it. This is an essential difference as compared to active materials with artificial or biological swimmers embedded in an otherwise inert surrounding medium such as water. The patterned LC electrolytes add a new dimension to active systems, as now both the medium and the dispersed particles can be used for energy input and departure from equilibrium. We construct a mathematical model of LCEK based on the Leslie-Ericksen approach. The model describes nonlinear phenomena such as charge transport in the direction perpendicular to the field, quadratic dependence of the velocities on the electric field amplitude, and formation of steady states of the system under an alternating current voltage driving, Fig.2. The model predictions show a very good agreement with laboratory experiments on nonlinear electrokinetics.

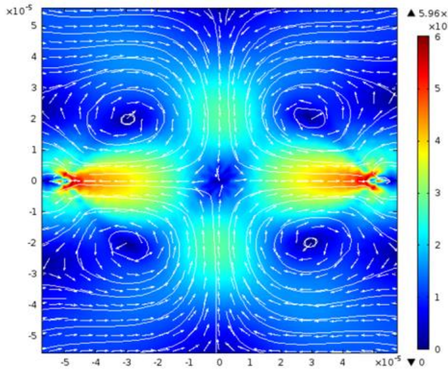

Figure 2. Numerical simulation of the electroosmotic flows in an LC electrolyte with two point singularities.

Future Plans

Dispersions of colloids in a nematic liquid crystal (LC) show a diversity of self-assembled structures guided by long-range interactions. It will be highly of interest to investigate the interaction between the colloids and different director distortions and study the dynamic processes involving LCEK flows. The self-assembly of colloids can be directed and separated by the director distortions and collected by LCEK flows. The dynamic approach to control self-assembled colloidal systems through LCEK in cells with patterned director field might open the opportunities in the microfluidic, lab on a chip, biological sensing and sorting applications. We plan both experiments and theoretical description of the colloidal assembly in patterned LC cells.

Broader impact (Optional for DOE grants/FWPs)

The experimental work is performed by graduate students who acquire diverse skills in physics and materials science. Last summer, an undergraduate student participated in the NSF REU (research experience for undergraduates) program and worked on the LCEK theme for 10 weeks.

Data Management and Open Access

The experimental and computational data are stored on the laboratory computers and are regularly updated. The data that represent a finished step in the research are disseminated through publications and public servers: http://link.aps.org/doi/10.1103/PhysRevE.92.052502; http://arxiv.org/abs/1510.01024; http://vinals.tiddlyspot.com/.

Accelerating Materials Discovery & Development

The project develops a fundamentally new approach to microfluidics that feature principal advantages over other forms, such as absence of mechanical pumps, possibility of AC electric field driving instead of the DC driving, ability to transport solid, fluid and even gaseous inclusions. The microfluidic systems based on our invention can be developed as commercial products. One patent application has been filed.

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Peng, C., Guo, Y., Conklin, C., Viñals, J., Shiyanovskii, S. V., Wei, Q.-H. & Lavrentovich, O. D. *Liquid crystals with patterned molecular orientation as an electrolytic active medium.* Physical Review E **92,** 052502 (2015).

High-Throughput Discovery, Development and Demonstration of Material Systems to Enable Low-Power NEMS-Based Computation

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Keywords: Nanoelectromechanical systems, tribology, tribopolymer, electrical contacts, surface contamination.

Project Scope Transistors are increasingly energy-inefficient. Radically different devices are needed to continue Moore's law and enable low power computing. One candidate, the nanoelectromechanical (NEM) switch (Fig. 1), *physically* opens and closes to turn signals on and off, operating at 10^3 times lower voltage, and 10^6 times greater energy efficiency than transistors. However, they suffer from reliability problems: the contacting electrodes must cycle nearly 10^{15} times without wear or contamination. **Materials and environments for this are lacking**. Our objectives are: (1) to understand the failure mechanisms and (2) to use a MGI approach to develop materials and operating conditions with ultra-high reliability.

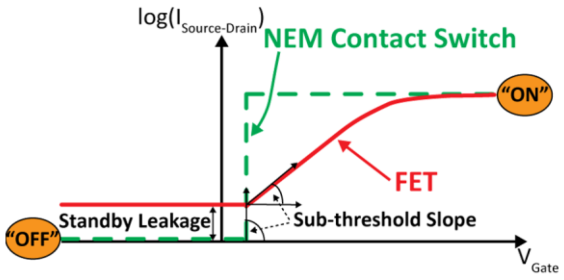

Fig. 1. Solid-state field-effect transistors (FETs) are fundamentally limited by a low sub-threshold slope and high standby leakage. NEM switches overcome both of these limitations to save energy.

Relevance to MGI Integrating computational modeling of atomic-scale contacts with nanoscale experiments enables high-throughput screening of the wide range of possible NEM electrode materials and operating conditions. We are characterizing existing Pt and RuO_2 electrodes to identify a set of descriptors to apply to new candidate materials. From these candidates, we have selected ones with required characteristics: high electrical conductivity, wear resistance, and – the most challenging aspect – tribopolymer (TP) resistance. The most promising candidates are tested in microscale devices and subsequently in nanoscale devices to ultimately identify materials and conditions that will be tested in actual NEM switches. Successful execution of this MGI paradigm will enable NEM switch technology, where quantum mechanical and molecular dynamics modeling of materials, reactions, and processes guides materials selection and device design.

Technical Progress The project involves five interconnected thrusts: 1. Contact material development/characterization; 2. Quantum chemical (QC) simulations of TP formation; 3. Molecular dynamics (MD) simulations of electrode behavior; 4. Material testing using MEM microswitches; and 5. Development of NEM switches. **Contact material development** focused on characterizing Pt_xSi ($1 \leq x \leq 3$) and RuO_2 candidate materials. These were identified via our initial screening process based on electrical conductivity, mechanical robustness, and hypothesized contamination resistance. For Pt_xSi, a method was developed to tune the silicide phase, showing that Pt_3Si is ideal, with much better mechanical properties than Pt while maintaining high conductivity. We developed methodology to obtain this phase with high purity, rendering it an appealing candidate material. We also produced Pt_xSi and RuO_2 AFM probes to test under NEM switch-like conditions using a novel high-throughput methodology. Additionally, we fabricated and are testing an *in situ* SEM heater to further study Pt_xSi synthesis and nanogap formation. Finally, we produced a large quantity of TP using macro-scale Pt-Pt wear testing to enable spectroscopic investigation. **QC simulations** modeled electrode surfaces with contaminants using density functional theory, showing how TP forms under pressure, and then recommending contamination-suppressing materials. We demonstrated a mechanical effect on TP formation: loads required for polymerization reduce on catalytically-active surfaces. Catalytic mechanisms for a pure metal and a conductive oxide were determined, providing guidance for selecting electrode materials, and suggesting that Pt_xSi is promising. **MD simulations** focused on the effects of TP thickness, electrode adhesion, and TP viscosity on nanocontact behavior via a parametric model designed to clarify trends, identify key variables, and determine mechanisms. When the TP is thick, metal/TP adhesion and/or TP viscosity is high, asperities are unable to displace TP to make electrical contact. The resultant small metal/metal contact leads to little metal transfer between surfaces and thus less wear, while preserving sufficient electrical contact. This suggests that some TP may be beneficial to long-term performance. **Material testing using microswitches** focused on (i) developing an infrastructure to rapidly coat MEM devices with new materials, and (ii) improving test throughput. To coat new materials on MEM devices, blanket coating (without the need of photolithography), die attach and wirebonding process techniques were developed. MEM switch substructures provided by Sandia National Labs were released, dried and coated with materials of interest (Pt and Pt_xSi so far) with a new fixture that enables simultaneous coating of 60 devices. Regarding test throughput, an *in situ* oxygen plasma cleaning apparatus with graphite electrodes, which eliminate contamination as demonstrated by X-ray photoelectron spectroscopy, was designed, constructed and demonstrated. The time to clean the switch surfaces reduced from ≈18 h (UHV bakeout) to ten minutes, enabling overall test throughput to be doubled. **NEM relay development:** Design and analysis was completed for a highly scalable third relay NEM switch geometry. This design uses a free-floating conductive shuttle, actuated by a combination of electrostatic force and acoustic pulses supplied by a piezoelectric actuator to bridge contacts to close the switch. Fabrication of the first prototype is nearly complete.

Future Plans The next phase involves full implementation of feedback loops between the different thrusts. **MD studies** will be augmented to incorporate reactive characteristics of TP precursor molecules determined from the **QC studies**, and TP characterization from the **contact material** effort. Since the **contact material** effort produced promising results for Pt_xSi, we will further examine Pt_xSi in the **QC studies** to verify the optimal stoichiometry, and test it in augmented **MD studies** and new Pt_xSi-coated **microswitches**. Promising results will motivate Pt_xSi **NEM relay material selection.** We will also undertake parallel studies of oxides of Ru and Re using **QC studies** and screening tests in the **contact material** effort. Work originating in each area will also continue. For **contact materials**, we will consider graphene and other 2D materials as electrodes. For the **QC studies**, we will: determine a set of descriptors for TP formation resistance, test the validity of these descriptors on the existing materials (Pt_xSi, RuO_2), and apply this to discover TP-immune materials. For **MD studies,** future work will focus on: (i) the effects of multiple cycles on contact/TP evolution, (ii) the effects of TP type (molecular structure and chemistry) on contact behavior based on more accurate, polymer-specific models, (iii) validating simulation predictions with experiment, and (iv) providing guidance on material system selection and contact design for long contact lifetimes. For the **microswitches**, we will test Pt_xSi contact material on microswitches with respect to performance and immunity to contaminants. We will determine and eliminate remaining failure mechanisms in promising materials. **NEM development** goals are to: (i) complete fabrication and testing of the highly scalable relay geometry under development, (ii) refine and iterate this same NEMS relay geometry and (iii) identify and design test structures in which to incorporate a selected set of contact materials.

Broader Impacts If successful, we will discover new materials and operating conditions that make NEM switches a viable technology for future low-power computers and portable devices. This has potential to save large amounts of energy worldwide. This work will also help maintain U.S. competitiveness in information technology by continuing technological progress in a key economic sector. Eight Ph.D. students conducting research in our labs will develop skills to lead future research in energy-efficient nanodevices, materials science, and tribology. Two undergraduate students are benefiting from direct involvement in the research. Our group is organizing an international workshop to address future directions for this research.

Data Management and Open Access All of our findings, including the database of material systems we create and the experimental and modeling methodologies we will develop, will be widely disseminated through research articles and conference presentations. We will share our material systems database through a web interface hosted on a wiki-based website that we call *NEMSMatWiki*, to be developed next year. The wiki will be searchable and editable by all, creating a community of knowledge-sharing researchers seeking the common goal of reliable NEM devices.

Accelerating Materials Discovery & Development At present, materials for NEM switches are not chosen or developed systematically but rather based on ad-hoc, trial-and-error methods predicated on accumulated knowledge, where available. In fact, NEM relays are not commercially available precisely because of the lack of knowledge of failure-resistant materials. By developing experimental and theoretical methods to screen candidate materials that overcome the hurdle of TP-based failure, we aim to accelerate the commercial feasibility of these devices. Two patent applications have been filed in support of this. Follow-on funding is still under consideration.

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Provisional patent applications

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2. *Methods, apparatuses, and systems for piezoelectric nanoelectromechanical relays*, G. Piazza and U. Zaghloul, U.S. Patent Appl.

Controlling Hierarchical Nanostructures in Conjugated Polymers

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Keywords: polymer, processing, electronic structure, morphology

Project Scope

Semiconducting polymers have achieved impressive benchmarks of performance. However, predictive control of morphology through tailored processing methods and molecular structure would lead to further major advances. We are designing semiconducting polymers which form solution-phase assemblies that lead to solids with hierarchical 3D transport pathways (Figure 1). The design of processing conditions will be enabled by efficient computational methodologies developed using experimental inputs. The development of scalable models to understand the role of domain boundaries in charge transport using high resolution electron microscopy of the hierarchical nanostructure will be key. These models will provide feedback to design next generation materials and guide the synthetic efforts, validating this methodology.

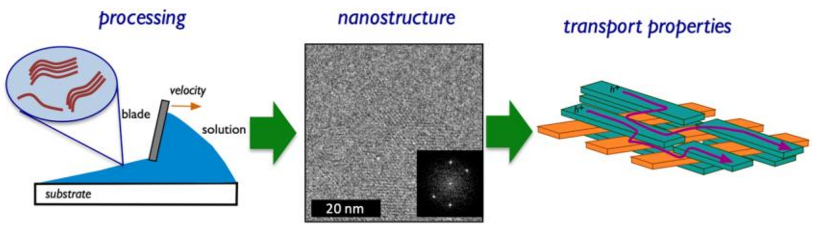

Figure 1. The charge transport properties of semiconducting polymers are controlled by nanostructured domains that sets the electronic coupling between polymer chains. Development of methods to predict how such structures arise from solution will lead to improvements in the design of new materials and processes for flexible electronic devices.

Relevance to MGI

Our research team has complementary expertise in computation (**Ganapathysubramanian**), physical characterization (**Chabinyc**), and synthesis (**Hawker**). We will accelerate our 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

The **Ganapathysubramanian**, **Chabinyc**, and **Hawker** groups have worked to define synthetic targets and structural information necessary to develop robust computational models that will allow coating processes to direct polymer assembly. To this end, we have designed and synthesized semiconducting polymers with unique structural building blocks and coupled these with experiments to determine best methods for measuring structures in solution to provide inputs for the predictive codes.

Hawker has designed and synthesized novel building blocks for control of hierarchical nanostructures in polymers that have unique steric and electronic properties. In one design, cyclic and acyclic sidechains were developed to control steric interactions in donor-acceptor polymers. Another key monomer developed is a versatile pentacyclic quinone building block, which can be obtained in a high yielding, one step process. These efficient synthetic methods are critical to allow us to produce libraries of polymers that will test computational models.

Chabinyc has studied the solution phase structure of several semiconducting polymers with varying backbone structure to determine the extent of aggregation using synchrotron small angle X-ray scattering (SAXS). The solution SAXS work provides the size and shape of aggregates a function of solvent composition, which will be used in computational models by **Ganapathysubramanian** to study solidification during coating process. Surprisingly we have found that very stiff chain polymers based on alkyl-substituted indacenodithiophene, a large conjugated repeat unit, do not show signs of aggregation in a variety of aromatic and non-aromatic solvents. These results have already influenced the choices of synthetic targets by **Hawker** for new polymers.

Ganapathysubramanian has worked on creating a massively parallel framework for modeling the solidification process which are defined by non-linear (Allen Cahn) equations. We have developed an adaptive methodology for the solution of general (linear and) non-linear time dependent problems that is especially tailored for massively parallel computations. The basic concept is to solve for large blocks of space-time unknowns instead of marching sequentially in time. The methodology is a combination of a computationally efficient implementation of a parallel-in-space-time finite element solver coupled with *a posteriori* space-time error estimates and a parallel mesh generator. We showcased this framework with applications involving linear, quasi-linear and non-linear diffusion equations and investigated how the coupled space-time refinement indicators for this class of problems affect spatial adaptivity. Finally, we showed excellent scaling behavior up to 150,000 processors on the Blue Waters machine.

Future Plans

Ganapathysubramanian will use experimental inputs defined by **Hawker** and **Chabinyc** to study solidification in semiconducting polymers from solvent using the framework described above. **Chabinyc** and **Ganapathysubramanian** are working to develop efficient analysis methods for high resolution transmission electronic microscopy images to study the nanostructures formed from solution and connecting them with transport properties.

Broader impact

The PIs on the project are training graduate student and post-doctoral researchers in MGI science under the award. Two female engineers are carrying out research on the project.

Data Management and Open Access

The **Ganapathysubramanian** group has a bitbucket page where all the software being developed is curated and stored. The PI’s will release the code in Fall/Winter 2015/16. **Chabinyc** is developing a means to disseminate X-ray and TEM structural data on polymers via the web.

Accelerating Materials Discovery & Development

Ganapathysubramanian has developed a methodology to reformulate the challenge of high throughput exploration during Process-Structure-Property analysis into the work flow of the MapReduce model in order to take advantage of advances in cloud computing with minimal specialized knowledge in High Performance Computing. The algorithmic details outlined in this work will serve as a template for the material science community to reformulate other high throughput materials science problems using the MapReduce paradigm.

Publications

None.

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

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

Project Scope

This research is focused on iterative design, processing, and characterization to gather the genomic data for material systems based on ternary Ti-B-X (X=Fe/Mo/Nb) compositions. Using computational calculations and the understanding of the phase stability, alloying, and solute partitioning of the X element between the metal and boride phases, a rich fundamental genomic material data will be created for Ti-B-X to simultaneously benefit material design in three material classes: metal-matrix composites, cermets and ceramics.

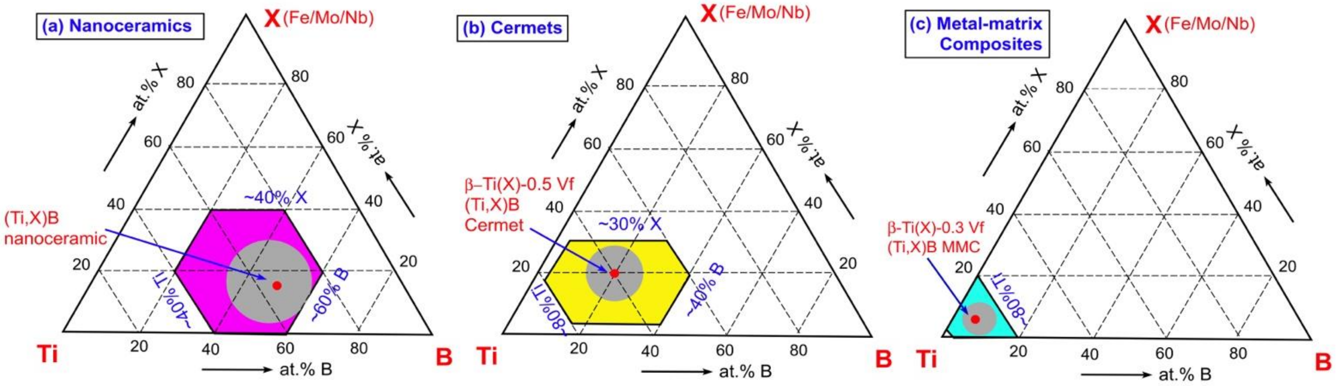


Figure 1. Compositions focused in the Ti-B-X system for material designs in three distinct material classes

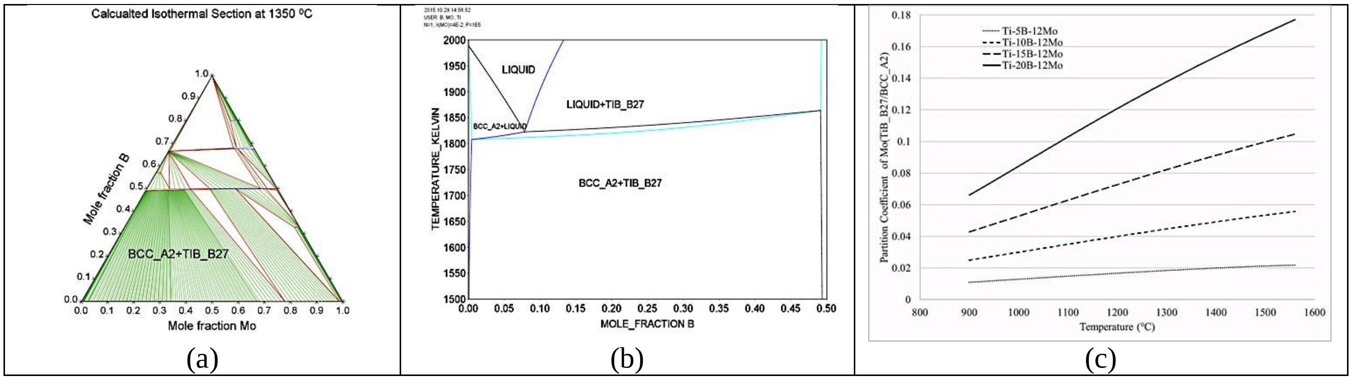
Relevance to MGI

The team is performing computational design, electric-field-activated synthesis, and application-specific characterization of three material classes (ceramic, cermet and metal-matrix composite (MMC)) emerging from the Ti-B-X system as a platform. The work is focused on core research themes 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 is progressing through material design, rapid synthesis, and standard and application-focused characterization to uncover the genome of this material system and to benchmark its properties against contemporary advanced materials.

Technical Progress

Progress is underway on three fronts: (i) initial composition selections for the Ti-B-Mo/Fe material classes are made by optimizing ternary phase diagram data and to identify regions for CALPHAD type calculations (ii) detailed evaluation of electric-field rapid processing system performance and (iii) discussions with the GOALI industry advisory panel. Composition domains for multiclass materials in Ti-B-X have been identified by synthesizing information of binary Ti-Mo/Fe systems and B-Fe/Mo systems. These are the focus points of CALPHAD calculations to establish phase domains and processing windows. A pulsed-DC electric-field-activated sintering unit has been designed and built in cooperation with GTAT, Santa Rosa, CA. The equipment was completed in summer 2015. Several material compositions are being processed and analyzed.

The computational design of the materials is progressing in two stages: (i) determination of various ternary Ti-B-Mo/Fe/V phase diagrams and (ii) identifications of stability domains of β-Ti+TiB based phases and processing conditions using these ternary phase diagrams. Calphad-based computational thermodynamics approach is being used for the first step, where lower order (i.e. binary) system descriptions are extrapolated to identify key compositions. Ternary interactions needed to improve ternary descriptions are obtained from these identified alloy compositions. For Ti-B-Fe, key compositions are identified and synthesis of these alloys is now underway. The optimized phase diagram information is stored in well-accepted .tdb format using the Thermo-Calc software. For the second step, isothermal sections (Figure 2(a)) at various temperatures have been determined and are used for compositional design. Vertical sections (Figure 2(b)) are used to find operating conditions i.e. temperature window for liquid phase sintering. Partitioning of solutes (Mo/Fe) between phases is being obtained from the thermodynamic modeling and optimization (Figure 2(c)).



(a) (b) (c)

Figure 2 Compositional Design of Ti-Mo-B system based MMC and element partition

Future Plans

This research is basing the Ti-B-Mo/Fe system as a platform for three material classes (Figure 1), each having a range of uses: (i) nanostructured ceramics based on (Ti,Mo/Fe)B rich compositions (volume fraction, $V_f > 0.98$ for hard boride phase) provide a locus for a new class of high-performance ceramics for wear-resistant bodies like ball/roller bearings, biomedical implants, nozzles etc., (ii) MMC compositions with low volume fractions of boride whiskers ($V_f \sim 0.1\text{-}0.3$) and with a large amount of tough, ductile phase show great potential to replace high strength steels (HSSs) for lightweight aerospace and automotive applications, (iii) compositions with intermediate boride content ($V_f \sim 0.6\text{-}0.9$) are essentially cermets competing with expensive WC-Co cermets.

The goal of this proposal is therefore to uncover the full genome of the Ti-B-Mo/Fe system while developing an iterative design approach that achieves increases in hardness, strength, wear resistance and toughness. We believe that: (i) the hardness and modulus of the binary boride phase, TiB, can be increased (Hv > 2500 kg/mm^2 and E > 500 GPa) by designing on the basis of ternary compositions, Ti-B-Mo/Fe, to form isostructural ternary borides (Ti,Mo/Fe)B; and (ii) the ductility and toughness of the Ti matrix can be engineered (>10% Elong.) by stabilizing the BCC beta phase by solid-solution formation in Ti by the same elements.

Broader impact

A. Advancing New Materials Design Data and Technology: First, in (Ti,X)B ceramics, the goal is to achieve high hardness of the dominant ($V_f \sim 0.98$) boride phase while also enhancing the ductility of residual titanium. Second, in MMCs, the ductility of the matrix beta-Ti will be enhanced to compete with HSSs. Third, the design of cermets with Ti(X) matrix and (Ti,X)B reinforcement phases fits naturally between the ceramics and MMCs.

B. Advancing Education Opportunities: The project supports one post-doctoral researcher, two graduate students at UofU and two at UIUC. At UIUC, PI Trinkle is engaged in training and developing high school science teachers to expand science education in the city.

C. Advancing Commercialization Opportunities: In the summer of 2015, the GOALI industry advisory panel met at the University of Utah. Potential commercialization opportunities were discussed. CoorsTek expressed an interest to develop a pressureless sintering process for the manufacture of titanium boride.

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 (hdl objects, in this case). This ensures that the data is publicly accessible.

Publications

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2. J. Du, A. P. Sanders and K. S. Ravi Chandran, “Synthesis of nano titanium boride at the lowest possible temperature,” **Scripta Materialia**, Submitted, December 2015.

Design and Synthesis of Novel Magnetic Materials

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Keywords: magnetic materials, genetic algorithms, pseudopotential-density functional theory

Project Scope

This collaborative research project implements new, transformative strategies for the design of novel magnetic materials, with special focus on sustainable materials containing earth-abundant and inexpensive elements. The project couples a strong *experimental effort* with recent *theoretical* advances in quantum modeling algorithms and software, data-mining techniques, and high-performance hardware to accomplish its objectives. Magnets play a crucial role in contemporary technologies, and this research focuses on the discovery of new Fe-Co-X phases with anisotropic structures, high magnetization, high Curie temperatures, high spin polarization and high magnetic anisotropy.

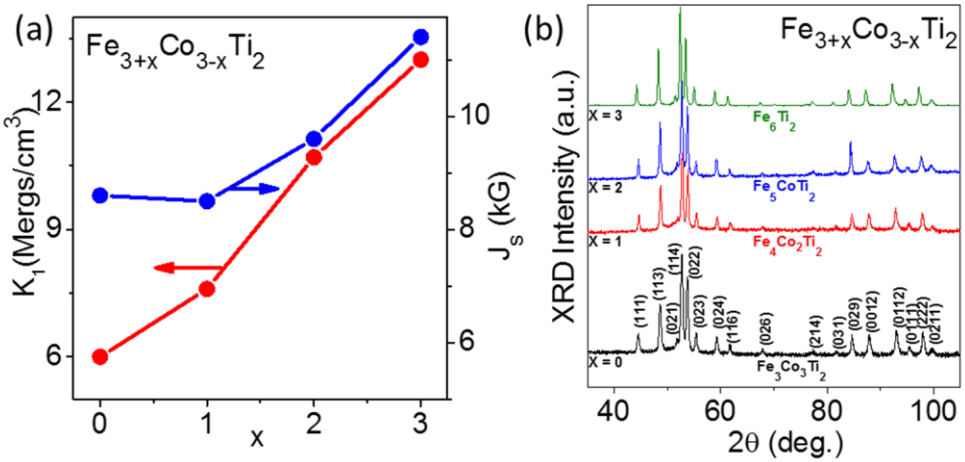

Figure 1. Properties of Fe_{3+x} $Co_{3-x}Ti_2$: (a) The measured K_1 and J_s at 10 K and (b) XRD patterns.

Relevance to MGI

The technical design and synthesis of new magnetic materials is a formidable problem, especially so given the myriads of possible combinations of composition and structure. This research uses computationally driven phase-diagram explorations and materials-structure prediction coupled with experiment to identify materials with desirable properties for magnetic applications. A new adaptive genetic algorithm coupled to first-principle codes is used for structure and property searches. The algorithm possesses the speed and efficiency of classical simulations, while maintaining the accuracy of quantum-based simulations. Concurrent, experimental research involves novel synthetic techniques and a comprehensive set of characterization methods.

Technical Progress

Initial work has been focused on improving the speed of the real-space pseudopotential *density-functional-theory* (DFT) code. In addition, we have obtained preliminary *adaptive genetic algorithm* (AGA) results on new metallic compounds of the form $Fe_3Co_3Nb_2$ and $Fe_3Co_3Ti_2$. Among our previously discovered $Fe_3Co_3X_2$ (X = Ti, Nb) compounds, $Fe_3Co_3Ti_2$ synthesized by rapid quenching exhibits appreciable magnetocrystalline anisotropy constant ($K_1 = 6$ Megs/cm^3) and saturation magnetic polarization ($J_s = 8.6$ kG) at 10 K and a high Curie temperature ($T_c \approx 550$ K). As shown in Fig. 1a, we have significantly improved K_1 (13 Megs/cm^3) and J_s (11.4 kG) by replacing Co with Fe in $Fe_{3+x}Co_{3-x}Ti_2$ alloys ($0 \leq x \leq 3$), which have potential as rare-earth-free permanent-magnet materials. $Fe_{3+x}Co_{3-x}X_2$ alloys form a crystal structure similar to that of $Fe_3Co_3Ti_2$ (hexagonal structure with a space group P-6m2) as revealed by the XRD patterns (Fig. 1b).

Using adaptive genetic algorithm (AGA), we performed crystal structure searches for Co_xN, with x=1, 2 … 8 up to 4 formula units per cell and have no constrains on the structure symmetries. Results of the formation energies from first-principles DFT-LDA calculations for the known phases and structures obtained from our AGA searches indicate it is possible for CoN, Co_2N, Co_3N and Co_4N to be synthesized in experiments because some structures from our AGA searches are energetically favorable. Moreover, first-principles calculations also indicate that some stable structures of Co_4N and Co_5N obtained from our AGA prediction exhibit very high magnetocrystalline anisotropy energy and reasonably high magnetic moment. We are in the process of further verifying these theoretical predations using other ab initio calculation packages. Experimental work at the University of Nebraska will focus on synthesis and characterization of these compounds to confirm the theoretical predictions.

Future Plans

We will perform computational phase-diagram exploration and materials-structure prediction to identify candidate chemical compositions and structures that have desirable properties for permanent-magnet applications. Structures of the nanoparticles and crystals will be predicted at the atomic level using a genetic algorithm with first-principles density functional calculations for the energy and properties evaluations. The first-principles *adaptive genetic algorithm* (AGA) developed at Iowa State University [1] will be used for structure searches. This AGA algorithm will be integrated with the real-space pseudopotential-density functional code, called PARSEC [2], developed at the University of Texas at Austin. This is expected to result in a highly efficient code for structural searches. Machine learning techniques will also be employed to study the correlations between the structures and the magnetic properties and to improve the AGA performance. Based on the low-energy structures obtained from the AGA search, we will employ cluster expansion techniques to expand the search for a larger number of atoms. The cluster expansion calculation will also be coupled with Monte Carlo simulations using the Wang-Landau algorithm for free-energy calculations in order to explore the alloy phase diagrams as the function of composition and temperature.

We are in the process of fabricating $Fe_{3+x}Co_{3-x}Ti_2$ nanoclusters ($0 \leq x \leq 3$), and additional high-anisotropy nanoclusters such as $CoFe_2C$ and Co_4N. The advantage of the cluster-deposition method is that the high-anisotropy building blocks can be combined with a high magnetization soft phase to form exchange-coupled nanostructured magnets with substantially improved permanent-magnet properties.

We will continue to perform adaptive genetic algorithm and first-principles calculations to predict the structures and magnetic properties of $Fe_{3+x}Co_{3-x}X_2$ ($0 < x < 3$, X=Ti, Nb), Fe-Co-C, and Fe-Co-N systems.

The groups at Iowa State and the University of Texas will develop algorithms and approaches to calculate the structures and magnetic properties of nanoparticles such as Co_3Nb and Co_4N. The theoretical results will be compared with the experimental ones from University of Nebraska-Lincoln.

Broader Impact

Our multicomponent broader-impact activities will center on the following efforts: (1) Graduate Education and Training, (2) Summer Intern Program, (3) Alice in Wonderland Program, (4) Nanocamp and STEM After-School Programs.

Data Management and Open Access

A notable aspect of our work will be to emphasize informatics and data-mining techniques as a means to elucidate important properties of magnetic materials and to analyze existing databases. In its simplest form data mining exploits underlying low-dimensional representations inherent in large data sets. Datasets that have many representatives of different types of objects are necessarily correlated and the correlations between different representatives can be exploited. For example, a question which can be answered by mining datasets of materials may be: Which compound is the most likely to have a certain property among a group? This can be guessed by establishing a distance between the compounds and then a neighborhood graph. We will apply machine learning techniques to search among Fe-based and Co-based binary alloys, those that have certain desirable characteristics. To do this we will exploit our computational codes for performing calculations to extract the features required for the analysis.

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2. W.Y. Zhang, P. Kharel, R. Skomski, V.R. Shah, X.Z. Li, and D.J. Sellmyer, “Structure and Magnetism and electron-transport properties of Mn_2CrGa-based nanomaterials,” AIP Advances, submitted.
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Exploring Multi-functional Molecular Electronic Materials

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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 (Wu, Zhang et al. 2013), 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

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.

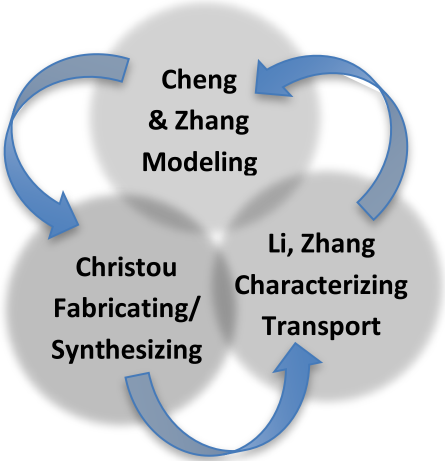

Fig.2 Team and tasks

Technical Progress

Two user projects, one theoretical on Quantum Monte-Carlo and one experimental on STM, at the Center for Nanophase Materials Sciences of the Oak Ridge National Lab are recently awarded to enhance our NSF-DMREF effort.

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} (Christou, Gatteschi et al. 2000, Christou 2005) 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. 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) 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.

Broader impact (Optional for DOE grants/FWPs)

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.

Accelerating Materials Discovery & Development

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.

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Publications

Collaboration to Accelerate the Discovery of New Alloys for Additive Manufacturing

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Keywords: Additive Manufacturing, Solidification, Microstructure, Viscoplastic properties, Data Science.

Project Scope

This project seeks to design a new β-titanium alloy that exploits the unusual characteristics of additive manufacturing (AM) using data-driven design. It integrates high-throughput combinatorial techniques, state-of-the-art materials characterization, computational methods, and data-science to: (1) discover and model the interrelationships between the alloy composition, the far-from equilibrium conditions of AM processes, and the resulting microstructure and properties; (2) describe key materials attributes using multi-dimensional, multi-spatial, and multi-spectral approaches; (3) determine hidden mechanisms between composition, structure, and properties using data science approaches; (4) validate mechanisms via computational modeling and critical experimentation; and (5) *design* a new material *for* AM.

Relevance to MGI

The activities of this multi-university project are intimately coupled. As the project seeks to provide *tools*, a series of "industrial dissemination" workshops will be held where companies focused on the implementation of AM will be informed of progress being made on the project, including both models, data, and materials discovery.

Technical Progress

This collaborative effort has made technical progress in the areas of selection, processing, characterization, and modeling. Regarding materials selection, a subset of binary titanium alloys has been identified that will vary fundamental thermophysical properties, including the enthalpies of mixing and fusion, as well as the undercooling parameter and growth restriction factors. These factors will allow us to vary the thermophysical properties in the same way that we vary the processing variables associated with additive manufacturing. In addition to the primary efforts focused on laser-based additive manufacturing, the team members are also exploring material deposited using different electron beam approaches to better inform the fundamentals of processing on the resulting microstructure. Of the binary systems that will be explored, the Ti-W, Ti-Fe, Ti-Mo, Ti-Mn, and Ti-Ni systems have been deposited and disseminated among the team members for subsequent analysis. All gradients have been characterized using scanning electron microscopy to begin to establish phase fractions at different isothermal holding conditions. Both the Ti-W and Ti-Fe systems have been characterized using far- and near-field high energy (synchrotron) X-ray diffraction microscopy (HEDM) to non-destructively characterize the as-deposited material, including preliminary assessments of the three-dimensional grain structures and elastic strain distributions. The Ti-Mn and Ti-Ni systems have been subjected to site-specific spherical indentation measurements and analysis protocols. During testing, a series of indentations were performed with 1 micron, 16 micron, 100 micron, and 1500 micron radii spherical indenter tips at specific locations. The material response is being analyzed to understand the effect of both composition and microstructure on the elastic and plastic response. In addition to these characterization techniques, a new precession electron diffraction study was undertaken to assess whether the crystallographic relationships, including any potential variant selection, could be determined on nanoscaled secondary α and athermal ω, which are beyond the scale resolvable using EBSD studies. The early results are promising. Regarding modeling, the efforts span techniques and length/time scales. COMSOL simulations under both inert atmosphere and vacuum have been performed to understand the role that various melt-pool physics might have on thermal gradients. The outputs, including the thermal gradients and some details regarding macro-level fluid flow are extracted from the COMSOL simulations and passed to a Lattice-Boltzmann (LB)/solidification method to accurately predict the solidification phenomenon. The LB method has been chosen because it gives the most complete control over coupling the physical phenomena (heat flow, fluid flow, diffusion, and solidification) during nucleation. To complement the process modeling, microstructure-property modeling focused on making statistically representative lamellar Ti microstructures that exhibit a range of morphologies and scales of the microstructural features. These synthetic microstructures are used in full-field micromechanical modeling to understand the links between microstructural features and the resulting mechanical response. These simulations are informed by concurrent efforts to understand the behavior of the constituent phases as discovered by the team under this project.

Future Plans

The team will: (1) deposit the full set of binary and ternary alloys as identified by their thermophysical properties; (2) disseminate the full set of alloys among the team members to characterize and inform the modeling activities; (3) establish a methodology to preliminarily integrate the macro-level multiphysics models afforded by COMSOL with the higher resolution L-B models being developed under the program; (4) reduce the existing synchrotron data and reconstructing 3D microstructures; (5) extract morphological data, strain data and orientation data on the various materials deposited under activity #1; (6) model microstructural evolution of the as-deposited microstructures under phase nucleation/grain growth/recrystallization using tools such as the Potts model and phase field model to understand how these materials respond to thermal treatments; (7) conduct accelerated material property measurements using spherical nanoindentation to develop single phase properties; (8) use data-driven approaches to establish processing-structure-property linkages; and (9) conduct viscoplastic modeling of the materials.

Broader impact

Critical to this project are the summer integration workshops and industrial dissemination workshops. The PIs conducted a summer meeting in 2015. In 2016, the summer meeting will involve the students. Initial dissemination to industry has been conducted during an existing NSF I/UCRC, with plans for an extra day devoted to disseminating information obtained in this program in 2016/2017. Students are communicating amongst the teams, and are currently holding telecons amongst the institutions.

Data Management and Open Access

As described above, establishing highly productive cross-disciplinary, distributed, collaborations is one of the core activities of this project. This project has built on ongoing efforts in Kalidindi's research group at designing, creating, and launching an open science collaboration platform called MATIN. A critical functionality that has guided the MATIN development thus far is the need to track and keep together all the data, codes, and discussions with connected (i.e., graphed) persistent identifiers, while keeping a low maintenance cost for the sustained operation of the collaboration platform. The digital recording of the code and data transformations that occur among the users of this collaboration platform provides rich new data that can be mined for best integration practices and workflows in all the endeavors (including research, education, outreach, and knowledge transfer).

References

None.

Publications

The first two papers have been submitted for review, and the first conference presentations were made in 2015. Multiple publications representing multiple groups are expected for 2016.

Helical Protein Assemblies by Design

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Co-Principal Investigator (Grigoryan): Departments of Computer Science and Biological Sciences, Dartmouth College, gevorg.grigoryan@gmail.com.
Keywords: Self-assembly, protein, peptides, designability, helical assembly

Project Scope

Molecular self-assembly is a fundamental principle of life, with cells having mastered this process to encode incredible diversity of function. Helical protein assemblies organize much of the intracellular and extracellular structure and direct all movement. The ability to emulate such functions by designing synthetic protein assemblies would transform modern molecular science, with far-reaching applications. This research will establish, validate, and make available to the community a novel framework for the targeted design of synthetic protein assemblies at atomic-level accuracy. This approach will merge significant advances in modeling and computational design with never-before-possible experimental techniques for structural determination at the atomic level.

Relevance to MGI

Currently, we are poised at a historical juncture in which rapid developments in genome sequencing, bioinformatic analysis, atomic resolution cryo-EM structural determination, and computational protein design, in combination with extant synthetic and analytical methods, presents an unprecedented opportunity to create protein-based supramolecular assemblies of precisely defined structure and controllable function. Computational methods will be employed to interrogate the protein structural database to identify designable interfaces within structurally robust protomers comprising tertiary motifs (TERMs) corresponding to stable secondary structure elements or entire folded protein domains. Suitable candidate sequences will be computationally optimized and synthesized using chemical or molecular genetic approaches. 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. Dramatic improvements in imaging hardware, reconstruction algorithms, and computational methods of structural refinement have provided rapid access to near-atomic resolution structures of native and synthetic helical assemblies, as we recently showed for a class of synthetic peptide assemblies.[1,2] These analyses will inform future rounds of computational modeling and design, thus establishing a dynamic feedback loop between theory and experiment.

Technical Progress

We have previously developed protein structure search algorithms that can estimate the natural designability of a given structural motif based on its abundance in the Protein Data Bank (PDB). Our approach towards the *de-novo* design of assemblies is based on the idea that any structure or interface can be decomposed into constituent local tertiary motifs (TERMs), such that the designability of the overall structure can be judged based on the designability of its component TERMs. Further, sequence statistics from structural matches for each TERM serve to identify features important to the formation of the motif. In fact, we have now shown that TERM statistics are indeed a reflection of underlying fundamental structure/sequence relationships.[3]

Our design procedure starts with the choice of a protomer structure, which can be an existing protein structure, a unit designed *de novo*, or even just an anchor motif around which to further organize the protomer. As a structural prototype, we focused on an assembly derived from a naturally abundant short α/β structural motif (Figure 1A). The next task is to find a helical (solenoid-like) assembly of protomer units to target in design. Such an assembly can be fully described with six parameters–helical radius (*R*), pitch (*P*), frequency (□), and three Euler angles defining the protomer's orientation in the helical reference frame (see Figure 1B). Each combination of parameters leads to specific lateral and axial interfaces—those between protomer units adjacent along the helical curve and along the solenoid axis, respectively (Figure 1B). So, applying our principle of designability, we can rapidly find the set of parameters that produce the most designable interfaces, by breaking each into its corresponding TERMs and describing their abundance individually (e.g., see Figure 1C). As a result, before the final protomer sequence is known (or, in cases of an anchor motif, even before the full protomer structure is complete), we can already build the most promising assembly topology to target in design. Applying this procedure to our initial α□β motif led to the geometry shown in Figure 1C. When the protomer is an incomplete anchor, as was the case with our α□β motif, additional structural elements or stabilizing loops are added at this point, guided by the constraint of making designable contacts with the existing assembly template (red regions in Figure 1C). Finally, once the assembly geometry is complete, computational sequence design proceeds using standard tools taking into account the positional amino-acid preferences emergent from TERM analysis of interfaces.

We have now also applied our procedure with a very different protomer—the structure of Maltose Binding Protein (MBP). The goal is to design an MBP variant that is stably folded as a monomer without maltose, and assembles into a solenoid upon binding sugar. For this purpose, both the monomeric and assembled states were considered, and a modified design procedure was implemented to find sequences whose specificity is modulated by sugar. The resulting assembled geometry is shown in Figure 1D. Experiments are currently underway to characterize designed sequences for both MBP and α□β-based assemblies.

Future Plans

Future plans encompass the following experimental aims in support of the hypothesis that the concept of designability of protein-protein interfaces can be employed as a mechanism to promote and control the association of small, folded protein motifs into helical assemblies of defined structure. **Specific Aim 1**: Prototypical structural motifs will be investigated as a designable scaffold for the construction of helical supramolecular assemblies in order to address the feasibility of this approach. Computational methods will be developed and validated using this motif as a test case. Synthetic assemblies will be subjected to cryo-EM analysis with direct electron detection to obtain high-resolution structures for comparison to computational model structures and permit further refinements of the algorithms. **Specific Aim 2**: The sequence space for computational design of helical assemblies will be more broadly addressed in terms of designable tertiary structures that are compatible with self-assembly using the protocols developed in Specific Aim 1. The structural differences between assemblies will be scored experimentally

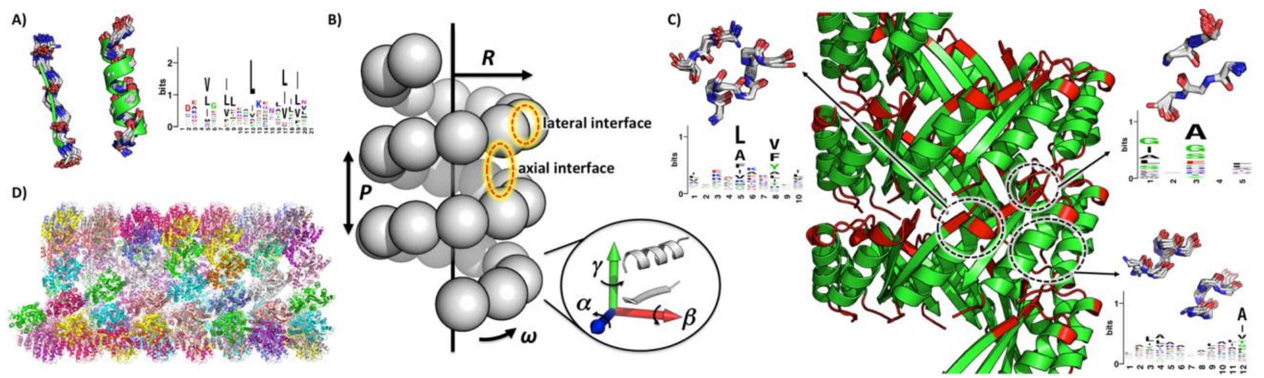

Figure 1. Computational design approach. A) The anchor motif for the α/β assembly (green cartoon) along with closely matching native representatives (gray sticks) and the sequence logo capturing native amino-acid preferences (right). B) Geometric parameters of a helical assembly. C) Design model of the α/β assembly for peptide **sol1** (red regions indicate additions to the α/β anchor motif made during the design process). Shown are three TERMs formed by various interfaces within the assembly (outlined with dashed circles) along with their native representatives (gray sticks) and resulting sequence logos. D) Designed helical assembly based on the ligand-bound form of MBP.

in terms of nanomechanical properties (persistence length, which is the flexural (i.e., bending) rigidity divided by kT), and will be compared to the values determined for protein assemblies in the literature and inform further rounds of computational design. **Specific Aim 3**: As a further test of our approach, we will develop computational methods for the design of heterodimeric systems in which two different protomers selectively interact with each other to form mixed rather than uniform assemblies.

Broader impact

Three core activities are proposed that will promote the broader impact of the scientific component of this research project. (1) An exchange program between the three academic institutions will be established that will permit students and postdoctorals to become involved in the different aspects of this research project. (2) A short (6-8 lecture) course will be constructed that focuses on design and structural characterization of protein-based assemblies with perspectives from across the chemical, and biological materials sciences. The three co-investigators would serve as lecturers in this course, each contributing 2-3 lectures of 50 minutes on topics related to their respective expertise. (3) We will create a presentation for the Atlanta Science Festival that relates scientific themes that form the focus of the proposed research to issues of broader, societal significance.

Data Management and Open Access

All published cryo-EM density maps will be deposited in the electron microscopy data bank and all published atomic models will be deposited in the protein data bank. Computational resources developed under these research activities (code, data files, structural models of design proteins) will be accessible on the Grigoryan lab website (http://grigoryanlab.org).

Accelerating Materials Discovery & Development

Structurally defined materials on the nanometer length-scale have been historically the most challenging to rationally construct and the most difficult to structurally analyze. Sequence-specific biomolecules, i.e., proteins and nucleic acids, have advantages as design elements for construction of these types of nano-scale materials in that correlations can be drawn between sequence and higher order structure, potentially affording ordered assemblies in which functional properties can be controlled through the progression of structural hierarchy encoded at the molecular level. DNA nanotechnology has evolved rapidly over the last decade due to the advantage that DNA interactions are “digital”, in the sense that the interface between oligonucleotides can be predicted from knowledge of sequence alone. In contrast, the rules that govern protein-protein interactions are more complex and difficult to predict, but may be more relatable to the interactions that govern the properties of most soft materials. The goal of the proposed research is the fabrication of a nanotechnological toolkit in which function can be encoded within archetypical protein assemblies on the basis of design principles derived from the structural models that we will develop.

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Constructing comprehensive models of hydrogen behavior at grain boundaries using high-throughput experiments

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Keywords: grain boundaries, hydrogen, high-throughput experiments, neutron radiography.

Project Scope

The goal of this project is to rapidly construct, analyze, and model an experimental database of hydrogen (H) solubility and diffusivity at thousands of individual grain boundaries (GBs) in nickel (Ni) and to determine how local GB plasticity affects these properties. This work will demonstrate the rapid extraction of detailed GB crystallography-processing- property relations from high-throughput experiments using limited computational resources. Many of the methods used to accomplish these goals are transferrable and may be applied to study GB-related behaviors in other settings, such as Li transport through battery electrodes or oxidation of GBs in steels.

Relevance to MGI

We combine novel methods for characterizing GB crystallographic character with state-of-the-art neutron reflectometry (NR) to investigate H behavior at numerous individual GBs. This data will be analyzed rapidly using automated image-processing methods, providing substantial coverage of the complete, five-dimensional space of GB crystallographic character. Based on this unique database, we will construct GB constitutive laws describing the behavior of H at GBs in Ni as a function of GB crystallography and local plastic deformation. These constitutive laws will be expressed in simple analytical form or as short scripts that easily run on a laptop. The physical mechanisms underlying GB H behavior will be inferred by relating trends in the experimental data to GB structure. This project addresses research priorities for structural materials identified in the MGI Strategic Plan [2], namely: *"Develop analytical tools for efficient extraction of process-structure-property linkages from large datasets that can be executed with desktop-scale computational resources."*

Technical Progress

We have applied for and received an allocation for conducting neutron reflectometry measurements at the BT2 thermal imaging instrument [3,4], which is operated as a user facility by the Radiation Physics Division of the Physical Measurement Laboratory at NIST. In our first set of experiments, we collected baseline neutron radiography data on commercially pure Ni samples provided by I. McCue and J. Erlebacher from John's Hopkins University. These samples were thermomechanically processed to contain large, through-thickness grains. We characterized all the GBs in this sample using a novel technique, termed "electron diffraction optical reflectance" (EDOR), which we pioneered in the previous award period of this project [1]. The preliminary results from this measurement are illustrated in Fig. 1.

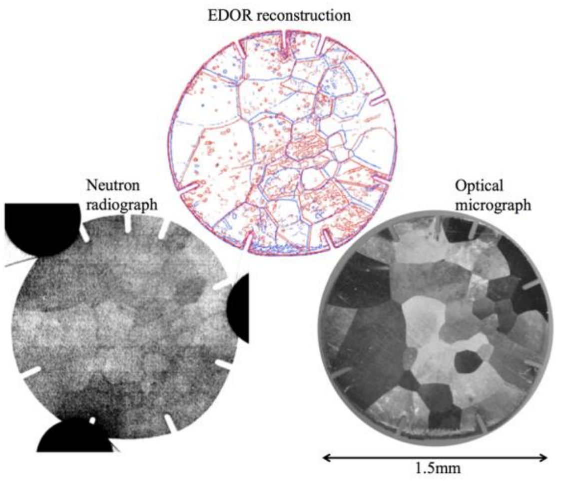

Fig. 1: Microstructure of a pure Ni sample with through thickness grains (bottom right); EDOR [1] reconstruction of the GB network in the sample (top); Neutron radiograph showing distinct signals from individual GBs and grains (bottom left).

Our initial investigations validate our approach for constructing databases of GB properties using high-throughput experiments. In particular, they demonstrate that we are able to fully characterize the complete crystallographic character of all the GBs in our samples using EDOR. This method integrates GB misorientations, determined using EBSD, with GB plane orientations, measured by correlating the locations of GB traces on opposite faces of samples with through thickness grains. Our investigations also demonstrate that our NR measurements are able to distinguish signals from individual GBs as well as from individual grains. We are currently investigating the source of these signals through detailed elemental analysis.

Future Plans

Our next step is to cathodically charge our Ni samples with H and conduct NR measurements to detect H at individual GBs. These measurements will be correlated to GB crystallographic character measured by EDOR. By collecting data for hundred or thousands of GBs, we will be able to begin constructing "crystallography-property" relations for H behavior at GBs.

Data Management and Open Access

The MATLAB scripts for EDOR have been submitted as Supplementary Information along with a manuscript describing the technique in detail [1]. Several groups at other institutions have already expressed interest in using EDOR and further developing it for their own particular interests. All neutron reflectometry data is being retained in accordance with the data management policy at NIST:

- https://www.ncnr.nist.gov/news/data_access_policy.html

Accelerating Materials Discovery & Development

Uptake of H leads to embrittlement in Ni-base alloys, causing a transition in fracture mode from transgranular ductile to intergranular brittle. The GB constitutive laws to be determined in this project will enable better predictions of H uptake and trapping to specific GBs in Ni-base alloys. This information will improve models of H-induced fracture in Ni-base alloys used in energy applications. It will also accelerate the development of HE-resistant Ni-base alloys through microstructure engineering.

The computational methods for constructing GB constitutive relations used in this project are transferrable to many applications beyond H at GBs in Ni. We will develop and disseminate these methods to the scientific community. Their potential future applications include detailed studies on H behavior in specific alloys of engineering interest or analogous investigations in other settings where GBs play a crucial role in material behavior (examples of which are given in BES basic research needs reports).

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DMREF: Collaborative Research: Designing and synthesizing nano-metallic materials with superior properties

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Keywords: nano-metallic material, flow localization, bicontinuous, design, synthesis

Project Scope

Our goal is to create nano-metallic materials (NMMs) that resist flow localization by engineering their architectures, interfaces/surfaces, and compositions via an iterative design process that integrates theory, modeling, and experiments. This project will impart to NMMs the ability to undergo large-scale, uniform plastic deformation, markedly advancing their potential for use in structural and functional applications. Our design strategy postulates a clear *performance metric* and identifies numerous *degrees of freedom* (DOFs), which define the design space. We will focus on NMMs with bi-continuous architectures, such as those in Fig. 1, because they offer a rich design space to explore.

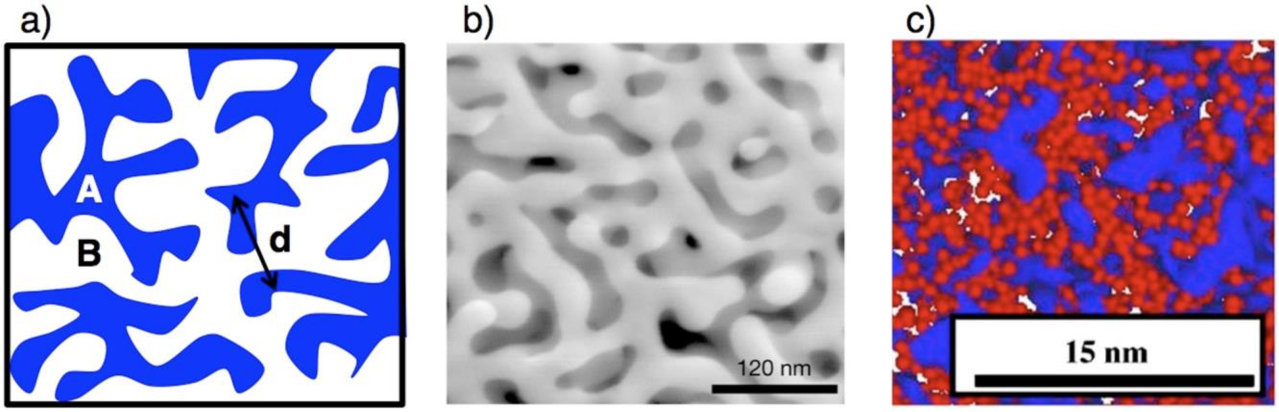

Fig. 1: Bicontinuous nano-metallic materials: a) schematic A-B composite with microstructural length d (d<100nm), b) nanoporous Au (A=Au, B=vacuum) [1], c) vapor co-deposited Cu-Nb (A=Cu, B=Nb) [2].

Relevance to MGI

Our *performance metric* is lack of flow localization in nanoindentation and micro-pillar compression experiments performed on the NMMs we design. It will be met through design over the following *DOFs*: surface and interface stresses, interface coherency or—for non-coherent interfaces—interfacial defect structure, interface shear resistance and susceptibility to slip transmission, ease of dislocation and twin nucleation, microstructural length scale, volume fraction of porosity or second phase, stiffness/hardness/hardening of second phase, interface curvature, and possibly many others.

The design space defined by these DOFs is so vast that it cannot be scanned by brute force experimentation or first principles modeling. To explore it comprehensively and efficiently, we will formulate reduced order models (ROMs) that relate DOFs to the performance metric using analytical expressions or short, fast algorithms. These ROMs will enable us to scan over multi-dimensional design spaces in reasonable time. To ensure reliability, they will also preserve the causal relations between DOFs and the performance metric, i.e. they must be based on the correct physical mechanisms. ROMs are also the primary link between successive iterations of our design process: after each iteration, we will revise our ROMs to reflect our increased understanding of the connections between our DOFs and the performance metric.

Technical Progress

This project will begin in January 2016.

Future Plans

Our work will follow an iterative "design-synthesize-test" cycle that scans the design space rapidly and integrates insights gained in each iteration by updating theoretical models connecting design parameters to performance metrics. The first iteration of this cycle will begin in January 2016.

Broader impact (Optional for DOE grants/FWPs)

This project will pursue several outreach objectives, including contributions to *MGI/ICME summer schools* organized at UM, *summer camps in materials design* for high school teachers, creation and dissemination of *educational web base modules*, *novel course development*, and participation in *summer camps for high school girls*. This project will also develop a diverse workforce *via* engagement and mentoring of undergraduate and graduate students as well as postdocs.

Data Management and Open Access

Our data management plan calls for the publication of analyzed data as supplementary information in scientific journals as well as for the retention of raw data for a minimum of five years and its open sharing upon request. Software and analysis codes to be developed through this project will be archived in publicly accessible repositories, such as NanoHub (nanoHUB.org): the NSF's Network for Computational Nanotechnology.

Accelerating Materials Discovery & Development

NMMs present significant advantages over conventional bulk metals, such as uniaxial strength above 2 GPa, fatigue and radiation resistance, and high strength-to-weight ratio. However, an impediment to widespread technological application of many NMMs is that they fail suddenly and with minimal uniform plastic deformation, almost as if they were brittle materials. In fact, most NMMs are inherently ductile and their apparent "brittle-like" failure is actually due to plastic flow localization. By designing NMMs that resist flow localization, the work proposed here will accelerate the transition of these materials from a research setting to commercial applications.

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Multifunctional Interface Materials by Design

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Keywords: Interfaces, Complex Oxides, Heterepitaxy

Project Scope

Our goal is to achieve an iterative cooperation between forefront theory and experiment that will determine the fundamental principles controlling new physical phenomena at oxide interfaces, and use these principles to design couplings between multiple orders at interfaces to generate new functionalities, and experimentally synthesize and investigate designed interfacial materials for novel electronic devices. Our theory team addresses the three required components. Our experimental feedback includes atomic-layer control synthesis, atomic-scale structural and spectroscopic characterization, and characterization of interfacial states.

Relevance to MGI

Controlling the interfacial orientation, atomic plane, and interfacial plane provides a landscape for new electronic phenomena in complex oxide heterostructures. Given the significant challenges, including synthesis, characterization, and unexplored atomic layer stacking sequences and bonding, this benefits from the MGI protocol of iterative feedback between theory, synthesis, and characterization. We have integrated iterative feedback loops in all stages of the research. The complex nature of multicomponent oxide materials and interfaces requires a first step of theory and modeling to identify promising directions. This includes first-principles calculations of electronic structure, phenomenological theory of structural properties and phase stability, and phase field modeling of mesoscopic properties. Synthesis is quite challenging, and incorporates feedback loops of in-situ RHEED, and ex-situ x-ray diffraction and scanning probe microscopy, basic evaluation of electrical and magnetic properties, and finally detailed experimental properties measurements, which directly feeds back to theory. Examples of particular systems are detailed in the next section.

Technical Progress

1. Emergence of Room-Temperature Ferroelectricity at Reduced Dimensions

The enhancement of the functional properties of materials at reduced dimensions is crucial for continuous advancements in nanoelectronic applications. Here, we report that the scale reduction leads to the emergence of an important functional property – ferroelectricity, challenging the long-standing notion that ferroelectricity is inevitably suppressed at the scale of a few nanometers. A combination of theoretical calculations, electrical measurements, and structural analyses provides tangible evidence of room-temperature ferroelectricity in strain-free epitaxial nanometer-thick films of otherwise non-ferroelectric $SrTiO_3$. It is shown that electrically-induced alignment of naturally existing polar nanoregions is responsible for the appearance of a stable net ferroelectric polarization in $SrTiO_3$ films. This

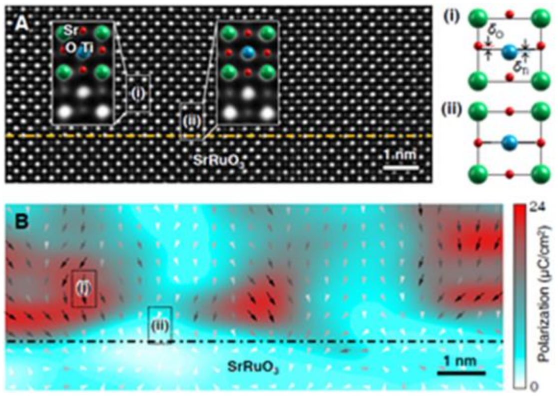

Figure 1. (**A**) Atomic-scale imaging of polar nanoregions showing the emergence of ferroelectricity in reduced dimensions predicted by theoretical calculations The (i) and (ii) regions are examples of polar and nonpolar regions, respectively, (**B**) Polarization vectors for each unit cell, estimated from atomic displacements in A.

finding can be useful for the development of low-dimensional material systems with enhanced functional properties relevant to emerging nanoelectronic devices. (see Figure 1 and reference 2)

2. Polar Metals by Geometric Design

We reported the discovery of new polar metal using a collaborative process involves the iterative feedback loop between theory and experiment. The tendency is for mutual exclusion of the two properties (polar and metal) in the same phase, which makes them quite interesting from a fundamental perspective and attractive for technology applications—if such materials can be found. We put forward a new design strategy of atomic scale control of inversion preserving displacements. We use thin film synthesis with atomic layer control to synthesize the materials, and explore the polar displacements by STEM, synchrotron XRD, optical and electrical measurements. We geometrically stabilize polar displacements in heteroepitaxial thin films grown on (111) $LaAlO_3$ substrates with geometrical constraints induced by the substrate. This approach will provide novel avenues for realizing new multifunctional materials with unusual coexisting properties. (see Figure 2 and reference 1)

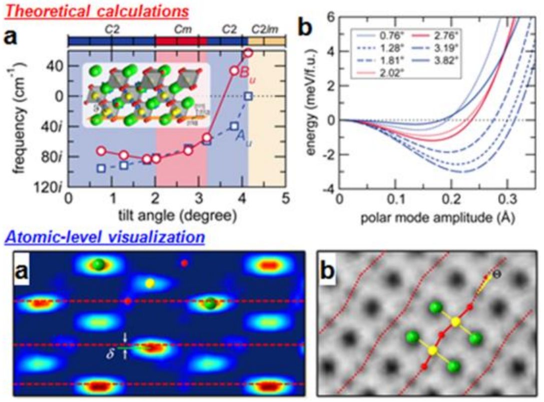

Figure 2. (Top) Geometric stabilization of polar $NdNiO_3$ via octahedral tilt engineering predicted by DFT calculations. (Bottom) The electron density maps and b, annular bright field (ABF) images in $NdNiO_3$ (111) thin films showing non-centrosymmetric A-site ions and suppression of octahedral tilting.

Future Plans

We plan to investigate several possible exciting applications of this new class of polar metals, in particular thermoelectric properties and polarization-dependent work functions. We also plan to investigate the giant longitudinal piezoelectric response of freestanding membranes of epitaxial PMN-PT relaxor ferroelectric film using an *in situ* TEM study and an *in situ* XRD study under an applied electric field. The deeper understanding of PMN-PT films and membranes obtained from this study will provide the firm knowledge base necessary for the future of microelectronic engineering.

Broader impact (Optional for DOE grants/FWPs)

The PI, Chang-Beom Eom, has been on sabbatical leave and appointed to the Peabody Visiting Professorship at the Department of Mechanical Engineering at MIT for the 2014 Spring Semester. He has developed and taught a new course “2.S997: Multifunctional Complex Oxide Materials by Design” at MIT with Prof. Alexie Kolpak, a faculty at the Department of Mechanical Engineering at MIT. The course syllabus is attached. The course covered the basic principles of bulk and heterostructure design, atomic and electronic structure/property prediction, atomic-layer controlled synthesis, atomic-scale structural and spectroscopic characterization, and the integrated theoretical/experimental development of design rules. A variety of specific device applications of novel multifunctional oxides will be discussed in detail. Eom has also participated in department research activities and develop new research collaborations with faculty at MIT.

Seven secondary school teachers from public and private schools in Puerto Rico came to Madison, WI for a summer workshop on communicating important ideas in materials physics to high school students. The workshop emphasized using technology in the classroom to communicate important aspects of materials, and included a visit to Bruker AXS, a world leader in materials analysis. Assisted by faculty and graduate students, teachers learned about and discussed basic ideas in materials design and analysis, then learned and used iPad software to develop interactive teaching modules, for both real-time interactive in-class use, and for off-line student use. Teachers presented their products on the last day of the workshop. Four UW-Madison graduate students (Aaron Wright, Alyssa Frey, Trevor Anderson, Chris Sundahl) mentored the teachers during the workshop.

Data Management and Open Access

Co-PI Chen's group has made significant progress in integrating research-level phase-field method based computer codes to a commercial software package. The package, namely μ-Pro® (http://www.ems.psu.edu/~chen/package/home.html), is to be released in 2016, and is expected to be the most efficient and the most multifunctional among all existing phase-field-method based software packages.

Accelerating Materials Discovery & Development

Sputtering is a common growth technique for many complex oxide materials but lacks the powerful *in situ* analysis techniques used to great advantage. We developed the integration of reflection high-energy electron diffraction (RHEED) into the sputtering environment and use it to study layer-by-layer growth of complex oxide heterostructures. This can be widely used to fabricate various multifunctional complex oxide heterointerfaces with atomic layer control. We filed the US patent application in 2015.

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Discovery and Design of Ferromagnetic Shape Memory Alloys by Quantum Mechanical Simulation and Experiment

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Keywords: Shape memory alloys, metamagnetic materials, magnetocaloric effect, phase transitions

Project Scope

This project seeks to accelerate the discovery of new ferromagnetic and metamagnetic shape memory alloys (SMAs) for use in solid-state cooling and refrigeration technology, through an approach that integrates theory, experiment, and high-throughput computation. Towards this end, we are (i) developing a computational infrastructure for high-throughput SMA search, (ii) validating the approach through experimental measurements, and (iii) applying this approach to a broad range of known crystalline materials and predicted compositions. The resulting database of experimental, computational, and structural results will be analyzed to reveal the underlying design strategies and principles, and the database will be made open to the community through a dedicated SMA materials design website.

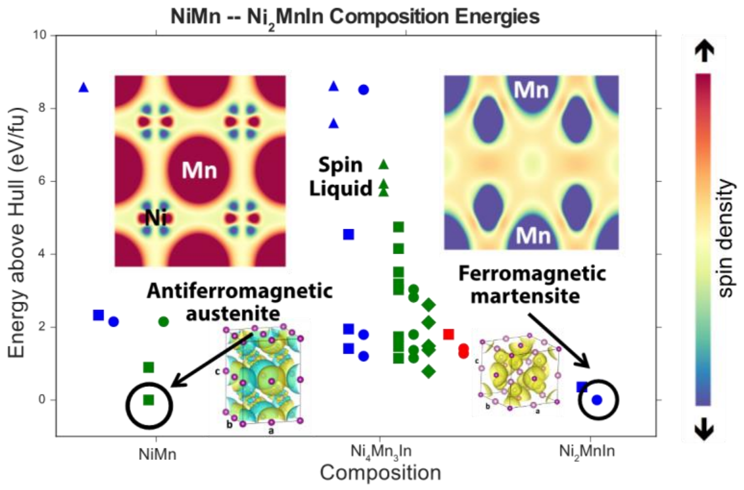

Figure. Composition-dependent total energies of Ni_2MnIn metamagnetic shape memory alloys for different spin configurations (ferromagnetic and antiferromagnetic and phases (austenite and martensite) according to first-principles electronic structure calculations and spin-lattice model. The spin-lattice model captures the existence of an intermediate composition spin liquid phase needed for high performance SMAs for applications in solid state cooling.

Relevance to MGI

Creation of SMA search and design strategies requires an iterative feedback loop between experimental measurements of the magnetocaloric response of crystalline materials and theory and computations. This necessity arises from the complex coupling between structure, composition, and magnetism in these materials. Our approach to overcome this challenge is to use first-principles computational results to provide input to a semi-empirical spin lattice model, which then can be used assess the magnetocaloric response. In the first year of the program, we have demonstrated the approach to several known magnetic shape memory alloys, and demonstrated a closed-loop cycle between experimental measurements and computational modeling of one particular class of SMAs, the Heusler systems which undergo martensite/austenite phase transitions.

Technical Progress

Our focus to date has been on building the infrastructure for high-throughput SMA candidate assessment. For this the main challenge is to reduce the dimension of complex parameter space to a smaller subset that is computationally tractable and predictive. Since SMAs exhibit a coupling between magnetism, lattice strain and deformation, composition, and temperature, capturing the essential physics with semi-empirical methods is challenging and requires development and assessment of effective physics-based models. Our approach to capturing the behavior is to carry out a parameter compression by mapping the response of the material onto an effective spin-lattice model which captures the interaction between the composition, the lattice strain, and the magnetism. The parameters of the spin lattice model are the crystalline magnetic exchange interactions (*i.e.* Heisenberg J) and their dependence on lattice strain, which can be readily calculated within standard density functional theory. As a preliminary validation of the approach, we have demonstrated its efficacy for two well-known Heusler shape memory systems (ferromagnetic Ni_2FeGa and and metamagnetic Ni_2MnIn), and in addition we have used it to predict the existence of ~4 new Heusler systems currently not reported in the ICSD. The figure illustrates the application of the model to $Ni_2Mn_{(2-x)}In_x$, spanning the composition range from x=0 to x=1. While properties such as SMA phase transition temperature and entropy changes upon phase transition are virtually inaccessible within the standard first-principles suite of tools (particularly for high-throughput search purposes), the spin lattice model gives us a direct, semi-empirical approach to estimating these quantities and assessing a candidate material.

Future Plans

The next stage of this program will be to implement the computational approach in a high-throughput manner, in order to scan the large phase space of Heusler SMAs, including compositional variations. The steps required to do this are (i) to automate the calculation of the parameters of the spin-model for different SMA compositions, (ii) to automate the for the calculation of phase transition temperature and entropy changes using a stochastic Monte Carlo approach, and (iii) to use the automated approach for SMA design, discovery, and assessment. A second primary future effort will focus on initiating the development of the online website and database that will serve as a public community forum and repository to share results on shape memory materials.

Broader impact (Optional for DOE grants/FWPs)

Our team is engaged in a large set of broader, educational activities that are aligned with the MGI philosophy. We have integrated aspects of this work into our courses, and we have developed hands on laboratory activities that demonstrate how shape memory alloys work, which we have used at summer camps that annually bring ~100s of high school students to the University of Illinois campus. At the team level, our program links several disciplines that historically have had limited interaction: the materials physics/magnetism community and the mechanical engineering community. Our team has also recently been invited to present these results at the 2016 International Conference on Plasticity, and we will be organizing a dedicated symposium at the 2017 Annual Meeting of The Minerals, Metals, and Materials Society (TMS) that focuses on the materials physics and materials informatics of shape memory alloys.

Data Management and Open Access

An objective of this program is to make all of our computational and experimental results accessible to the public, including data analysis and design tools. With the computational infrastructure now in place, we will initiate the process of developing an online website, www.shapememorydesign.org, and associated database that will enable users to import and export computational and experimental data for various classes of shape memory materials. Various analysis functionalities will be available through the website.

Accelerating Materials Discovery & Development

This program accelerates shape memory materials discovery, deployment, and design through the establishment of a validated infrastructure for rapid computational assessment of candidate materials. The infrastructure allows for rapid convergence on optimal material compositions in this large parameter space. Opportunities for commercialization are enhanced by knowing in which parts of compositional phase space to focus. Current challenges include the development of crystal growth techniques to synthesizing the predicted compositions so that their properties can be characterized through measurements in the laboratory.

Publications

1. Garrett J. Pataky, Elif Ertekin, and Huseyin Sehitoglu, *Elastocaloric cooling potential of NiTi, Ni2FeGa, and CoNiAl*, Acta Materialia **96**, 420-427 (2015).

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

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Website: http://www.chem.indiana.edu/DMREF
Keywords: molecular design • organic semiconductors • patterned nanostructures • 3D self-assembly • multiscale modeling

Project Scope

Our objective is to understand how atomic-level interactions drive the hierarchical assembly of molecular building blocks into patterned organic materials. We focus on mesoscale ordering of flat organic molecules onto graphite that are of interest as organic semiconductors, including bulk heterojunctions for organic photovoltaics. For CAD, Deductive Multiscale Simulator software will be developed and use Pade approximants and density field variables. We hypothesize that co-facial contacts between synthesized molecules direct 3D self-assembly and that edge-edge contacts code for 2D patterning. We expect to show ordering of molecules into heterojunctions composed of ~20-nm domains of p- and n-type materials.

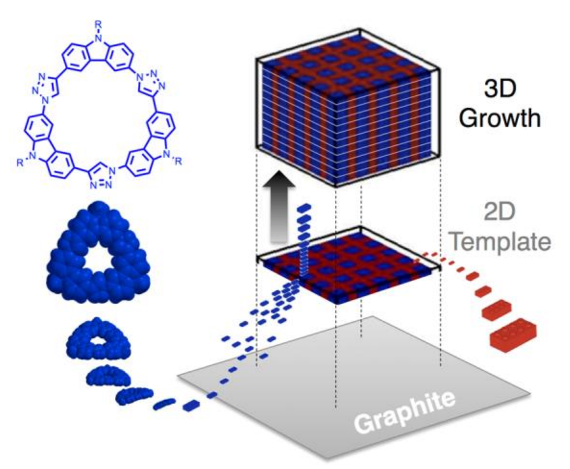

Figure 1. We will design molecular building blocks (blue and red) to self-assemble on graphite into programed 2D patterns that can grow into controlled 3D bulk heterojunctions.

Relevance to MGI

This project addresses the challenges of MGI by using an innovative multiscale modeling approach in close collaboration with expertise in organic design and synthesis and real-space surface characterization. The multiscale approach allows us to not only observe the long-range ordering and phase behavior of the organic self-assemblies in 2D and in 3D, but also to account for atomic-level interactions that allow detailed insight into the coding of the molecular building blocks. The atomic level theoretical description is introduced with interatomic and intermolecular force fields (FF). The atom description is correlated to atomic precision in organic building block design and synthesis and to submolecular-resolution scanning tunneling microscopy (STM) characterization of the assemblies. The characterization and simulation of long-range ordering will lead to insight related to the long-term goals of the project, and of the DMREF program, to develop functional materials properties based on rational design. Interaction between theory, synthesis, and characterization researchers occurs in weekly face-to-face meetings involving PI, Co-PIs, postdocs, and graduate student researchers.

Technical Progress

Since issuance of the award, we have published our first set of results describing the synthesis and the hierarchical self-assembly of tricarb macrocyclic molecules (*see* Figure 2A) in 2D (*see* Figure 2B) and in 3D (see the paper for details, 10.1002/chem.201503161). This was an early study in the project and so did not benefit from the multiscale modeling theory, but has been extremely useful in developing input to force field calculations and for designing further experiments. The high-resolution STM achieved in this study (Figure 2B, orange-tinted image) allowed us to characterize the lateral tricarb-tricarb contacts (inset to Figure 2B) in a detailed way. Correlation with DFT calculations provided insight into the atomic-level coding of close-contact interactions that drive the extended nanoscale structure. 3D packing was observed and attributed to partial pairing of dipoles (Figure 2A) between faces of the molecular building blocks.

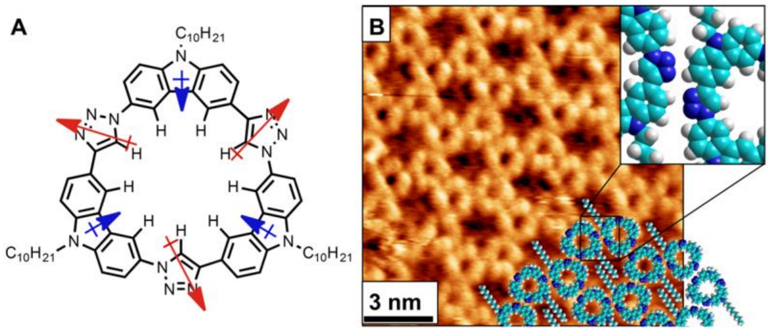

Figure 2. (A) Molecular structure of the tricarb macrocycle showing the dipoles helping to guide 3D assembly. (B) STM image, packing model and inset of nearest neighbor contacts that guide 2D patterning

Future Plans

Our plans are to deepen the integration between theory and experiment for the programmed molecular self-assembly and structuring of organic materials. We have one central goal – to understand and predict how atomic level details of a molecule direct its hierarchical assembly.

Initially, we are being guided by experimental results to test the accuracy of the FF-based simulations. We will then shift to a hypothesis-driven CAD approach. In these first steps, molecules are designed to enable us to learn the rules of self-assembly while expediting all components of the research. Ideally, designs should employ functional groups with reliable inter-molecular FF and molecular sizes to expedite simulations while the molecular syntheses should be facile, and self-assembly conditions should be amenable to STM imaging and sub-molecular resolutions.

As an example, alkoxybenzene was synthesized (Figure 3A) and self-assembed onto graphite. That self-assembled structure serves as a test of newly developed FFs and multiscale modeling codes. We have had some success in correlating experiment to simulation (Figure 3B cf. 3C) but further developments are needed. All team members participated in the new designs (Figure 3D) to provide a series of input to test and refine the FF, modeling, and our fundamental understanding.

Long-term, we expect to establish both the knowledge base and the simulation software to provide other researchers with the ability to conduct virtual experiments on how to design molecules to hierarchically assemble into a specific structure. We hope to provide a partial solution to the reverse design problem by allowing 2D patterning to be separated from 3D growth. Nevertheless, it does provide a platform for forward engineering of organic nanostructures.

We will showcase the approach by challenging ourselves to formulate a new n-type molecule that will self-assemble into a 3D hierarchically organized material.

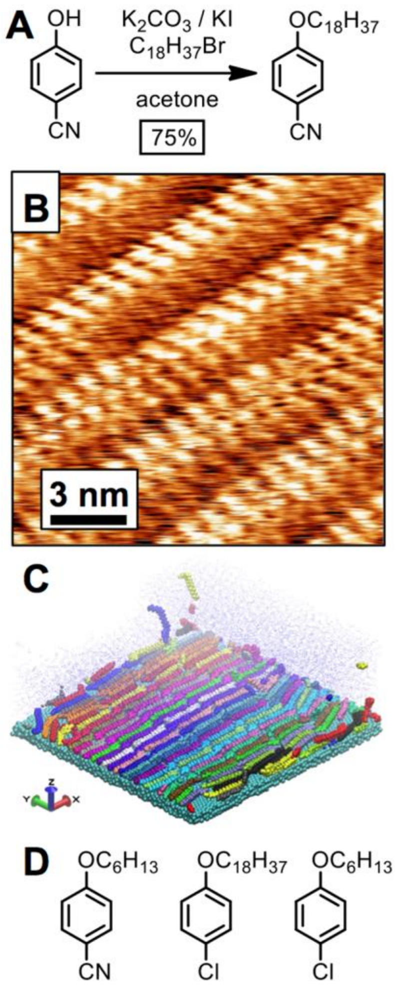

Figure 3. (A) Synthesis of alkoxybenzene, (B) STM image of their 2D patterning, and (C) MD simulation of their packing. (D) New set of molecules designed collaboratively with feedback between synthesis, imaging, and simulation.

Broader impact

We are implementing plans to impact communities outside of the immediate DMREF team. (1) We will organize a symposium on “Computer-aided design of hierarchical self-assembled materials” at the Fall 2018 American Chemical Society meeting. This symposium will promote the MGI philosophy to participants. (2) The multiscale software will be open-source and made available through nanoHUB for the scientific community. This will have immediate impact on other researchers in the field. (3) Outreach to high schools is planned for showcasing nanoscience with use of an educational atomic force microscope, related to our characterization approach. These efforts will involve graduate students. (4) The team will recruit under-represented groups to participate in research. We have already attended a graduate recruiting fair at the southeast / southwest combined regional ACS meeting in November 2015 to recruit students and promote diversity in graduate education and in our DMREF team. These efforts will continue to develop with other specific recruiting efforts and sponsorship of summer research visitors.

Data Management and Open Access

The output of this project, including data, codes, and structures, will be made available through the project website, nanoHUB, and peer-reviewed publications. We have recently published a first result from the project in *Chemistry – A European Journal* (DOI: 10.1002/chem.201503161). This publication includes a detailed description of the novel molecular synthesis of the macrocycle tricarb, as well as detailed structural characterization of the self-assembled 2D nanostructures. A new project website has been established at http://www.indiana.edu/dmref to provide a way to make research results and modeling codes publicly accessible.

Accelerating Materials Discovery & Development

The project will enable acceleration of materials discovery by augmenting the more time consuming experimental-based cycle of synthesis-characterization with a virtual cycle of CAD to narrow the design space from upwards of 100 molecules to just 10 or fewer. It should be possible to accomplish, at the end of the project and with the simulation software available, the 2-fold speed up of design and testing. Towards commercialization, we are planning to provide insights on how to control the structural ordering of possible organic photovoltaic systems. Thus, we must also overcome the hurdles associated with testing the optoelectronic properties prior to consideration of making this into a commercially relevant technology. While we have had no interactions with industry, we have been approached by CRANE Naval Base with possible interests in organic electronics. It is too early for patents, and follow-on funding from more applied sources and entrepreneurial activities.

Publications

1. S. Lee, B. E. Hirsch, Y. Liu, J. R. Dobscha, D. W. Burke, S. L. Tait, A. H. Flood, *Multifunctional Tricarbazolo Triazolophane Macrocycles: One-Pot Preparation, Anion Binding, and Hierarchical Self-Organization of Multilayers*, Chem. Eur. J. **21**, online (2015). **Back Cover Art | Hot Paper |** 10.1002/chem.201503161.

Synthesis of Colloidal Crystals Guided by Particle-Based Theory and Simulation

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Keywords: metamaterials, directed assembly, classical density functional theory, Monte Carlo, parallel tempering.

Project Scope

In this project we use a combination of theory, simulation, and experiment to discover and synthesize new crystalline metamaterials. Directed assembly of colloidal particles in suspension is employed to make the materials. Particle geometry and interparticle interaction are engineered to enable access to a wide variety of equilibrium crystal structures. New formulations of classical density functional theory (cDFT), embedded in an evolutionary structure-sampling algorithm, and parallel tempering Monte Carlo (PTMC) simulation are employed to guide the experiments. The final results of the project will be codes and heuristics that accelerate the development of metamaterials based on colloidal particle assembly.

Relevance to MGI

The three components of this program – theory, simulation, and experiment – are integrated on several levels. A unique feature of our project is the capability of Bevan's laboratory to precisely measure colloidal interaction potentials using advanced microscopy techniques; the potentials employed in the theory and simulations are therefore high-fidelity representations of real experimental systems. The theory and simulation efforts are also integrated. The PTMC simulations are used to improve and verify the accuracy of the cDFT tool at key locations in parameter space. Once the cDFT tool has reached a sufficient level of accuracy for a given interaction potential, it is used to map out thermodynamic phase diagrams over a broad range of potential parameter space, which in turn are used to guide the more computationally expensive simulations to the most interesting regions for further refinement. The phase diagrams based on theory and simulation then guide the most expensive and time-consuming task, which is experimentally realizing a target colloidal system and making crystals. Finally, experimental characterization of the crystal structures serves as a final check on the predictions of theory and simulation.

Technical Progress

For the theory component of the project, we have developed a new cDFT for the Yukawa potential (a common basic element of potentials used to model colloidal systems) using a perturbation theory based on fundamental measure theory and the pair correlation functions of the hard sphere system in the liquid and solid phases. This cDFT is based on previous work on Lennard-Jones systems [1]. We have made predictions of solid-fluid phase diagrams for single-component Yukawa systems that are significantly more accurate than previous perturbation theory. For the simulation component of the project, we have written a PTMC code with pressure as a tempering variable. This code will be used for structure discovery for model colloids with hard sphere type interactions. By simultaneously simulating the system over a range of pressures from low to high the method makes it possible to cross barriers separating local and global free energy minima. The code has been tested for hard spheres and is now being implemented in MPI to allow for the efficient sampling of large numbers of replicas. For the experimental component of the project, we have performed microscopy studies on several particle systems being studied in simulations, and for each of these systems, we have also matched pair potentials and MC simulations to experimental observations. The systems studied to date include binary sized particle mixtures, Janus particles in external fields, and anisotropic particles with connections to dumbbell shaped particles. These initial results can be matched to preliminary modeling studies in an iterative fashion to find systems in which models can predict assembled colloidal microstructures.

Future Plans

Our next steps in the theory are to (1) extend the cDFT tool to include mixtures, (2) compute phase diagrams for binary mixtures of Yukawa-type colloids that are asymmetric in charge and size, (3) embed the cDFT free energy computation engine in an evolutionary structure-sampling algorithm, and (4) improve the accuracy of the cDFT engine through comparison with simulation and experiment. Our next steps in the simulation are to (1) continue with our development of PTMC using pressure as a tempering variable, (2) extend the work to colloidal hard dumbbells and a study of solid-solid transitions, (3) develop codes for hard sphere mixtures and Yukawa mixtures and, using hyper parallel tempering MC (HPTMC), study replicas with different compositions and variations in interaction parameters such as the mixture size ratio, and (4) study Janus colloids and other systems with low coordination number, directionally specific interactions that can give rise to a multiplicity of non-close-packed crystalline lattices. Our next steps in the experiments are to (1) develop realistic colloidal potentials in experimental systems that match those being explored in modeling studies, (2) design experimental systems that enable tuning of potentials through systematic variations in static material parameters (e.g., systematic variations in van der Waals attraction via gold film thickness on Janus particles) or dynamically tunable properties (e.g., induced dipoles amplitudes involving polarizable materials in external electric fields or superparamagnetic materials in magnetic fields), and (3) explore dynamic pathways involving binary, Janus, and dumbbell colloids to achieve predicted low free energy configurations to avoid trivial dynamically arrested amorphous configurations.

Broader impact

Content on colloidal assembly has been added to graduate core and elective courses at both UMass and JHU. At JHU, a module from this research is being developed for incorporation into Bevan’s work with SABES (STEM Achievement in Baltimore Elementary Schools), a $7.4M 5-year NSF-funded project that aims to boost STEM education for elementary students in specific Baltimore City neighborhoods.

Data Management and Open Access

The codes in this project are still under development and the data are being used for benchmarking performance. Therefore we have not yet released any results into the community.

Accelerating Materials Discovery & Development

This project focuses on the cyber-enabled discovery and synthesis of new crystalline metamaterials by self-assembly of colloidal particles in suspension. Metamaterials have unique periodic structures that can be used to manipulate electromagnetic or mechanical energy. The results of the project will provide scientists and engineers with improved tools for identifying colloidal systems of interest, predicting stable crystalline structures, and guiding synthesis of the new materials.

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Publications

None yet.

Programmable Chemomechanical Materials

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Website: http://fraden.brandeis.edu/research/bz.html
Keywords: nonlinear dynamics, active matter, soft-robotics, responsive gels, chemical oscillators

Project Scope

The objective of this project is to develop purely synthetic, chemomechanical materials that emulate biological processes, such as the beating of a heart, at programmable rates and rhythms. The materials will operate autonomously, execute multiple functions and be externally triggered to modify their behavior. Two sub-systems, one for control and one for actuation, will be developed and integrated. The team of four investigators will synthesize new chemo-responsive gels, elucidate the mechanisms of operation through molecular-level characterization, model performance through theory and computer simulation, and engineer devices using microfluidics and 3D printing.

Relevance to MGI

We have divided our project into four main thrusts headed by four senior investigators (**bold**) and two collaborators (**blue**): (1) the synthesis of chemo-responsive hydro-gels (**Xu** and **Ye Zhang**), (2) fundamental studies into the structure of the gel (**Schmidt-Rohr, Zhang**), (3) continuum modeling the chemo-mechanical coupling between the gel and the oscillatory chemical reactions (namely the Belousov–Zhabotinsky (BZ) reaction) (**Irving Epstein**), and coarse grained microscopic simulation of gel behavior (**Hagan**) and (4) higher level engineering of networks, microfluidics, and control systems (**Fraden**). Our team is set up to proceed from fundamental investigations to applied systems in these areas in parallel so that insights gained in one branch can quickly be disseminated into the others. Naturally, in the course of building and testing devices, new phenomena will be encountered that will need a theoretical underpinning. Conversely, theoreticians in the group can help propose auxiliary experiments to test specific hypotheses as they are generated. If one considers the more than 60 year time lag between Turing's initial hypothesis of morphogenesis [1] and the experimental realization of the canonical system using the BZ emulsion [2], the advantages of theoreticians and experiments from classically disparate fields occupying the same lab is clear. Understanding and controlling non-linear and non-equilibrium reaction-diffusion dynamics is a fundamental challenge in many fields besides soft robotics, including condensed matter physics [3] [4], biology, chemistry, computation, ecology, engineering and medicine [5]. Our project thereby naturally contributes to, and is inspired by, many fields.

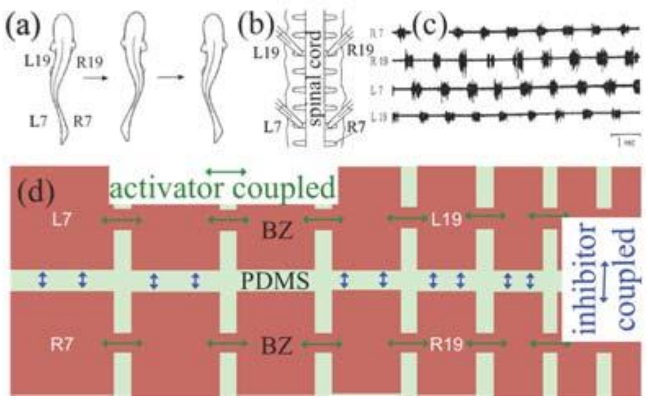

Fig. 1: Central pattern generator. (a) Waves of muscle contraction in swimming fish. (b) spinal cord with left and right paired neurons. (c). Time trace of neural firings for two pairs of neurons. (d) Our proposed schematic of implementation using the BZ system.

Technical Progress

Using emulsions and PDMS wells to house BZ reactor cells has allowed us to tune the transport between BZ regions and create systems that behave much differently than a non spatially structured BZ system. Namely, we can switch between activator and inhibitory-coupled wells by making small changes to geometry. These two limits have vastly different dynamical properties, which we plan to exploit in device design. In the former state, the system transmits chemical waves typical of the BZ system; in the latter, out of phase oscillations between neighboring cells occur. We've successfully created hexagonal and square arrays of PDMS wells with varying ratios of inhibitory to excitatory coupling, and are using this system to both quantify the coupling strength (which will be useful for higher level device design) and to more broadly understand how network structures give rise to different attractor states, which are identified by their spatiotemporal patterns.

Future Plans

We plan to address two fundamental challenges in the design of chemomechanical materials. The first is to understand and develop mechanisms of volume transitions in redox sensitive gels, by which forces can be actuated. Materials engineered from a selection of promising building blocks will be probed over length scales ranging from nanometers to millimeters in order to fully elucidate gel structure and dynamics. These findings will be fed into computer models, which will in turn inform the chemical synthesis of next-generation materials with desirable properties. The second challenge is to engineer a control mechanism comprised of the aforementioned array of micron-scale compartmentalized reactors that contain the BZ solution, and are physically networked via diffusion. The network exhibits externally selectable spatiotemporal patterns of chemical activity. The versatility of this control subsystem will be maximized by varying crucial properties of these reactors, including coupling strength and network topology, and employing feedback-based synchronization.

Coupling the control and actuation sub-systems will yield chemically responsive gels that can change volume in concert with predictable and tunable chemical activity. Such materials will have attributes heretofore found only in living matter, such as flexibility in mammalian tongues, pulsatile contractions in human intestines, and heliotropism in plants. Thus, this work will establish a new paradigm of precise and programmable chemomechanical control for the fledgling field of soft robotics. But one example of what is attainable with our proposed systems is shown in Fig. 1. By utilizing a combination of activator coupled PDMS wells (rows) and wells coupled through inhibitory dynamics (columns), one can emulate the basic functionality of a spinal cord. The schematic shown will be capable of manifesting a sinusoidal actuation pattern by alternately activating top and bottom gel groups attached to the wells.

Broader impact (Optional for DOE grants/FWPs)

Reaction-diffusion systems, oscillating chemical reactions, microfluidics, chemomechanical transduction, and engineering of soft machines are visually appealing phenomena, displaying fascinating behavior and involving elegant and sophisticated mathematical, physical, chemical and computational modeling. Research in these areas is broadly appealing and inspirational to young scientists, and will provide the training needed to begin a STEM career. Each year we will organize a team of 3-5 undergraduates with backgrounds from chemistry, physics and computer science to work together on this interdisciplinary research for a year-long project starting full-time in summer and culminating in their senior thesis. To increase diversity in the STEM fields, the Brandeis MRSEC has a partnership with Hampton University, a HBCU, through which Hampton undergraduates spend a summer at the Brandeis REU and continue research back at Hampton under the supervision of a Hampton professor. We will leverage that existing network to engage Hampton Prof. Samuel (Chem. Eng.) to host a team of Hampton undergraduates at Brandeis as part of the Brandeis REU. They will work together as a team with the other Brandeis undergrads during the summer, and after their return to Hampton, they will be supervised by Prof. Samuel. One possible undergraduate project will be constructing gelbots, inspired by fish, as in Fig. 1. Graduate education: A one-day, hands-on workshop given annually will be led by this project's 5 graduate and undergraduate student researchers to a target audience of other science graduate students at Brandeis. This interdisciplinary team of chemists and physicists, theorists and experimentalists will devise and lead hands-on exercises involving computer modeling and experiments in non-linear dynamics. Our philosophy is that teaching is an effective way to learn – for both the teacher and the student!

Data Management and Open Access

Given the early stage of the project, new experimental results have not yet been made available. However, provisions are in place to adhere to the data management policy required by the NSF.

Accelerating Materials Discovery & Development

The end goal of our project is to create materials with high levels of embodied intelligence and functionality. As with many microfluidics-based technologies, creating a stand-alone system that operates over long periods of time and without expensive peripherals is a challenge. The BZ-gel chemical system has two drawbacks. Firstly, the system only behaves predictably when it is consistently supplied with fresh reactants. Secondly, the gel that we functionalize to respond the BZ reaction degrades over time. As we develop our understanding of the proposed system, we plan to engineer ways of minimizing degradation of the polymer and maximizing the active life-time of the BZ cell-arrays; this will both enable longer term experiments and robustness for real world operation of soft devices.

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Computationally Driven Discovery and Engineering of Multiblock Polymer Nanostructures using Genetic Algorithms.

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Keywords: Block Polymers, Self-Assembly, Inverse Design, Global Optimization

Project Scope

We have accelerated the design and discovery of novel self-assembling nanoscale block polymer microphases. We tackled two computational problems that limit the rate of materials development: (i) the "forward problem" – given a polymer formulation, compute the most stable self-assembled nanostructure; and (ii) the "inverse problem" – given a target structure and properties, select the least complex polymer formulation that self-assembles into the target mesophase. Our program is combined with the development of sophisticated synthetic methods for new sequences of multiblock polymers and comprehensive characterization methods for complex phases. In addition, we developed an open-source computing platform for predicting particle-forming phases in block polymers.

Relevance to MGI

We tightly integrate three components: (i) a new computational approach for identification of thermodynamically stable phases of a specified block polymer formulation and formulation optimization; (ii) new synthetic strategies for fine control of composition, sequence, and architecture of multi-species, multi-block polymers; and (iii) advanced characterization of novel phases. In an iterative approach, the synthesis and characterization assist with refining free interaction parameters in the theoretical model, and the computational search identifies interesting synthetic targets in the high-dimensional phase space.

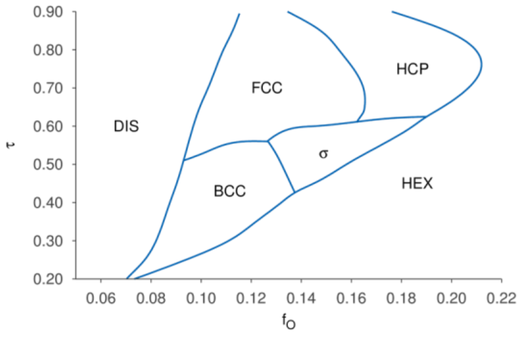

Figure 1. Phase diagram for poly(styrene)-poly(isoprene)-poly(styrene)-poly(ethylene oxide) tetrablock polymers as a function of the fraction of the PEO block (f_O) and the asymmetry (τ) between the polystyrene blocks for T=180C. DIS = disordered, BCC, FCC, HCP = conventional sphere packings, HEX = hexagonal cylinders, σ = Frank-Kasper σ phase.

Technical Progress

A major result in the past year is an iterative theory-experimental approach to the discovery of novel sphere forming phases in tetrablock terpolymer melts. In this part of the project, we started from a hypothesis that sphere-forming regions of the 7-dimensional phase diagram for a tetrablock terpolymer should produce complex phases due to small free-energy differences between candidate phases. By computing the region of stable body-centered cubic (BCC) relative to competing disordered and hexagonally packed cylinder phases, we defined a domain of synthetic interest for poly(styrene)-poly(isoprene)-poly(styrene)-poly(ethylene oxide) (SIS′O) as a function of the volume fraction of the O block and the asymmetry of the S blocks, $\tau = N_S'/(N_S' + N_S)$, where N_S is the degree of polymerization of the interior S block. We synthesized SIS′O polymers within the sphere-forming region of the predicted phase diagram, and indeed discovered a cornucopia of unexpected particle phases in addition to BCC. To explain these results, we returned to SCFT simulations, now matched to the precise experimental composition parameters (see Figure 1).

Theory predicts much of the phase diagram, including the Frank-Kasper σ phase and an A15 phase; we find that these two complex particle phases are very close in free energy, likely within uncertainty in the interaction parameters used in the model. This observation set up a subsequent round of experiments to determine if small changes in polymer composition can stabilize the σ or other phases, and to use observed phase transitions to refine model interaction parameters for improved theoretical predictions. Remarkably, nine distinct sphere-forming phases have been identified and this discovery has produced new concepts regarding access to equilibrium versus metastable states in multiblock copolymers.

We have made other significant advances in both theory and experiment. On the theory side, we developed two different methods for accelerating materials design and discovery. In the first, we addressed the forward problem by developing a real-space genetic algorithm as a global optimization wrapper around existing self-consistent field theory (SCFT) local optimization software. This method predicts, without guidance, the globally stable structure of a specified polymer formulation. To validate the method, we applied it to known phases in melts of diblock copolymers. The second method solves the inverse problem: predict polymer formulations to achieve a target morphology. To this end, we developed a Particle-Swarm Optimization (PSO) method that optimizes in the space of polymer formulation variables. We applied the method to the design of a multiblock polymer blends in thin films that self-assemble to target complex heterogeneous patterns. We also developed an approach that solves the commensurability problem for lattice models of block polymers. On the experimental side, we have been laying the foundation for further work, in addition to the major synthetic/characterization effort required for the SISO experiments described above. We developed a new method for solvent annealing of thin films of multiblock polymers that should prove critical to experimental realization of the pattern predictions arising from the PSO simulations. Likewise, we have made advances in synthesis of frustrated ABC block polymers, which are the "missing link" synthetically to realize simulation predictions for ABCA terpolymers. We have also developed a robust procedure to the preparation of ABCA' tetrablocks with arbitrary composition and asymmetry that combines multiple polymerization techniques and precision protection/deprotection schemes.

Future Plans

We have two major goals for the remaining 8 months of this project: (1) For the SISO system, we are now in position to develop a detailed understanding of the σ phase in tetrablock terpolymers. (2) We will implement an iterative refinement program for deducing model interaction parameters from observed structures. We will also finalize several manuscripts describing results in the Technical Progress and Data Management sections.

Broader impact (Optional for DOE grants/FWPs)

This project has supported, in part, four graduate students and two postdocs at Minnesota, and two graduate students and the PIs at UCSB. Importantly, the close connections between students in experiments and theory have fostered a MGI mentality within the project. This philosophy was most evident in the SISO phase diagram, requiring close connections between the entire team.

Data Management and Open Access

We implemented several improvements to the open-source polymer self-consistent field (PSCF) code, along with a "cookbook" routine that allows users with little experience with SCFT to generate phase diagrams similar to Figure 1. We envision this approach as "SCFT for the Masses" and will build and publicize a new website for dissemination.

Accelerating Materials Discovery & Development

The PSO approach identified above will be applied immediately to address difficult design problems in next-generation microelectronics patterning in collaboration with researchers from Intel, Samsung and SK Hynix, along with their chemical suppliers. The I,S,O multiblock materials targets in other parts of this project are to date primarily of scientific interest. However, the experimental and theoretical tools we have developed, and the collaborative workflows that we are continuing to improve, have clear potential to impact a range of industries from the development of advanced membranes to components of energy, medical, or photonic devices.

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Midwest Integrated Center for Computational Materials (MICCoM)

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Website: http://miccom-center.org/

Keywords: List up to 5 keywords. Do not use terms such as 'MGI', 'synthesis', or 'computation' that would apply to all projects.

Project Scope

The Midwest Integrated Center for Computational Materials (MICCoM) develops and disseminates interoperable open source software for quantum, classical, and particle-continuum simulations, as well as data and validation procedures, enabling the community to simulate and predict properties of functional materials for energy conversion processes. Emphasis is on interfaces, the transport across them, and the manipulation of matter under conditions far from equilibrium.

Relevance to MGI

The Center's design principle has been conceived under the premise that, in order to accelerate the discovery of innovative functional materials, it is not sufficient to compute the properties of the end product; it is critical to simulate and validate the assembly processes that occur during synthesis and fabrication. In addition, in order to design materials relevant to energy technologies, it is essential that the basic mass, charge, and energy transport phenomena involved in energy storage and conversion processes be understood. Most of these phenomena, e.g. electron transport, are inherently quantum mechanical and require a first-principles treatment. Others, such as ionic transport, occur at the molecular scale. It is therefore necessary that electronic-structure methods be coupled to appropriate dynamical descriptions of matter, thereby providing the means to capture all the relevant length and time scales of importance to a material's performance within simple, streamlined computational workflows. Acquiring the ability to predict transport and dynamical properties of heterogeneous materials across multiple length scales represents a paradigm shift for the materials science community. MICCoM will enable such a shift by adopting a multi-scale approach, linking quantum, classical, and continuum simulation codes (see Fig.1), together with integrated database and validation procedures.

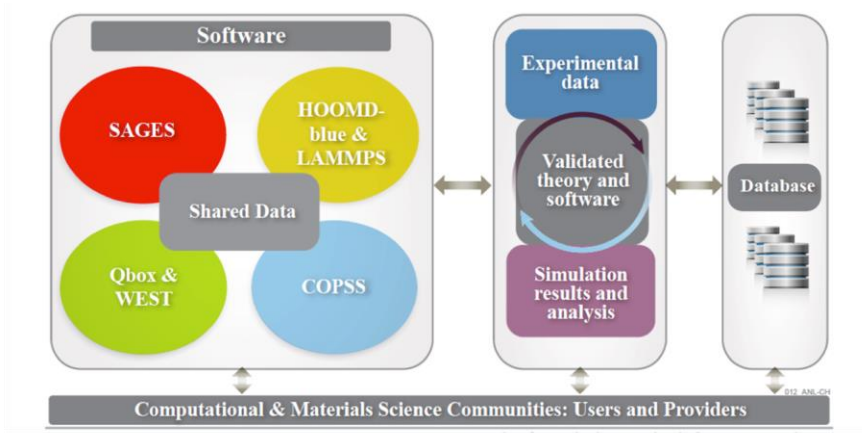

Figure 1. Summary of MICCoM gctivities and Goals. The four circles on the left represent the four main suites of codes that will be made interoperable.

Expected Technical Progress

The Center develops methods and delivers and maintains codes to compute transport coefficients from first principles, based on density-functional and many-body perturbation theory (Qbox: http://qboxcode.org/ and WEST http://www.west-code.org/codes), integrated within ab initio molecular dynamics simulations (Qbox); these coefficients will serve as inputs to continuum particle codes (COPSS suite of codes: http://ime-code.uchicago.edu/) that will predict the effect of applied fields on a material's structure and performance. Within a client server strategy, quantum (Qbox) and classical Molecular Dynamics (MD), and Monte Carlo codes (LAMMPS and HOOMD-blue) will be coupled and enhanced through a suite of advanced generalized-ensemble sampling techniques (SAGES), which will in turn operate in tandem with continuum codes. This approach will enable simulations of assembly processes of nano- or meso-building blocks of arbitrary shapes, with designer electronic properties. Importantly, through a marriage of forefront quantum MD, advanced sampling, and particle-continuum coupling, MICCoM will enable ab initio based calculations of the free energy of complex materials (and its derivatives with respect to field variables), both at equilibrium and far from equilibrium.

Future Plans

MICCoM will deliver computational tools for: (1) simulation of controlled assembly of designer building blocks of arbitrary shape, and with engineered functionalities, into nano- and meso-structured heterogeneous materials; (2) prediction of the thermal, mechanical, and transport properties of such materials, and (3) interpretation of experimental data in terms of well-defined atomistic and molecular processes. Such tools will be applied for the discovery of emergent properties for energy conversion and storage in complex, heterogeneous materials. The focus on transport properties is motivated by their central role in energy conversion processes. One of MICCoM's technical goals will be that of providing validated codes to simulate mass, electronic and thermal transport from first principles up to the continuum scale. Ab initio simulations will be performed on building blocks, where users will seek to identify electronic or dielectric properties, excited states, and electronic transport properties. Building blocks will include metallic and semiconducting nanoparticles. Coupled classical and quantum simulations will be used to describe the medium for assembly and, in particular, the interfaces that arise between medium, building blocks, and distinct phases. Coupled continuum-particle strategies will be used to describe the assembly of building blocks in specific media, at equilibrium or far from equilibrium, under applied external fields. Having arrived at desirable assemblies, MICCoM tools will also be able to describe dynamic processes, such as sintering of co-assembled blocks of different composition and shape into organized, heterogeneous structures. Similarly, MICCoM's software will describe annealing of multi-component melts in such a way as to lock in metastable, nanostructured features as the temperature is lowered, eventually forming solid matrices with embedded nanoparticles. In all cases, special emphasis will be placed on providing analysis tools, reference experimental data, and templates for interpretation of data aimed at unraveling the effects of solid-solid and solid-liquid interfaces on material properties.

Data Management and Open Access

MICCoM will develop a Materials Data Environment (MDE) to integrate and track all data and metadata associated with the interoperable codes developed within the Center. Researchers interested in using and/or developing codes, and/or using data will be able to access the MDE operated by MICCoM, or alternatively install their own MDE. In either case, they will be able to: (a) use validated data from experiment, theory and simulations, (b) run codes in higher-level ensemble or workflow patterns and (c) produce, store, and exchange data products that are described by trustable provenance and metadata. While codes and workflows will be runnable without an MDE, its use will enhance validation, replication, and dissemination. The MDE design will also allow users to add their own tools, for example to incorporate (and then share and track) specialized analysis methods.

Accelerating Materials Discovery & Development

Within the MGI strategy, it is essential that predictive computational tools be developed and deployed to design synthetic materials from specific building blocks while incorporating consideration of efficient assembly routes into the design process. The four elements that MICCoM's software and validation strategies will address include the objects or building blocks to be assembled, the medium for that assembly, the fields that one might apply to guide the assembly and the physical properties of the assembled material, with focus on transport processes.

Multiscale Theory and Experiment in Search for and Synthesis of Novel Nanostructured Phases in BCN Systems

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Co-Principle Investigator: Valery I. Levitas, vlevitas@iastate.edu; Aerospace Engineering, Iowa State U.

Co-Principle Investigator: Yanzhang Ma, Mechanical Engineering, Texas Tech University, y.ma@ttu.edu.

Keywords: BCN system, phase transformations, shear, multi-scale simulation, rotational diamond anvil cell.

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 theory and 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, using conditions to stabilize these high pressure phases for processing at ambient pressure. We start with known superhard phases of carbon, boron, boron nitride, cubic cBC_2N, B_4C, and use the theory to discover new compositions and phases for nanostructured composites expected to have dramatically improved properties.

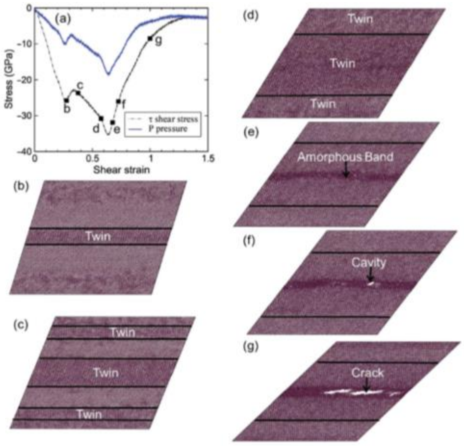


FIG. 1 QM derived ReaxFF Reactive Dynamics simulation of shear failure in boron carbide ceramic (unit cell has 216,000 atoms). This shows the successive processes of twinning, amorphous band formation, cavitation, and then failure. From ref. 1

Relevance to MGI

The methods we develop for *first-principles* based atomistic *reactive dynamics* simulations (millions of atoms for milliseconds) based on quantum mechanics (100s atoms for picoseconds) that we apply here to superhard ductile BCN ceramics will be important for many other MGI projects requiring QM accuracy for predictions and simulations of structures and mechanical properties on complex materials with realistic distributions of grain boundaries, defects, and impurities. The methods we develop for *continuum level* simulations at nano-, micro-, and macro-scales (based on parameters from the atomistic scale) to simulate processing conditions (sequence of pressure, shear, and temperature) to synthesize the predicted optimum system will be important in many other MGI projects to predict the conditions needed to synthesize predicted materials. The experimental techniques developed here using RDAC to combine large *plastic shear deformation* at high pressures and temperatures to synthesize new material polymorphs, atomistic simulations experimentally provides a new tool for experimental realization of MGI designs.

Technical Progress

***Atomistic modeling*—**To discover new superhard but ductile ceramics, we are scanning composition space for materials containing the B_{12} icosahedral cluster motif observed in superhard boron and boron carbides. The current materials are superhard but brittle, but we hope to find equally hard materials that are ductile. To simulate brittle failure requires ~200,000 atoms per cell for single grain systems and ~5 million atoms/cell for more realistic multigrain systems with typical distributions of defects and impurities. To carry out first principles based reactive dynamics simulations (RDS) on these systems, we developed the ReaxFF reactive force field based on QM RDS on cells with 100s of atom. Figure 1 shows the RDS of brittle failure in boron carbide using a periodic cell with 216,000 atoms.[1] This captures the processes for failure in ceramics. From these simulations we discovered that the fundamental mechanism involves reactions of the middle B in the CBC chain with a C-B inter-icosahedral bond that breaks during shear. [1] This opens up the icosahedron, leading to a higher density amorphous phase that induces tension that leads to cavitation, crack formation, and failure.[1]

Using these discoveries we searched for new compositions that would have 2- or 1-atom chains. We discovered a promising system, replacing the CBC chain with SiSi, which at the QM perfect crystal level is much more ductile.[2] We are now developing ReaxFF to test more realistic million atom per cell RDS. We are also using ReaxFF to test novel synthetic strategies to ensure that Si only connects between cages. As we explore new icosahedral compositions for hardness and ductility, we are also calculating band gaps and other electronic properties to identify other possible applications of the new compositions. In order to quickly and routinely obtain accurate band gaps we showed that the B3PW hybrid DFT method is best (0.2 eV accuracy,[3] Fig. 2)

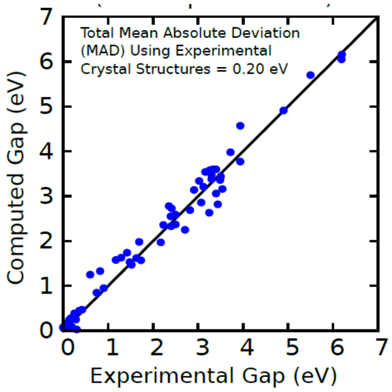
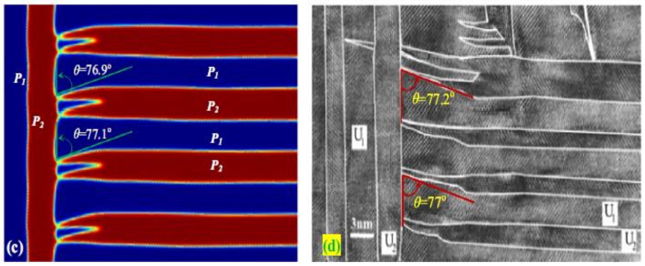


Figure 2: B3PW hybrid DFT band gaps versus low-temperature experiment for 61 materials.
Mean absolute deviation (MAD) in eV from experiment: 0.20 (B3PW), 0.36 (GW), 1.09 (PBE). Compared to PBE (VASP) the costs are 1.1 for B3PW (CRYSTAL), >100 for GW. Ref. 3

- ***Continuum modeling*—**We developed new phase field approaches for stress-induced phase transformations between *any number of* phases. This describes each phase transformations with a single order parameter with no explicit constraint equation, which allows analytical solution to calibrate each interface energy, width, and mobility. This reproduces desired phase transformation criteria via instability conditions; introduces interface stresses, and allows for a controlling presence of the third phase at the interface between the two other phases. We developed a finite-element method (FEM) to predict nanostructure formation for multivariant martensitic transformations. Results are in a quantitative agreement with the experiments (Fig. 3).
- We developed a comprehensive phase field theory (and FEM algorithms) with specific models for coupled phase transformation and dislocation evolution at large strains. We performed extensive studies of their mutual effect and derived simple phase equilibrium conditions at the phase interfaces and for the entire samples.
- We developed large strain theory to describe plastic flow and simplified the theory for plastic strain-induced phase transformations under high pressure at the macroscale (also using FEM). These methods were applied to modeling plastic flow and strain-induced phase transformations in traditional and rotational diamond anvil cell under high pressure and large plastic shear, allowing various experimental phenomena to be interpreted.
- ***Experiments***--We performed RDAC experiments on such materials as graphite, C_{60}, lead and $B_{12}As_2$. Findings include: (1) Formation of a new polymeric amorphous C60 phase at ~10 GPa. It has increased sp^3 bonding, leading to a superhard material quenchable to ambient conditions. (2) Transformation of graphite to lonsdaleite (hexagonal diamond) and then to a diamond-like amorphous phase as the pressure increases continuously to 6.9 GPa. The quenched amorphous phase has increased sp^3/sp^2 ratio, leading to a super hard phase. (3) application of large plastic shear to soft solids like lead can regenerate homogenous pressure by shear, making them good pressure transmitting media for shear.

Figure 3. Stationary solution for two-variant martensitic nanostructure exhibiting bending and splitting martensitic tips based on the new multiphase phase field theory (left) compared with experimental (from Boullay et al. 2001) (right)



- **Future Plans**
- Atomistic methods: (a) **Near term**: large scale (millions of atoms) long time (milliseconds) reactive dynamics simulations (using ReaxFF) of predicted $(B_{11}C)Si_2$ and $(B_{10}C_2)Si_2$ sytems to validate the superb ductile and hardness predicted by QM. Simulate the synthetic strategies for forming the desired composition (cage vs. chain). (b) **Longer term**: extend the search over the periodic table of possible chain compositions for high hardness and ductility. (c) Predict band gap and other properties for these new compositions to identify promising compositions for other properties.

- Continuum methods (a) advance our three-scale continuum theory for plastic strain-induced phase transformations under high pressure and utilize it to model synthesis of amorphous and nanocrystalline superhard phases for BCN based systems in RDAC (b) search for ways to control Pressure Transitions and (c) to seek for new phases.
- Experiments: To perform strain-induced synthesis experiments in RDAC with in situ diagnostics to realize the optimal pressure-shear loading path predicted from the multiscale simulations.
- Combined: To iteratively couple modeling at each scale and experiments to improve models and identify material parameters, 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

The methods for large scale atomistic simulations (millions of atoms for milliseconds) and for multiple time scale continuum simulations of phase transformation and coupling this with RDAC experiments will likely impact the MGI developments of new and improved materials for energy, environment, water, sustainability. More specifically Superhard but ductile materials have numerous applications in cutting, polishing, and drilling tools for various industries (including the oil industry) and as components of composite materials. Synthesizing new superhard materials stable at ambient conditions may revolutionize these fields. Our incorporation of the theory, computational, and experimental methods into the materials science and chemical engineering curriculum (both undergraduate and graduate) will rapidly advance this new expertise into the science and engineering communities. One graduate student, 2 post docs, and 2 undergraduate students will receive training on Multi-paradigm simulations and experiments. Special programs at Caltech, ISU, and TTU are being used to attract students from under-represented groups. Results are being disseminated broadly via seminars, workshops, conferences, and short courses.

Data Management and Open Access

All data will be published in public journals and proceedings. After publication, the copyright is granted to the publisher and the data can be accessed by the public for non-commercial purposes. The data can also be shared in collaborations with the data creators. The data user can access the information through published journal without of charge for data access. The long term maintenance and preservation of the database also rests with the journal, which has the safeguards and the longest-term-storage capability.

The metadata will be stored and displayed through the Texas Tech University website. The metadata will include the experimental data, the data analysis, and the conclusive points along with the references to the journal where the data is published. The metadata will be updated within 3 months of obtaining new data. We will store the data for 3 years.

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Design of Multifunctional Catalytic Interfaces from First Principles

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Keywords: 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 the development of quantitative reactivity predictions and, ultimately, genome-based catalyst screening.

Relevance to MGI

The effort focuses on developing 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. We are developing detailed computational models of these interfaces, with a goal of generalizing these models to identify fundamental descriptors suitable for rapid computational screening of catalytic materials. Experimental synthesis, characterization, and kinetic measurements also form a central, indispensable part of the project and are tightly coupled to the modeling efforts. Multiple synthesis strategies are employed, including incipient wetness, coprecipitation, colloidal deposition, and organic solution synthesis, and the resulting catalysts are characterized with HRTEM and STEM and rigorously tested to elucidate accurate reaction orders and activation barriers for water-gas shift and related chemistries. The data to emerge from these efforts inform our computational models, and the computational analyses, in turn, suggest alternative catalyst formulations to explore.

Technical Progress

Catalyst study and design efforts over the past year have been focused on the water-gas shift (WGS) reaction, a model chemistry involving conversion of CO and H_2O to CO_2 and H_2 that plays a central role in catalytic processes ranging from reforming to biomass conversion. Two case studies from the past year's efforts follow.

1. *WGS catalysis on platinum alloys*. Synthesis of a series of approximately ten binary platinum alloys by incipient wetness techniques, and correlation of the measured kinetics on these samples with the results of DFT calculations, has led to the identification of the adsorption energy of OH, a key intermediate in most WGS mechanisms, as one of the reaction descriptors. The experiments and modeling further suggest that a bifunctional mechanism is operative for Pt alloys that expose more oxophilic heteroatoms on the surface, and this correlation of experimentally measured rates and theory-determined descriptors may serve as a basis for further screening studies of Pt-based alloys for WGS activity.

To further explore the effect of metal/oxide interfaces on WGS chemistry in Pt alloys, a series of PtCo bimetallic catalysts were prepared. The WGS rate at 300°C could be promoted by a factor of nine with cobalt at a Pt:Co ratio of 1:3. Leaching of the catalyst selectively removed surface CoO_x's while preserving a metallic PtCo alloy core (Figure). The WGS kinetics of the leached catalysts were about 2.5 times lower than the monometallic Pt sample but were similar to the kinetics on a homogeneous Pt_3Co catalyst, demonstrating that the interface between the PtCo particles and the CoO_x phases promotes WGS. Analogous results have been obtained by depositing thin Na oxide films on the surfaces of CNT-supported Pt nanoparticles; the resulting structure promotes WGS by a factor of 25 compared to pure Pt nanoparticles.

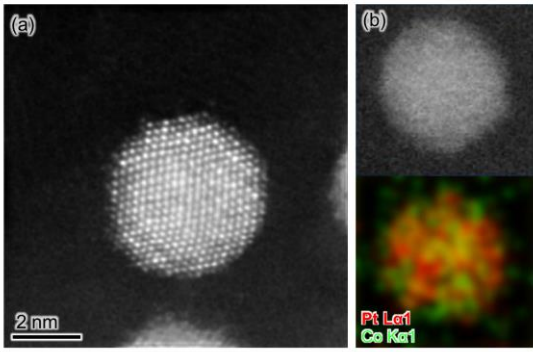

Figure. Pt-Co nanoparticles after leaching. (a) STEM images, and (b) XEDS map.

2. *Au nanoparticles on oxide supports.* We have developed and extensively explored a computational model of MgO-supported Au nanowires. The combined DFT/microkinetic model shows excellent agreement of calculated and activation barriers and reaction orders with detailed kinetic experiments. The model has further demonstrated that the adsorption energies of both CO and OH at the Au/MgO interface are crucial descriptors for the reaction rate. The work has also explored the effect of doping the MgO substrates on the reactivity of the Au/oxide interface. Exciting preliminary results suggest that scaling relationships, previously established in simple metal and oxide surfaces, also exist at the doped Au/oxide interfaces and relate binding energies of key WGS intermediates to the binding energies of hydroxyl groups at the interface. These relationships, which can provide a large reduction in the independent parameter space needed to fully describe the kinetics and ultimately screen for enhanced catalysts.

Future Plans

We will continue to pursue our coupled theoretical/experimental effort in WGS studies on Pt alloys and oxide-supported Au nanoparticles. The computational effort will focus on refinement of metal/oxide interface models via comparison to TEM and kinetic measurements. We will also begin combinatorial screening by systematic modification of the interfacial structures through doping and binary alloying. Promising candidates to emerge from this analysis will be synthesized and tested experimentally. Experimental efforts will involve further development of promising heterodimer-based synthesis strategies, combinatorial experimental screening of metal/oxide systems for WGS activity, and further development of aberration-corrected TEM for atomic resolution of catalyst interfaces.

Broader impact (Optional for DOE grants/FWPs)

Multiple graduate students are being trained in state-of-the-art computational, theoretical, characterization (TEM), and kinetic techniques. The PIs are additionally making sustained and significant investments in the intellectual development of a targeted number of economically disadvantaged high school students to encourage them to pursue STEM in college. In summer of 2015, the PIs hosted multiple such students as summer interns for a period of two months each. The projects were very successful; one of the interns is continuing research during her senior year of high school. Additional community-level outreach, in the form of weekly visits to local high schools, is taking place at the co-PI's institution (JHU), while Purdue PIs organized and facilitated a day-long, catalysis-themed workshop for 16 talented high school students in central Indiana in June 2015. The students were exposed to state-of-the-art catalyst theory and participated in hands-on experiments for fuel cell and TEM operation.

Data Management and Open Access

The project generates both electronic and print data which integrate experimental studies and molecular simulations. Publication in the peer-reviewed literature provides the primary means of disseminating and archiving the primary products of the research, including all laboratory and computational procedures, results, and analyses of those results. After publication, the results will be incorporated into growing online databases.

Accelerating Materials Discovery & Development

The integration of molecular modeling, STEM/TEM characterization, kinetic measurements, and advanced synthetic strategies is accelerating identification of catalytic descriptors at metal/oxide interfaces, providing a theoretical framework for design of multifunctional catalysts that promote chemistries such as water-gas shift.

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High-Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling

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Co-Principal Investigator: Giulia Galli, Institute for Molecular Engineering, University of Chicago, gagalli@uchicago.edu
Co-Principal Investigator: Eric Schwegler, Lawrence Livermore National Laboratory, schwegler1@llnl.gov

Keywords: first-principles, ab initio, electronic structure, molecular dynamics, density functional theory.

Project Scope

This project aims to develop scalable, high-performance software for First-Principles Molecular Dynamics (FPMD) simulations, and use it in investigations of materials relevant to energy conversion processes. FPMD simulations combine a quantum-mechanical description of electronic structure with the statistical description provided by molecular dynamics (MD) simulations. New algorithms are developed to improve the efficiency of simulations on large parallel computers, and to enable the computation of spectroscopic properties (Raman and infrared spectra. The software is used in investigations of aqueous solutions and liquid/solid interfaces relevant to photo-electrochemical cells. The algorithms are implemented in the Qbox code, distributed under a GPL open-source license.

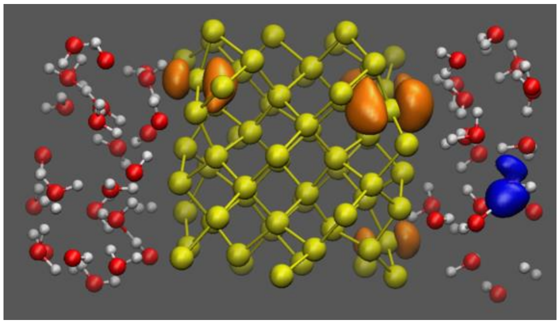

Figure 1. Model of a silicon/water interface showing isosurfaces of extended (gold) and localized (blue) electronic orbitals. The methods developed in this project allow for efficient computation of hybrid-DFT electronic structure in complex interfaces in which orbital localization varies.

Relevance to MGI

First-principles simulations allow for investigations of the electronic properties of materials in realistic conditions (e.g. finite temperature, or presence of defects). The approximations used in the simulations (i.e. the level of description of exchange and correlation in electronic structure) are validated by comparing predicted structural properties (e.g. pair correlation functions in liquids) and electronic properties (e.g. optical absorption, band gap, Raman, IR spectra) with results obtained in well-controlled experiments. Validated approximations are then used in predictive simulations of complex structures, such as solid/liquid interfaces.

Technical Progress

<u>Algorithm development and implementation in the Qbox code:</u>

a) We have completed the implementation of the electric enthalpy functional allowing for molecular dynamics simulations in the presence of a finite electric field. This feature was validated against an implementation of Density Functional Perturbation Theory (DFPT) in Qbox.

b) We have completed the implementation of hybrid-DFT molecular dynamics using the recursive subspace bisection (RSB) approach to accelerate the calculation of the exchange operator. We have demonstrated that this approach can be used in inhomogeneous systems (such as e.g. surfaces or interfaces) where the localization properties of orbitals are widely varying [1].

Development of accurate norm-conserving pseudopotentials: We have developed a new method for generating optimized norm-conserving Vanderbilt (ONCV) pseudopotentials in the form recently proposed by D. Hamann. The optimization is based on the computation of the lattice constants of several hundred solids and a comparison with all-electron results obtained with the FLEUR code. We have generated and published a table of ONCV potentials for all elements up to Bi (Z=83). The resulting set of norm-conserving pseudopotentials allows for electronic structure calculations and molecular dynamics simulations of materials with the same accuracy as obtained with the projector augmented wave (PAW) method or ultrasoft (USPP) potentials. ONCV pseudopotentials require a simpler implementation than PAW or USPP potentials, leading to better algorithm scalability [2].

Validation of DFT and hybrid-DFT approximations in water and ice: Accurate modeling of water is essential in order to obtain realistic properties of solid/water interfaces. We have performed first-principles molecular dynamics simulations of water and ice using both DFT (PBE) and hybrid-DFT (PBE0) approximations of the exchange-correlation energy. We determined equilibrium densities and compressibilities. Results show that the PBE0 functional yields a lower density in both ice and water with respect to PBE, leading to better agreement with experiment for ice but not for liquid water. Approximate inclusion of dispersion interactions on computed molecular-dynamics trajectories led to a substantial improvement of the PBE0 results for the density of liquid water, which, however, resulted to be slightly lower than that of ice [3].

Ab initio calculations of IR and sum-frequency generation spectra: We have developed a framework for the computation of sum-frequency generation (SFG) vibrational spectra in semiconductors and insulators. The method is based on density functional theory and maximally localized Wannier functions. SFG spectroscopy is used to characterize the structure and dynamics of surfaces and interfaces, which are ubiquitous in energy conversion devices. The computational framework was validated in calculations of SFG spectra of ice [4]. In addition, we have applied our approach to the calculation of IR spectra to carbonates under pressure [5].

Future Plans

Future research will focus on further development of scalable algorithms for the computation of DFT and hybrid-DFT electronic structure, taking advantage of the localization properties of Kohn-Sham orbitals through the recursive bisection approach. Algorithms will be designed to make optimal use of the new Intel Knight’s Landing (KNL) architecture that will be deployed in 2016 at major DOE facilities (LBNL, ANL).

Data Management and Open Access

All software developed in this project is available in open source form under the GPL license. The Qbox code is available at http://qboxcode.org. Pseudopotentials used in simulations and reference data are available at http://fpmd.ucdavis.edu/potentials/index.htm and http://www.quantum-simulation.org.

Broader impact (Optional for DOE grants/FWPs)

The Qbox code developed in this project is available in open source form. It has been used as a teaching tool in graduate classes at UC Davis and at the University of Chicago.

Accelerating Materials Discovery & Development

The availability of accurate computational prediction methods is expected to accelerate materials discovery by reducing the number of materials to be synthesized after computational screening is performed. The development of predictive methods for surface-sensitive spectroscopic data is a key ingredient of this strategy.

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Combinatorial Methods to Enable Rapid Prototyping of Polymeric Pervaporation Membranes for Biofuels

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Keywords: biofuels, combinatorial screening, polymer membranes, molecular dynamics, pervaporation

Project Scope

A key challenge in the production of both bioethanol and biobutanol is energy-efficient recovery from dilute aqueous fermentations. Pervaporation is a leading candidate to replace energy-intensive distillation processes. Through a synergistic program of high-throughput combinatorial experiments, data-driven thermodynamic modeling, and predictive molecular simulations, we are developing a rapid prototyping paradigm to accelerate design of *polymeric pervaporation membranes*.

Relevance to MGI

Combinatorial synthesis of copolymer membranes produces a library of materials differing in two independent variables (e.g., hydrophilicity and crosslink density). Equilibrium swelling measurements in pure and mixed solvents provide interaction parameters for a new, multi-component, equilibrium thermodynamic model. Experimental data and interaction parameters are inputs to simulations, which predict component diffusivities in membranes. Prediction of permeability selectivity and component transport rates completes the design loop by linking performance metrics with molecular-level inputs.

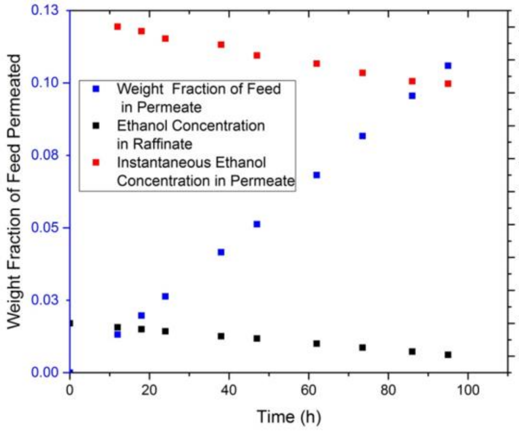

Figure 1. Pervaporation trial with a composite membrane based on a (30% PHEA, 70% PBA) random copolymer. (Godbole et al., *ACS Combi. Sci.*, **2015**, 17 (11), 663-670).

Technical Progress

Recent experiments addressed the complex problem of predicting permeability selectivities (α_a) and ethanol flux (J_e) for large test matrices of membrane samples. Based on measurements with actual membranes, predictions for α_a based on pure-component diffusivities and equilibrium distribution coefficients were found to underestimate the selectivity of the membranes for alcohol, likely due to vapor-liquid equilibrium phenomena at the membrane-vacuum interface. Accurate measurements of α_a and J_e were obtained by conducting pervaporation trials with selected materials chosen from the sample matrix based upon their equilibrium selectivity for alcohol. **Fig. 1** shows pervaporation data for a representative polyacrylate copolymer (PHEA= poly(2-hydroxyethylacrylate), PBA= poly(n-butyl acrylate). The measured values of selectivity and alcohol flux were α_a = 3.6 to 4.0 and J_e =6.0 g m^{-2} h^{-1}, respectively. The model polyacrylate system we used for method development produces modest selectivities for ethanol that are insufficient for commercial applications, but some of the materials tested produced very high ethanol fluxes, suggesting that continued studies of polyacrylates are warranted. The significant challenge remaining is to improve predictive methodologies such that fabrication and testing of membranes is not necessary to obtain reasonable estimates of α_a and J_e.

Molecular dynamics (MD) simulations were performed to study the structure of water molecules inside three polyacrylate materials having different amounts of hydrophobic and hydrophilic polymer segments. The structure and dynamics of the hydrogen bonding between the water molecules were studied. At the equilibrium swelling condition, water molecules created large clusters in the most hydrophilic system, PHEA (**Fig. 2)**. The probability of water-water hydrogen bonding increases as the hydrophilicity of the polymer increases due to enhanced absorption of water. Water molecules tend to aggregate in the system, and subsequently, their properties approach those of bulk water. The same membranes with low and fixed amounts of solvents (water and ethanol) were also examined; water molecules did not create clusters and they made hydrogen bonds predominantly with polymer segments. The dynamics of the solvent molecules is strongly coupled with that of polymer segments, especially in membranes with a low amount of solvent.

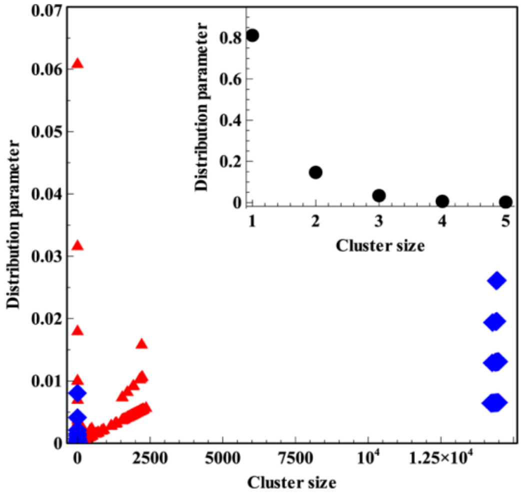

Figure 2. Cluster size distribution of water molecules in gels swollen to equilibrium. Results are shown using the following symbols: PBA (in inset, ●), P(BA50-HEA50) (▲), and PHEA (◆).

Future Plans

Future work on simulations will focus on the dynamics of water and ethanol molecules in polyacrylate copolymer membranes to elucidate the mechanisms governing molecular diffusion. Theoretical modeling efforts will focus on applying our multi-component equilibrium thermodynamic model to develop a more realistic model of mass transport in pervaporation membranes. Experiments will focus on extending screening methods to more hydrophobic (alcohol-selective) polymers, which are challenging to study due to their comparatively low solvent absorption.

Broader Impact

Our DMREF project provides training to a diverse group of Ph.D. candidates and undergraduate researchers, including underrepresented persons, to equip them with the research skills needed in the future workforce in the materials and renewable energy fields. Results from this work are being disseminated to researchers in bioenergy and materials research via professional meetings, while journal publications and a database of membrane materials (under development) will make the work available for education of the general public. Students from our team have so far received two awards for excellent posters and one award for an oral presentation after presenting at regional and national meetings.

Data Management and Open Access

A code that was developed last year based on the simulated annealing polymerization technique to prepare polymer structures from a well relaxed monomer mixture with 100% conversion has been extended to create polymers with desired overall conversion or individual monomer conversion. In addition, the code has the ability to restrict reactivity between the monomers. As inputs, the code requires a LAMMPS[1] data file of reactant mixture and a parameter file that specifies the desired conversion and reactivity pathways.

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Design and Testing of Nanoalloy Catalysts in 3D Atomic Resolution

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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 is on the synthesis of Pt based metallic alloys with transition metals M (M=Fe, Co, Ni, Cu, Cr, Mn, V, Mo etc). 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.

Relevance to MGI

The team of three PIs will synthesize new nanocatalysts with designed compositions and shapes (Huang), image the positions of all atoms in 3D resolution using the world's most powerful electron microscope (Miao), and carry 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 will lead to rational design rules to optimize catalyst performance (ORR, hydrogen oxidation). The development and validation of predictive multi-scale simulation tools further benefits the computational user community and improvements of related materials.

Technical Progress

We have developed a class of highly active and ultra-stable catalysts for oxygen reduction reactions (ORR), by doping the composition of Pt_3Ni surface layers with various transition metals (M). Mo-Pt_3Ni/C demonstrated ~4 times higher activity than the undoped Pt_3Ni/C, and nearly two orders magnitude higher activity than commercial Pt/C, while at the time exhibiting ultra-stability that greatly outperform bothPt_3Ni/C and Pt/C. This work simultaneous addresses the long lasting critical challenges in fuel cells regarding the low activity and durability of Pt ORR catalysts, and brings fuel cell technology one step closer to broad applications. Our studies also provide a new strategy to enhance catalyst performance, which can contribute to more efficient chemical production and refinement process, reducing the associated negative environmental impact.

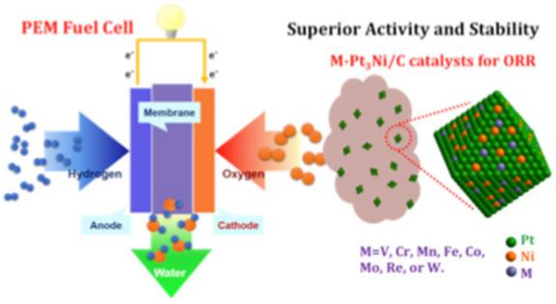

Figure 1. Development of highly active and ultra-stable catalysts for oxygen reduction reactions (ORR), which is the critical rate and cost limiting reaction in fuel cells by changing the composition of Pt_3Ni octahedra surface layers. [1].

At the same time, our team for the first time, demonstrated the determination of the 3D coordinates of thousands of individual atoms and a point defect in a materials with a precision of ~19 picometer. From the coordinates of these individual atoms, we measured the atomic displacement field and the full strain tensor with a 3D resolution of 1 nm and a precision of 10^{-3}. The ability to precisely localize the 3D coordinates of individual atoms in materials and identify point defects in three dimensions is expected to transform our understanding of materials properties and functionality at the most fundamental scale. [2] Meanwhile a hybrid experimental and computational approach was applied to systematically elucidate biomolecule-dependent structure/function relationships for peptide-capped Pd nanocatalysts. [3]

Future Plans

Planned immediate future work involves the deterministic synthesis of binary and ternary Pt and Pd based alloy nanocrystals, guided by molecular simulation, the three-dimensional characterization of nano-alloy catalysts at atomic resolution and model refinements, as well as the prediction, testing, and optimization of catalytic activity. More emphases will be placed on integration of the experimental and theoretical efforts, including (1) 3D atomic scale tomography characterization of the ternary PtNi-M nanocrystals, and (2) the development theoretical models using ab-initio and reactive molecular dynamics simulation (using CHARMM-INTERFACE) to predict the activity of theses nanocatalysts. Also, correlations between the observed structures and the reliability of current interatomic potentials to predict alloy nanostructure and thermodynamic stability (EAM, INTERFACE) will be explored to result in eventual improvements.

Broader impact (Optional for DOE grants/FWPs)

The multidisciplinary, collaborative environment where theory and computation guide and complement the selection, synthesis and characterization of nanoparticles with high catalytic activity will offer a unique training experience for graduate students, undergraduate students, and outreach participants. The team will pay particular attention to recruit students from underrepresented groups and currently includes a minority PhD student at U Akron. UCLA PIs have recruited undergraduate students as well as high school students in the project through existing REU programs and the Center for Excellence in Engineering and Diversity (CEED) program at UCLA. The PIs will also participate in an annual Engineering Career Day for High School students, teachers, and parents (U Akron), the annual Research Experiences for Teachers program (UCLA), the High School Summer Research Program (UCLA), as well as the coordination of the ACS Chemistry Olympiad for the Akron local section, which includes hands-on laboratory studies for selected High School students.

Data Management and Open Access

Accurate force fields and new computer codes will be disseminated via NanoHub, the NIST atomistic potentials repository, Heinz's research webpage, and the Accelrys/Biovia community site to reach a broad user and developer community. Original data on nanocatalyst structure from equally sloped tomography as well as structural models will be fully disclosed in publications as part of the Supporting Information. All other experimental and computational data related to the project will be well organized for long-term storage including backups.

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Rapid Design and Engineering of Materials Systems for Nanomanufacturing via Directed Self-Assembly

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Keywords: block copolymers, self-assembly, meso-scale

Project Scope

This project endeavors to (1) develop a general modeling and design platform for nanostructured block copolymer systems that can accelerate the design of such nanostructured soft matter and (2) use this platform to design new nanostructured functional materials and processes. To address this challenge, a minimum set of experimental characterizations, an higher fidelity meso-scale energetic model, high speed GPU computing methods, and a novel stochastic simulation technique are being combined to develop a robust structure prediction method for complex block copolymer systems. The successful completion of this work will include the accurate prediction of structure-property relationships for high χ block copolymers and the use of these relationships to design new self-assembling nanostructured polymer systems for semiconductor manufacturing and organic photovoltaic applications.

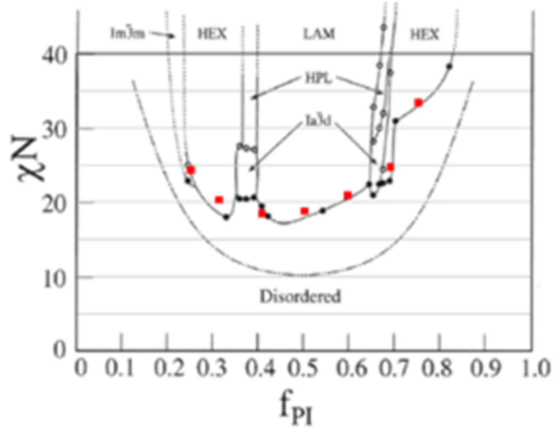

Figure 1. Phase behavior as a function of χN and isoprene fraction for poly(styrene-b-isoprene) showing comparison of experiment [1] (open/closed circles) and our meso-scale simulations (red squares) The parabolic shaped order-disorder transition line is the one obtained from more commonly used mean-field technqiues.

Relevance to MGI

Design of nanostructured block copolymer materials and processes that utilize them is quite challenging and time consuming due to their complex phase behavior. Given that many of the current applications for such materials are in thin film form (e.g. integrated circuit patterning, organic photovoltaic cells, etc.), the presence of interfaces in these applications make such systems even more complex. Many fundamental questions remain about the design and behavior of block copolymer systems in both bulk and thin film form and their development is in general rather Edisonian. While some progress has been made in rapid modeling of these systems (e.g. mean field methods), such modeling methods do not in general capture the full richness of behavior exhibited by many block co-polymer systems. In particular, block copolymers that exhibit vastly different physical properties between their constituent blocks (i.e. as in the case of many high-χ polymers) and the presence of free surfaces and interfaces greatly complicates such analyses. Figure 1 shows an example of the experimental phase diagram for poly(styrene-b-isoprene). Figure 1 also shows the order-disorder transition (ODT) boundary as predicted by using simple mean field methods. As can be seen, simple mean field models do not provide a good match to the complex experimentally observed ODT line. Much of the modeling work to date on block copolymer systems has used such mean field theory approaches that describe the block copolymer system in terms of a single polymer enthalpic parameter (χ parameter). In order to better close the loop between modeling and experimental behavior of block copolymer systems, and thus enable predictive design of such block copolymer materials, the proposed work involves development of methods to implement a multi-parameter meso-scale model for block copolymers that includes hompolymer interaction parameters and interaction parameters between the constituent polymer blocks. Manipulation of these parameters independently provides a tighter coupling with the experimental systems and the prediction of their complex phase behavior. By independently manipulating these three parameters we have had some success in accurately predicting some of the complexity observed in real block copolymer systems (see the red squares in Figure 1 which show modeling of the PS-b-PI ODT). This new meso-scale modeling approach will be coupled with larger long-time polymer dynamics simulations to allow us to predict the self-assembled morphologies in complex block copolymer systems as a function of relevant experimental variables and at a rate to allow for computationally guided materials design. These larger long-time simulations will be made possible through the combination of the meso-scale model with high speed GPU computing based molecular dynamics simulation techniques and an efficient simulation enhancement method known as Protracted Colored-Noise Dynamics which allows for faster exploration of the polymer phase space.[2]

Technical Progress

Previously we have shown how relevant materials parameters, including molecular weight distribution,[3] surface topology,[4] multi-block structure, and surface topology effect the morphology of self-assembled lamellar and cylindrical structures in block copolymer thin films. Similarly our long-time simulations of defect annealing have provided information on the mechanism by which such defects can be annealed away and on their stability and expected frequency. This information will ultimately be used to design high χ polymers for advanced materials based on self-assembled block copolymers.

Since the initiation of this award we have completed the synthesis of many structures of one of our target block copolymer systems, namely poly(styrene-b-hydroxyethylmethacrylate) or PS-PHEMA. Several block copolymer systems will be synthesized and characterized in this project to provide experimental data sets from which to parameterize and validate modeling results. Small angle scattering has been used to characterize part of the phase diagram of this PS-b-PHEMA system. Preliminary simulations of both bulk and thin films of high χ polymers containing asymmetric block physical properties have been carried out. These early simulations show dramatic differences in the behavior between such high χ polymers and the more widely studied low χ polymers such as PS-b-PMMA.

Future Plans

We will continue to examine the PS-b-PHEMA system as our first model system from which to develop the block copolymer simulation and design methodology of interest in this work. Additional small angle x-ray scattering (SAXS) studies will be performed to complete the phase diagram characterization for this system. This data, in conjunction with homopolymer parameters determined from other measurements, will be used to fit the aforementioned meso-scale energy model to produce an accurate model of this high χ system and to validate its predictive capabilities. Next, this validated model will be used to predict details of the morphology of self-assembled thin films for PS-b-PHEMA. Using this model, the effect of changes in copolymer structure and interfacial layer composition will be explored systematically through simulation to find the optimal conditions under which the PS-PHEMA system produces small, defect-free, stable lamellae thin film structures that can be used in advanced semiconductor patterning applications via directed self-assembly. Additional work will be performed to expand the modeling capabilities to include processing methods that involve solvent annealing of such block copolymer thin film systems. Additional block copolymer systems will be explored both experimentally and through simulation as the methodologies developed in this work mature both to test the methods and demonstrate their utility in accelerated design of such materials and processes.

Broader impact

This rational approach wherein a validated model is used to explore the impact of polymer composition, structure, and processing variables on resulting material morphology and properties promises to be a very general method for computationally guided materials design in block copolymer systems. Current target applications for the work include semiconductor nanopatterning and organic photovoltaic materials, and it is expected that the work pursued through the project will result in advancements in both fields. This DMREF program currently engages 6 graduate students on a full or part-time basis and includes students from Chemical Engineeing, Chemistry, and Materials Science and Engineering. We plan to expand broaden the exposure of students to such computationally guided materials design methods through inclusion of project content into a recurring graduate level molecular modeling class at Georgia Tech taught by Professor Ludovice. We also plan on doing one or more radio shows about this project and related computationally guided materials design methods on a weekly radio show produced by the PIs at Georgia Tech on WREK-Atlanta. Our involvement in other community outreach activities, e.g. the Atlanta Science Festival, high school science engagement programs, etc. will also allow us to more broadly engage younger students and the public concerning such advanced topics.

Data Management and Open Access

As the project progresses, output data will be made available on a public website in an accessible format (the generic format used by the VMD program). We have already coded the PCND algorithm into the massively parallelized GPU program HOOMD developed at the Department of Energy and the University of Michigan. Once validated, this code will be available on the HOOMD site to users at no cost. All other simulations and codes will be available through a Georgia Tech website maintained through the SMARTECH platform at Georgia Tech's Library.

Accelerating Materials Discovery & Development

An objective of MGI is to discover, develop, and deploy new materials twice as fast at a fraction of the cost. How is the project accelerating materials discovery and development over what would be possible without use of the MGI approach? Although these are fundamental research projects, please comment on prospects for commercialization. What hurdles must be overcome to make this a commercially relevant technology? Describe any interactions with industry (especially for GOALI projects). Have any patent applications been filed? Has follow-on funding from more applied sources been pursued? Are any entrepreneurial activities (such as I-corps or SBIR) underway? Please limit to 150 words.

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Publications

None to report.

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 will be the integration of the computational methods with a synthetic, characterization, and design cycle. As a team, we will 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 will speed-up the discovery of new catalysts.

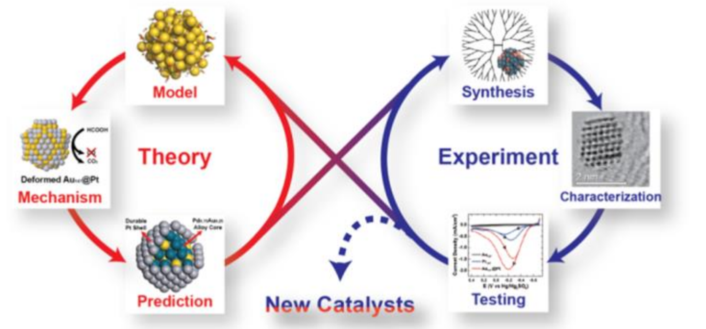

Figure 1. Design cycle for understanding catalytic function and increasing the rate of material discovery.

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 will be confirmed using electron microscopy, X-ray absorption spectroscopy, and electrochemical methods. Each of these methods will be combined with DFT-based Monte-Carlo calculations to evaluate candidate structures according to their calculated stability.[3] Finally, the activity of the NPs will be measured and compared with the calculated expectations. Discrepancies between experiment and theory will be 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 will be able to determine appropriate reactivity descriptors, reaction mechanisms, and ultimately accelerate materials discovery.

Technical Progress and Future Directions

Our project, which has just started, will focus on the four following specific tasks:

1. Computational screening of catalysts: For certain reactions on model catalysts, the chemical properties which facilitate activity are understood. In the case of oxygen reduction, for example, a good reactivity descriptor is the binding energy of oxygen to the catalyst surface. Using this quantity as a target, many compositions and structures of catalysts can be screened to find stable candidates for synthesis. Computational methods, including discrete optimization (e.g. genetic algorithms) and gradient-based optimization (e.g. alchemical derivatives), will be developed for this task. Predictions of trends (see Figure 2) in the relationship between structure and function will be used to identify particles for synthesis, characterization, and measurements of catalytic activity.[4]

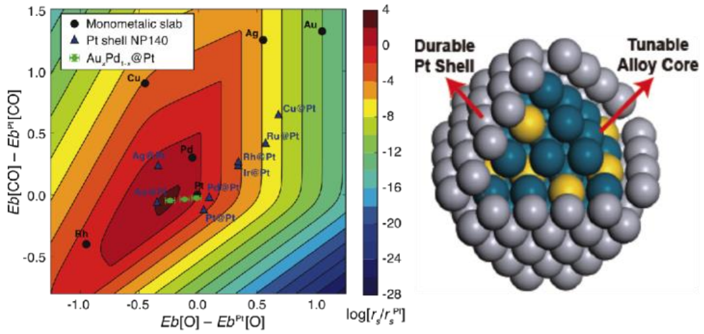

Figure 2. (left) 2D volcano plot shows how the activity of CO oxidation is related to the binding energy of CO and O; **(right)** Structural model of the $Pd_xAu_y@Pt$ NP.

2. Computationally assisted structural characterization: Most experimental tools for the characterization of nanoparticles provide structural data, but not enough data to uniquely determine the structure with atomistic precision. Examples include transition electron microscopy (TEM), which provides a projected image of a few nanoparticles, electrochemical measurements of adsorbate-surface interactions, and extended x-ray adsorption fine structure spectroscopy (EXAFS), which gives ensemble-average short-range information of local bonding in the NPs. In the case of EXAFS, a model is required to interpret the raw data in terms of representative NP structures. TEM is used to give credence to any such model, because it can test whether the particle size and composition distributions are narrow. For all three techniques, DFT calculations help by providing a base model of the geometry and by evaluating the quality of potential structures that are consistent with experiment from their calculated stability. In this task, the machinery for combining DFT calculations with TEM and EXAFS data will be developed for the improved determination of NP structures at the atomic scale.

3. Determination of active sites and reaction mechanisms: The core of a design cycle for new materials must include an understanding of the correlation between material structure and function. For catalysis, this is tied to a determination of the reaction site and mechanism. In some cases, mechanisms and corresponding reactivity descriptors are fairly well known. In this project, however, we will focus on bi-functional catalysts including either two metals in proximity or a metal/metal-oxide interface where the mechanism(s) of reaction are not well-understood. With a combination of DFT calculations of available reaction mechanisms, kinetic modeling, and correlations to expected variations in NP structures and compositions, mechanisms and reactivity descriptors will be identified and used in subsequent screening-synthesis-characterization-evaluation cycles.

4. Synthetic and characterization techniques: The computational acceleration of catalyst design can only succeed if the theoretical structures identified can be synthesized. In our design cycle, computational screening will initially focus on particles that we know can be synthesized. In subsequent iterations we will advance our synthetic techniques towards interesting particles which we do not have experience making. For example, many of the particles predicted to be active for CO oxidation are bifunctional in the sense of having one component that interacts with O_2 and a second with CO. A synthetic tool that we have started using is the underpotential deposition of a shell metal on a core (described at the end of this section) which can be used to cover particular facets of the core. Galvanic exchange is another technique that allows the substitution of shell metals for which underpotential deposition is not possible. Finally, we will aim to synthesize NPs with distinct oxide and metallic components such as in a Janis structure. We have made tin oxide particles, [5] but not yet metal/oxide particles. A second experimental challenge that we will address is the characterization of nanoparticles with complex structures. This effort will involve state of the art *in situ* TEM, quantitative scanning TEM and EXAFS, which will give quantitative and dynamic structural information about the catalysts both after synthesis and over the course of the reaction.

Broader impact

At The University of Texas at Austin (UT), the Henkelman and Crooks groups lead sister nanomaterials research streams in our flagship Freshman Research Initiative (FRI). In this program, freshman undergraduate students are placed into research laboratories and given the opportunity to participate in active research projects rather than experiencing the traditional freshman chemistry laboratory. In the experimental FRI stream, roughly 30 students synthesize DENs, characterize them, and measure their catalytic activity, currently for the reduction of p-nitrophenol. In the computational stream, roughly 15 students calculate the stability of bimetallic NPs and the binding of reactant molecules to their surface. As part of this project we will better integrate these two groups so that the theory and experimental streams coalesce. This will provide an outstanding opportunity for peer interactions, because the theory students are sufficiently advanced to teach the experimentalists the basics of DFT and vice versa. The proposed effort to model bi-functional catalytic DENs for reactions such as CO oxidation will be included in our streams so that undergraduates can become a part of the proposed research effort, working directly with graduate students and faculty funded by this effort. There is a similar emphasis on undergraduate research at Yeshiva University and the University of Pittsburgh. As part of this project, undergraduate students will be given the opportunity to travel between research locations to stimulate interactions between the various undergraduate researchers on the project team.

Data Management and Open Access

All products will be made available to the public via a web portal that will be hosted at the Texas Advanced Computational Center (TACC). As a partner for the NSF XSEDE project providing multiple high-end computational, visualization, and data analysis and storage resources, TACC has significant experience hosting and archiving research data via dedicated web portals, global file systems and mass storage facilities. The web portal will not only make the software and data available to the public but also it will expose the metadata enabling anyone to intelligently search through the data repository.

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Fragment-Based Quantum Chemistry for Non-Covalent Interactions and Excitation Energy Transfer

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Keywords: Intermolecular Interactions, Excitons, Quantum Chemistry

Project Scope

This project aims to develop, implement, and test new fragment-based algorithms for efficient calculation of non-covalent interactions and exciton transport in large systems composed of "soft" materials, *e.g*, organic semiconductors. The methods to be developed rival the accuracy of traditional, post-Hartree-Fock quantum chemisty calculations, yet the natural parallelizability of the fragment-based approach makes them affordable even in large systems (*e.g.*, several hundred atoms or > 50,000 Gaussian basis functions).

Relevance to MGI

For non-covalent interaction energies, validation against high-level *ab initio* benchmarks demonstrates that accurate relative energies can be predicted at substantially reduced cost, relative to traditional quantum chemistry. This is the first step toward predicting accurate energies of different structural polymorphs, and to performing condensed-phase simulations with these low-cost methods. For excitation energy transfer, we have demonstrated accurate and scalable-parallel results out to systems with hundreds of chromophores (thousands of atoms), and shown that the energetics of organic semiconductors change *qualitatively* upon passing from a system with tens of chromophores to a system with 100+ chromophores. The latter calculation is only tractable using the methods developed as part of this work.

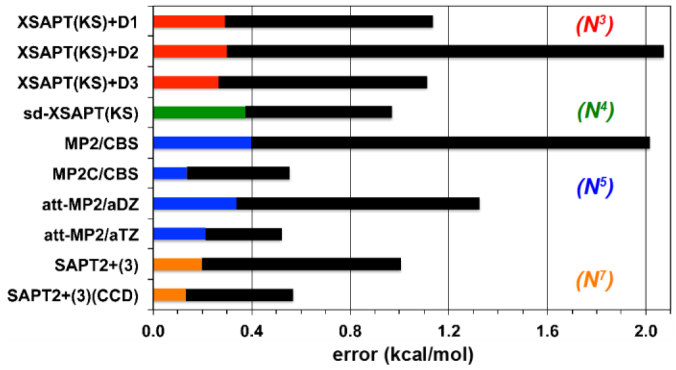

Figure 1. Error statistics, vs. complete-basis CCSD(T) results for S66, for a variety of quantum chemistry methods. Shown are the mean absolute errors (colored bars, with the color-code according to how cost scales with system size) as well as the maximum errors (black bars).

Technical Progress

In the context of non-covalent interactions, we have developed an "extended" version of symmetry-adapted perturbation theory that we call "XSAPT", in which monomer-based self-consistent field calculations are combined with a perturbative (and trivially-parallelizable) description of intermolecular interactions. This approach lends itself to a variety of further approximations, or differing cost and accuracy, depending on how the dispersion (van der Waals) interactions are treated. A particular variant that proves successful at low cost is called XSAPT(KS)+D, which combines Kohn-Sham DFT for the monomers with SAPT for the intermolecular interactions, but with empirical atom–atom potentials for dispersion (the "+D" correction). Dispersion potentials are parameterized in a fully *ab initio* way using high-order SAPT to extract *ab initio* dispersion potentials for a training set of dimers, then fitting these results to damped $C_6/R^6 + C_8/R^8$ potentials. Results in Fig. 1 show that our third-generation version of this method, XSAPT(KS)+D3, affords a mean accuracy of 0.3 kcal/mol with respect to complete-basis CCSD(T) benchmarks, and a maximum error of about 1 kcal/mol.

Regarding excitation energy transfer, we have developed an *ab initio* implementation of the Frenkel-Davydov exciton model, in which collective excited states in a system containing multiple, electronically-coupled chromophores are expressed in a basis of easily-computable monomer excited states. The whole approach is trivially parallelizable and we have extended it to systems with 150+ chromophores, obtaining excitation energies within 0.2–0.3 eV of benchmark results but in calculations that take days (not months) on commodity hardware (not supercomputers). Results in Fig. 2 demonstrate that the energy-transfer dynamics in an organic semiconductor can change qualitatively when one is able to use a model system containing significantly more chromophores than what is achievable using traditional quantum chemistry methods.

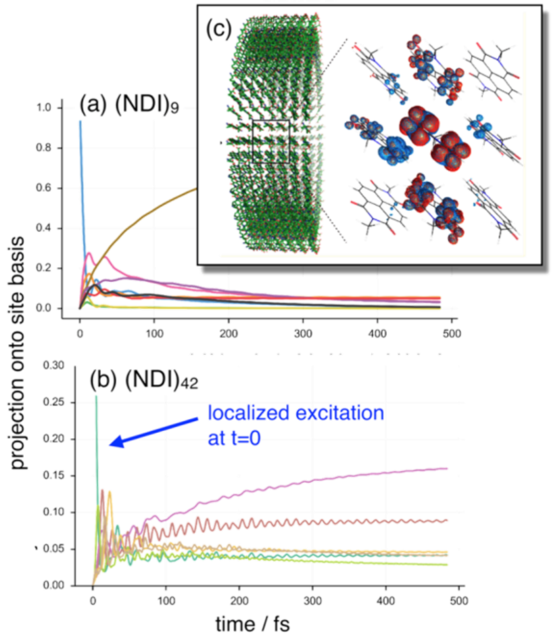

Figure 2. Population dynamics of a localized excitation of (a) a 9-mer and (b) a 42-mer of a naphthalene diimide (NDI) nanotube that is shown in (c). Very different dynamics are observed in the smaller system as compared to the larger one.

Future Plans

On the XSAPT front, we are currently working with Prof. Lee Woodcock (U. of South Florida) to combine this approach with his “non-Boltzmann Bennett” enhanced sampling approach, which is intended to perform QM/MM calculations by using MM dynamics to drive the sampling with only occasional QM calculations. In this way, we can use very large QM regions, given the low cost of XSAPT, and the intent is to study ligand binding to proteins at an *ab initio* level. We are also working to incorporate three-body dispersion corrections into XSAPT, along the lines of the Tkatchenko-Scheffler many-body dispersion method, and then to use this approach to compute ligand-dependent C_6 parameters for the metal ions in metal-organic frameworks. This is a collaboration with Prof. Brian Space (also at U. of South Florida) to do force-field development for gas adsorption onto metal-organic frameworks.

In terms of the *ab initio* exciton model, we are currently using this model in an attempt to achieve a mechanistic understanding of singlet fission in crystalline tetracene and pentacene. Due to the low cost of the model, we can include far more “QM” chromophores as compared to previous calculations performed on these systems.

Broader impact (Optional for DOE grants/FWPs)

Funds from this grant have so far been used to support five Ph.D. students at various points in their education, plus a fraction of a postdoc who has been involved with this as well as other projects. One of the Ph.D. students has graduated and is currently interviewing for academic positions while another will graduate in a few months and has a postdoctoral position at Cornell, after which he, too, will pursue an academic job. Collaborations have been established with two other DOE-funded PIs (Dan Chipman at Notre Dame and Lee Woodcock at U. South Florida). The PI has given a webinar describing the XSAPT methodology, which is available here: https://www.youtube.com/watch?v=bkAQnFkrUKY&feature=youtu.be. A short online presentation for the Journal of Physical Chemistry Letters is also available, which describes our work on the many-body expansion: http://pubs.acs.org/iapps/liveslides/pages/index.htm?mscNo=jz401368u. Another online presentation describes our *ab initio* exciton model: http://pubs.acs.org/doi/suppl/10.1021/acs.jpclett.5b02109.

Data Management and Open Access

Our many-body expansion methods are based on a stand-alone, open-source code that acts as a driver for an electronic structure program. (Currently, it works as a driver for the Q-Chem, NWChem, and Psi4 electronic structure programs, the latter two of which are open source.) Our XSAPT and *ab initio* exciton models have been implemented in Q-Chem but with sufficient details in the peer-reviewed literature such that they can easily be ported to other packages.

Accelerating Materials Discovery & Development

All of the aforementioned methods are interfaced with the Q-Chem electronic structure program, making them available to all materials researchers, both academic and industrial. The fact that these methods are high-accuracy but reduce the computational scaling (with respect to system size) quite dramatically means that they can be applied to much larger systems --- and thus systems that are more representative of real materials --- than was previously possible. An SBIR grant (with Q-Chem) may be pursued in the future in order to better parallelize these approaches so as to exploit petascale computing resources available to DOE.

Publications

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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.

Technical Progress

No significant new insights can be reported at this time.

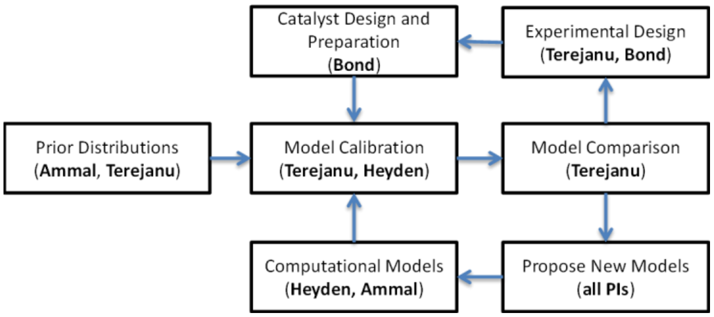

Figure 1. Uncertainty quantification pipeline and interconnectivity of the tasks.

Future Plans

As a case study for our integrative approach, we have chosen the hydrodeoxygenation (HDO) of succinic acid (SUCC) in aqueous media over supported multimetallic catalysts (Fig. 2). This chemistry could allow for the selective production and facile recovery of bio-based 1,4-butanediol (BDO), γ-butyrolactone (GBL) and tetrahydrofuran (THF).

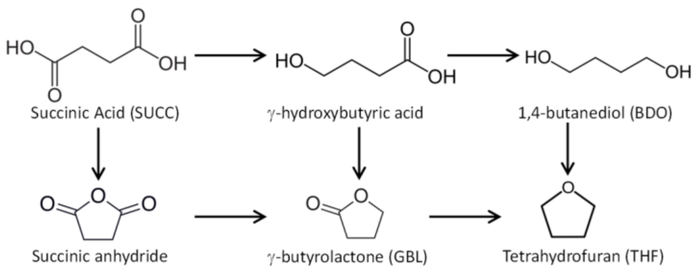

Figure 2. Pathways for the HDO of SUCC to BDO, GBL, and THF.

The project involves preparation of well-defined and well-dispersed bimetallic clusters of tin (Sn) adsorbed on ruthenium (Ru), platinum (Pt) or rhodium (Rh) deposited on amorphous silica or carbon supports. The catalysts will be characterized in detail with respect to structure, composition, and surface acidity, and then evaluated in the SUCC HDO reaction. A multiscale strategy will be used for the computations based on DFT methods and techniques developed in the investigators' laboratory aimed at reducing uncertainties in the estimation of free energies. Uncertainties in both the experimental and computational analyses will be subjected to Bayesian statistical analysis. Refinements to both the experimental and computational methods will be made to minimize the uncertainties and obtain meaningful comparisons between theory and experiment.

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 proposed work will require 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. 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.

Accelerating Materials Discovery & Development

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.

Mechanics of Three-Dimensional Carbon Nanotube Aerogels with Tunable Junctions

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Keywords: rigid rod networks, junction characteristics modulation, mechanical properties, superelastic.

Project Scope

The goals of this research program are to combine experimentation with simulation to develop a systematic and comprehensive understanding of how the mechanical properties of single-walled carbon nanotube (SWCNT) aerogels, *i.e.*, three-dimensional (3D) networks of SWCNTs, depend on pore geometry, pore size distribution, and the characteristics of the junctions between nanotubes to improve the performance and to predict an optimal design of SWCNT-based porous structures. The educational, training and outreach activities include: training undergraduate and graduate students in interdisciplinary experimental and computational research, incorporating the research results into advanced undergraduate- and graduate-level courses taught at CMU, and interacting with TMS to spearhead initiatives designed to support women in the minerals, metals, and materials professions at all levels.

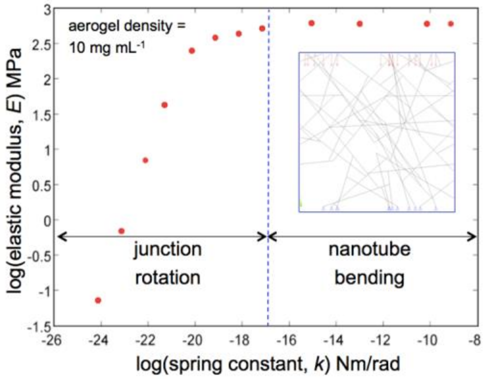

Figure 1. Elastic modulus versus junction strength for 2D SWCNT networks. Inset shows the network structure and loading.

Relevance to MGI

In this project, we are developing a 3D mechanical model for SWCNT aerogels that includes realistic network structures as well as nanotube and junction properties that approximate experimental systems. We are then using this model to predict the mechanical properties in compression, including modulus and hysteresis, as a function of network and junction parameters. Our goal is to computationally survey the range of available SWCNT aerogel properties in order to provide insight and guidance to accelerate development of these technologically significant materials.

Technical Progress

1. Computationally survey the range of available SWCNT aerogel properties by varying the network and junction properties (Holm). In order to understand the properties of nanotube junctions, molecular dynamics simulations were used to characterize the van der Waals interactions between nanotubes. The results were incorporated in a novel "pre-strained" network model to reproduce the observed elasticity and failure behavior of pure, unmodified CNT aerogels. The mechanical response of unmodified (van der Waals interactions) and strongly-bonded (crosslinked) aerogels were compared.

2. Fabricate and characterize 3D SWCNT aerogels with diverse junctions and explore applications of these materials (Islam). Techniques to modify the junctions between nanotubes using graphene and boron nitride materials were developed, and the resulting mechanical properties of these aerogels were measured (DOI:10.1039/C5NR01981H). In addition, applications of these aerogels were explored. For example, the high porosity of SWCNT aerogels allowed them to be used as scaffold for fabrication of polymer composites with high elastic moduli. This approach is similar to current methods used in industry, making this approach suitable for rapid implementation (DOI:10.1021/acsnano.5b00170). The high porosity of SWCNT aerogels has also allowed their usage as high-rate performance electrodes in electric double layer electrodes (DOI:10.1016/j.nanoen.2015.05.028). Further, the highly compressible and elastomeric graphene-coated SWCNT aerogels allowed construction of supercapacitors with high volumetric capacitances of ~5−18 F/cm^3 in aqueous and room temperature ionic liquid electrolytes, respectively, which are 50−100 times higher than comparable compressible supercapacitors (DOI:10.1021/acsami.5b01384). A new class of aerogels from co-networks of graphene and nanotubes was developed with significantly larger pore distributions. Electrodes fabricated from this class of aerogels significantly improved power density of an enzymatic biofuel cells that can also be recharged (DOI:10.1021/am507801x). Finally, since these classes of materials are expected to find applications, it is inevitable that nanotubes will be exposed to cells. We investigated the effects of nanotube exposure to both embryos and mammalian cells (DOIs:10.1002/jat.3203, 10.1039/C5TB00705D, 10.1021/acsami.5b04851, and 10.1002/jat.3255).

Future Plans

Computational activities will focus on: (1) **Developing a new finite element method code for 3D CNT networks.** In exercising the 2D finite element model, developed using the ANSYS code package, we encountered a variety of numerical and computing challenges. For the full 3D network model, we will write our own finite element code, optimized for sparse networks of high aspect ratio, stiff members connected by complex junctions. (2) **Performing MD simulations of nanotubes and nanotube junctions coated by a continuous graphene layer.** Graphene coating is observed to increase the elastic modulus and alter the stress-strain behavior of CNT aerogels. We will incorporate a continuous graphene layer in MD simulations of individual nanotubes to measure changes in elastic modulus and buckling stress. (**3) Utilize the 3D network model to explore the phase space of network parameters and junction properties.** Nanotube junctions may be modified by a variety of means, including wetting, coating, that changes the deformation and failure of the junctions. We will apply the 3D CNT network model across a range of network densities and junction properties (spring constant, failure strain) to determine systems that yield the desired mechanical response. These results will inform experimental efforts to optimize CNT aerogels.

Experimental activities will focus on: (**4) Developing methodologies to synthesize continuous graphene layer on carbon nanotube networks.** We have recently discovered that reinforcing the node structure with few-layer graphene, nanotube network can completely recover from compressive strains of over 90% with no observed fatigue. This sharply contrasts the unreinforced SWCNT aerogel, which undergoes plastic deformation at 9% strain, and sees fatigue at even lower strains. We will create a superelastic porous system with ultrahigh elastic modulus, and characterize physical properties. (**5) Creating new aerogels of boron nitride (BN) or boron-carbon-nitride (BCN) nanotubes.** We have recently observed that carbon nanotubes could be converted to BN o BCN nanotubes in the presence of boric acid. We will perform detailed experiments to convert carbon nanotube aerogels to BN or BCN aerogels.

Broader impact

Two graduate students are being trained in computational and experimental materials science. Work related to this grant has generated nine peer-reviewed journal articles and sixteen conference presentations. Results of this project were incorporated in undergraduate and graduate courses at Carnegie Mellon University, as well as in two K-12 outreach activities. In addition, the outcomes of the PI chaired the First TMS Summit on Creating and Sustaining Diversity in the Minerals, Metals, and Materials Professions (DMMM1) is available at http://www.tms.org/meetings/2014/diversity/resources.aspx. The PI presented and led a discussion on "The role of graduate education in fostering and sustaining diversity in the materials profession" at The Future of Graduate Education in Materials Workshop, held at the University of California Santa Barbara in June 2015, sponsored by NSF.

Data Management and Open Access

All computational simulations are performed using open access code platforms (ANSYS for finite element calculations, LAMMPS for MD simulations). Full experimental and computational data sets, including metadata such as input decks and initial structures (computation) or conditions and protocols (experiment), will be included as online supplemental information in all publications resulting from this work. In addition, all codes and data are archived at CMU via a GitHub instance and available upon request.

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Iterative Theoretical Morphology Prediction, Synthesis, and Characterization of Novel Donor Oligomers for Accelerated Materials Discovery

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Keywords: morphology, charge-transport, structure-property, multiscale, discotic.

Project Scope

Our theory-synthesis-device team tests methods to predict organic photovoltaic (OPV) donor molecular structure and morphology, synthesizes new molecules, and tests these in devices. We are studying new oligomers, including a novel type of 2-D trefoil discotic oligomer, and new device architectures. Model crystal structures and molecular dynamics (MD) calculations simulate morphologies and charge transport properties of thin films and BHJ devices. Synthesis of promising new candidates is followed by measurements of device properties. Success is measured by the correspondence between prediction and experiment and by increases in device PCE.

Relevance to MGI

Morphology prediction is combined with synthesis and device testing to accelerate the discovery of more efficient OPV devices. Using QM and MD simulation methods, we build up morphology predictions and then use them to calculate hole mobilities. New oligomers, including novel discotic trefoil donor molecules, are being synthesized and will be combined with fullerene acceptors for testing in OPVs. The results of these experiments will guide future designs.

Technical Progress

Project 1: Development of a conformational library for oligomer/polymer design

In OPV devices, active layer morphology and the frontier energy levels of the donor and acceptor material influence efficiencies. The conformational behavior of donor oligomers has been investigated; we have computed the torsional potentials of 2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene (BTTT). We benchmarked 11 common DFT methods and 3 Pople-style basis sets, and found that ωB97XD achieves the best results. To establish general rules for conformational preferences and barriers to planarization, we computed conformational potentials on common subunits of electronic organic materials.

Project 2: Correlating crystal packing with charge transport

In order to understand the influence of atomistic features of packing motifs on charge transport in various systems, ab initio, stochastic sampling, and molecular dynamics were used to calculate charge mobilities in oligomers using Marcus theory. We conducted an electron mobility benchmarking study of single-crystal and thin-film mobilities of electron acceptors. Single-crystal mobilities fell within one order of magnitude of experimental values, while mobilities calculated from disordered morphologies showed weaker with experiment.

The electron mobility benchmarking study, and a prior hole mobility[4] benchmarking study, serve as a basis for a number of collaborations with experimental groups, within and outside of UCLA, on the effect of crystal packing on calculated charge transport based on Marcus theory. In these collaborations, we have studied helical aromatics, curved aromatics and planar nanographenes. To further advance this methodology, we have successfully used USPEX, an evolutionary crystal structure prediction program developed by the Oganov lab at Stony Brook, with plane wave basis sets to predict crystal structures of simple aromatic hydrocarbons: benzene, naphthalene, anthracene, and tetracene, and we are now applying these methods to new discotic heteroacenes.

Project 3: Discotic heteroacenes

We have designed discotic oligomer **1** as a donor material (see Fig. 1). The Garg group has developed methodology to synthesize the both the 4,5-indole trimer core and the 5,6-indole trimer core using indolyne chemistry. Although the structure of the 5,6-indole trimer is planar, the 4,5- indole trimer is helical. The marked difference in ground state structures of the two cores provides a foundation for future study on the differential electronics, packing, and charge transport of helical and planar discotics molecules.

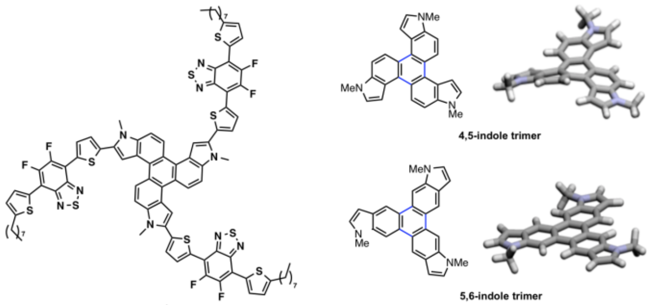

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Figure 1. Left: Target discotic oligomer. Right: Calculated structures of the 4,5- and 5,6-indole trimers using ωB97X-D/6-31G+(d,p).

Project 4: Dopant-free organic hole transport materials

Donor-acceptor (D–A) molecules were synthesized and implemented as dopant-free hole transport materials (HTM) in perovskite solar cells for efficient charge extraction.[8,9] To compare the effects of different D–A small molecule HTMs on the performance of perovskite solar cells, molecular structures containing electron-donating and electron-withdrawing cores were synthesized. Fabricated devices exhibited PCE as high as 16.2% using small molecule DERDTS–TBDT with an electron-donating core as the HTM.

Future Plans

Project 1: Development of a conformational library

Work is currently underway toward the development of a database that will provide calculated conformational data for a variety of oligomer or polymer subunit combinations to the scientific community. Specifically with regard to the rotatable single bonds that connect two subunits of an oligomer or polymer, the geometries and energetics relating to deviation from planarity will be provided to allow scientists to rapidly construct realistic oligomer geometries for visual inspection or as starting points for morphology calculations.

Project 2: Correlating crystal packing with charge transport

In order to unite crystal structure prediction methods with charge transport prediction, we are conducting a three-part benchmarking of (1) several plane-wave basis sets for USPEX crystal structure calculations; (2) hole and electron mobility calculations on the twenty lowest-energy crystal structures calculated by USPEX; (3) mobility calculations on MD-disordered morphologies from part 2.

Project 3: Discotic heteroarenes

Future work by the Garg group will focus on trimerization of the phenyl-substitued indolynes to form an extended core. Computations will guide the optimization of the synthetic methodology of the trimerization reaction in order to increase regioselectivity. We will use USPEX to predict the crystal structure packing of the 4,5- and 5,6-indole trimer cores. Mobility will be calculated for the twenty lowest-energy crystal structures. Analogous linear heteroacenes, like regioisomerically pure *anti*-anthradichalcogenophones, will also be synthesized.

Broader Impact

The participants have all been involved in undergraduate mentorship and collaborations with groups outside of UCLA. Yu Jin, an undergraduate student from Zhejiang University, visited the Houk lab as part of the UCLA CSST program. During this past summer, Yu became involved in the conformational library project, using DFT to study conformational behavior of OPV oligomers and polymers in order to establish design rules. Outside of the classroom, the Garg group continues to perform outreach activities with the Los Angeles community like chemistry demonstrations to elementary school children. The Garg group has also developed a new educational tool called "BACON at UCLA," an online tutorial designed to help connect organic chemistry to topics in human health and pop culture. Lastly, DMREF participants Janice Lin, Steven Lopez, and Tejas Shah are members of OCDS (Organization for Cultural Diversity in Science). Among other activities, OCDS hosts outside speakers at UCLA and sends speakers to give talks at other universities and conferences such as SACNAS.

Data Management and Open Access

Our results are primarily disseminated by published work and conference presentations. Our labs have published several hundred manuscripts over the past 5 years, and are eager to share scientific results. Our results have been presented through lectures (>200 invited lectures since 2008). This practice will be continued, and laboratory websites will be maintained to showcase our studies and associated publications.

Accelerating Materials Discovery & Development

The prime example of the benefits of the MGI approach toward acceleration of progress is the ongoing development of novel discotic oligomers for OPVs. Development requires a cooperative effort from all three groups, which would not be possible without the tightly knit DMREF collaboration.

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Real Time Control of Grain Growth in Metals

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Keywords: Grain growth control, temperature control, Phase Field model, Monte Carlo method, SEM

Project Scope: This project focuses on developing the methodology and algorithms necessary to actively control materials processing to achieve a target microstructure. Our major contribution is the synthesis of experimental characterization, process control, and microstructure simulation to predict, monitor and control microstructural evolution during materials processing. In this project we focus on thermal processing of polycrystalline metals, specifically control of grain growth in Cu, but the methods we develop should be extensible to a broader range of processing parameters and materials.

Relevance to MGI: The mechanical properties of metals, such as ductility, strength, and fatigue resistance, are directly linked to microstructural characteristics resulting from thermo-mechanical processing. Thus, active control of the processing conditions, through iterative cycles of processing, measurement, modeling and feed-forward /feed-back control, to create a desired microstructure and resulting macroscale properties is a major priority for materials manufacturers and for the MGI. In this project we are integrating simulation and modeling of a ubiquitous materials processing tool – grain growth in polycrystalline metals by thermal processing – with feedforward and feedback control algorithms to guide the system towards a proscribed microstructure and thus desired mechanical properties.

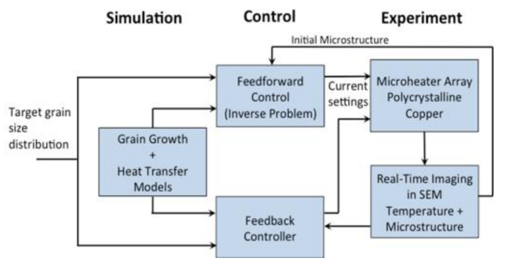

Figure 1: Overview of the sensing – simulation – control cycle

Technical Progress: Our two over-arching project goals are (i) To enhance predictive capability for the relationship between thermal processing and microstructure in polycrystalline metals, through coupling of in situ real time observation with simulation of microstructural evolution as a function of thermal trajectory; and (ii) To subsequently control microstructural evolution by regulating the temperature distribution using model-based feedforward control and measurement-based feedback control. This approach requires progress in multiple activities: 1) We have developed a ten zone multi-zone resistive heater, upon which polycrystalline Cu films are deposited, and that can be operated within a scanning electron microscope (SEM). The design of this heater array targets temperatures in the range 350 – 450^o C, through raising of the base temperature to 200-300^{o}C from an SEM heating stage, in combination with controlled temperature excursions in each Ti micro-heater strip zone. This enables programmable temperature distributions across the sample area. The thermal design of the heater array has been guided through extensive finite element analysis (FEA) modeling. 2) Within the SEM, we are developing a novel set of real-time characterization methods to simultaneously measure microstructure (using secondary electron imaging), crystallography (using electron backscattered diffraction EBSD patterns) and temperature (using diffuse scattering from EBSD patterns), in order to study the microstructural response to controlled sets of inputs to the multi-zone heater and resulting temperature fields, and to compare the observed evolving microstructure to predictive models. Extension to 3D imaging and correlation of 2D-3D grain models will be enabled through tomographic imaging in dual focused electron and ion beam systems. We have successfully integrated the micro-heater array into the SEM and demonstrated control of the heater element currents and temperatures (at this stage, using resistance as a proxy) during SEM imaging. 3)

Detailed discrete (Monte Carlo) and continuum (phase field) grain growth models are being developed to predict both microstructural trajectories as functions of time and temperature, and the local dependence (gradient) of microstructure upon time and temperature. Detailed comparisons of experimental results with Monte Carlo (MC) simulations have been made, and show a substantially higher kurtosis in grain size in the experimental images; this is due to persistence of smaller grains without substantial grain growth in the experimental observations. 4) From a combination of simulations and experimental data, the sensitivity of microstructural characteristics, e.g. grain size distribution, to heater settings are being characterized. From these sensitivities, using inverse problem solving techniques, we are predicting the optimal heater setting histories to obtain a prescribed microstructure. 5) The combined information from modeling and real time observation (and specifically triggered by deviations between the two), are then used in a combined feedforward and feedback control strategy for real-time control of microstructure evolution. Initial control strategies were demonstrated for feedforward control of the desired temperature distribution of FEA models of the heater array, by solving the inverse problem for a constant heat input. We have since demonstrated extensive coupling of control strategies with both experiment and simulation, using both the standard proportional-integral control method, and the consensus control method based upon an imposed graph interconnection of the output measurements. These methods have been applied in the past year to control of (i) The set of ten heater elements ex-situ to the SEM, using Ti line resistance (and hence temperature) as the control output variable, ii) To coupled FEA – MC models, where the control algorithms are used to control heater elements in the FEM model, in turn driving grain growth in the MC model, with the MC grain size distribution used as the control output variable; and (iii) To the control of individual heater line resistances / temperatures in-situ in the SEM.

Future Plans. For the remainder of the current project, we will focus on demonstrating and refining integrated sensing-simulation-control loops of the evolving microstructure during in-situ heating with multi-channel control in the SEM. The next (renewal) phase of our project will focus on two major goals: (i) Mapping control capabilities across a temperature-stress-property ternary "phase diagram" using in-situ methods within the SEM at the micro-scale and (ii) Examining extension to macroscopic samples used as test structures by our industrial partners who create raw metallic materials, and who process them into desired shapes and function. The goal of the latter is to extend our methods into practical materials manufacturing conditions.

Broader impact: A "core body of knowledge" has been implemented for the participating graduate students, combining selected graduate courses and a half-day "mini symposium" on the science of grain growth. The graduate students have spent extended period working in other PIs' laboratories. Multiple undergraduate students have participated, including contributions to phase field and Monte Carlo simulation development, and development of grain delineation algorithms from experimental images. A project symposium was held as part of the annual RPI Center for Automation Technology and Systems Advanced Manufacturing Conference in Oct 2015, that attracted many industrial participants, and generated multiple potential collaborations.

Data Management and Open Access: Relevant simulation and experimental results are shared among team members, and data / results stored on the project wiki site. The full team meets biweekly. During the next six months, project relevant data sets and products will be made permanently available to the external community (research advances and findings will of course also be published in the scientific literature).

Accelerating Materials Discovery & Development: We believe our approach to integrating fabrication, sensing, modeling and control can be transformational in accelerating materials processing cycles. Real-time control algorithms enable us to direct experimental materials processing pathways onto simulated trajectories that result in desired microstructure and properties. This allows us to understand what physical processes are absent and/or incompletely accounted for in the simulations, and also enable us to discover predictive experimental pathways towards desired microstructures. Our renewal proposal will explicitly focus on bridging the gap between the current microscopic systems and macroscopic systems of direct relevance to manufacturing industry.

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(1) Yixuan Tan, Chengjian Zheng, John T. Wen, and Antoinette M. Maniatty, "Inverse heat transfer analysis for design and control of a micro-heater array". *Inverse Problems in Science & Engineering*, in resubmission
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Computationally Guided Design of Multicomponent Materials for Electrocatalytic Cascade Reactions

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Keywords: Catalysis, Energy, Nanomaterials, Cascade, Electrochemical

Project Scope

We are developing catalytic materials that allow greater efficiency in energy-demanding reactions. We are developing components that can be integrated into multi-site catalytic cascades, and developing computational tools to predict the performance of these components and the eventual cascade. Our efforts have constructed a microkinetic model for a cascade system, demonstrated the benefits of an electrochemical cascade for oxidative coupling of methane, and used oxide coatings to protect selective catalytic sites. Our poster this year concentrates on our work using self-assembled monolayers on metal nanoparticles to alter catalytic activity and selectivity.

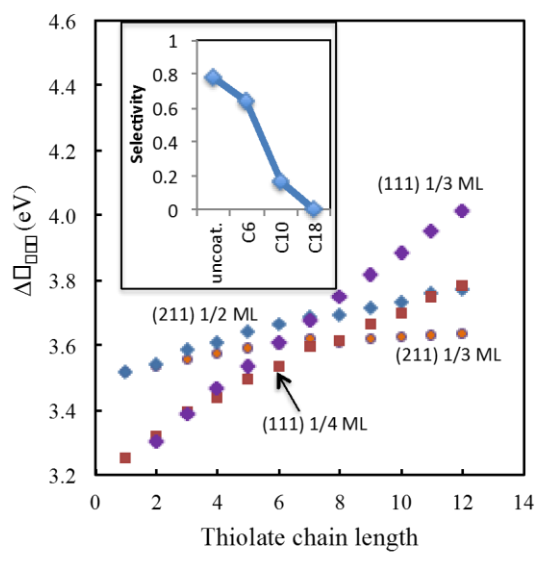

Figure. DFT calculations show that the adsorption strength of n-alkyl thiolates on Pd favors step sites at low chain length and coverage, but favors terrace sites at high chain length and high coverage. Inset: predicted trends in site preference versus alkyl chain length agree with experimentally measured trends in selectivity for decarbonylation of furfuryl alcohol.

Relevance to MGI

An alternative approach to catalytic conversion will be developed using multi-component, multi-active site materials. Communication between active sites will be controlled by the selective transport of energetic intermediates. A computationally-guided design framework will 1) utilize atomistic and electronic structure methods to optimize individual catalytic components, and 2) construct a coupled microkinetic/transport model to guide construction of the multi-component material. Synthesis, fabrication, characterization, and reactivity studies will validate computational models and realize the enhancements offered by the catalysts. Nanoparticles with self-assembled monolayers (SAM) will serve as a component in catalytic cascades, where the SAM both alters particle selectivity and controls access to only specific reactants in the cascade.

Technical Progress

For the DMREF PI's meeting, we will present results in one specific area of our project, the modification of catalyst activity and selectivity using organic self-assembled monolayers. The Medlin group has shown that self-assembled monolayers (SAMs) formed from organic thiolates as selectivity modifiers for supported metal catalysts. In prior studies of furfural and furfuryl alcohol hydrogenation over Pd/Al_2O_3 catalysts, it was found that application of octadecanethiol (C18) coatings resulted in a dramatic reduction in the decarbonylation (DC) rate with only a small change in the hydrodeoxygenation (HDO) rate, leading to high HDO selectivities. Diffuse reflectance infrared spectroscopy (DRIFTS) measurements conducted after CO adsorption on the catalysts showed that the SAM selectively eliminated terrace rather than defect sites. This result was surprising, since one would expect thiolate adsorbates to form stronger metal-sulfur bonds at undercoordinated Pd atoms presents at defects. To understand these results, and to begin building a platform for control of sites at organic-inorganic interfaces, we have conducted complementary experimental and modeling studies of the modification of Pd surfaces with alkanethiols having different chain lengths. We have applied density functional theory (DFT) methods to illustrate that thiolates bind stronger to uncoordinated edge sites at low coverage or with short alkyl chains (see Figure). For longer alkyl chains and higher coverage, however, van der Waals interactions drive preferential binding on terrace sites, leaving step edges exposed. Based on these DFT results, we have demonstrated that longer chain SAMs are necessary to promote HDO/DC selectivity. DFT studies of the reaction energetics further demonstrate that decarbonylation is slowed by higher coverage of SAMs due to the larger ensemble of atoms necessary to allow for binding of both furyl and carbon dioxide products.

Future Plans

Both experimental and computational efforts are continuing towards using SAMs to modify access to metal nanoparticle sites and catalytic selectivity. Future efforts will seek to incorporate SAM coated particles as part of a catalytic cascade, in which the SAM controls access to the catalytic surface while a second site supplies active intermediates to increase overall activity and selectivity. The current efforts have been focused on establishing the ability to combine computational and experimental studies to understand SAM performance, and subsequent efforts will emphasize utilizing these capabilities for design. We have also studied the use of inorganic (rather than organic) films for similar purposes.

Broader impact

Research efforts are integrated with educational and outreach activities to broaden the impact of the proposed work. Five graduate students are involved in this project. Undergraduate researchers are integrated into research efforts at the four partner institutions, involving these students in multi-disciplinary work with exposure to our collaborative team. Undergraduate researchers are drawn from programs that target underrepresented groups, including Penn State’s Women in Science and Engineering Research (WISER) and Wayne State’s Michigan-Louis Stokes Alliance for Minority Participation (LSAMP) programs. Collaborative teaching approaches are being explored, and have included other project participants visiting the University of Michigan to provide interactive lectures on various energy technologies. Collaboration with the Michigan Science Center has been established and co-PI Nikolla has taken part in their “Ask the Expert” series. Nikolla has given presentations and demonstrations on energy conversion systems and the effect on the environment. The Nikolla group has also organized a GO-GIRLs Keeping in Touch Workshop “Material Girls Get Energetic!” this summer, to enhance the interests of middle and high school underrepresented female students from the local Detroit schools in science and engineering.

Data Management and Open Access

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

Accelerating Materials Discovery & Development

Providing a rationale for complex catalyst behavior that is based on atomistic structure and elementary reaction kinetics enables predictive design based on inherent materials properties. Such rationale design can produce active and selective catalysts with behavior distinct from their separate components.

Publications

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Extreme Bandgap Semiconductors

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Website: http://djena.engineering.cornell.edu/projects_dmref.htm

Keywords: Semiconductors, Bangap, Isotopes, Heterostructures, Doping.

Project Scope

The goal of this DMREF proposal is to develop the materials science of extreme bandgap semiconductors such as BN, AlN, Ga_2O_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. Guided by rigorous mathematical and first-principles theory and modeling, the 4-PI team will collaboratively explore the fundamental epitaxial growth, polarization-induced conductivity control, band anticrossing in highly mismatched materials, and effects of isotope engineering on electronic and thermal transport to lay the foundation for a nascent area with rich scientific and technological relevance.

Relevance to MGI

The last two decades witnessed revolutionary advances in electronics and photonics by moving from ~1 eV gap semiconductors (Si, GaAs) to ~3 eV GaN and SiC. A similar quantum leap to xBGS materials with gaps of ~5-6 eV has the potential to seed vast application arenas, and simultaneously advance the fundamental material science and the physics of materials. The proposed research project has the potential to be transformative in the field of material science and condensed matter physics under the umbrella of the Materials Genome Initiative because the research thrusts will develop:

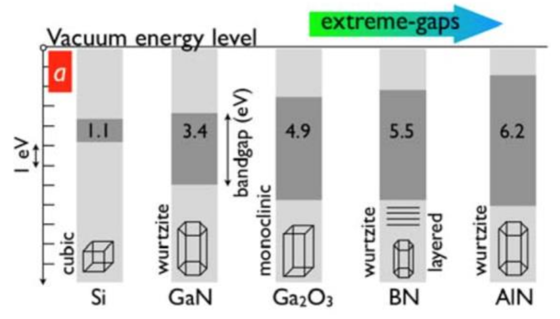

Figure. Extreme Bandgap Semiconductor materials (xBGS): (a): Compared to Si, and even GaN, the xBGS materials such as AlN, BN, and β-Ga_2O_3 have extremely large bandgaps, and crystallize in richer structural phases. Their growth and physical properties forms the basis of the proposed research project.

- First principles predictive theory of electronic, optical, thermal properties of xBGS materials.
- Epitaxy of new xBGS nitride and oxide semiconductors, isotope alloys and heterostructures.
- Novel methods for controlling conductivity of xBGS materials.
- Understanding and control of the interplay of competing 3D vs 2D crystal phases.
- Understanding of high-field optical, electronic, thermal phenomena.
- Understanding of cation band-anticrossing physics.
- Novel paradigms of isotope (neutron) engineering of opto- and thermo-electric properties.
- Will lay the groundwork for sustained leadership and creation of a new research field.
- Will provide potential for a lasting legacy.

Technical Progress

The project commenced in October 2015. A more substantial project report will be available in after 1 year of the project. At this stage, the PIs have

a) Identified students and postdoctoral scholars for the project,
b) Begun biweekly teleconferences for the DMREF project, and

c) begun technical discussions for theory and modeling and experiments, the data and samples to be exchanged have been identified, initial sets of samples have been grown.

Future Plans

The work spans epitaxy of xBGS materials, to understanding their electronic, optical, and thermal properties. We divide the work into 4 close-knit thrust areas, starting with predictive first-principles theory as the guiding force behind the experimental thrusts, and closing the loop at every step.

Thrust 1-Theory and Modeling (Kioupakis): Kioupakis will perform first-principles calculations based on density functional theory and related techniques to predictively model the structural, electronic, optical, and defect properties of the studied materials, and to guide the experimental efforts.

Thrust 2-xBGS Heterostructure Epitaxy of xBGS materials (Jena, Kioupakis): We will explore the growth and properties of (Al,B,Ga,In)N alloys and heterostructures and Ga_2O_3, In_2O_3, Al_2O_3, and their alloys and heterostructures. Their 3D and 2D crystalline forms, and their chemical doping will be explored by direct epitaxial growth.

Thrust 3-xBGS Electronic & Optical Properties (Xing, Jena, Kioupakis, Pop): The optical properties of xBGS materials will be explored with a combination of predictive theory and photo- and electro-luminescence and absorption/reflectivity measurements. Spectral measurements of the band structure, band offsets, carrier lifetimes, dopant and defect energy levels, polaronic and excitonic effects, and the effect of strain on xBGS materials will be performed. In combination with experiment, the Bethe-Salpeter Equation (BSE) method will be used to study the optical and excitonic properties of xBGS.

Thrust 4-xBGS Structural and Thermal Properties (Pop, Jena, Kioupakis): Complementary tools such as HRTEM, SEM, AFM, and X-Ray diffraction (XRD) will be employed to comprehensively study the structural properties of the epitaxially grown xBGS materials and their heterostructures. The thermal properties of xBGS materials such as Seebeck coefficients, thermal conductivities of bulk, heterostructures, and nanostructures, and isotope engineering of their thermal properties will form the fourth thrust of the project.

Broader impact (Optional for DOE grants/FWPs)

The proposed project will result in the training of graduate students in the fascinating emerging field of xBGS material science, with their many fundamental electronic, optical, and thermoelectric properties. In addition to expanding existing outreach programs, new activities with a special focus on high-school students and underrepresented groups via Research Experience for Teachers (RET) programs and direct visits for in-class demonstrations are proposed. The PIs will build on an already strong record of mentoring young women and underrepresented graduate students, as well as publishing with their undergraduate researchers. That the team is distributed between Notre Dame, Michigan, and Stanford with complementary expertise will be exploited by regular exchange of students for experiments, as well as theory and modeling work, to foster a truly collaborative mindset in the project. The dissemination of research by journal publications, presentations at conferences, its inclusion in courses taught by the PIs (e.g. developing new lectures on xBGS topics), and online (e.g. through up-to-date PI websites and the NSF-sponsored nanoHub.org) will ensure the outreach of the research proposed to the widest possible audience.

Data Management and Open Access

The codes and data will be made available with NanoHub (see above). In addition, a website [http://djena.engineering.cornell.edu/projects_dmref.htm] will list publications, highlights, and substantial outreach activities.

Accelerating Materials Discovery & Development

The combined theoretical and experimental approach followed here for extreme-bandgap nitrides and oxides is made possible by the MGI fit. At this point of time, there is no other agency that supports this sort of forward-looking and exploratory research, which strangely also has a high potential for immediate commercial impact. The supporting letters from two companies (HexaTech and Tamura Corp.) with whom we have exchanged samples, and co-authored scientific papers supports this assertion. Because extreme-bandgap semiconductors will enable electronic, photonic, and potentially thermoelectric devices that reach operation regimes far beyond what current state of the art materials do, this MGI is expected to result in fundamental advances that also have commercial impact. The PIs will pay close attention to this aspect as the project matures.

Analysis and Optimization of Polymer Networks for Emerging Applications

Principal Investigator: Jeremiah A. Johnson, Department of Chemistry, Massachusetts Institute of Technology, jaj2109@mit.edu.
Co-Principal Investigator, Bradley D. Olsen, Department of Chemical Engineering, Massachusetts Institute of Technology, bdolsen@mit.edu.

Keywords: polymer networks, gels, hydrogels, primary loops, mechanical properties.

Project Scope

A deeper understanding of polymer networks at molecular level has the potential to transform our engineering of these ubiquitous materials. This project aims to develop and test theories for predicting the number of primary loops, the major molecular defects, in polymer networks, providing design guidance for the structural, mechanical, and transport properties in these ubiquitous systems. The results of this project will provide new synthetic strategies, experimental methods, computational approaches, and theoretical developments related to the microstructure of polymer networks.

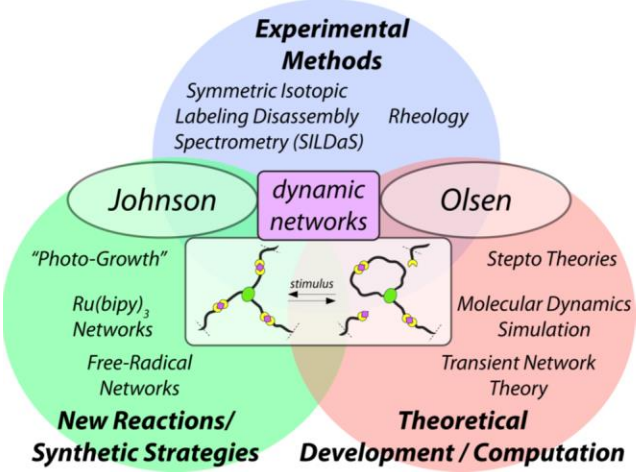

Figure 1. This project aims to analyze and predict new properties of polymer networks through the synergistic application of physical characterization techniques, synthetic strategies, and theoretical developments.

Relevance to MGI

This project has pioneered a new method to directly measure the concentration of loops and bridges in a polymer network using mass spectrometry. This technique provides the ability to fundamentally test theories of polymer gel formation (rate theory and Monte Carlo theory models for gel formation kinetics) and polymer network mechanics (affine and phantom network theories). The work here consists of synthesizing new network materials, testing their mechanical properties and chain configurations, and using this new data to iteratively test and improve the theories describing polymer networks and gels.

Technical Progress

As introduced last year, an advanced analysis method, "Symmetric Isotopic Labeling Disassembly Spectrometry" (SILDaS), has been developed to quantify primary loops in tri-functional model network materials. This strategy enables the analysis of a more universal range of network systems compared to our previously developed concept called "Network Disassembly Spectrometry" (NDS),[1] where an asymmetric macromer (the polymer bridge between two junctions) with restricted molecular weight has to be designed purposefully. Furthermore, in order to simplify the synthetic process, a mass-labelled macromer has employed to replace the previous isotopically labelled one. In this case, a new term called "Symmetric Mass Labeling Disassembly Spectrometry" (SMLDaS) is also introduced. The quantification of primary loops was then conducted in a tetra-functional network system and published recently.

One of our goals in this project is to study the influence and contribution of loops on the mechanical property of polymer networks. The phantom network theory and the affine network theory have both been developed to relate the modulus of polymer networks to the density of elastically effective chains, ν. Both theories predict that the shear modulus of a gel, G', can be quantified by the equation $G' = C\nu kT$, where kT is the thermal energy and C is a constant that has a value of 1 for the affine network model and $1-2/f$ for the phantom network model, where f is the functionality of network junctions. Unfortunately, the validity of these theories has not been demonstrated experimentally due to difficulty of quantifying ν. The fraction of elastically ineffective chains measured from SILDaS allows us to address this issue and the contribution of molecular defects to mechanical property has be evaluated by rheological measurement. The resulting data provided experimentally estimated values of C, thereby differentiating between the different network models. In the rheological measurements, 1 mm thick samples will be cast into a Teflon molds and then be punched out to form 12 mm diameter disks and loaded onto the oscillatory shear rheometer using parallel-plate geometry. A series of gels containing various fractions of loops have been synthesized *via* varying the initial concentrations of macromers and crosslinkers. Both tri- and tetra-functional gels system showed C values that were very close to those ones derived from phantom network theory, i.e., 0.33 for trifunctional and 0.50 for tetrafunctional gels, respectively. A modified rate theory has been developed to demonstrate that all different orders of cyclic topologies are a universal function of a single dimensionless parameter characterizing the conditions for network formation. The theory is in excellent agreement with both experimental measurements of hydrogel loop fractions and Monte Carlo simulations without any fitting parameters. Furthermore, in order to describe the effects of loops on the mechanical properties of polymer gels, a modified phantom network theory has been developed, which demonstrates that small loops (primary and secondary loops) have a vital effect on the modulus of the gel. This theory is in good agreement with the experimental measurement of the decrease of the modulus with the loop fraction without any fitting parameters. A manuscript related to this work is in preparation.

We have also been working on other sub-projects under this grant: (1) An air-friendly crosslinking reaction involving Michael-addition of oxonorbornadiene was investigated. This provides an opportunity to perform kinetic studies via an *in situ* gelation experiment on rheometer stage. In addition, the temperature-prompted retro-Diels-Alder (DA) reaction of resulting adducts provides a cleaner and simpler method for gel degradation. (2) Polymer networks containing well-defined metal-cluster based junctions have been synthesized. These systems were characterized by small-angle neutron scattering (SANS), solid state nuclear magnetic resonance (ssNMR) spectroscopy, rheometry, and molecular dynamics (MD) simulation, and determined to be highly loop-rich. This work was also published very recently. (3) Another novel loop analysis method using a crosslinker-label instead of a macromer-label has also been developed and has provided very consistent data compared to the previously developed SILDaS method.

Future Plans

Other parameters to be adjusted include the molecular weight of macromer, higher functionality number f (> 4), and potentially the molecular weight distribution of macromer. Macromers employed in this project will be focused on PEG first and extended to other types such as polystyrene (PS) or polydimethylsiloxane (PDMS). Polymer networks in a bulk state formed from PDMS macromer will be of particular interest due torubbery properties attributed to the subzero glass transition temperature and melting point of PDMS. The crosslinker will also be extended from a multifunctional small molecule to a macromolecular crosslinker, e.g., chain-end functionalized multi-arm PEG. Accordingly, the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) will be employed to analyze the latter system for SILDaS.

While existing rate theory and Monte Carlo theories have been able to successfully capture the reaction kinetics and concentration-dependence of loops in polymer networks when the reactive groups are present in a 1 to 1 ratio, experimental data has been generated for networks that have off-stoichiometric reagents, and the rate and Monte Carlo theories pioneered by Stepto[3] and published by the PIs do not capture even at a qualitative level the trends in the experimental data. Therefore, modifications to these theories are being developed that may have the ability to more accurately capture the process of network formation in off-stochiometric systems. This understanding will also guide us to perform semi-batch experiments which can potentially control the loop fraction but still maintaining the volume fraction of polymers.

Broader impact

A deeper understanding of polymer networks at molecular level has the potential to transform our engineering of these ubiquitous materials. It will advance discovery of novel self-healing materials, tunable filtration devices for removal of toxic agents from wastewater, and matrices for cellular and tissue engineering, in addition to having an immediate impact on a myriad of industrial products from coatings to tires.

Data Management and Open Access

The codes for rate theory, Monte Carlo simulation and modified phantom theory to calculate gel modulus are being posted on the Olsen group website. All data for this project is also being archived on a server which is backed up internally using multiple drives and off-site on a daily basis to provide for data security. Other laboratory data that is not generated digitally is stored in lab notebooks that are archived in the Johnson and Olsen labs.

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Center for Emergent Superconductivity
Designing New Correlated Electron Systems

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Co-Principal Investigator: James N. Eckstein, Lucas Wagner and Daniel Shoemaker, University of Illinois at Urbana-Champaign, Laura H. Greene, Florida State University, Duck-Young Chung, Mercouri Kanatzidis Argonne National Laboratory, Cedomir Petrovic, Genda Gu and Ivan Bozovic, Brookhaven National Laboratory
Website: https://www.bnl.gov/energy/ces/

Keywords: Superconductivity, Correlated Electron Systems, Antiferromagnetism, Combinatoric Synthesis, Quantum Monte Carlo.

Project Scope

The overarching goal of our Materials Genome work is to discover new families of high temperature superconductors (HTS). This would have major scientific and potentially large technological significance. The question is how to accomplish this. Our approach has been multipronged - theoretical, computational and experimental. The links among these activities create close knit feedback loops in which fundamental theory and experiment provide physical descriptors that should lead to the desired correlated electronic structure.

Relevance to MGI

This work extends MGI concepts to phenomena as complex as superconductivity and correlated electron matter. We do this with guidance from our study of the fundamental mechanisms of high temperature superconductivity which notes that in all known cases HTS emerges from a correlated parent phase. Correlated electronic systems exhibit extraordinarily useful properties, but they are fundamentally difficult to solve and expensive to simulate and verify. We are searching for MGI descriptors that will allow us to systematically search for new materials systems that have strong electronic correlations and efficiently attempt to synthesize them. We are developing tools to do this by bringing researchers spanning the entire process from fundamental theory to computational materials science to chemical synthesis to measurement of important physical properties. Specifically, we are using Quantum Monte Carlo simulations (QMC) to obtain realistic parameters for effective models such as Dynamical Mean Field Theory (DMFT) and Density Functional Theory (DFT). These efforts feed predictions to experiment which in turn feedback to theory. This integrated program constructs an engine for intellectual feedback throughout the effort.

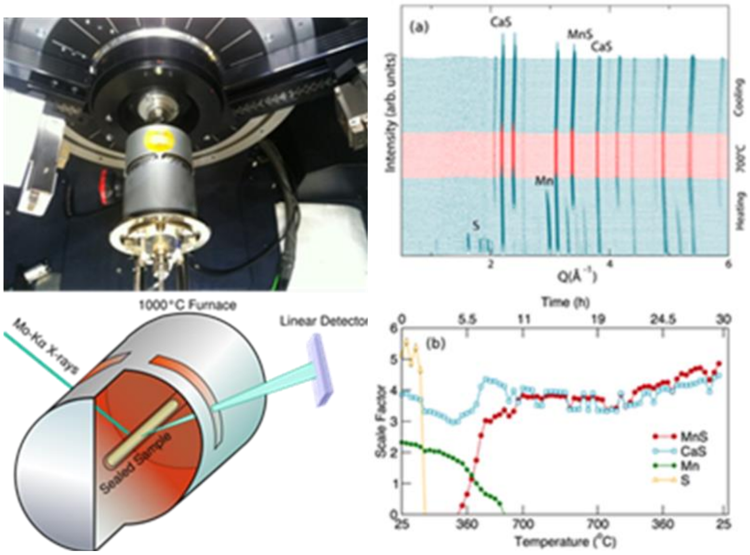

Figure. Left panel shows a picture and schematic of our new in-situ XRD system that allows the structures evolving in chemical reactions to be followed in real time. Right panel shows evolution of chemical phases occurring as a function of time and temperature during study of the Ca-Mn-S ternary system.

Technical Progress

The fundamental mechanisms component of the CES and our work on vortex matter have provided us with specific suggestions regarding what a new HTS material family should look like. These lead to material descriptors which are an integral part of genomic analysis and computational prediction of properties. They form a hierarchical set we create by looking at common features of existing HTS phases. The known families are the cuprates, the Fe-based compounds and various heavy Fermion phases (HF) that exhibit superconductivity. (For

HF phases the ratio of the critical temperature to the Fermi temperature, T_C/T_F, is large and for this purpose they can be considered examples of HTS.) In all of these compounds the chemical motif of the conducting molecular orbitals is simple and two dimensional, predominantly nearly tetragonal. In all of them superconductivity emerges from a highly correlated electronic system exhibiting strong quantum antiferromagnetic fluctuations. Additionally, the superconductivity is tunable with such control parameters as carrier doping and pressure. We have postulated that the best candidates for new HTS families are similar in these regards.

The experimental strategy of our synthesis effort is to develop fast, efficient, and high-information-content methods to synthesize the compounds predicted by computation, while feeding stability, properties, and doping descriptors back to the computational effort. Our genomic computational efforts have highlighted two classes of materials that provide insight into correlated electron behavior in unexplored environments. (1) New compounds, where DFT-calculated stability is a descriptor, and (2) known compounds where the synthesis is known to be possible from the literature but no properties are known. Our experimental work spans the whole gamut of synthesis, from ceramic to single crystal and from bulk to atomically layered thin film.

We developed a materials prediction and synthesis process in which computation provides prediction for synthesis of new phases and agile synthesis (bulk and thin-film) provides rapid feedback.

- We have analyzed the statistics of false-negative and false-positive materials predictions and determined the trade-offs to evaluate which predicted new phases should be grown based on estimates of computational accuracy. The final result is that one new phase can be expected to be found if approximately thirty phases that end up being false positives are attempted.
- We have computed DMFT parameters using QMC simulations, providing a bootstrap for predicting dynamics.
- We developed a rapid bulk synthesis process illustrated in the figure in which real time XRD patterns are obtained during processing as a function of time and temperature. One ternary system can be explored in a week.
- We have modified an existing materials discovery (14-source) MBE system to carry out combinatorial synthesis at low temperature. We explored ten materials systems and discovered one new phase.
- We have studied doping of transition metal boride phases as predicted by density functional theory. We found that magnetism is controlled by doping that changes the valence of the transition metal, similar to HTS.
- We have employed surface/interface doping with electrical field effect and explored carrier doping in transition metal oxide thin films.

Future Plans

We will continue to exercise our prediction/synthesis engine during the next year, focusing on 3d and 4d transition metal chalcogenides. We will attempt to focus our search more effectively on phases with high temperature phases that are tetragonal. We will use QMC to predict DMFT parameters for new materials systems in order to find new candidate structures that should exhibit strong electronic correlations.

Data Management and Open Access

Our program has a web page located at https://www.bnl.gov/energy/ces/. Data is shared among investigators across our center via biweekly Skype meetings involving all of the groups. These meetings can be joined by outside investigators, and to obtain access please contact one of the program PIs.

Accelerating Materials Discovery & Development

Because we bring together fundamental theory, Quantum Monte Carlo, Dynamical Mean Field Theory with Density Functional Theory, we provide a way to make contact between single particle calculations and accurate many-body calculations. This provides cheap predictions that are likely to do a reasonable job of accounting for strong electronic correlations. Furthermore, we should be able to identify specific predictions of electronic correlations and chemical phase stability. Our ability to rapidly survey specific compositional phase diagrams via both bulk synthesis as well as non-equilibrium synthesis provides a way to quickly verify prediction of new stable phases and strong electron correlations.

Ten Publications

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Engineering Strong, Highly Conductive Nanotube Fibers Via Fusion

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Keywords: Carbon nanotube fiber, Electrical fusion, Structure transformation.

Project Scope

The primary research objective of this project is to create strong and highly conductive fibers for applications in aerospace, high power density energy storage, lightweight cabling/wiring, structural health monitoring, and more. To accomplish this goal, our research focuses on a novel carbon nanostructure engineering process called electrical fusion creating covalently bonded molecular junctions (cross-links) between nanotubes, and transforming them into other desired seamless sp^2 carbon nanostructures (multiwall nanotubes or multilayered graphene). The research includes studying the best way to organize the carbon nanotubes into the network, as well as studying the best way to fuse nanoscopic filament, carbon nanotubes, together by applying controlled electric voltage across the network. The optimal nanotube network structures and organizations and electrical fusion processes will be identified through experiments and simulations, and by using data mining to understand the complex relationship between how the fused networks are made and how they perform.

Relevance to MGI

In this project, we are combining the results from experimental, modeling, and data mining to create and optimize high performance carbon nanotube fibers with exceptional properties. All of experimental processing parameters and experimental results of carbon nanotube fusion experiments are transferred to an online database that integrates the effects of structural parameters, extracted from coarse-grained computational studies, via data mining capabilities. The database captures all experimental parameters and results, applies machine learning algorithms (e.g., clustering, outlier detection) to help tune the best experimental processing parameters, and can also be used to predict the structural transformation and properties of fused carbon nanotube fibers. The computational simulation extract structural information from the original and fused carbon nanotube fibers to simulate the process of structure transformation of carbon nanotube fiber to investigate the mechanism of carbon nanotube fusion. By leveraging data mining, machine learning and simulation, we can guide the progress of the current experiments to create the fibers with high performance and unique properties. This should shorten the time to optimize the parameters as compared to experimental methods. For example, through reorganizing the breakdown voltages of carbon nanotube fibers with several certain lengths from the experiments, the data analysis system and simulation tools can predict the breakdown voltage of carbon nanotube when we vary the nanotube length, which can greatly enhance future experimental results.

Technical Progress

During the first year of this project, we designed and built a multifunctional and large-scale electrical fusion system for carbon nanotube fibers enabling electrical fusion under ultrahigh vacuum, controlled temperature, and in-situ electrical and thermal properties characterizations. The carbon nanotube (CNT) fibers have been fused using this new electrical fusion system, and apparent morphology change of fiber have been found, the fused fiber has much higher surface density and enhanced alignment than the pristine one, and original double-walled nanotubes (DWNT) structure of pristine fiber was transformed into multi-walled (MWNT) and graphitic structures with significantly reduced defects in nanotubes. By controlling the frequencies of applied voltages during fusion, the percentage of multi-walled and graphitic structures has been increased, which may help reveal the mechanism of the fusion of carbon nanotubes. We also developed the tensile test and torsion test platforms, CNT yarns are wet-twisted from CNT tapes with different twists (0.5, 1.0, and 1.5 rot/mm) before fusion. Fusion significantly increased the stiffness of the as-spun low and medium twist yarns by 22% and 23% respectively; but only 7% for high twist yarns. Whereas the strength decreased by 27%, 53% and 58%, for low, medium and high twist respectively. For the data mining and computational simulation, the corresponding database and simulation program have been established based on the experimental parameters and data.

The computer simulations, tailored to relate fiber-scale structural features on the fiber strength, have been performed to investigate the effect of fiber alignment, density length distribution and macroscale parameters such as bulk twist. Our coarse-grained model has been adapted to generate experimental-scale fiber configurations with complex variations of these parameters (i.e. they are not individually controlled), and we extract the stretching, flexural and twist rigidities of the resultant configuration. These results are integrated with experimental processing parameters through the online database combines these aspects with experimental processing parameters to extract the multi-scale dependencies.

We have compared our initial online database, which will shortly be remotely accessible by the broader research community. The database is indexed by sample IDs. A sample ID is a global identifier mapped to a unique carbon nanotube sample. Each entry in the database contains the information of a single experiment for each sample, and includes such searchable parameters as experiment type, experiment environment, existing properties of the sample carbon nanotube, and final properties resulting from processing. Our current experiment types include: i) breakdown voltage test, ii) I-V test, iii) fusion treatment, iv) torsion test and v) tensile test.

As part of developing this online system, we have developed a complete data dictionary for catalogue all data and data types stored in our system. We utilize this data dictionary during the data cleaning process that occurs during import of the data.

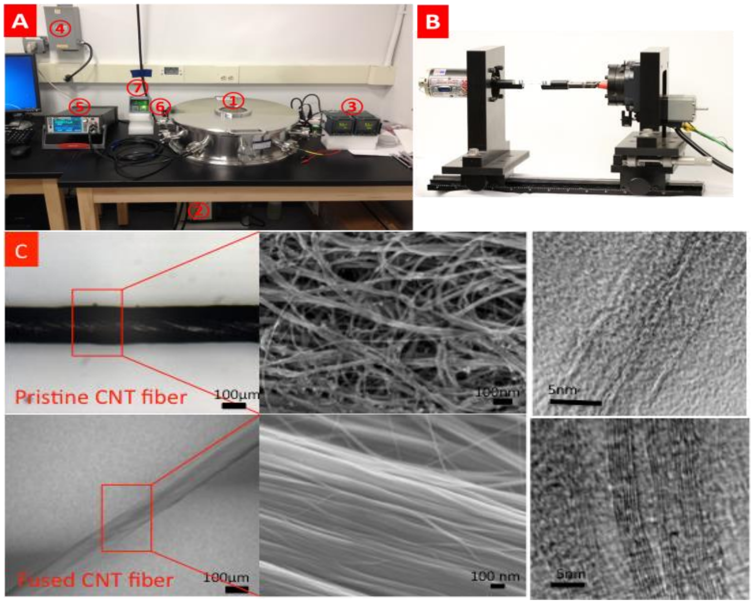

Figure 1 (A) New electrical fusion system (①ultrahigh vacuum chamber; ②mechanical pump; ③thermal controller; ④power transformer; ⑤multifunctional power and measurement meter; ⑥ water cooling system; ⑦pressure gauge) (B) Torsion test platform (C) SEM and TEM images of original CNT fiber and fused CNT fiber.

Future Plans

We will investigate the effect of other electrical fusion parameters; particularly higher frequency, lower pressure and higher temperature and characterize related structural transformation of CNT fibers. The electrical, thermal and mechanical properties will also be measure to obtain desired and highly controlled fusion condition to create a super CNT fiber. The data mining and computational simulation will integrated all the experimental parameters and results to further optimize the fusion process and understand the structure transformation during electrical fusion.

Broader impact (Optional for DOE grants/FWPs)

Building a novel electrical fusion system greatly impacted participating graduate and undergraduate students understanding how to design and fabricate experimental system, which will help them to learn the knowledge about materials science, vacuum technology, thermal transfer technology, and circuit design, etc. Also through this project, students learned various materials characterization methods (microscopes and electrical and thermal measurement techniques). Also students learned how to prepare a journal paper as well as conference presentation. Also two high school students presented their research results in the Young Scholar Program 2015 research presentation: James Zhou, Gary Hu, Ji Hao, Yung Joon Jung, “Engineering carbon nanotube fibers using a mechanical twisting method” Young Scholar Program 2015 research presentation, Boston. Jack McGrath, an Electrical and Computer Engineering undergraduate, play a key role in the development and testing of the online database system. The computational team has developed modules for elementary and middle schools, based on Raspberry Pi and Arduino platforms, to introduce school children to coding via sensing based applications. In particular, the SenseHat module on Raspberry Pi was made to introduce students to dynamic sensing via embedded temperature and pressure sensors. A small presentation on “Introduction to Coding with Interacting Physical Systems” was made in Wakefield elementary school along these lines.

Data Management and Open Access

An objective of MGI is to make data and computer codes publicly accessible: to integrate digital data, software, and program outputs into the community. Please describe how this project is addressing this objective. How has the project provided the community with access to its outputs (data, codes, samples, *etc.*)? Please identify URLs and DOIs (counted as 1 word each) where data and code are available. Please limit to 150 words.

The project is developing an online data repository that will be available to users through a secure login. The system will provide access to the existing dataset, the modeling tools, and machine learning/data mining tools. To add significant value to the data maintained in the database, we are building a machine learning framework that can provides for training a regression model. Our current effort is to build construct a regression model that can correlate results from our experimental modeling work with the properties of a processed carbon nanotube sample. This model could help us better understand the strengths/weaknesses of our modeling environment , and should help to produce carbon nanotubes with the desired set of properties.

Accelerating Materials Discovery & Development

Our current results about the structure transformation of CNTs in the CNT fibers from double walled CNTs to the graphitic nanostructure, which make the application of our electrical fusion method from microscale fusion to the several millimeter or even longer. This result will make people have chance to operate the nanostructure transformation at macroscale to create more promising applications including lightweight but highly functional aerospace platforms, strong, robust, and stretchable conductors, high power density/high energy density system for energy storage, multifunctional membranes and sensors, fast moving and low-voltage actuators, super tough fibers, and more. And also the new built electrical fusion system also can be redesigned to accommodate the requirement of industry, and for the established database and simulation program, it will help to push forward to find more carbon nanotube fibers with high performance and unique properties. A patent related to the electrical fusion method has been field.

Publications

The project has led to four published journal articles, and three more are in preparation.

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“Printing highly controlled suspended carbon nanotube network on micro-patterned superhydrophobic surface“ B. Li, X. Wang, H. Jung, Y. Kim, J. Robinson, M. Zalalutdinov, S. Hong, J. Hao, KT. Wan, Y. Jung, Scientific Reports **5**, 15908 (2015)

"Shaping van der Waals nanoribbons via torsional constraints: Scrolls, folds and supercoils" A. Shahabi, H. Wang, and M. Upmanyu, Scientific Reports **4**, 7004 (2014)

“Printing highly controlled suspended carbon nanotube network on micro-patterned superhydrophobic surface“ B. Li, X. Wang, H. Jung, Y. Kim, J. Robinson, M. Zalalutdinov, S. Hong, J. Hao, KT. Wan, Y. Jung, Scientific Reports **5**, 15908 (2015)

"Shaping van der Waals nanoribbons via torsional constraints: Scrolls, folds and supercoils" A. Shahabi, H. Wang, and M. Upmanyu, Scientific Reports **4**, 7004 (2014)

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. We will 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 the interesting mixed systems that can result from their predicted large band offsets. Ab-initio calculations will help guide the experimental work on this system and also be applied to other II-IV-nitrides. We will construct and maintain a fast-responding, publicly accessible website and database for this project.

Relevance to MGI

The close iterative feedback between synthesis, *ab-initio* calculations, device simulations, and measurements of lattice, electronic and optical properties is illustrated schematically in the figure. Our group has already put this plan into practice in work done preceding this award. This work includes *ab-initio* band structure calculations, synthesis and characterization of $ZnSnN_2$ and $ZnGeN_2$, and the development of a theory of octet-rule preserving cation ordering in the heterovalent ternary nitrides that is an alternative to the theory of random placement of atoms on the cation sublattice.[1] These two models predict very different band gaps for $ZnSnN_2$ and each may in fact apply in different circumstances. Another example especially relevant to this grant is our design of a type-II nitride quantum well light-emitting diode structure with improved overlap of the electron and hole wave functions, based upon the large band offsets between $ZnGeN_2$ and GaN, that results in a six-fold improvement in the spontaneous emission rate.[2] Our group will be uniquely placed to grow this and other mixed binary-heterovalent ternary nitride heterostructures by metalorganic chemical vapor deposition (MOCVD). Our first publication, listed below and partially supported by this new award, will accelerate the development of strategies for achieving controlled doping of $ZnGeN_2$.

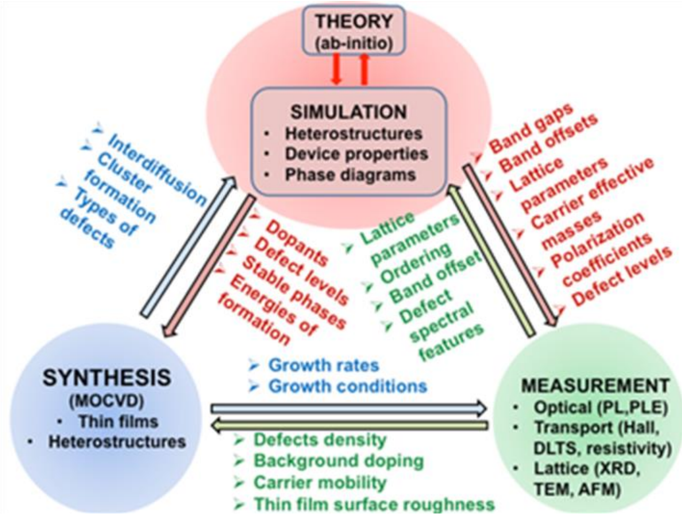

Figure. Illustrated closed-loop, iterative interactions between synthesis, theory and measurement.

Technical Progress

A computational study of native defects and doping in $ZnGeN_2$ has been done using density functional theory, with partial support from this grant in the finishing stages of the work. Energies of formation and energy levels were calculated for Zn, Ge and N vacancies, Zn_{Ge} and Ge_{Zn} antisite defects, the n-type dopants O_N and Ga_{Zn}, and the p-type dopant Ga_{Ge}. Cation antisite defects were found to be the dominant native defects. Ga should act as a p-type dopant but not much more effectively than intrinsic doping by Zn_{Ge}. The n-type doping observed so far in $ZnGeN_2$ in the few cases studied is tentatively ascribed to O_N, although at the growth temperature of 1200 K these should be compensated by the formation of native antisite acceptors Zn_{Ge}^{2-}, in contrast with the case of GaN for which no low energy compensating acceptors exist. Work on the role of exchange defects, *i.e.* defect complexes of Zn_{Ge} and Ge_{Zn} close to each other, and vibrational spectra of an alternative structures of $ZnGeN_2$, the $Pmc2_1$ structure are in progress.

The design of the custom MOCVD instrument has been updated with a dual-chamber design (one chamber dedicated for both II-IV-N_2 and III-N growth, and the other for III-N growth only) with shared load-lock chamber that allows the transferring of materials between the two chambers without exposing to the atmosphere. The instrument quotation has been finalized with the vendor and currently is going through the CWRU institutional review. Lab renovation and infrastructure set-up for the MOCVD instrument is in progress.

Future Plans

The three major goals in the first year of the program are (1) to finalize the design, acquisition and installation of the custom MOCVD instrument that will allow us to grow both binary and II-IV-nitride heterostructures, (2) create, populate and promote a publicly accessible database for the heterovalent ternary nitrides and related compounds, and (3) extend *ab-initio* computational studies to include, strategically, some of the thirty or so other II-IV-nitrides for which band structures and fundamental properties have not yet been calculated or measured.

Specific goals and the work plan for the four years of this program are summarized 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 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, leading to identification of defects through interactive feedback with *ab-initio* computations
- 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 through incorporation of Ga in the $ZnGeN_2$ growth
- Control the doping of both n-type and p-type $ZnGeN_2$
- 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 and other substrates
- Expand the theoretical and computational database of properties of the materials systems, including surface properties, elastic constants, phonons, and defect levels
- Refine our models of the defect physics, including cation ordering, through interaction between theory and experiment
- Do computational studies of surface reconstruction and defects relevant to the experimental growth studies

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, will contribute 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. Dissemination of new and archived results via an interactive website-accessed database available freely to the community with rapid updates, including critical evaluations and comprehensive inclusion of both theoretical and experimental results, will 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 will be established at CWRU with assistance from the IT department. 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 lm-suite at http://www.lmsuite.org/ to which the co-PI W. L. is a contributor. He has also participated as lecturer in hands-on workshops of these methodologies.

Accelerating Materials Discovery & Development

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.

Important hurdles for commercial applications will be to achieve synthesis of high quality $ZnGeN_2$ materials and their doping, and synthesis of $ZnGeN_2$-GaN heterostructures.

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Publications

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High-throughput computation and machine learning for understanding and designing catalysts

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Keywords: Heterogeneous catalysis, transition metals, oxidation, dehydrogenation

Project Scope

This project has two related goals, both of which involve using high-throughput computation and machine learning to study and design transition metal catalysts. First, in order to understand the surface structure and catalytic performance of nanoporous Au and other AgAu alloys, a machine learning algorithm will be trained to predict the surface energies of AuAg alloys with adsorbed O. Second, in order to screen Cu alloys for their catalytic performance for anhydrous formaldehyde production, a machine learning algorithm will be trained to predict the reaction energetics of methanol dehydrogenation on Cu alloys.

Relevance to MGI

Our computational work is part of a larger effort by the IMASC Energy Frontier Research Center. Currently, researchers at IMASC are developing a toolbox of synthesis techniques for synthesizing bimetallic alloys with a particular composition and structure. Therefore, our predictions for effective catalysts can be tested experimentally, and feedback can be given to refine our prediction method. Other researchers are carefully characterizing nanoporous Au and similar systems, allowing us to check some aspects of our predictions of the structures of these systems. For example, the model active site for O_2 dissociation we have identified has a similar activation energy to that measured by experimentalists within IMASC. Within the computational effort, the machine learning framework will be developed as the data are generated, allowing a data-driven approach to both data generation and data analysis, with an overarching goal to develop a materials library through theoretical screening of the surface composition of alloy catalyst materials under working conditions.

Technical Progress

- Modeling of the active surface structure of nanoporous gold

Nanoporous Au is a mesostructured gold-silver alloy with 1-3% silver content. It is an effective catalyst for several oxidation reactions, including oxidative coupling of methanol. Previous work has shown that the dissociation of oxygen (O_2) is a critical step in these oxidation reactions, but it is unclear how nanoporous Au dissociates O_2, as a convincing model of the active site has not been identified. Here, we attempt to find a site that is both stable under reaction conditions and has a low barrier for O_2 dissociation.

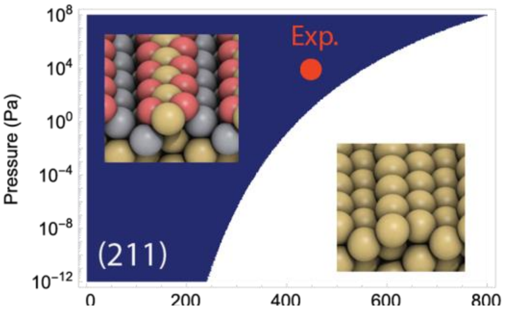

Figure 1. Phase diagram for the stepped (211) surface facet of an AgAu alloy such as nanoporous Au. The phase diagrams for the terrace facets, (100) and (110), indicate that they are inactive for O_2 oxidation, but the AgAu(211) structure shown here is stable under reaction conditions and has a low barrier for O_2 oxidation.

Using the ab initio thermodynamics framework, the free energy of surface structures can be calculated based on their total energies from DFT. Therefore, by calculating total energies of several hundred surface structures, we are able to determine which surface structure is most stable under various sets of conditions. This analysis indicates that the terrace facets (111) and (100), are Au-terminated under reaction conditions. Therefore, they are unlikely to be able to dissociate oxygen. In contrast to the terraces, the stepped facets (110) and (211) are predicted to have Ag at the surface (see Figure 1). In both cases, the Ag sits in the rows next to the step atoms.

To test the activity of these AgAu step sites for O_2 dissociation, the dissociation barrier was calculated on the AgAu(211) surface pictured in Figure 1. The calculated barrier was 0.36 eV, lower than on Ag(110), which can easily dissociate O_2 at room temperature. There is good agreement between theory and experiment, particularly in comparing nanoporous Au to Ag(110). Therefore, the AuAg(211) structure appears to be a good model for the active site on nanoporous Au.

- Modeling alcohol dehydrogenation on Cu surfaces

Current technologies for formaldehyde generation from methanol also generate water in situ, and it is energy intensive to separate the formaldehyde out from the water. Dry dehydrogenation of methanol would obviate the need for this separation, and would also generate H_2, a useful byproduct. As a first step in discovering novel Cu alloy catalysts for methanol dehydrogenation, we have studied methanol and ethanol dehydrogenation on the Cu(110) surface. The results are in clear agreement with experimental work: methanol can dehydrogenate to methoxy, but no further reaction occurs, while ethanol can dehydrogenate to acetaldehyde. Based on our understanding of pure Cu, design of Cu-based alloys is now possible.

Future Plans

While the materials genome approach has not yet been effective in fueling the successful discovery of new heterogeneous catalysts and their more rapid deployment and incorporation into processes in the chemical industry, our EFRC is moving synergistically to pave the way for this.

Our work has given insight into the nature of the active site for O_2 dissociation on nanoporous Au, but a more realistic picture will require consideration of the complex structure of nanoporous Au, as well as explicit consideration of the configurational entropy using Monte Carlo simulations. To perform these simulations on complex structures, a machine learning algorithm will be trained that can predict the energetics of O adsorbed on various AgAu structures.

To design Cu-based alloy catalysts for methanol dehydrogenation, a machine learning algorithm will be trained that can efficiently predict the adsorption energies of the relevant intermediates on each alloy surface of interest. This will require generation of a large number of adsorption energies using DFT, as well as development of a novel machine learning approach.

Data Management and Open Access

We are currently implementing a database that will be available to the public through our website in the next few weeks. The database will initially contain several hundred data points of relaxed coordinates and energies from DFT, and will grow to contain thousands or tens of thousands of data points throughout the course of the project.

Accelerating Materials Discovery & Development

Using machine learning to screen materials for their catalytic performance could, at least in principle, allow new materials to be screened in seconds and for a negligible cost. This initial screening would likely be approximate, but could identify candidates for more careful study. Hence, we will be able to rapidly identify promising materials for catalyzing methanol dehydrogenation. Using previously developed relationships between adsorption energies of various adsorbates, materials could be screened for a wide variety of other reactions. By predicting structural energies, materials could be screened for both stability and catalytic performance.

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Network for ab initio many-body methods: development, education and training

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Website: http://www.qmcpack.org
Keywords: electronic structure, many-body methods, validation, high-performance computing

Project Scope

This project aims to advance the theory, implementation and practical application of high-accuracy ab initio many body quantum Monte Carlo (QMC) methods to accelerate the discovery and characterization of advanced materials and enable sciences critical to DOE missions. The project is organized around developers and users of the open-source QMC package QMCPACK. The project specifically supports methods development and applications, aims to foster the collaborations among developers and users, and to educate new computational materials scientists. The intended outcomes include software, efficient workflows, and data repositories as well as scientific applications.

Relevance to MGI

A grand challenge of quantum mechanical materials modeling is be able to accurately predict the properties of materials without empiricism. This is important for wholly new materials and properties, where no data is available to fit, and for properties and conditions that are experimentally difficult or costly to access. QMC methods are able to achieve this because the methodology is – in principle – systematically improvable, enabling approximations to be tested. Validation is in part performed using standard test sets and established material properties. For example, we have recently confirmed that the binding energies of the S22 van der Waals test set are accurately reproduced with QMC. This set is very well characterized by quantum chemistry and therefore usable for validation. After establishing the accuracy of QMC, we studied the properties of black phosphorous, [1] an emerging layered material with semiconducting band gap and high carrier mobility of interest for applications. Although previous QMC studies for graphene have shown that modern van der Waals methods can treat graphite with acceptable accuracy, in the case of layered phosphorous we find a large and unexpected reorganization of the electronic charge density. This demonstrates that this phase of phosphorus should not be considered a pure van der Waals material, and also exposes significant weaknesses in current density functional theory (DFT) approximations. The QMC calculated lattice constants are in good agreement with experiment, lending credence to the calculations.

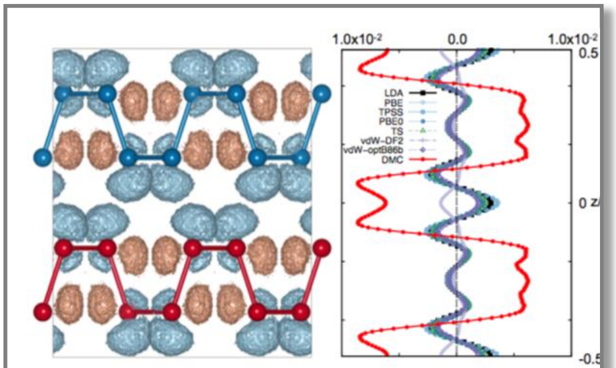

Figure 1. (Left) Charge reorganization induced by the interaction of black phosphorous layers. (Right) Large qualitative differences in charge transfer between density functional theory predictions and QMC (red), from Shulenburger et al. Nano Letters **15** 8170 (2015).

We have utilized a similar approach to provide predictions of high pressure properties of materials that are difficult to access experimentally. To understand the phase transitions of MgO [2], we first validate the ambient condition properties using experimental data. The density/pressure dependent energy is then obtained from QMC calculations and combined with DFT-derived dynamics data to obtain the Gibbs free energy. The final hugoniot was then used to infer the location and type of the B1-B2 phase transition. We note that the very high precision required in this work challenges not on the QMC but also some common technical choices in the DFT calculations.

Technical Progress

In the past year we have made both methodologically-related improvements and computational or code-related improvements. Firstly, as an example of methodological improvements, we have studied how to efficiently move from single determinant to multiple determinant calculations for molecules. This step essential to reduce the nodal-error, due to the fermion sign problem, which is often the largest source of systematic error for light element systems. Studying stretched configurations of a C_2 molecule we were able to demonstrate that well-chosen orbitals result not only in smaller nodal error, but also a smoother and faster convergence to exact results when combined with multiple determinants. Although chemical accuracy for small molecules is considered readily achievable, our scheme enables a much quicker and therefore cheaper convergence.

Secondly, as an example of an important computational improvement, we have modernized the QMCPACK development infrastructure to increase accessibility, portability, and maintainability. This includes a set of validation tests against known mean-field, quantum chemical, and QMC results. Although currently only for variational Monte Carlo methods, these tests provide important validation and considerable surety in the code, compilers, libraries, and system hardware and software.

Future Plans

In terms of scientific applications, we will focus on topical energy-relevant materials where standard quantum mechanics based approaches are suspect. In terms of technical developments, we will concentrate on characterizing and then reducing the systematic errors introduced by the use of (1) the fixed-sign approximation in diffusion quantum Monte Carlo and (2) pseudopotentials and their evaluation in diffusion quantum Monte Carlo. These errors are well understood and controlled for in light element systems but are not well-enough studied for heavier elements or for materials under extremes of pressure. In terms of computational developments, we are adapting QMCPACK to be able to run efficiently on the next generation of supercomputing systems (both next generation GPU and Intel Knight's/Xeon Phi). E.g. QMCPACK is one of the application readiness projects at the Oak Ridge Leadership Computing Facility for the next generation Summit machine.

Data Management and Open Access

QMCPACK is a fully open source code, available at http://www.qmcpack.org. The project takes specific care to ensure that all the dependencies are also open source, thus permitting reproduction of results and a fully open source capability for ab initio materials and chemical computation. To help facilitate reproducibility we have introduced a lightweight workflow management system that is compatible with the leadership-level computing facilities where QMCPACK is likely to be run. An automated test/validation capability is being developed, and currently provides a thorough test of the variational Monte Carlo capabilities. Outputs are standardized XML and HDF5 for interoperability with data analysis tools or larger materials property databases. To facilitate direct collaboration on methods and implementations, the development source code repository is now publically accessible (http://qmcpack.org/downloads/development-svn/). This has the latest source code updates and bug fixes.

Accelerating Materials Discovery & Development

QMC methods are reaching a stage of maturity and accuracy where they can be used to benchmark themselves, and where they can be applied in a timely manner to newly discovered or topical materials such as phosphorene, and provide essential validation to other computational methods. These materials often have interactions and electronic structures that preclude an MGI approach using established DFT-based approaches.

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10 Relevant Project Publications

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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[1–3] provide an attractive alternative. However, despite intensive study, a reliable design principle for purely organic phosphors is 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.

Technical Progress

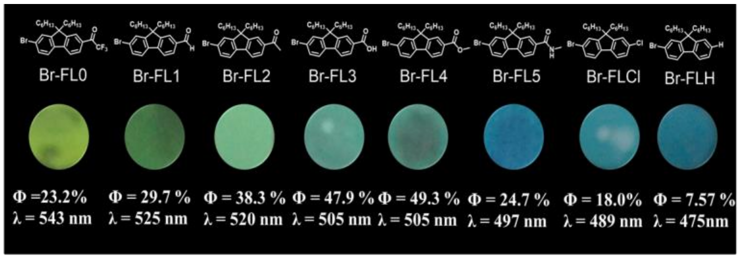

Fig. 1 Chemical structure of compounds Br-FL molecules and their phosphorescence color upon UV irradiation (365 nm) under inert gas atmosphere.

The main goal pursued during this project period has been to unequivocally identify the molecular design principles that facilitate all-organic phosphorescence. To this end we explored the roles of and interplays between non-covalent atomic bonding, spin-orbit coupling, transition rates between electronic states, and the stabilization of molecular vibrations. Accordingly, we used computation to study the influence of molecular conformation on electron relaxation and photophysical properties of a series of biphenyl derivatives. The calculated absorption and emission properties of the series as well as phosphorescence quantum yield are in good agreement with the available experimental data. The spin orbit coupling values and the S→T intersystem-crossing matrix elements and crossing rate constants are also explored as a function of the twist angle between the rings. Inspired by the “heavy-atom effect”, seen with addition of iridium or osmium, bromine has been used to effect efficient room-temperature phosphorescence in an organic crystal. Using molecular simulations, we ascertained that the underlying mechanism is (i) based on halogen bonding between the bromine and oxygen in adjacent molecules, which (ii) enhances spin-orbit coupling between these species.

We also investigated a series of fluorine derivatives (Fig. 1a), controlling the electron-withdrawing power of the carbonyl group via the choice of halide. Given the weak mesomeric effect of the carbonyl group, the fluorene derivatives exhibit blue-shifted phosphorescence, reduced phosphorescence lifetime, and high quantum yields. By substituting the carbonyl group with a chlorine atom and embedding the fluorine molecule in an amorphous polymer matrix, relatively strong phosphorescence is achieved (QY=18%). Compared to bromo-fluorene with aldehyde (Br-FL1), iodo-fluorene(I-FL1) does not phosphoresce. However, by modifying the carbonyl group, iodo-fluorene bright phosphorescence with QY as high as 45% is achieved. I-FL5 phosphoresces as brightly as Br-FL5, which contradicts the common knowledge about the heavy atom effect. Instead, it suggests that the heavy atom effect is due to the influence of the carbonyl group on the electron-density around the halide atom. TD-DFT calculations to elucidate the relationship between chemistry, electronic states, and phosphorescent properties of these fluorene derivatives are currently underway.

Future Plans

Experimentally, separation of multi-varied influences on phosphorescence processes such as phosphorescent radiative decay, non-radiative decay, and singlet-to-triplet intersystem crossing is very difficult. Computational exploration of fluorene derivatives with varying carbonyl groups and halide atoms will provide insight into the room temperature phosphorescence behavior. Immediate next steps in our research will be to (i) further explore the effect of substitution on the singlet-to-triplet intersystem crossing rates; (ii) deconvolute the $T \rightarrow S0$ radiative vs. non-radiative transition rates for each member of the above series, as well as for twisted and planar biphenyls molecules; (iii) optimize the molecular architectures of fluorene molecules for bright and deep blue phosphorescence; and (iv) using computation, predict the absorption, fluorescence, and phosphorescence experimental spectra for strategic members of the above series of molecules, both in their crystalline forms and in solution, so as to elucidate the basic phosphorescence mechanisms in these materials. Based on our computational analysis of experimental observations, we thrive to establish fundamental design rules of purely organic phosphors.

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 will 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.

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An Expert Ab Initio Transition-State-Theory-Based Master Equation Code

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Keywords: master equation, pressure dependent, transition state theory, ab initio, gas phase kinetics.

Project Scope

The goal of this project is to develop expert codes for accurately predicting the kinetics of gas phase chemical reactions. The ab initio transition state theory based master equation (AITSTME) approach provides the basic framework for this effort. The code development effort is designed to facilitate all aspects of the implementation of the AITSTME approach while also increasing its utility through further advances in its theoretical underpinnings. A successful code package will be widely used in the modeling of key reactions in combustion chemistry, atmospheric chemistry, astrophysics, and chemical vapor deposition, for example.

Relevance to MGI

The AITSTME approach provides predictions of the temperature and pressure dependence of chemical reaction rate coefficients, which can be used to effectively derive the chemical genome for various gas phase environments. Our recent two-dimensional master equation study of the HO_2 system aptly illustrates the validation effort for this project (cf. Figure below). Other validations are being performed through various collaborations, where the code is currently being used to explore the combustion chemistry genome and the predictions are being compared with a great variety of experimental measurements.

Technical Progress

We have continued to develop and expand our general-purpose AITSTME software package, termed PAPER (Predictive Automated Phenomenological Elementary Rates). The central element is a new master equation system solver (MESS) for complex-forming chemical reactions with multiple wells and multiple bimolecular products. The code includes a variety of features for (i) solving the master equation, (ii) incorporating advanced treatments for the transition matrix, and (iii) for examining the outcome of the kinetics. Currently, the solution features include parallel direct diagonalization of the transition matrix, a low-eigenvalue method for low temperatures, well truncations as appropriate, and limited use of quadruple precision for problem cases. The transition matrix allows for multidimensional quantum and semiclassical treatments of torsions, anharmonic treatments of umbrella modes, IR radiative transitions, inclusion of external reactants, automated connectivity, a variety of collisional energy transfer kernels, and a number of “standard” statistical models. The output features include automated merging of species, evaluation of product energy distributions, hot reaction probabilities, and time dependent species populations. Many of these features are only available in the MESS code. Considerable effort was devoted over the last year to increasing the stability, utility, and efficiency of this code.

Various ancillary codes, that are directly coupled to the MESS code and are part of the PAPER package, provide a number of additional features. For example, the VaReCoF code allows for the parallel implementation of direct variable reaction coordinate transition state theory, the DiNT code implements Direct Nonadiabatic Trajectory simulations, the OneDMin code estimates Lennard-Jones parameters from detailed intermolecular potentials, and a python script generates PLOG modified Arrhenius fits for all reaction channels over a complex potential energy surface.

The MESS code is proving to be of great value for studying the kinetics of complex systems. For example, Alexander Mebel, a world leader in the exploration of potential energy surfaces for PAH forming reactions, recently spent a sabbatical at Argonne with the express purpose of learning to use the PAPER package of codes. As a first step, Alex used the codes to predict the temperature and pressure dependent kinetics of the reactions involved in the conversion from phenyl to naphthalene via the HACA mechanism. This analysis demonstrated the key importance of treating the pressure dependence, which has been ignored in all prior combustion modeling studies. These results have led Alex and our group to initiate a long term collaboration to predict the temperature and pressure dependent kinetics of all the main pathways involved in the conversion from one to two or three aromatic rings. Such an analysis, which would not be feasible without the PAPER software package, should significantly improve the fidelity of PAH formation mechanisms used in combustion models.

We have also continued our work on coupling the two-dimensional master equation (2DME), in energy E and angular momentum J, with accurate calculations of collision induced E and J transfer rates. This work has involved further code development, together with a new application to H + O_2 (+M) → HO_2 (+M), which is the most important recombination reaction in combustion. The resulting predictions are in remarkably good agreement with the extensive experimental data (cf. the Figure), and allow for a more accurate description of the dependence of the kinetics on various colliders. Interestingly, the results indicate a much more gradual approach to the low-pressure limit than was previously assumed on the basis of the one-dimensional master equation calculations.

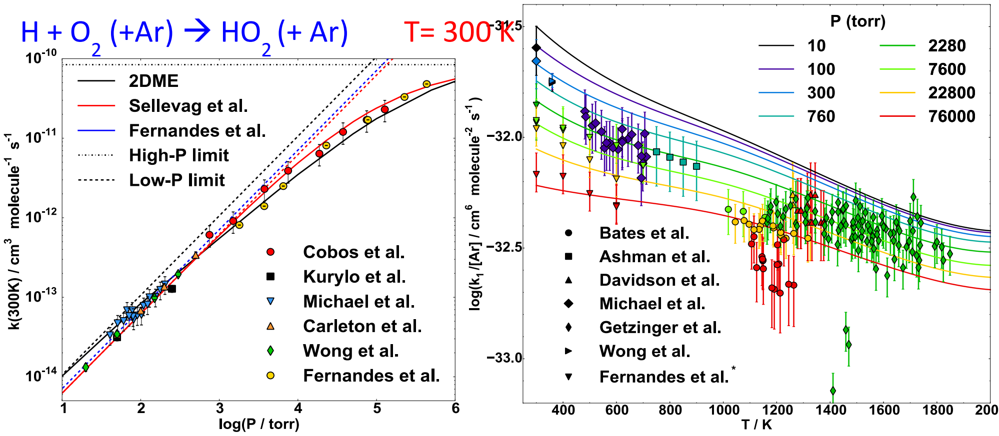

Figure Caption: Temperature and pressure dependent a priori predictions for the H + O_2 recombination rate coefficient compared with experiment.

In another recent application, we predicted the kinetics of the O + C_2H_4 spin-forbidden reaction by incorporating a nonadiabatic statistical treatment of intersystem crossing in the ME approach. This method is sometimes called “nonadiabatic transition state theory,” as the operating equations have similarities to conventional transition state theory. The weak nonadiabatic coupling was modeled using the Landau-Zener expression, which was validated against a more detailed multidimensional approach in our earlier work. The resulting a priori product branching was found to agree well with available room temperature experimental results and with an earlier empirical ME calculation. However, the results of the a priori and empirical ME calculations differ from one another at elevated temperatures (where no experimental results are available), thus emphasizing the usefulness of fully a priori predictions.

Future Plans

Continued progress in the automation of the kinetic predictions will require further consideration of the coupling to ab initio electronic structure evaluations. Further work on more general programming of the 2DME is also planned. Another topic of interest involves the development of coupled master equations that treat a succession of reactions without the presumption of thermalization at each stage of the reaction.

A systematic study of intersystem crossing for several O + alkene and alkyne reactions is underway. This study will make use of several of the codes newly developed for this project, allow us to quantify the accuracy of the ME approach when applied to spin-forbidden reactions, and will result in the development of improved strategies for treating intersystem crossing.

Data Management and Open Access

We have distributed our AITSTME master equation code (MESS) and ancillary programs in PAPER to select users (~20 groups thus far) for the purposes of beta-testing. A manual describing this code has been prepared and a web release of the code is planned for sometime in January. Two other codes that were developed as part of this work are freely available online:

DiNT: Direct Nonadiabatic Trajectories. A molecular dynamics program for adiabatic and nonadiabatic chemistry, version 1.1; A. W. Jasper, C. M. Oana, and D. G. Truhlar, Sandia National Laboratories and University of Minnesota (2013). http://sandia.gov/~ajasper/dint

OneDMin: A code for calculating Lennard-Jones parameters from detailed intermolecular potentials; A. W. Jasper and J. A. Miller, Sandia National Laboratories (2013). http://sandia.gov/~ajasper/onedmin

Future efforts will continue to expand our suite of released codes, including new codes for locating crossing seams, sampling crossing seams, and calculating nonadiabatic fluxes. We will also incorporate our previously published Monte Carlo sampling schemes into our transition state theory codes to allow for more complete a priori treatments of vibrational anharmonicity. Other codes, such as our 2DME code and VaReCoF code, will be made available as manuals are written for them and as they become more stable.

Accelerating Materials Discovery & Development

We have been distributing our codes as freeware, in part because the industrial market for gas phase kinetics is quite limited. Nevertheless, we have a vision of expanding to treat whole classes of kinetics via large scale simulations of many reactions, at which point there may be interest in commercialization of our efforts.

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Coupling Electrons, Phonons, and Photons for Nonequilibrium Transport Simulation

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Keywords: multiphysics, quantum transport, nonequilibrium, nanostructure, time-dependent

Project Scope

The objective of this project is to develop versatile computational tools for accurate simulation of the far-from-equilibrium and time-dependent quantum transport in realistic semiconductor nanostructures driven by high-intensity dc or ac electromagnetic fields. The key challenge is to capture the strong coupling between electrons, phonons, and electromagnetic fields in the same simulation, self-consistently and at every time step.

Relevance to MGI

This project addresses semiconductor-based nanostructured functional materials, with focus on their electronic, phononic, optical, and plasmonic properties in the nonlinear and transient response regimes. While the bulk materials are well characterized, many new properties emerge upon nanostructuring and are accessible in experiments. This work accurately predicts the functional properties of semiconductor nanostructures in experiments under high-frequency and high-intensity excitation.

Technical Progress

We studied the effects of phonon mode conversion and Rayleigh surface waves (they are similar to the waves we feel in an earthquake) on thermal transport in rough nanostructures. Mode conversion among bulk modes has little influence on thermal conduction, but the effect of the conversion into Rayleigh waves is sizeable: with increasing surface disorder, Rayleigh waves readily localize (Fig. 1) and draw energy away from the propagating bulk modes, which lowers thermal conductivity [1].

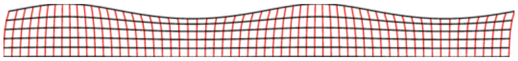

Figure 1a. A Rayleigh wave propagating along a free surface on the top. Wave amplitude decays with increasing distance from the surface.

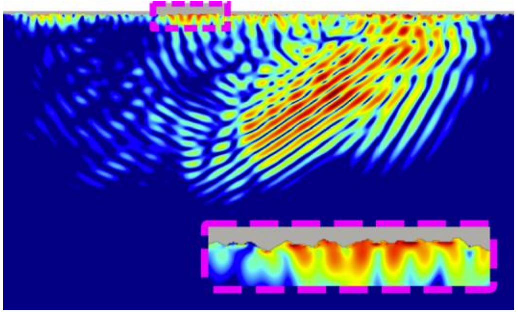

Figure 1b. Colorized energy-density profile after a longitudinal acoustic wave scattered from a rough surface, converting partially into a localized Rayleigh wave (enlarged in box). Maurer and Knezevic [1].

We introduced a method for calculating the dielectric function of nanostructures with arbitrary band dispersions and Bloch wave functions. The response of a dissipative electronic system to an external electromagnetic field is calculated by a self-consistent-field approach within a Markovian master-equation formalism (SCF-MMEF) coupled with full-wave electromagnetic equations. The SCF-MMEF accurately accounts for several concurrent scattering mechanisms. The method captures interband electron-hole-pair generation, as well as the interband and intraband electron scattering with phonons and impurities. We calculated the dielectric function, complex conductivity, and loss function for supported graphene. From the loss-function maximum, we obtained plasmon dispersion and propagation length for different substrate types [nonpolar diamondlike carbon (DLC) and polar SiO_2 and hBN], impurity densities, carrier densities, and temperatures (Fig. 2). Plasmon propagation lengths are similar on polar and nonpolar substrates, and are on the order of tens of nanometers, much shorter than previously reported [2].

Future Plans

The PI will 1) analyze excitonic energy transfer in carbon nanotube aggregates for photovoltaics and 2) combine first-principles calculations with vertical and lateral quantum transport and coupling with full electrodynamics to investigate how 2D materials and van der Waals heterostructures interact with light far from equilibrium.

Data Management and Open Access

Raw data, source code, and figures are being stored for at least three years past the award end or publication, whichever is later. The codes will be made publically accessible (GPL-v3) within the next several years.

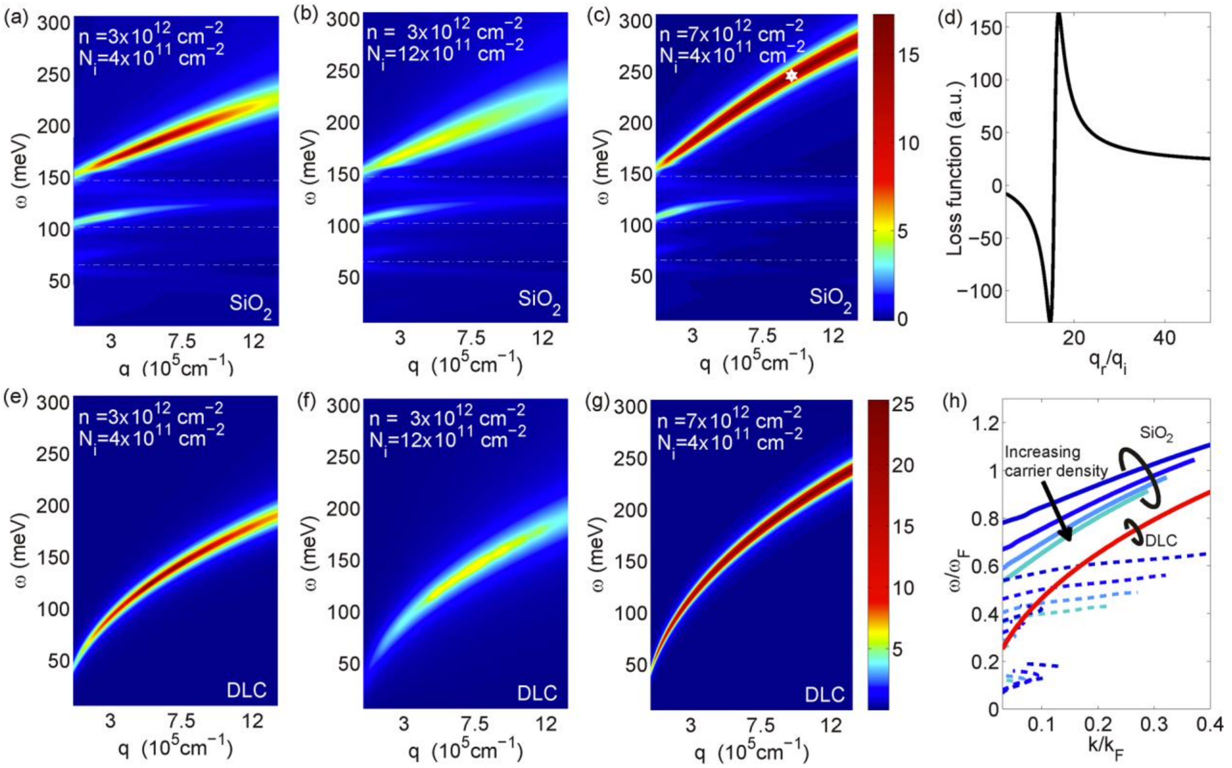

Figure 2. The loss function (related to the inverse of the imaginary part of the dielectric function), represented by color, for graphene supported on SiO_2 (polar material, with strong influence of surface optical phonons, panels a through c) and diamondlike carbon (DLC, a nonpolar material, panels e through g) as a function of wave vector and frequency for different electron densities n and impurity densities N_i. The peak of the loss function gives the plasmnon dispersion (panel h), while the peak width is related to scattering with dopants and phonons and can be used to calculate the plasmon propagation length. Karimi, Davoody, and Knezevic [2].

Accelerating Materials Discovery & Development

This project will reveal novel nonlinear and transient transport properties of semiconductor-based nanostructured functional materials. The work can expand their applications into environments with high-intensity electromagnetic fields or large thermal gradients and enable new applications..

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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 shape and function. While 3D printing processes have restrictions that present 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 (in the future, we will also use a specialized printer using biomaterials). 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.

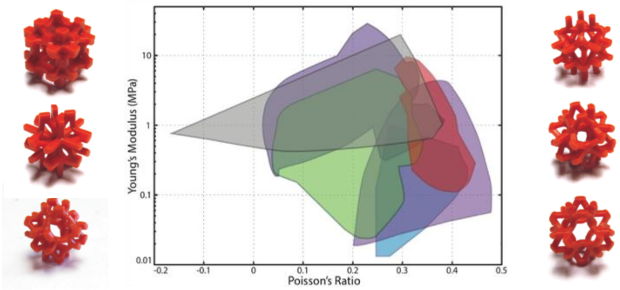

Figure 1. Space of parameters covered by 6 families of 3d patterns with distinct topologies discovered by combinatorial optimization.

Technical Progress

During the last year, the progress was made in several directions:

1. We have completed the development of a full 3D printing design pipeline using our macro-micro approach, for objects whose macroscopic geometry is relatively simple (subsets of rectilinear grids). The pipeline includes:

a. Robust inflation and meshing of truss-like patterned structures.
b. Combinatorial topology optimization for discovery of families of patterns yielding the largest possible space of achievable material properties.
c. Manufacturability criteria for stereolithographic printing validated with fabrication.
d. Shape optimization of periodic patterns, within a constrained space of parameters to achieve specific target properties for 2D and 3D patterns with enforcement of manufacturability constraints.

2. We have performed an initial exploration of objects whose macroscopic geometry is more complicated (eg curvilinear), that require non-square/cubic tilings and irregularities in the grid, to achieve adaptation to the boundary; in particular, we have considered the reduction of pattern design for non-square cells to the problem of pattern design on regular cells with an anisotropic target functional.
3. We are developing a new computational approach to *maximum-stress* shape optimization of patterns, aiming to reduce susceptibility of the designed structure to brittle failure. This effort includes an initial exploration of the optimization process in 2D. A part of the proposed formulation is worst-case design analysis.

Future Plans

As noted above, we are beginning to consider the design of structures whose macroscopic geometry is curvilinear. Also important is the development of methods that permit the microstructural length scale to vary (for example using small pores near the boundary but large pores deep in the interior). Our initial approach involves subdividing the macroscopic design domain with a (mostly regular) quadrilateral (in 2D) or hexahedral (in 3D) mesh. Such a mesh can conform to the boundary, and it permits control of the microstructural length scale (by controlling the sizes of the quadrilaterals). However, defects in the mesh are expected to influence the relationship between microstructural patterns and macroscopic elastic behavior.

Another current thrust is the development of methods for avoiding brittle fracture. This is important for many applications -- including bone scaffolds, which are typically made from hydroxyapetite (a brittle ceramic that's friendly to bone). The main idea is to make sure that the stress (determined using linear elasticity, for a worst-case boundary load) lies pointwise within an appropriate set of "safe stresses". This project offers many new challenges, since it involves a pointwise rather than average objective, and since it involves worst-case rather than fixed loading.

Finally: while we are currently using finite element methods to solve our elasticity problems, we plan to consider the use of boundary integral methods as an alternative. One advantage of boundary integrals is the accuracy they offer in evaluating the stress at the boundary -- a key task in our work on avoiding brittle fracture.

Broader impact

Two Computer Science PhD students are already involved in the project. A student in the Biomaterials department is being recruited. We expect each junior participant to engage in more than one aspect of the project. For example, one of the Computer Science PhD students has already acquired a significant experience in experimental measurements, under the guidance of the dental school co-PIs. Another example: a stereolithography 3D printer purchased with the award (marketed as B9Creator) has an open hardware and software architecture, and is maintained by the students involved in the project, and was used by other groups at NYU for their projects.

Data Management and Open Access

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.

Publications

J Panetta, Q Zhou, L Malomo, N Pietroni, P Cignoni, and D Zorin, *Elastic textures for additive fabrication*, ACM Transactions on Graphics (TOG) **34** (4), article 135 (2015)

Brookhaven National Laboratory – Rutgers Center for Theoretical Spectroscopy and Computational Material Design for Strongly Correlated Materials. DMFT-Mat-De-Lab

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Keywords: Software Development, Strongly Correlated Electron Systems, Software and Methodology validation

Project Scope

Strongly correlated materials hold a promise of revolutionary functionalities ranging from low-loss energy transmission to superior thermoelectric performance. However to understand and predict their properties and functionalities is a difficult task which requires new concepts and highly non-perturbative approaches. To advance discovery in this area tools for theoretically guided experimental exploration are needed. Inspired by the successes of the DMFT (Dynamical Mean Field Theory) based methodologies, we propose the development and the validation of a methodology by which a user can rapidly and easily characterize strongly correlated materials and so reveal their possible functionalities starting from structural information. The software tools and the validation tests will be open source and available to the community.

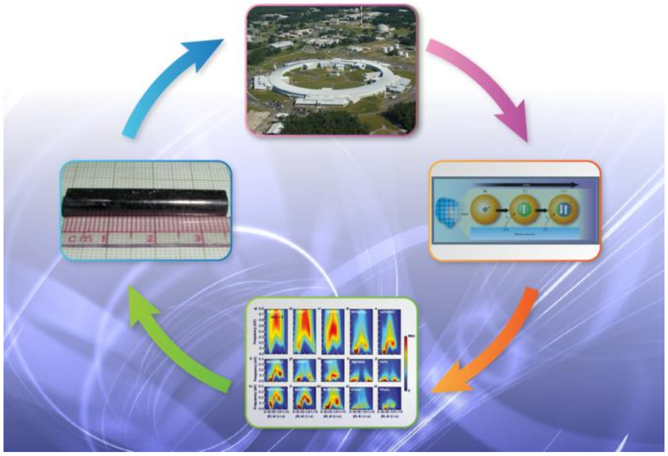

Figure: Key concepts in this proposal are software development for strongly correlated materials based on the Dynamical Man Field Theory (DMFT), leading to theoretical spectroscopic results of realistic materials which in turn are measured by our experimental colleagues. The comparisons provide feedbacks in further improving the capability of our codes to describe strongly correlated electron systems with predicting power, which boosts discovery and design of novel functional materials.

Relevance to MGI

The vast majority of the theoretical tools in use, in the MGI project are based on implementations of the density functional theory. In contrast, the electronic structure of strongly correlated materials is not well described by band theory, which prevents theoretical tools as viable and reliable guides in discovery and design of novel materials in MGI projects. It is the very goal of the development of DMFT-MatDeLab to enlarge the scope of efficient and accurate theoretical investigations to strongly correlated materials. It will enable scientists working on strongly correlated systems to theoretically characterize these systems and concomitantly permit strongly correlated material design to flourish.

Two validation modes will be used. First a small database of spectral data on typical strongly correlated materials will be compiled and compared with the results of LDA+DMFT, LDA+RISB and M-QPGW calculations. A second validation mode will be to carry out the design of functional material, for example, thermoelectric materials building on analogs of the FeSb2 system. This will require multiple integrations of theory and experiment, and would evaluate the quality of the tools to be developed in a material design context.

Future Plans

We envision three complementary DMFT based approaches to electronic structure. LDA+DMFT is a good compromise between speed and accuracy for generating spectra. LDA +RSIB is computationally much faster, and gives rapid access to total energies in situations where crystal fields splitting, spin orbit coupling and multiplet effects are important. GW+DMFT is computationally slower than LDA+DMFT but offers a path to a fully controlled approximations for strongly correlated materials.

Postprocessing modules to make contact with spectroscopic and transport measurements will be developed, in particular estimating the thermoelectric power, and to interface with the existing software for RIXS. To connect with low energy theories, a framework for molecular dynamics for strongly correlated models and connections between electronic structure calculations and Landau Ginzburg like approaches will be developed. Collaboration with computer scientists will ensure that the codes developed run in future high performance architectures. Validation against experiments of standardized codes will be carried out.

Broader impact (Optional for DOE grants/FWPs)

As part of the development of DMFT-MatDeLab, we will tie into the community of users of the National Synchrotron Light Source II (NSLS-II) as well as the nanotechnology center, carrying out research on strongly correlated electron materials.

We expect that as the very important outcomes of this proposal, user-friendly and well-documented computational packages will be highly beneficial to scientists in the entire community of strongly correlated materials by providing a set of standardized tools as the available famous tools such as VASP and Wien2K for weakly correlated systems.

Data Management and Open Access

The codes developed validated and optimized in the course of this project will be made available to the community via github, and links in the project website.

Inverse Design of the Self-Assembly of DNA-Grafted Colloids

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Keywords: anisotropy modeling, self-assembly, orientation driven organization, DNA, genetic algorithm.

Abstract

The self-assembly of DNA-grafted nanoparticles has garnered considerable interest in recent years. However, many of these efforts focused on the usage of spherical nanoparticles, which limits us to the formation of only a handful of crystal lattices. Recent synthetic advances have directed attention towards the usage of anisotropic particles for self-assembly. Here we combine experiments and theory on a series of DNA-grafted nanocubes to understand the structures that form and the factors that control them. Our studies indicate that shape anisotropy of the building blocks, not only directs where DNA linkers graft onto the particle (i.e., preferably to corners vs. faces), but also how they pack and orient themselves relative to each other. This results in a whole range of new crystal structures, and also enables the system to selectively transition between different sub-lattices of the same crystal class (e.g., a FCC structure where the cubes are either oriented face-to-face or face-to-edge). These results emphasize anisotropic self-assembly as a powerful new tool that allows for precise and directed control of nanoparticle self-assembly.

Project Scope

There has been increasing interest in programmable self-assembly for materials fabrication. While the traditional Edisonian approach has led to the development of several new theories and simulation results, it is limited in that it does not allow for design of the building blocks to form desired structures. An *a priori* approach involves determining the correct set of parameters with which to construct the initial building block so that they will preferentially self-assemble into any pre-defined target morphology. Here, we propose to develop a design framework that couples an optimization protocol to a rapid forward model to accelerate the design of the building blocks of interest (i.e., vary size, shape, and ligand densities) that can assemble into desired structures.

Relevance to MGI

The current state of the art method for DNA-mediated self-assembly revolves around the usage of isotropic particles of varying sizes, grafting densities. The two sets of colloids are grafted with complementary DNA single strands; the base pairing of these strands leads to nanoparticle self-assembly below the DNA base pairing transition. However, the use of spherical building blocks only yields few lattices. Due to recent synthetic advances, attention has shifted towards the self-assembly of DNA-grafted anisotropic particles in an attempt to expand the space of accessible lattices. Here, we combine experiments and theory to probe our understanding of the assembly of DNA-grafted nanocubes. Our studies indicate that anisotropy not only directs where ligands graft onto the particle but also affects how they pack and orient themselves, giving rise to an orientation-directed self-assembly. Furthermore, these new features enable the system to selectively transition between different sub-lattices of the same crystal class. This new ability to accurately model the assembly of non-spherical building blocks promises to revolutionalize this field of research.

Technical Progress

Previous works by Torquato and Dijkstra suggest that the packing entropy directs cubic particles to assume simple cubic (SC), face-centered cubic (FCC), and body-centered cubic (BCC) lattices depending on the size ratios of the colloids. The grafting of DNA to these cubic systems, which creates anisotropic coronas around the cubes, introduces directional attractions that overwhelm these entropic effects and directs their self-assembly. As a result, we expect these coronas to dramatically alter the traditionally expected morphologies as compared to the hard-core entropic packing observed previously. In order to address this issue, use the superellipsoid form $\left(\left|\frac{x}{R_x}\right|^r + \left|\frac{y}{R_y}\right|^r\right)^{t/r} + \left|\frac{z}{R_z}\right|^t = 1$ to describe arbitrarily shaped colloids, e.g. sphere, cube, cylinder, cross, and octahedron – through the tuning of the two parameters r and t. We then combine this with the Daoud-Cotton to capture the packing entropy experienced by a grafted chain on different parts of these superellipsoids. Our result indicates that the size of the DNA-grafted particle scales as $R \sim r_o \Omega^{-3/5} N^{3/5} \upsilon^{1/5} l^{2/5} f^{1/5} \left(\frac{l}{r_o}\right)^{3/5}$, where r_o is the size of the core, N is the number of monomers on each graft, υ is the excluded volume of the graft, f is the grafting density (chains/area), l is the Kuhn length, and Ω is a parameter that defines both the shape of the core and the position of the graft on the surface of the particle. Comparison of the theory to experimental data yields a similar 5x preferential packing towards the corner and edge of the nanocubes (Fig. 1). This preferential attachment of DNA chains is critical since, ignoring it, yields incorrect predictions for the structures that form (i.e., Fig. 2b vs. 2c/2d).

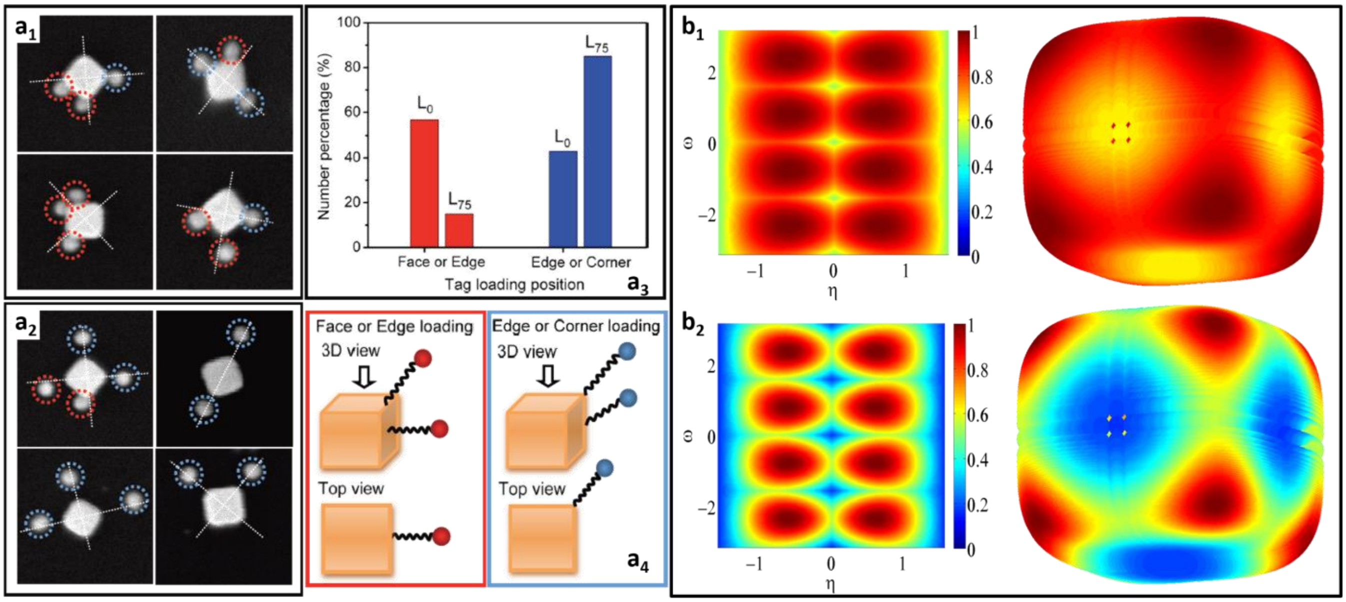

Figure 1. a SEM images of nanocubes hybridized with marker particles using DNAs of lengths L_0 (a1) and L_{70} (a2) (field of view is 100nm). Schematic of face-or-edge binding (c3) and edge-or-corner binding for marker particles (a4). Histogram of binding sites for marker particles for linkers L_0 and L_{70} obtained from SEM images (a3). b). Scaling model prediction of preferential attachment. (b1) Predictions for L_0. (b2) Predictions for L_{70}. Left: probablity distribution function (pdf) calculated at various points on the particle (defined by the angles ω and η). Right: pdf mapped to particle surface. The probability shown is a relative probability scaled to range between 0 and 1.

To study self-assembly, we graft ligands to both Au and Ag nanocubes and determine the resulting lattice structures. To model these two different elements we note that they have different van der Waals radii, and hence lattice spacings – this restricts the maximum number of ligands that can be grafted. Using this fact, for the Ag-nanocubes, we predict transitions from a SC to the FCC to two BCC sublattices – edge-edge (EE) and corner-corner (CC), respectively – with decreasing size ratio. For the Au-nanocube system, the transition goes straight from a SC to a BCC lattice. However, the resulting BCC lattice is one that has not been observed previously. Close inspection reveals that this new lattice is a BCC with its unit cell shifted 45° along both the x and y-axis while holding the origin in the same position –"a zig-zag BCC" (BCC-ZZ). The difference between the observed morphologies immediately suggests that the core type itself plays a much more direct role in self-assembly than previously believed (Fig. 2). These results are in excellent agreement with experimental findings.

Future Plans

It is clear that anisotropy not only allows us to access previously unobserved structures, but also gives rise to orientation-directed self-assembly. The ability of the superellipsoid model to create different shapes immediately suggests the possibility of ``mix-and-match" approach for inverse design - that is we use particles of different shapes in order to search for new stable lattice structures. One additional aspect of interest is the effect of preferential attachment of linker of varying lengths onto the surface of anisotropic particles. We could graft linkers of varying lengths onto the same particle. The result will be a particle whose effective shape differs dramatically from its initial building block. This insight leads to the idea of selective design of new molecular building blocks through the tuning of preferential grafting via grafts of different sizes.

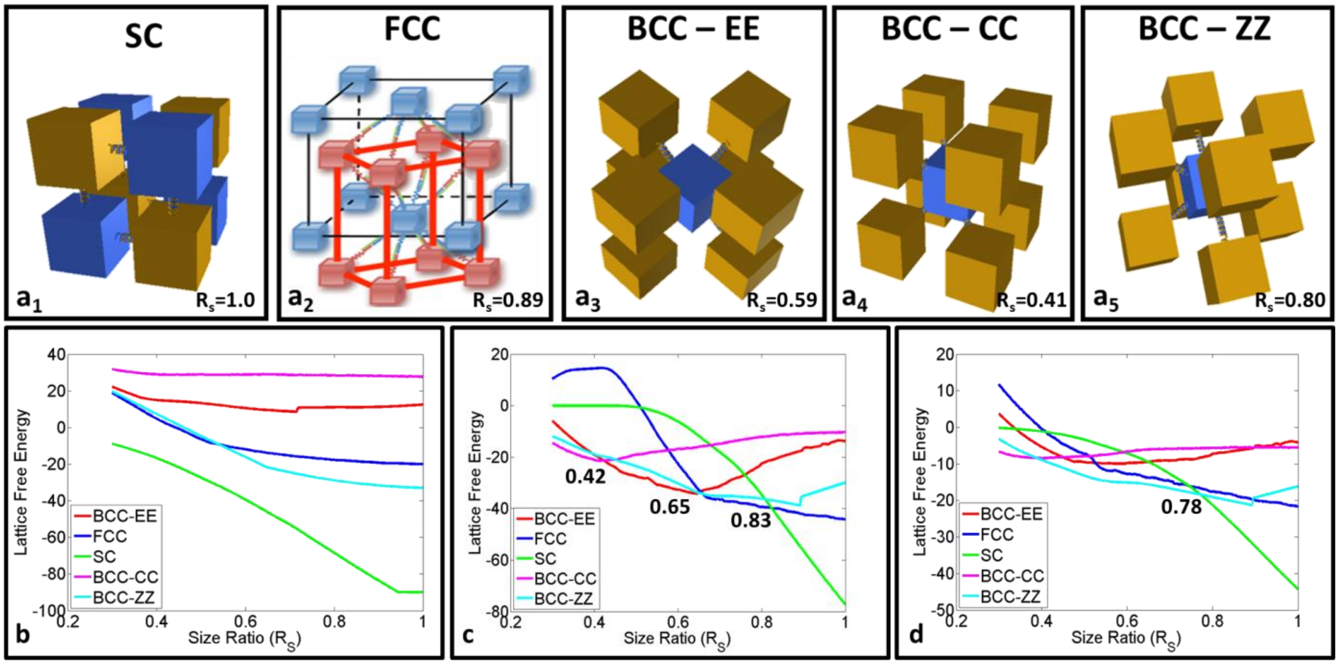

Figure 2. a). Crystal structures of observed experimentally. b). Isotropic grafting. c). Preferential grafting – Ag nanocubes. d). Preferential grafting – Au nanocubes. No transitions observed for isotropic grafting. Correct transitions observed for preferential grafting in both Ag and Au systems with good agreement with experimental data.

Data Management and Open Access

The final version of our inverse design framework combining both our new theory and optimization will be made available on the Kumar group website at www.columbia.edu/cu/kumargroup.

Accelerating Materials Discovery & Development

Our analysis reveals that shape anisotropy creates an entropic driving force that directs the packing of linkers of varying lengths on the particle, producing a preferential attachment effect. Additionally, we observe the emergence of orientation-directed self-assembly as the energetic driving force behind the phase transitions observed. By considering shape, stoichiometry, size, graft density, core, and orientation parameters, we have 9 separate parameters to consider in our design toolkit. Here, the power of our inverse design framework comes into play as a brute force search for the optimal design parameter is impractical whereas our optimization protocol allows for a rapid search through the phase space and convergence to the target parameters.

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Engineering Strength and Toughness into Metals

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Keywords: Twin mesh engineering, twin nucleation, strength, toughness, HCP metals

Project Scope

The DMREF program, between University of California at Davis (UCD), Georgia Institute of Technology (Georgia Tech) and Los Alamos National Laboratory (LANL), responds to the challenge of accelerating materials discovery and implementation by constructing a fundamental knowledge base to design materials from basic principles that have specific combinations of strength and toughness. A synergistic experimental-modeling approach is implemented to strengthening and toughening in HCP metals via the concept of "twin mesh engineering". Hypothesis is that twin-mesh, two or more intersecting arrays of twins within a grain, can be engineered to attain unprecedented combinations of strength and toughness in HCP metals.

Relevance to MGI

The DMREF program is to promote materials discovery and design with close, iterative feedback loop between materials processing, properties, and modeling. The approach will be applicable to HCP metals that commonly deform by slip and deformation twinning. Ex-situ and in-situ mechanical deformation experiments on Mg and Zr will be carried out systematically to explore the orientation dependence of twin mesh formation and expansion. The analyses will be directed with a view towards advancing the atomistic and polycrystalline plasticity models. These models will be used to predict the textures and deformation processes needed to create microstructures profuse with twin meshes. For validation, bulk processing and characterization on polycrystalline Mg and Zr will also be performed. Finally, constitutive model predictions and mechanical test results for strength and toughness will be compared and linked back to the twin-mesh microstructure. For instance, ex-situ EBSD-deformation studies validated the modeling results which predict that deformation twins nucleate preferably at existing low angle grain boundaries. Furthermore, new findings from EBSD suggest that newly created sub-boundaries by slip during deformation also promote twin nucleation in the vicinity. On the basis of these findings, new models are being developed to elucidate the details of twin nucleation and twin-slip interactions.

Technical Progress

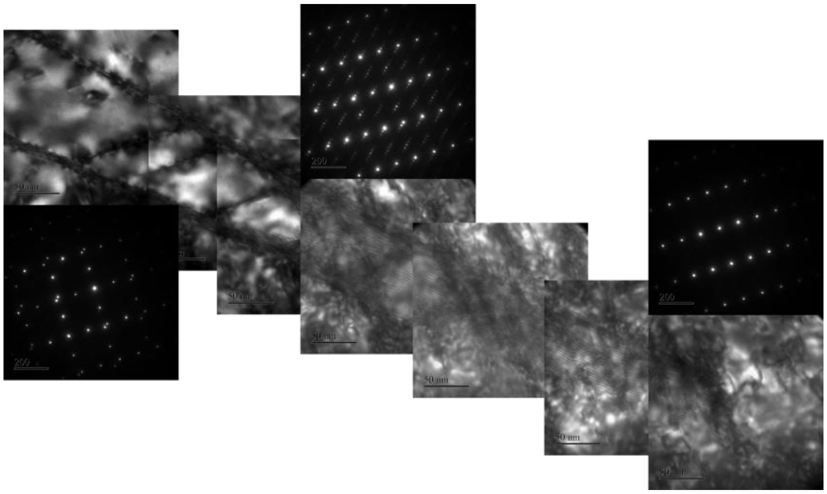

Figure 1: A stitched micrograph of a twin tip, and corresponding diffraction patterns for selected areas: right, regular pattern for the parent grain; left, regular pattern for both twin and parent grain; middle, peculiar pattern for the "transition" area from the twin tip to parent grain.

Both in-situ and post-mortem TEM studies have resulted in abundant novel discoveries concerning twinning mechanisms. Figure 1 is just one example: a twin tip in a slightly deformed pure Mg rolled plate was observed in detail. Whereas a regular twin is evident from both the bright field image and the corresponding diffraction pattern on the left, a peculiar diffraction pattern for the "transition" area from the twin tip to the matrix was recorded. There are arrays of many extra diffraction spots, and direction of the arrays corresponds to that of the twin plane. Therefore these extra spots are likely caused by nano-sized embryonic twins which are difficult to observe using TEM due to their small size and the thickness of the TEM sample. In addition, detailed diffraction contrast imaging for the dislocation configuration in the vicinity of the twin tip revealed that a band of <c>/<c+a> dislocations is ahead of the twin tip, suggesting a "slip band conversion" twin nucleation mechanism.

We have also started advancing our HCP single and polycrystalline modeling tools to account for multiple twin variants and twin types within individual crystals. Moreover, an in-situ TEM study is being pursued at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory, in order to: (1) capture the initiation of twinning events; (2) study the dislocation structure in the vicinity of embryonic twins; (3) therefore understand the nucleation mechanisms of twinning and the possible interactions between slip and twinning. Particularly, novel designs of in-situ TEM samples developed in our research program allow us to confine the twinning event(s) to desired extent, enabling us to study different stages of twinning.

Future Plans

This DMREF program will tightly integrate experimental and modeling efforts across UCD, Georgia Tech and LANL. To engineer twin meshes, existing theoretical models will be used to guide *in-situ* experiments and in turn, experimental results will be used to formulate and/or refine physical models that can ultimately be used to increase the accuracy of model predictions. Three fundamental questions for HCP metals will be answered: First, is slip an essential precursor to twinning and if so, how does it influence twin nucleation and thickening? Second, how are twin/slip and twin/twin interactions accomplished? Third, what texture and deformation conditions are needed to produce a high density of twin meshes? The mechanistic information derived from TEM and in-situ deformation experiments will be used to refine existing physical models, and formulate novel ones as new mechanisms are discovered.

Broader impact (Optional for DOE grants/FWPs)

The broader impact of the DMREF program is a solution to the long-standing problem of strengthening and toughening in HCP metals via an ingenious notion of ***"twin mesh engineering"***. The research formulates the scientific framework required to design twin meshes that can be used to attain unprecedented combinations of strength and toughness in HCP metals. This approach has a generic application to materials that deform by twinning. The DMREF program facilitates complementary collaborations and academic exchanges through mutual visits, in particular with participation of students at graduate level between LANL, Georgia Tech and UCD. For instance, one UCD graduate student supported by this DMREF program has already visited LANL for model development. The research activities are to provide excellent educational experiences for the graduate students involved. Students are encouraged to present their research at national and international meetings. Relevant interdisciplinary research activities can provide the students an in-depth understanding of scientific phenomena in materials science and engineering.

Data Management and Open Access

The Data Management Plan (DMP) is to be created and maintained to: (1) ensure the preservation of the data collected through the DMREF program, as well as any results derived from associated research; (2) provide the appropriate protection of intellectual property generated from the DMREF program; and (3) implement the dissemination and sharing of the associated research results created from the DMREF program. This DMP covers the data to be generated and collected through the collaborative research for the DMREF program at UCD, Georgia Tech and LANL. The majority of information generated will be stored and archived through both publication in the research literature and on a website. With each file there will be a pdf document describing the source, the data acquired and the data format. Access to the archived data will be granted for noncommercial research-based individuals or groups.

Accelerating Materials Discovery & Development

The first year of this project was principally focused on enhancing our fundamental understanding of twin nucleation and growth, and their various interactions using both experimental techniques and modeling approaches. The materials development through the concept of "twin-mesh engineering" remains an on-going effort.

Publications

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First-Principles-Based Design of Spintronic Materials and Devices

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Website: http://heusleralloys.mint.ua.edu
Keywords: Heusler, Half-Metal, Slater-Pauling, Spintronics, Formation energy

Project Scope

There are three interacting components of our project. First, the theory team aims to make reliable predictions for new spintronic materials based on our hypothesis of how half-metallic Heusler alloys form (Figure 1). Second, the experimental team attempts to synthesize the most promising materials to determine their basic structural, electrical, and magnetic properties. This information is fed back to the theory team to refine their predictions. Interesting bulk systems are then investigated in thin film form, allowing more advanced characterization and heterostructure growth, providing further feedback to theory. Iteratively refining this process is the overall goal of our project.

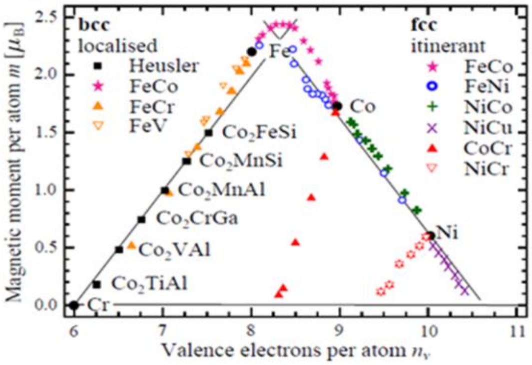

Figure 1. The magnetic moment of 3*d* elements and their binary alloys can be estimated from the total number of valence electrons. Almost all ternary Heusler alloys show this Slater-Pauling tendency. When there are $3e^-$ per atom, there is a gap or pseudo gap in one spin channel near the Fermi energy, creating a half metallic ferromagnet. This is the starting point for rational design of new half metals.

Relevance to MGI

Our project utilizes a close, iterative feedback loop between synthesis/processing, properties/measurement, and theory/modeling. Our database of calculated properties is examined for interesting new alloys that have calculated formation and ordering energies that indicate they may be synthesized. The alloys are synthesized by arc melting and annealing and by sputter deposition and annealing. After synthesis they are characterized by X-ray diffraction, metallography, scanning electron microscopy, electron dispersive spectroscopy, and magnetometry. Often, as we illustrate below, additional first-principles calculations are used to better understand the results of synthesis processing and characterization.

Technical Progress

The theory component has produced a survey of nearly 1000 Heusler alloys whose properties are already available to all at https://heusleralloys.mint.ua.edu. The full Heusler and half-Heusler data are available and the inverse- Heusler data has been calculated, checking is nearly complete, and it will soon be uploaded to complete the database. The experimental team assisted in the production of the website by helping to find references to both the experimental and theoretical literature. The experimental references were used to distinguish between those materials that were already well known, and previously unknown alloys that from the calculations appeared interesting/promising. The latter were further evaluated for suitability for fabrication with available resources. Inspired in part by the discovery of the layered-full-half-Heusler system (joint theory/experiment), the most recent theory work is oriented more towards layered Heusler systems with a paper under review and interfaces between Heuslers and other spintronic materials such as MgO.

An intriguing example of the interplay between theory and experiment is the recent work on FeTiSb alloys. Fe_2TiSb was identified by the experimental team as interesting based on the theoretical prediction that it was a near half metal with negative energy of formation, and no previous investigations. Interpretations of the experimental results were discussed in bi-weekly meetings of the theory and experiment teams. Puzzling experimental results on the Fe stoichiometry were partially resolved when half-Heusler database became available. It became clear that there might be a competition between the full- and half-Heusler phases. Calculations with moderately large supercells indicated that the alloy might consist of alternating layers of the full- and half-Heusler. A collaboration with Northwestern University established (via cluster expansion) that the most likely form of the equilibrium phase is full and half-Heuslers subunits layered along the (111) direction. We currently are evaluating the (Fe,Co)TiSb system, with the primary idea being to see if there exist other layered Heusler phases within the phase diagram.

The experimental team continues to evaluate the calculations, and is focusing presently on Fe_2MnGe, and Cr_2MnGe. Fe_2MnGe has already proven quite interesting: while theory suggests the $L2_1$ phase is a stable ferromagnet with a moment of $3\mu_B$/formula unit, the experiments actually find a remarkably stable hexagonal DO_{19} structure with an even higher moment of $5\mu_B$/formula unit. It will be interesting and valuable for the theory team to follow up on this to see if the stability of DO_{19} phases is common for prospective Heusler alloys. Experimentally, it will be extremely important to measure magnetic anisotropy in thin films. Given the hexagonal structure and c/a ratio (~1.25), one can anticipate a large magneto-crystalline anisotropy, which could be important for applications. This effort is currently underway (see below). These results also point out the power in the MGI approach: even though the database was not quite right in this case, it still led us to an extremely interesting material, and ascertaining the failure mode will only improve the theoretical efforts.

Future Plans [300 words]

We have very recently begun sputter co-deposition of Fe_2MnGe films with *in situ* annealing. We were quickly able to reproduce the bulk result of $4.9\mu_B$/formula unit (Figure 2). This gives us great confidence that we will soon be able to grow epitaxial films and perform more detailed structural and magnetic studies. We have also begun a more detailed theoretical study in collaboration with Rohan Mishra (Washington Univ., St. Louis) to understand why the DO_{19} structure is more stable than the Heusler phase. Our initial results indicate the stability of DO_{19} results from strong correlations of Fe and Mn *d* electrons. Depending on the degree of correlation included in the calculation (*U*), there is also a ferro- to ferri-magnetic transition (Fe and Mn spins antiparallel in the latter case). This makes Fe_2MnGe a highly unusual material – both structural and magnetic ordering are highly sensitive to strong electron correlation. Our future work will include more detailed calculations making use of the bulk experimental data, as well as more detailed structural and magnetic characterization of ordered thin films. These results indicate the importance of careful feedback between experiment and theory in the MGI approach – in this case, it revealed the importance of strong correlations which may have otherwise gone unnoticed.

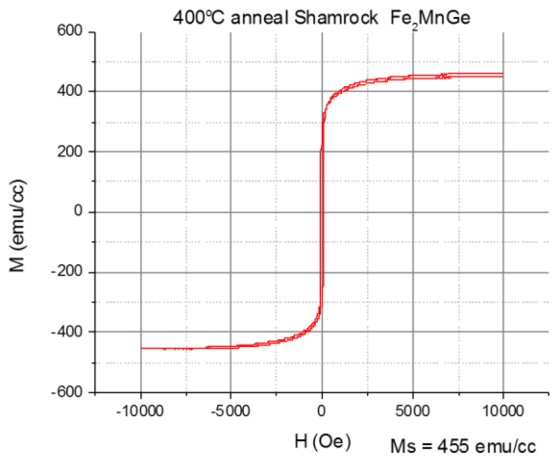

Figure 2. Room temperature magnetometry of a thin film Fe_2MnGe sample. The observed moment is $4.9\mu_B$/formula unit, consistent with our bulk work.

In our work on FeTiSb, in which we identified a new type of layered Heusler phase. In examining the mechanisms giving rise to it in more detail, we believe it to be only a single example of a new class of materials. We have predicted that the SnTiSb system should exhibit similar behavior, and the experimental team is currently working to verify this prediction.

Broader impact

We have been espousing the MGI philosophy and detailing our project outcomes at public talks, conference presentations, departmental colloquia, and in journal publications. Specifically, we have made a particular effort to include an overview of the goals and philosophy of the MGI, as well as our particular implementation. In our case, this means first-principles materials discovery, followed by bulk growth of the target material and a detailed study of its properties. The experimental phase then provides valuable feedback to the theoretical efforts - did the compound exist as predicted? Did its properties match predictions? Why not? The process of refinement and feedback is critical to improving the MGI, and stress this point in particular.

The survey and website now allow anyone to access a consistent set of calculations of the properties of Heusler alloys. Most importantly, it links to the oqmd database of calculated alloy properties which makes it much easier to estimate the probability that the alloy can be fabricated. Several papers are in various stages of preparation.

Data Management and Open Access

The Heusler alloy database is currently hosted at UA and publicly available. NIST has indicated an interest in hosting our databases as part of their participation in the MGI. We are also investigating other alternatives.

Accelerating Materials Discovery & Development

One major finding in our project initially is the utility of bulk synthesis in bridging the gap between theory and thin films and heterostructures. Bulk work allows us to quickly screen compounds at a fraction the time and cost of thin film synthesis. Given a starting point from theory, we can within a few weeks have bulk material synthesized, structure determined, and basic physical characterization performed. This very quickly gives the theory team feedback to refine their calculations and predictions. Once we know the bulk properties, it is far easier to decide which materials are sufficiently interesting to pursue in thin film form. Once thin film results are established, along with a growth recipe, commercialization particularly by the information storage industry is expected to be rapid for materials with desirable properties. As a follow-up to this project, we are in the process of developing an IRG for a MRSEC submission.

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Designing Tunable Au-Based Bimetallic Nanocatalysts

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Keywords: bimetallic catalysts, site-directed synthesis, structure-function catalysis.

Project Scope

The increasing demand for more optimal catalysts requires more efficient and selective catalysts that are less harmful and relatively inexpensive. Gold-based bimetallic nanocatalysts provide greater tunability in nanostructures and chemical compositions than their monometallic counterparts due to undeniable advantages resulting from the alloying "synergy" of gold and a second metal. With recent advances in nanoscience and nanotechnology, it is becoming easier to synthesize, manipulate, and characterize tunable Au-based bimetallic nanocatalysts.[1,2] We are computationally designing and subsequently synthesizing tunable catalysts to improve the reactivity, selectivity, and stability; thereby increasing catalytic efficiencies.

Relevance to MGI

On the basis of strong scientific and application-driven interests in bimetallic nanocatalysts, we are computationally designing Au_nAg_m and Au_nCu_m bimetallic nanocatalysts and expanding our first principles knowledge to other Au-based catalysts. Ultimately, our goal is to build a detailed structure-function mapping of Au-based bimetallic nanocatalysts. *We are currently developing a set of high-throughput algorithms that will create structure-property maps to further enable the design of nanocatalysts for energy and environmental applications.* The impetus for this project lies in the need to develop schemes that build on the multitude of material properties, accurately predicted and measured at the nanoscale, for designing functional materials with tailored properties at the mesoscopic scale.

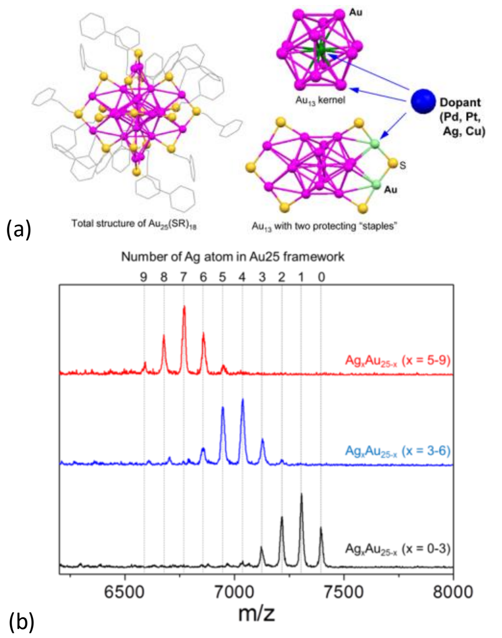

Figure 1. (a) Three types of sites for dopant atom(s) in the crystal structure of icosahedral $Au_{25}(SC_2H_4Ph)_{18}$, including the icosahedral center (dark green), within the icosahedral shell, and in the surface (light green sites) staple-like motifs. **(b)** MALDI-MS of three different $Ag_xAu_{25-x}(SR)_{18}$ nanoalloys. Each peak corresponds to a specific number of silver atoms doped into the Au_{25} framework, as labeled on the top of the figure; for example, x =1 indicates a single silver atom incorporated into the Au_{25} framework and results in the $AgAu_{24}$ nanoalloy, with the total number of metal atoms retained at 25.

Technical Progress

Structure of the $Au_{25-x}Ag_x$ Systems. With respect to Ag or Cu doping, using $Au_{25}(SC_2H_4Ph)_{18}$ as an example, the dopant atom(s) can be accommodated in three types of atomic sites (shown in Fig. 1) - 1) at the icosahedral center (green), 2) within the icosahedral shell, and 3) in surface (light green) staple-like motifs. By controlling the molar ratio between gold precursor ($HAuCl_4$) and silver precursor ($AgOOCCH_3$), different numbers of silver atoms were doped into the $Au_{25}(SR)_{18}$ framework (*i.e.*, the gold atoms are replaced by silver atoms). The composition of $Ag_xAu_{25-x}(SR)_{18}$ nanoclusters (from low silver content to moderate and then to high silver content) was determined by matrix-assisted laser desorption ionization mass spectroscopy (MALDI-MS) (see Fig. 2). The intensity of the peak in MALDI-MS corresponds to the relative abundance of each species. The red MALDI-MS spectrum shows a high amount of silver doping, where the most abundant species is $Ag_7Au_{18}(SR)_{18}$.

*CO Oxidation on the $Ag_xAu_{25-x}(SR)_{18}$ Catalysts***.** The catalytic activity of $Ag_xAu_{25-x}(SR)_{18}$ towards CO oxidation was evaluated and compared with $Au_{25}(SR)_{18}$ to determine the impact of the second element in the bimetallic nanocatalyst. For convenience, the three silver-doped Ag_xAu_{25-x} groups shown in Fig. 1 (b) are labelled according to their most abundant species, *i.e.*, Ag_1Au_{24}, Ag_4Au_{21} and Ag_7Au_{18}, respectively. We find that the Ag_1Au_{24} nanoalloy catalyst shows comparable activity to that of the undoped Au_{25} nanocluster catalyst. We also find that the catalytic activity for CO oxidation decreases as the degree of silver doping increases, which is different from the case of conventional Ag-Au alloy nanocatalysts. The Ag_7Au_{18} nanocatalyst exhibits the lowest catalytic activity towards CO oxidation. The observation of systematic decreasing of CO oxidation activity with increasing number of silver dopants in the Au_{25} framework demonstrates that the catalytic activity in the atomically precise nanocluster system can be tuned on an atom-by-atom basis.

High-throughput Evaluation of $Ag_xAu_{25-x}(SR)_{18}$ Nanocluster Structures. Using our local orbital density functional theory code called FIREBALL, we find that for Ag_3Au_{22} the predominant location of Ag atoms is within the icosahedral shell. After benchmarking these results with VASP, we confidently proceeded to examine hundreds of random structures of Ag_6Au_{19}, Ag_7Au_{18}, and Ag_8Au_{17} to determine the predominant locations of the Ag atoms in each of these stoichiometries. From a computational point of view, a significant distinction from lower quantities of Ag substitution is that a very large searching region is needed to cover more candidates as Ag doping increases. In summary, our results indicate that the greater doping of Ag at the core sites leads to more energetically favorable the confirmations. More specifically, once we increase the numbers of Ag atoms to 6, 7, or 8 sites out of 25 sites, the preferred doping sites exist within the icosohedral core. From the lower energy results, we have evaluated the Fukui functions (functions of nanocluster reactivity) and we can draw conclusion as to why the CO oxidation decreases with increasing Ag doping.

Future Plans

While our chosen prototype is was the $Ag_xAu_{25-x}(SR)_{18}$ bimetallic nanoparticle, we have obtained a framework which can be generally applicable for predictive modeling of other Au-based nanocatalysts. We are now focusing on high-throughput calculations of reactive properties for larger Au-based nanocatalysts to guide and refine a research framework "*aimed at understanding fundamental chemical structure and reactivity and fundamental intermolecular interactions that underpin and will enable the future discovery and design of new materials with predetermined properties and multifunctional capabilities.*" We are exploring the reactivity as a function of several key properties: the size, shape, composition, and stoichiometry. The size and shapes of these chosen Au-based nanocatalysts are determined both by what is experimentally feasible and what is predicted to be optimal *vis-à-vis* the desired functionality, the chemical reactivity of Au-based bimetallic nanoparticles.

We will utilize data from synthesized and characterized structures as feedback elements in our alloyed Au-based nanoparticle designs. We focus on the following tasks moving forward:

- Detailed computational modeling of chemical reactivity for small (< 2 nm) Au-based bimetallic nanoparticles
- High throughput modeling of larger (> 2 nm) Au-based bimetallic nanoparticles (investigating different size, shape, composition, and stoichiometry)
- Au-based bimetallic nanoparticles (small & large), building properties for a structure-property database.

Broader impact

Our proposed research will benefit energy technology that is currently being pursued by experienced researchers at the National Energy Technology Laboratory and this collaboration will continue to promote regional collaboration regarding catalyst design in energy applications. The proposed research will boost the current interdisciplinary collaborations along existing established pathways and thus will impact regional outreach and educational impact for students. We continue to engage under-represented student populations in their research programs and they will continue to cultivate broadened participation for their professional preparations. The National Energy Technology Laboratory is engaged with industrial partners and the research knowledge gained and catalysts designed will extend to these industrial partners.

Data Management and Open Access

Currently, our electronic-structure software package FIREBALL with molecular-dynamics capabilities is freely distributed.[3,4] We have developed a Fukui-function evaluator (using the core components of our FIREBALL code) to http://fireball-dft.org. We are currently in the final development stages of a new, more user-friendly, stream-lined FIREBALL code with full molecular dynamics capabilities. In later stages, as this project progresses, we will port a newly "stable" source of all software components of our FIREBALL software to our website with a copy at Sourceforge (or another third party sharing resource).

Accelerating Materials Discovery & Development

There are aspects of the reactivity development that has attracted the attention of researchers affiliated with BASF, Inc.'s Center for Excellence in Catalysis. We have recently joined that team due to the research progress that we have made under the DMREF funding. We are pursuing a materials genomics approach to investigate other industrial catalysts using our tools developed with DMREF funding.

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A Computational + Artisan Approach for New Materials Discovery

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Keywords: 2D Materials, Machine Learning, DMFT, Transition Metal Oxides

Computational design of materials to meet specific technological applications is gaining an increasing importance. The ability to compute and screen a large number of compounds satisfying specific targets, but decoupled from the ability to process and understand the obtained data, is not necessarily leading to the discovery of new materials with improved features. Great benefits could be obtained from exploiting computational tools along with concepts coming from basic sciences to manage one-by-one small sets of calculations under the guidance of a well-trained and intuitive practitioner. By means of computational modelling we propose a series of new compounds with appealing features demonstrating that they can be obtained upon careful inspection of the physical and chemical properties of the virtual sub-products. Assisted by advanced computational algorithms (machine learning), complex set of equations involved in the materials characterization are solved with great accuracy.

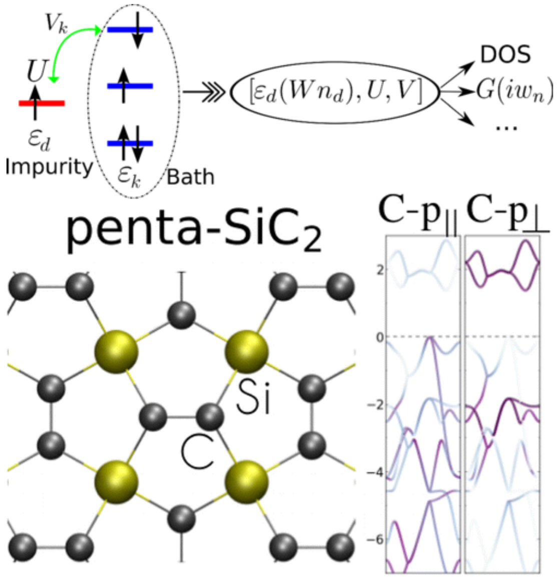

Figure. Machine learning and density functional calculations speeds up the solution of the equations involved in the prediction and description of new compounds.

Project Scope

We aim to demonstrate that an approach based on detail inspection of the intermediated compounds issued from massive calculations is a convenient route for materials discovery. Assisted by our own developed machine learning algorithms and guided by the experience amassed through the analysis of structure-property relationships of individual compounds, we studied a large gamut of material properties, ranging from the electronic properties of 2D compounds, to the transport properties of defected 1D channels, and model systems of the DMFT. Numerous publications from our groups demonstrate that raw high-throughput calculations are not enough when it concerns the discovery of new compounds with physical properties not measurable with a simple scalar, such as band inversion or permanent magnetic moments.

Relevance to MGI

Our two initiatives run in parallel, namely an artificial intelligent based methodology for solving equation involved in the description of correlated materials is developed simultaneously to density functional studies for the prediction of new compounds. Both types of initiatives are expected to converge with the creation of a data base upon collection of experimental data from various groups with experience on measuring the electronic properties of transition metal oxides based compounds with optical and spectroscopic techniques. Also, in an on-going study implying the collaboration from our groups with an experimental team at Argonne is expected to determine the origin of the measured band gap in manganite-nickelite heterostructure.

Technical Progress

Various algorithms based on computational science approached for Physics have been coded, tested, and validated for the prediction of model compounds. Our computational predictions of new compounds with interesting electronic and magnetic properties are gaining increasing attention from the scientific community. Numerous articles have been published in this regard in prestigious journals or are about to.

Future Plans

Our goal is to gather information on a large set of compounds, with special focus on transition metal oxides, to create a data base of public access. Allowing the community to have access to our codes we expect to increase the capabilities of the algorithms via the implementation of new features. Thus, our model systems could be complemented with real materials, whose theoretical or experimental description would constitute the input information for the machine learning algorithms. In contrast to the general trend of intensive calculations for several materials characterization, one of our next steps is moving on to the systematic description of the dynamical properties of a single material requiring large sets of calculations. Granted with a DoE INCITE proposal for large super-scale calculation in leadership computing resources, we aim to push forward the first-principles simulation of uranium based material under extreme physical conditions.

Broader impact (Optional for DOE grants/FWPs)

Several people are being benefited from the project training. Two postdoctoral appointees have gained a broad experience on the definition of relevant physical problems, the use of high-performance computational resources, and proposal writing. Several students at both Columbia University and ANL make the most of the computational resources and training courses under the project framework.

Data Management and Open Access

So far, intensive work on the design, implementation, and validation of the various computational approaches used throughout the project has been done. Public release of our codes is in the pipeline.

Accelerating Materials Discovery & Development

The development of the machine learning based algorithms has resulted in a great gain of calculation speed without loss of accuracy in the computation of many body properties of model systems, and of transmission coefficients for electron channels. Future implementations of the same approaches for real materials will determine the final speed gain which is supposed to be comparable to model systems. Regarding the new predicted compounds, the mixed approach of computational + manual design is yielding results of doubtful success within the traditional MGI framework based on high-throughput screening of binary and ternary compounds. Public reports and on-going publications are available on the new compounds.

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Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling

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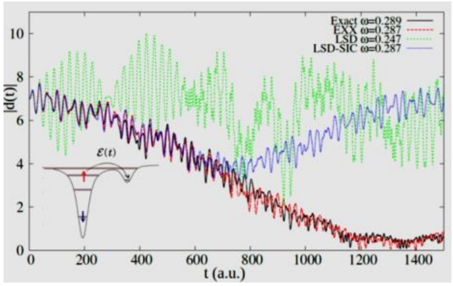
Keywords: time-dependent density functional theory, coupled electron-ion dynamics, charge-transfer, non-equilibrium, non-adiabatic

Project Scope

The goal is to develop a method for electron-ion dynamics in solar cells, using time-dependent density functional theory (TDDFT) for electrons and semiclassics for nuclei, capturing trajectory branching and relaxation in a more theoretically sound way than current methods. Properties of functionals required for *full* transfer of charge, as opposed to merely a calculation of charge-transfer excitation spectra, will be identified and implemented into new approximations, especially for simulations beginning after initial photo-excitation. Semiclassical nuclear dynamics based on the exact factorization of the molecular wavefunction will be developed: the time-dependent potential energy surface (TDPES) incorporates all non-adiabatic electron-nuclear correlation effects.

Relevance to MGI

The computational studies that complement the experiments and syntheses of solar cell candidates routinely use TDDFT with Ehrenfest or surface-hopping to model the effect of coupling to nuclei. It is unclear that the exchange-correlation functionals currently used are reliable and accurate enough for charge-transfer processes, and further unclear that the non-adiabatic effects provided by Ehrenfest/surface-hopping are realistic. We are investigating simple models of charge-transfer dynamics for which exact solutions are available, testing functionals and finding essential aspects needed, and finding features of the TDPES that correctly approximate non-adiabatic effects. These models will be used to validate our new method.



Dipole moments under weak resonant driving under the respective resonant frequencies, where the amount of transferred charge is inversely related to the degree of violation of our new exact condition.

Technical Progress

We found new step features in the exact correlation potential that do not appear in calculations of spectra, but are present in non-perturbative dynamics. A step structure associated with the transfer of charge develops, as well as an oscillatory step with a faster time-scale, both of which require non-adiabatic and spatially non-local density-dependence. Lack of these structures in approximations result in their failure to transfer charge, explaining recent results of others on small molecules. We derived a decomposition of the potential into a component that depends on the exchange-correlation hole, and a component that is kinetic in origin. Although both contribute to the non-adiabatic step, the contribution is often larger in the kinetic term.

We propagated with the best possible adiabatic approximation, i.e. the exact ground-state functional (“adiabatically-exact”). We found that, despite sometimes capturing charge-transfer excitations and ground-state step features in dissociation, adiabatically-exact propagation fails to transfer charge across a model molecule. Full charge-transfer *dynamics* is harder for functionals than calculating charge-transfer energies.

Still, ALDA predicted charge-transfer reasonably well in the light-harvesting carotenoid-porphyrin-C60 triad, leading us to investigate beginning *in a photo-excited state*. If the initial Kohn-Sham state is also chosen excited, no charge-transfer step should appear, although an oscillatory step remains, so approximations might perform better. Indeed we found that the simple EXX achieved resonant full transfer on a two-electron model. Other functionals however failed, and understanding this led us to uncover a new exact condition on the functional with general implications for time-resolved spectroscopy. When a field driving a system is turned off, the Kohn-Sham potential typically continues evolving, yielding time-dependent Kohn-Sham frequencies. The exchange-correlation kernel must cancel this time-dependence, yielding an exact condition, typically violated by approximations.

Earlier work with collaborators from MPI-Halle derived a new formalism for coupled electron-ion dynamics where the exact molecular wavefunction can be factored into nuclear and electronic wavefunctions. The nuclear wavefunction satisfies a Schroedinger equation with a scalar potential, called the time-dependent potential energy surface (TDPES) that contains all the coupling to external fields as well as to the electronic degrees of freedom exactly, and a vector potential containing possible Berry phase effects. In exploring features of this TDPES, we found that quasiclassical propagation of an ensemble of nuclear trajectories on the exact TDPES is accurate in describing branching of a nuclear wavepacket in a model non-adiabatic charge-transfer event in the Shin-Metiu model. This suggests that it is the correct starting point for mixed quantum-classical methods. Further, we related features of the exact surface to aspects of surface-hopping, like velocity renormalization. We also see hints of a force-induced decoherence. We used the exact factorization to define the exact potential acting instead on the electronic system, and compared this to traditional potentials used to study laser-induced electron localization, a technique developed for attosecond control of electrons, and charge-resonance enhanced ionization. Errors in the localization asymmetries and ionization rates predicted by the traditional potentials can be explained by features in our exact potential missing in the former.

Future Plans

We will focus on implementing the exact condition mentioned above, that prevents spuriously detuned resonances. The spurious detuning plagues approximate functionals in use today when the electronic system has evolved far from its ground-state, impacting a range of applications, including level alignment in solar cell candidates after photoexcitation and the ensuing charge-transfer dynamics. We also will develop new approximations that either utilize initial-state dependence to minimize the impact of the step structures that we found to be present in the exact functional that are missing in approximations, or that model important parts of these structures, and we will determine the system-size scaling of these non-adiabatic features.

We will develop a new coupled-dynamics method based on the exact factorization approach. We identified features of the time-dependent exact potential energy surfaces on which the nuclei evolve, that are responsible for wavepacket branching and decoherence, and now we are ready to develop a practical approach from first principles. Our proposed approach treats the nuclei semiclassically, coupled to TDDFT electrons via simplified electron-ion correlation terms arising from the exact factorization.

Broader impact (Optional for DOE grants/FWPs)

Several postdocs are being trained under this project, developing programming and analytical thinking skills, and awareness of the current challenges in computational materials research. They attend several conferences a year where they are exposed to more applied research groups in computation and experiment, and discuss with others there the challenges and what is needed from the more theoretical side.

Data Management and Open Access

On our group website, a list of in-home codes are given with a brief description, including which publications of ours use which codes. Viewers are asked to email me to request the code and explain for what purpose. The code will be shared if in a sufficiently stable state.

Accelerating Materials Discovery & Development

This project investigates the accuracy of currently-used functionals in TDDFT, which is today routinely used to predict and design materials. The rigorously-based electron-ion dynamics method being developed sheds light on traditional methods and overcomes challenges those methods have. This kind of fundamental research is important for building reliable and practical methods for materials discovery. Success of the project will yield accurate, practical, and predictive methods, sound in their basic theory, to model electron and nuclear dynamics in solar energy conversion. The ultimate goal is to use these tools for the computational design of new materials for solar cell devices of high efficiency.

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Laminated Elastomeric Composites with Anisotropic Shape Memory

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Keywords: Shape memory polymer; elastomer; composite; electrospinning; origami

Project Scope

Shape memory elastomeric composites (SMEC) previously developed by the PI's (Mather's) group were prepared by embedding a polymer fiber network in an elastomeric matrix, providing a simple yet very versatile approach[1] for preparing shape memory polymers with novel properties, such as anisotropic shape memory effects, non-affine cold programming, and water-induced shape recovery. The goal of this project is to investigate the structure-function relationship of the anisotropic SMEC (ASMEC) and its laminates, and through the fundamental understanding and modeling to guide and enable the discovery of new shape memory behaviors and applications.

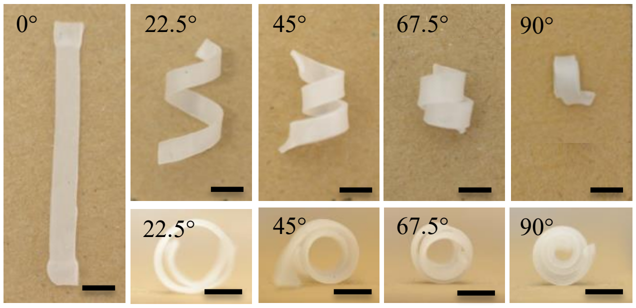

Figure. Representative images of curled bilayer ASMECs, indicating the pitch in the top row and the radius of curvature in the bottom row. Scale bars represent 4 mm.

Relevance to MGI

The development of isotropic and anisotropic SMECs is a highly integrated project involving experimental, theoretical, and computational work. Collaboration between the PIs allows for an in-depth investigation of the structure-function relationship of the materials and for a fundamental understanding of the physics and mechanics that influence observed behaviors. Theoretical models from PI Qi were first verified based on the ASMEC and laminates fabricated by the PI Mather with known material composition parameters, such as fiber and matrix properties, fiber volume fractions and orientation. These models were then used by the PI to predict the behaviors of the ASMEC and laminates with optimized anisotropic shape memory behaviors as well as shape change. These predictions were compared with materials fabricated. Such iterative approach establishes a deep understanding of the underlying physics of the material behavior, improves model fidelity, and thus expedites the broader applications of the promising processing method for ASMEC.

Technical Progress

(i) A constitutive model for mechanically activated ASMEC lamina

The ASMEC lamina consists of an elastomeric matrix reinforced by an aligned amorphous polymer fibrous network. By utilizing the plastic-like behavior of amorphous polymers at low temperatures, a temporary shape can be fixed upon unloading since the induced plastic-like strain resists the contractile force of elastomer matrix. After heating to a high temperature, the permanent shape is recovered when the plastic-like strain recovers. A 3D anisotropic thermoviscoplastic model is developed. In this model, the matrix is treated as a thermoviscoplastic solid, and the fibrous mat is treated as a mixture of amorphous and glass phases which evolve from one to the other as the temperature changes. The anisotropic viscoplastic property of the fibrous mat is captured by considering an isotropic fibrous network superimposed with an oriented fibrous network, with each part a different time dependent viscous property assigned. Good agreement between experiments and simulations demonstrates ability of present model in capturing the anisotropic viscoelastic behavior of ASMEC. The mechanically fixed shape memory behavior of ASMEC was simulated and effects of loading rate and fiber volume fraction on plasticity shape memory property of ASMEC were investigated.

(ii) Water origami

The PI Mather recently reported a water triggered self-folding mechanism by applying electrospun PVAc fiber mat. This PVAc fiber mat 'restore' unrecovered strain during stretching by rotating drum in the manufacturing under room temperature. This fixed strain can be gradually released under water initiated plasticization effect and the material shrinks. When water diffusion starts from top surface of a PVAc fiber mat sheet, a graded distributed material shrinkage along thickness induced by water diffusion will bend the PVAc fiber mat sheet, and finally a self-folding of the sheet is attained. A chemo-thermomechanical coupled model has been built to get a clear understanding on this water activated self-folding mechanism. The type II diffusion model is applied and a viscoplastic constitutive relation is developed to capture water-temperature dependent inelastic material property. The model is calibrated and implemented for the finite element analysis, and the self-folding of the PVAc fiber mat is simulated.

Future Plans

We are in the middle of the final year of our DMREF project. We have developed a preliminary model to capture the activation of the newly developed water-triggered origami with a polymeric web. The model shows a good qualitative comparison with experiments. We will refine the theory and conduct more experiments to obtain good quantitative comparison and then to use the model for design applications.

Broader impact

Several graduate and undergraduate students have contributed to the work described, and as a collaborative and highly integrated project, the students are exposed to and trained in a multitude of materials research areas. As the research is being conducted in an academic setting, the student researchers' group members also benefit from discussion of the projects. An outreach program established by members of Mather's group focuses on educating middle to high school aged students on materials research and engineering. Dr. Qi recruited two middle school teachers to conduct a 10 week research in his group.

Data Management and Open Access

Ten papers were published in the past[2-11] and one invention disclosure was filed, all citing NSF/DMREF support. One more manuscript is in preparation. Data generated are available through contacting PIs.

Accelerating Materials Discovery & Development

Dual electrospinning (electrospinning-based deposition of a mixture of two polymer nanofiber jets) was initiated under this project as a rapid means to fabricated ASMEC lamina. This lead to the discovery that the method is general it is ability to prepare polymer blends of two (2) or more compositions, with prescribed fine scale of blending, < 1 µm. As a materials discovery tool, dual electrospinning can be used to rapidly prepare new blends and examine structure-property relations for comparison with model predictions or to aid in model refinement. Thus far, the work has led to two publications and one invention disclosure, all citing NSF/DMREF support. Co-PI Mather presented the approach to Lubrizol, Inc., under a non-disclosure agreement with Syracuse University for possible co-development.

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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, we propose 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[1]. 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.

Technical Progress

On the theoretical/modeling front, the team led by Nelson and Bowick has used a combination of the theory of thin elastic plates and large-scale numerical simulations to study effects of thermal fluctuations on 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. With a coarse-grained transfer matrix approach, we how shown how thermalized ribbons respond to pulling and bending forces over a wide spectrum of temperatures, forces and ribbon lengths [2]. We have also studied in detail the effect of a slit on a graphene cantilever (Figure). Surprisingly, a slit down the middle of a graphene ribbon can actually lower the mean-square height fluctuations rather than raise it [3].

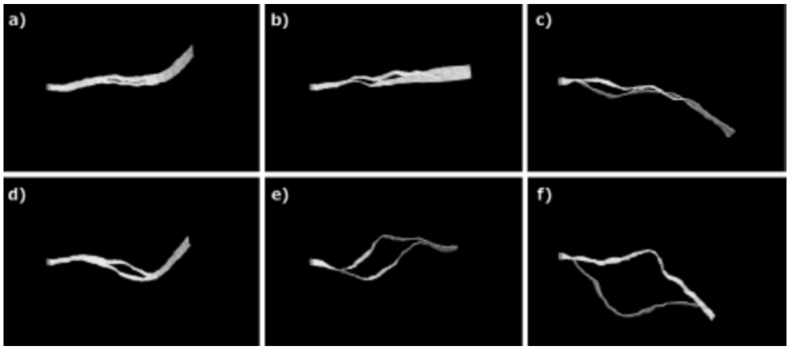

Figure. Snapshots of simulated ribbons with slits undergoing thermal fluctuations. The slits are centered in both dimensions, and extend 30% (a,d); 60% (b,e); and 90% (c,f) of the total length of the ribbon. In (a-c), the two sides of the ribbon remain close to one another, while in (d-f), a large gap is apparent as the two sides of the ribbon fluctuate in opposing directions. Taken from [3].

On the experimental front, we have made significant progress in a number of areas:

(1) The entire team has collaborated closely to identify the best device geometries to address the most important open questions in the basics of graphene mechanics, including fluctuations. This was done over a series of weekly Skype meetings and in-person visits. We identified a number geometries for amplifying the effects of thermal fluctuations, and identified a number of other key geometric motifs (slits and nets, e.g.) that will be the building blocks for kirigami metamaterials. Experiments on these geometries are currently underway. When completed, this will reflect our first full iterative feedback loop from theory to modeling to experiment and back to theory.

(2) A critical need of the project is to measure both static and dynamic fluctuations in graphene membranes with improved time and spatial resolution. To that end, we have developed a high resolution interferometric technique to image the height fluctuations in 2D membranes with ms and nm scale (in height) resolution. Initial results show that there are reproducible static fluctuations in larger sheets, but these are much diminished in thinner sheets. We are now moving on to study the dynamic fluctuations in these devices using this technique, and we expect a publication to be submitted by early 2016.

(3) We have also created atomically thin graphene bimorphs that can bend/fold graphene. In particular, we can now deposit nm-thick silicon dioxide or metal layers by atomic layer deposition and subsequently transfer graphene onto these layers to create the world's thinnest bimophs. These bimorphs show reproducible bending in a controlled and dramatic fashion as a response to a variety of stimuli, including heat, pH, ion concentration, etc. This is an exciting step forward with many potential applications. We expect to finish up this work in the coming months and submit a publication to a major journal. (Note: this bimorph work is also partially funded by the Cornell MRSEC.)

Future Plans

Over the next year, we plan to:

(1) Finish up measurements of static/dynamic fluctuations in graphene cantilevers, including comparison to theory and simulations, and then write up these results. This will provide the bedrock foundation for all the remaining work, including metamaterials and design tools.
(2) We will finish experiments on bimorphs and write up a manuscript on the topic for a major journal.
(3) In a joint theory/experiment/simulation effort, we will attempt to design a graphene kirigami metamaterial that is maximally flexible. This will enhance the effects of thermal fluctuations that are one of the main topics of this grant. We expect this project to fully demonstrate the design loop, from theory and simulation to experiments and then back to theory and modeling.
(4) We will launch a website on 2D materials origami/kirigami, with both scientific and public outreach components.

Bowick and Nelson have hired a joint postdoc Michael Moshe from the Hebrew University of Jerusalem to work solely on the project goals in the next three years. He started September 1. McEuen and Cohen support a postdoc, Marc Mishkin, who is leading the experimental effort, as well as graduate students.

Broader impact (Optional for DOE grants/FWPs)

Cohen and McEuen, combined, gave presentations at 6 conferences/workshops over the past year covering the research funded by DMREF. In addition, they have given approximately 20 seminars/colloquia at universities. All together, these lectures reached thousands of scientists. McEuen has also given multiple public lectures, including the first in a new series at the University of Washington. It can be found online here: http://uwtv.org/watch/SXBHvbRgHHE/. David Nelson's outreach efforts this year included a free public lecture in early July, 2015, at the University of Colorado, Boulder on the crumpling and wrinkling of polymers and membranes. In addition Bowick has presented at Cornell in December 2014 and at Saclay (Paris) in June 2015. Finally, we have, in cooperation with Nature magazine, produced a YouTube video describing our graphene kirigami work: https://www.youtube.com/watch?v=PsIqicBrsQQ. The paper was primarily completed before the beginning of this grant, but the current team participated in creating the video. To date, it has over 23,000 hits.

Data Management and Open Access

This collaborative project (CSH: Cornell-Syracuse-Harvard) will generate a diverse set of theoretical, computational and experimental data that will be of interest to communities in materials science, physics, engineering and chemistry. To unite the diversity in data type and geographical spread of the CSH team, a centralized computer facility for data storage and access will be created. The computer cluster will be housed in the Green Data Center at Syracuse University, and managed by the Syracuse University Information Technology and Services group. This server will be backed up daily on offsite servers at partnering institutions. Individual research groups will be provided password-protected access to the cluster to store and save their data. The team will follow strictly the NSF guidelines related to the data management procedures. No personal protected information of any type will be used and all results of the proposed fundamental research are intended for broad dissemination through publications and presentations.

Accelerating Materials Discovery and Development

What constitutes a new “material” here is 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, combining theory, design, manufacture, and testing in a closed loop is speeding up our ability to explore the possible phase space of these materials. By understanding the 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 have potential applications in number of areas, the most obvious being sensing. As the technology develops, we will seek out specific applications and partners for commercialization.

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2. A. Kosmorlj and D. Nelson, *Response of thermalized ribbons to pulling and bending*, submitted.
3. Emily Russell, Rastko Sknepnek, and Mark J. Bowick, *Stiffening Thermal Membranes by Cutting*, submitted.

Publications

1. Emily Russell, Rastko Sknepnek, and Mark J. Bowick, *Stiffening Thermal Membranes by Cutting*, submitted, http://arxiv.org/pdf/1508.01528v1.pdf

2. A. Kosmorlj and D. Nelson, *Response of thermalized ribbons to pulling and bending*, submitted, http://arxiv.org/pdf/1508.01528v1.pdf

Multiscale Design of Hard and High Temperature Resistant Coatings by Computation and Experiment

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Keywords: High temperature coatings, hard coatings, thermal barriers, ab-initio molecular dynamics, distinct element method simulations.

Project Scope

The goal of this collaborative research is to design and develop a new class of protective (Zr,Si)-B-C-N coatings, coalescing computational investigation and experimental realization and characterization. Applying a hard coating, which bonds strongly to the surface of the material, prevents excessive abrasion and provides the needed shield towards mechanical impacts. At high temperatures and in an oxidative environment, however, many hard coatings quickly deteriorate due to thermal instability and chemical degradation. Thus, there is a need to develop hard, thermally stable and oxidation resistant coatings for high temperature (>1500° C) applications.

Relevance to MGI

The project couples multiscale computations and experiment to merge the high-temperature oxidation resistant properties of Si-B-C-N and high hardness properties of Zr-B-C-N systems. The predictive effort spans from atomistic to multiscale distinct element method simulations to formulate solid predictions of the optimized compositions. These predictions provide critical guidance for synthesizing coatings with targeted properties (hardness, thermal conductivity and high temperature oxidation resistance). We expect that in these new coatings, the desirable properties will coexist, resulting in a new generation of protective layers.

Technical Progress

Our HRTEM studies of amorphous $Si_{30-32}B_{10-12}C_{2-4}N_{49-51}$ coatings showed that they remain amorphous when annealed to 1700° C in air and combine good hardness (20-22 GPa) with an extraordinary oxidation resistance.[1] The high temperature oxidation resistance is attributed to formation of an outer amorphous SiO_2 layer and an inner nano composite layer of finely distributed h-BN nano crystals embedded in an amorphous SiO_2 matrix. Molecular dynamics simulation studies confirmed this hypothesis and now we are looking at possible ways to further maximize these properties. We have computed the thermal conductivity and thermal contact resistance between h-BN and SiO_2. Remarkably, we found that a single BN layer (~1 nm) provides the same thermal resistance as a 60 nm thick a-SiO_2. Thus, BN interfaces can be used as efficient thermal insulators.

Using classical molecular dynamics, we investigated the thermal and mechanical properties of amorphous SiBN ceramics with different boron content: Si_3BN_5, $Si_3B_3N_7$, $Si_3B_9N_{13}$ as well as amorphous Si_3N_4 and BN. By using equilibrium MD simulations, we found that the thermal conductivity (κ) of the SiBN systems increases with BN/Si_3N_4 ratio, and such discrepancy remains at high temperature up to 2000 K. Our calculations indicate that κ of amorphous SiBN ceramics can be tuned between 2 to 8 W/mK by BN/Si_3N_4 ratio, and an-isotropic κ can be realized by the BN phase segregation after annealing. Increasing the BN content will increase the Young's modulus, elastic range and ultimate stress, and this effect is robust at high temperatures.

Experimental studies on the Zr-B-C-N coating system revealed tremendous differences in properties (oxidation resistance, hardness and electrical resistivity) with a slight change in the N_2 plasma content. The $Zr_{41}B_{30}C_8N_{20}$ coating was found to possess the highest hardness (37 GPa), modulus (317 GPa) and electrical conductivity (electrical resistivity of 1.7×10^{-6} Ωm). The coating consists of nano-needle structures which have a length of about 40 nm and a width of ~10 nm. The nano-needles are composed of ZrN and/or Zr(B,N) nano-domain structures (~2 nm) that are semi-coherently joined via Zr-N monolayer interfaces. However, its oxidation resistance is limited to 550° C. We used ab-initio molecular dynamics simulations with a melt-quench approach to generate at least six configurations for $Zr_{42}B_{32}C_8N_{18}$ composition each with 100 atoms in the simulation box. Formation of small nuclei which are characteristic of a nanocrystalline structure rather than amorphous was also observed. Searching for new materials that combine oxidation resistance (SiBCN) and high hardness (ZrBCN), Si additions to the latter system were theoretically explored. Ab-initio MD simulations were used to obtain the mechanical properties of various compositions on four tie-lines in the ZrB_2, Si_3N_4, ZrN ternary diagram. We compute high hardness for compositions that are low in Si_3N_4 and high in ZrN. Increasing the amount of Si_3N_4 decreases hardness, primarily via decreasing the shear modulus. Only if Si_3N_4 is added at the expense of ZrB_2, the system retains high hardness values. Therefore, we project that a balance between Si_3N_4 and ZrB_2 must be sought to achieve hard coatings with improved oxidation resistance.

Future Plans

Future activities will mainly focus on the (Zr,Si)BCN system. The objective is to incorporate additions of Si in ZrBCN in order to increase the oxidation resistance while maintaining the nanocrystalline composite structure. We have developed and already tested a classical potential for Zr. We are currently using this potential to understand the mechanical and thermal properties of Zr-B-N heterostructures and compare the obtained properties with predictions formulated based on ab initio calculations. Next, we would like to expand on exploring the properties of ZrSiBN ceramics. The experimental effort will involve synthesis and characterization of compositions along the tie-lines of the ZrB_2, Si_3N_4, ZrN ternary diagram studied by the MD simulations. Our expectation is that moderate Si additions can maintain the nanoscale composite structure observed in the ZrBCN system while forming a Si-N based tissue layer around the nanoscale domains increasing the oxidation resistance. We also plan to utilize our preliminary work on the HfSiBCN system (replace Zr by Hf) that can exhibit an oxidation resistance up to 1600° C. In recent studies, we found that replacement of Zr by Hf presents a high potential alternative for these coatings and thus, we included Hf-Si-B-N coatings in our plans. MD simulations will be conducted to optimize compositions that exhibit attractive combinations of mechanical and thermal properties along with oxidation resistance. Following the theoretical predictions, compositions of (Zr,Si)BN and (Hf,Si)BN coatings presenting attractive combination of properties will be synthesized and their structures and properties will be characterized experimentally in order to accelerate coating development.

Broader impact

The focus of this research - the discovery of new coatings working under extreme conditions - can find application in multitude of critical components such as turbine blades, reusable launch vehicles, hypersonic vehicles, and thermal barrier applications. The research program is integrated with a multi-layered education and outreach program involving curricula development, exposing students to a novel interdisciplinary field, and summer camps. At UTA, two female Ph.D. students (one in materials science and one in chemistry) have taken their dissertation research on the project. A Postdoc was also involved under the supervision of Kroll in Chemistry department. A new *Nanotechnology Certificate* was inititated last fall 2015 at UTA for undergraduate science and engineering students. Meletis and Jiang have been involved in the UTA College of Engineering ***Materials Camp for Kids 2015*** (July 25, 2015, with 18 students from 4th and 5th grade) and ***2015 American Society of Materials Summer Camp*** (July 18, 2015, with 27 students 7 to 12 years old). At UMN, one graduate student, one undergraduate (Hispanic), and one post-doc are directly involved in this work. The results obtained in this research enriched the well-attended Computational Nanomechanics course developed by Dumitrica. Also, at UMN undergraduates from Pi Tau Sigma Honors Society are engaged in activities of the American Ceramic Society, including the UMN version of the Ceramic Mug Drop Contest.

Data Management and Open Access

Ab-initio molecular dynamics simulations are using the Vienna Ab Initio Simulation Package that is commercially available. For modeling of amorphous structures, an in-house code (Continuum Random Network Generator, CORANGE) is used. Both, VASP and CORANGE produce ASCII results are stored in the project data and are publically available. The force-field development is using the Tersoff-potential and the REAX-ForceField approach that are implemented in the LAMMPS package available from Sandia National Laboratory. Mesoscopic mechanical simulations are performed with the code PFC3D provided by Itasca Inc. All the developed parameters for the atomistic potentials, as well as the parameterization of the contact models for the PFC3D, are reported in our publications. The mesoscopic part of the distinct element method working with PFC3D is freely available via the Office for Technology Commercialization, University of Minnesota. All experimental data are reported in our publications.

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Next-generation Nanostructured Polymer Electrolytes by Molecular Design

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Keywords: batteries, lithium, polymer electrolytes, synthesis, screening, computation, modeling.

Project Scope

The objective of our project is to develop safe, robust, and efficient nanostructured polymer electrolytes for large-scale lithium batteries used in electric vehicles and grid applications. Our approach combines expertise in theory and simulation, polymer synthesis, and polymer electrolyte characterization, to facilitate accelerated discovery of new polymer electrolytes. State-of-the-art theoretical and coarse-graining methods drive the screening and design of new polymer electrolytes, as well as provide the detailed understanding of ion diffusion mechanisms. Our goal is to develop a polymer electrolyte with conductivity larger than that of the current state-of-the-art polymer electrolyte (PEO). We have several new synthetic targets inspired by recent theoretical predictions,[2,5] and a recently developed coarse-grained model[2] will enable the screening of hundreds of candidate polymers over the next year.

Relevance to MGI

Our approach fully embodies the MGI approach, consisting of a cyclic, iterative process wherein theoretical and experimental research components are utilized to accelerate materials discovery. The theoretical research component provides detailed, mechanistic insights into the molecular processes that govern the polymer electrolyte material properties and tools required to screen candidate polymer electrolyte materials. This allows for more efficient exploration of parameter space and reduces the number of polymer electrolyte materials that need to be experimentally synthesized and characterized, focusing efforts on polymer materials with promising properties. Meanwhile, the experimental research components provide explicit tests of the theoretical predictions and methodologies, thus leading to better simulation approaches, an improved understanding of lithium diffusion in polymer electrolytes, and physical realizations of polymer materials with improved conduction properties. An ongoing dialogue between the experiment and theory groups ensures that the structures studied by the theory group are limited to those that the synthesis group can make. Promising polymer electrolyte candidates identified by theory will then be synthesized in the laboratory, and their ion transport characteristics will be measured.

Technical Progress

Modular synthesis (Coates), electrochemical characterization (Balsara), and molecular simulation (Miller and Wang) were combined to investigate lithium-ion transport in a new family of polyester-based polymers and in the canonical poly(ethylene oxide) (PEO) electrolyte.[1] Both experimental and theoretical results showed that the conductivity in PEO was more than an order of magnitude greater than that present in the polyester-based polymer electrolytes, despite small differences in the measured glass-transition temperatures. Our theoretical analysis not only revealed key mechanistic differences between the ion transport processes in PEO compared to the polyester-based polymer electrolytes, but an analysis of spatial distribution of lithium-ion solvation sites in the polymer provided a new framework for the general evaluation and prediction of ionic conductivities in polymer electrolyte materials.

These insights were used to develop a coarse grained model for ion transport in which ion diffusion occurs via transitions between viable solvation sites in the polymer, and the coarse-grained variables are connected to polymer-specific properties.[2] Importantly, all model inputs are readily determined from relatively short (5-20 ns) MD simulations. Figure 1 illustrates the results of a benchmark study on a series of polyethers. The figure shows good agreement between long timescale (>300 ns) MD simulations and kinetic Monte Carlo simulations based on the model (CS-DBP). Both sets of results indicate that PEO and P(EO-TMO) exhibit superior lithium-ion diffusivity than the remaining polymers. Importantly, the relative performance of the polymer electrolytes can be interpreted based on the coarse-grained variables present in the model, such that the performance of a given polymer electrolyte can be understood on the basis of its underlying physical properties. However, the results from the coarse-grained model are more than 100x more efficient to calculate than those of the MD trajectories, highlighting the potential of the model as a tool for screening candidate polymer electrolytes at reduced computational cost and for saving human and monetary resources.

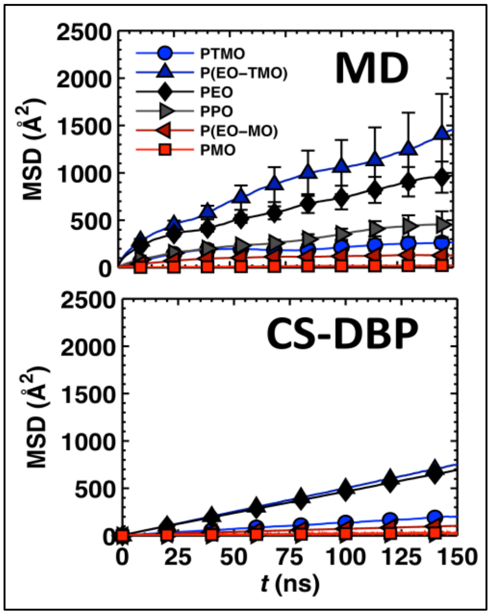

Figure 1. Comparison of Li+ mean-squared displacements (MSD) obtained from molecular dynamics (MD) and our coarse-grained model (CS-DBP).

We have also investigated the apparent connection between conductivity and the connectivity of lithium-ion solvation sites experimentally. A series of polyethers with varying number of consecutive EO units and carbon-linker lengths were synthesized at Cornell via Acyclic Diene Metathesis (ADMET) polymerization followed by hydrogenation with Crabtree's catalyst. These samples were sent to Berkeley, where electrolytes were prepared by homogeneous mixing of the polymers and lithium bis(trifluoromethanesulfone)imide (LiTFSI) salt. To elucidate the effect of the carbon linkers on ion conduction without the conflating factor of polymer mobility, the conductivities for the different polymers were compared at a fixed distance from their glass-transition temperatures, enabling exctraction of a new variable called the experimental connection factor, f_{exp}, which reports on the extent to which conductivity differs from ideal expectations based on PEO. Complementary theoretical analysis examined how varying the composition of the polymers affected the connectivity between possible lithium-ion solvation sites. Figure 2 shows a comparison between f_{exp} and a theoretical metric reporting on the connectivity of lithium-ion solvation sites. This analysis shows that variations in f_{exp} indeed provide an experimental signature of changing the connectivity among lithium-ion solvation sites.

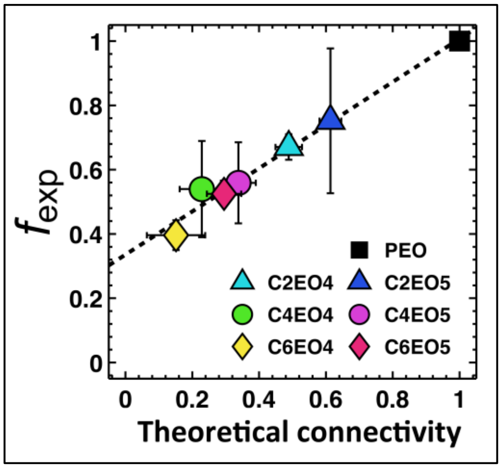

Figure 2. Correlation between the experimental connection factor f_{exp} and a theoretical metric reporting on the connectivity of lithium-ion solvation sites.

Future Plans

To date, we have identified several polymer electrolyte materials[2,5] that are predicted to have improved properties compared to PEO. These structures are either being actively pursued as synthetic targets or inspiring new synthetic targets based on their composition. Experimental characterization of these polymers will guide any refinements of the coarse-grained model, thereby systematically improving future predictions. Additionally, we are developing an automated protocol for force-field parameterization that can be coupled to our coarse-grained transport model to facilitate the large-scale screening of polymer electrolytes with more diverse chemistry and topology. Beginning early in 2016, we aim to perform an initial theoretical screening of more than 400 candidate structures. A subset of the polymers that exhibit promising lithium-ion diffusivity and polymer properties will be selected as synthetic targets. Additional long-time molecular dynamics simulations will be used characterize the ion-transport mechanisms that will guide further selection of targets.

Broader impact (Optional for DOE grants/FWPs)

Our project provides an ideal platform for training and educating students and postdoctoral researchers in the area of materials research and education. Being a fully integrated theory-synthesis-characterization project, the students and postdoctoral scholars are involved in all three aspects of the research. A web-based discussion group has been set up where these junior researchers are regularly (on a weekly basis) discussing research progress, exchanging ideas, analyzing results and planning the next stage. In addition, all-hands web-based meetings are held once a month where students or postdocs from each of the groups give a presentation of the newest results.

Data Management and Open Access

A primary goal of this DMREF project is to broadly disseminate our findings to interested parties. A primary mode for achieving this aim will be through publication in peer-reviewed journals. However, we will also develop and maintain a web-based Polymer Electrolyte Archive for the duration of the proposed research that will allow outside parties to directly access and download posted experimental and simulation data. Compiled experimental and simulation data will be uploaded by the four collaborating research groups, using password protection. All posted data will be available to the general public for download, without password protection. Data will be released to the website after it is accepted for publication, and the appropriate citations will be indicated on the website. The source code for all programs that are written as part of this DMREF project will also be made available on the Polymer Electrolyte Archive.

Accelerating Materials Discovery & Development

This research program tightly couples experimental synthetic and characterization efforts to computational and theoretical studies of the candidate polymer electrolyte materials. By combining aspects of theory, synthesis, and characterization, we have been able to gain insights that are deeper and broader than would otherwise have been possible, which is crucial for rational design of new polymer electrolytes. Moreover, using theory to test proposed structures saves time and material resources in our screening efforts, and the development of our coarse-grained model significantly increases the number of materials that can be tested before experimental characterization. This permits us to investigate polymers with new chemistries before investing significant synthetic effort.

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Mechanistic and Microstructure-Based Design Approach for Rapid-Prototyping of Superalloys

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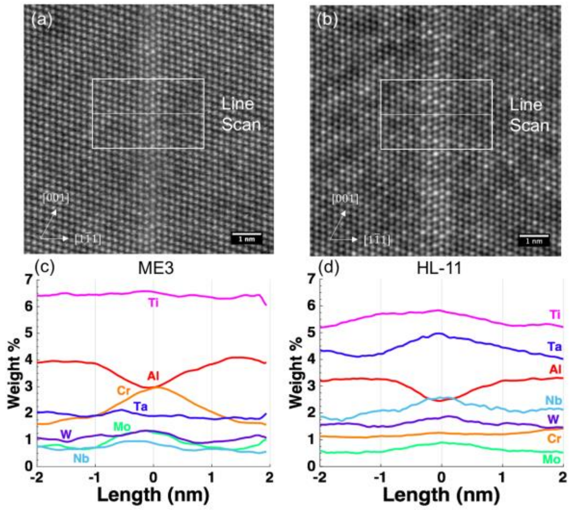
Keywords: Superalloys, creep, electron microscopy, density functional theory, phase field and crystal plasticity.

Project Scope

Breaking away from traditional, incremental superalloy development, a new design paradigm will be implemented in this GOALI program with the GE-Global Research Center using a novel materials data analytics (MDA) applied to an integrated experiment/modeling exploration of a sparse set of high-order (6-component) compositions, thereby extracting key physics-based correlations for alloy design. A novel, rapid-prototyping approach to alloy processing will enabling nimble exploration of the inter-related effects of composition, microstructure, deformation mechanisms and creep response, and producing a validated 7-component powder metallurgy alloy with 50°C improvement in creep capability over the present generation commercial alloy ME3.

Relevance to MGI

Rapid prototyping of six-component cast and wrought polycrystals, as well as single crystals of the same alloys, will be integrated in three alloy variant feedback loops with first-principles, phase field and crystal plasticity models. Advanced characterization at each length-scale will guide development of quantitative and predictive understanding of alloying and microstructure effects on creep. The materials data analytics will employ non-linear dimensional reduction to aid the design of experiments and physics-based modeling, and to assess the results, in order to predict an optimized seven-component composition and microstructure, which will be produced as a trial PM alloy for evaluation of its enhanced creep performance.



(a) and (b) HAADF-STEM images obtained on a [110] zone axis revealing segregation along a SESF in ME3 and HL11, respectively. In (b), a “grid-like” ordering consistent with the eta phase. Integrated line scans across faults in (c) ME3 and (d) HL11, showing distinctly different segregation phenomena. These alloys have significantly different creep strengths, which are related to the propensity for the microtwinning mechanism.

Technical Progress

The initial matrix of six-component alloy compositions has been developed in consultation with GE-GRC. These compositions provide large variation on crucial elemental constituents, while maintaining similar γ’ volume fraction and γ’ solvus temperature based on predictions using Thermocalc. The actual volume fraction and solvus temperature (determined via differential scanning calorimetry) will be measured and disseminated for thermodynamic model refinement. GRC is presently establishing a workable thermomechanical processing procedure, including a multi-axis forging (MAF) practice, in order to develop homogeneous, low retained texture microstructures with an average grain size of ~50 mm. This goal has already been achieved for one of the initial alloys, and additional trials are in progress. Once processing parameters are refined, this rapid prototyping approach will enable production of high-order alloy polycrystals much more rapidly and cost-effectively than is possible via conventional powder metallurgical routes.

Based on recent experimental advances in our understanding of creep in two more complex commercial alloys, ME3 and HL11, we have already modified the initial set of alloy compositions that will be studied. Fundamental studies of single crystals of these alloys have determined that alloy HL11 is remarkably stronger than alloy ME3 in creep between 700-800°C, which is the critical temperature range for the disk materials. In depth investigation using diffraction-contrast scanning transmission electron microscopy (DF-STEM) has revealed that this difference is directly related to the frequency of microtwins present following creep deformation. The more creep-resistant alloy (HL11) has a much lower frequency of twins. Furthermore, inhibition of twinning in HL11 appears to be directly related to a new strengthening mechanism that has been revealed by atomic-resolution imaging using high-angle annular dark field (HAADF-STEM) and compositional analysis using advanced energy dispersive spectroscopy (EDS). Distinctive elemental segregation at stacking faults within the γ' phase in the two alloys is observed, with γ formers segregating to faults in ME3, while η phase rich in Ta and Nb forms at the stacking fault in alloy HL11. Density functional theory calculations have also determined that subsequent shearing of these stacking faults in order to form microtwins is relatively easy in ME3, while a substantial energy barrier is associated with the same twin-thickening in alloy HL11 due to the stabilizing presence of the η phase. This novel strengthening mechanism suggests that the effect of Ta is essential to include in our initial alloy matrix, and thus one of the six-component alloys will include 4 wt% Ta.

Future Plans

This is but one example of the feedback between experiment and modeling that will be utilized extensively in this program. As polycrystalline and single crystal alloys are produced by GRC, creep testing and post-deformation mechanism analysis will be performed using electron channeling contrast imaging (ECCI), microstructure-scale digital image correlation, DF-STEM, HAADF-STEM, and atomic-scale EDS. Results will be integrated in three alloy variant feedback loops with first-principles, phase field and crystal plasticity models, and with advanced characterization at each length-scale, to develop quantitative and predictive understanding of alloying and microstructure effects on creep. The MDA will employ non-linear dimensional reduction to aid the design of experiments and physics-based modeling, and to assess the results, in order to predict an optimized seven-component composition and microstructure, which will be produced in a trial PM alloy for evaluation of its enhanced creep performance.

Broader impact

Superalloys are critical, enabling materials with broad impact in aerospace and energy technologies. Computational and experimental tools for efficient material design are desperately needed to accelerate alloy insertion. Coordinated application of these complementary techniques will also provide a roadmap for future alloy development strategies. Dissemination of the approaches and results will be communicated via professional society short-courses (live and on-line) which will benefit students and professionals. The team is also dedicated to producing vibrant course content for high school Materials Science teachers/students.

Data Management and Open Access

To coordinate and manage data for the entire project, we will use web-based tool DMP Online (http://dmponline.dcc.ac.uk/), where we will build and edit a customized plan complying to NSF funder requirements. Animations will be posted at the PI's institution websites. An instructional module will be uploaded at NSF funded NanoHub portal at Purdue University. No additional support is required to maintain these websites. The team is exploring the best options for hosting the raw and analyzed data including commercial services such as Citrine Informatics Open Data Platform (http://citrination.com), Materials Resources LLC MiCLOUD (http://www.icmrl.com). Source code for the developed software will maintained by the PIs in an open repository and be distributed by Bluequartz as plugins/filters for DREAM.3D (http://www.icmrl.com).

Design of Nanoscale Alloy Catalysts from First Principles

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Keywords: nanoparticles, alloy catalysts, CO_2 reduction

Abstract

The major goal of this project is to develop and validate an approach to design alloy nanocatalysts. 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 will be validated by electrocatalytic studies for CO_2 reduction. The integration of these two thrusts will lead us to a rational approach towards advanced catalytic materials for complex chemical processes.

Project Scope

We are developing and validating a way to design alloy catalysts using density functional theory and the cluster expansion approach. The computational approach is iteratively improved by comparing computational predictions with experimental results on the structure and catalytic properties of nanocatalysts. To demonstrate and evaluate our approach, we aim to design Cu-based alloy catalysts for highly active and selective CO_2 reduction.

Relevance to MGI

The predictions generated by our computational models are being 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.

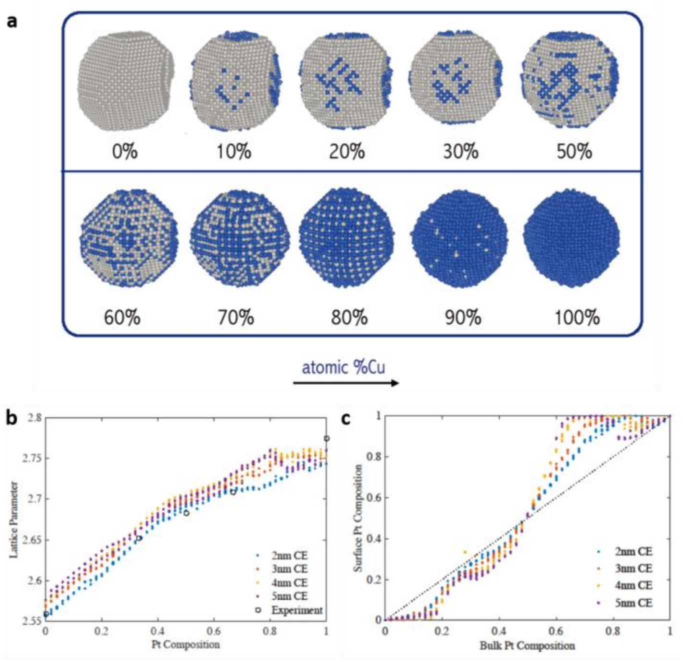

Figure 1. (a) Shapes of Cu-Pt nanoparticles from cluster expansion calculation (Cu blue, Pt gray); (b) Lattice parameters of Cu-Pt nanoparticles in comparison with experimental data; (c) Corresponding surface compositions.

Technical Progress

Thrust 1. We have generated the necessary training data and developed cluster expansions for Cu-Pt and Cu-Ni nanoparticles, enabling us to rapidly predict the energies of nanoparticles as a function of composition, particles size, and temperature

(Fig. 1a). We have used these cluster expansions in Monte Carlo simulations to predict the equilibrium structures of nanoparticles for comparison with experiments. These predictions are in good agreement with lattice parameters derived from XRD data on synthesized nanoparticles (Fig. 1b). We have also predicted a trend in the surface composition of the nanoparticles (Fig. 1c), which will be compared to the atomic structures characterized by scanning transmission electron microscopy (STEM).

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) spectroscopy, respectively. In particular, we have developed the synthesis of highly dense Cu nanowires (Fig. 1 a and b) 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). We have also employed DFT calculations to predict the catalytic properties of various Cu facets (Fig. 2d). It was found that the overpotential for reduction of CO_2 to generate hydrocarbon products is 0.79 V for Cu(211), 0.77 V for Cu(110), 0.94 V for (100) and 1.07 V for Cu(111), respectively. The predicted superior performance of Cu(110) was further validated by surface structure analysis based on temperature-programmed CO desorption (CO-TPD) and OH_{ad} electrosorption.

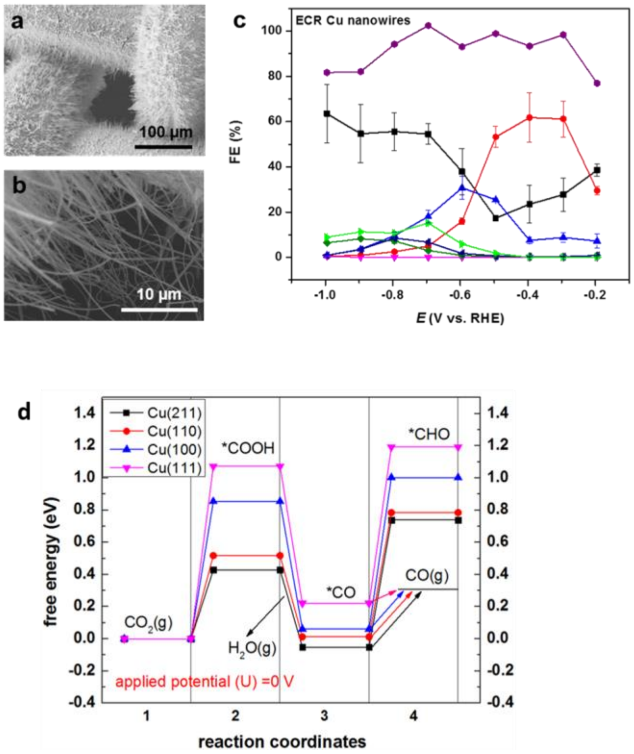

Figure 2. (a, b) SEM images of Cu nanowires grown on Cu mesh by electrochemical reduction of CuO nanowires. (c) Faradaic efficiencies (FEs) of various products obtained from CO_2 reduction on the electrochemically reduced Cu nanowires. (d) The free energy diagrams of CO_2 reduction on various Cu facets.

Future Plans

It is planned to continue the efforts on the two thrusts. In thrust 1, the focus for the coming year will be placed on finalization of the structure model for alloy nanoparticles and experimental validation for the surface sompositions, depending on the particle size, shape (facets), composition and synthetic conditions. In thrust 2, it is aimed to extend the electrocatalytic studies to Cu-based alloy catalysts, including both nanowires and nanoparticles, focusing on comparative studies by both computation and experiments to build up structure-property relationships.

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 will include a female high school student from a largely minority Baltimore City public school, who will gain 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 will be archived and made available for sharing, as will the computational tools developed for this project. Detailed descriptions of the computational and synthesis methods used will be published in peer-reviewed literature and student theses.

Publications

1. D. Raciti, K. J. Livi, C. Wang, *Highly Dense Cu Nanowires for Low-Overpotential CO_2 Reduction,* Nano Lett. **15**, 6829-6835 (2015).

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 simplified quasi-2D synthesis amenable to processing-structure linkages, a nanoscopic 2D sheet-like structure that overcomes diffusion limitations and provides high surface area, and facile membrane fabrication by coating processes. Our approach interlinks advanced multiscale modeling of N2DMs, development of novel N2DM data analytics methodologies, and extensive synthesis and characterization experiments, in a cyclic and mutually validative workflow.

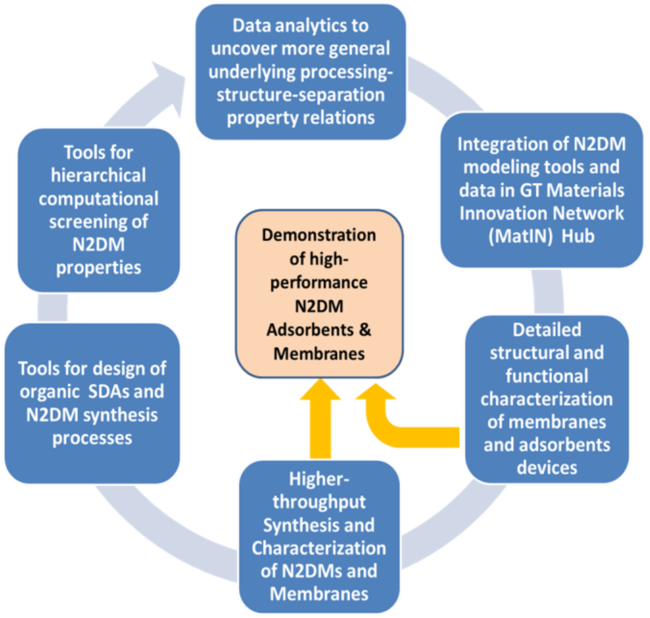

Figure. Workflow of a "genomic"-based approach to discovery and development of functional nanoporous 2D materials (N2DMs) for adsorbents and membranes.

Relevance to MGI

Our strategy exemplifies the "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 two important applications (adsorption-based ethylene/ethane separation and membrane-based H_2/CO/CO_2 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* Wiki-based sharing and evaluation of large datasets, code and protocol repositories, and open-source-format data repositories.

Technical Progress

The project officially began in October 2015. Three graduate students have recently been hired from the Fall 2015 entering class after preliminary discussion and presentation of the project. A project kickoff meeting was held on Dec 22, 2015 and work will commence in January 2016. Additionally, the PIs have utilized a small seed grant (Jan-July 2015) from Georgia Tech's Institute for Materials to demonstrate a GitHub-based collaboration on structure elucidation of nanoporous materials using metal-organic frameworks (MOFs) as an example (see: http://rossverploegh.github.io/Hybrid-ZIF-Structure-Elucidation/). The learnings from this activity will be used in setting up the DMREF-supported collaboration on N2DMs.

Future Plans

Current N2DMs show exciting promise as adsorbents, catalysts, and membranes. The vast range of possible new N2DM structures, and their complex dopant and cation distributions, create tremendous opportunities and wide-open challenges to discover and exploit their fundamental 'genomic' characteristics. By creating the first comprehensive 'genomic' approach to reliable PSP linkages for N2DMs, our team will develop high-performance N2DMs and membranes for energy and chemical production applications (H_2/CO/CO_2 membrane separations for biomass utilization, and ethylene/ethane adsorptive separations for energy-efficient olefin production). In doing so, we will also create a broadly applicable framework of tools and knowledge for exploiting N2DMs in a range of membrane-based and selective adsorption-based molecular separation processes.

Broader impact

We will produce a cadre of STEM workforce members (at least half of whom will be women or underrepresented minorities) 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 will substantially 'MGI-enable' the GT educational curriculum and expose a large number of students to next-generation materials design and discovery, *via* new course materials on the theme of 'Nanoporous Materials Design for Sustainability'. Our program creates 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 our PhD-track, UG, and K-12 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 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

This project has begun in October 2015, no publications to report yet.

Predictive Theory of Transition Metal Oxide Catalysis

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The scope of this effort is to establish a fundamental understanding of oxide surfaces to a level where electronic structure-based simulations can be utilized to quantitatively predict the catalytic properties for reactions relevant for energy conversion. Due to lack of "exact" computational solutions for complex oxides, we benchmark the theoretical methods against carefully designed experiments including accurate syntheses of well-defined surface structures of oxides, detailed characterization using synchrotron methods and the free electron laser at SLAC, and the most accurate measurements of adsorbate-surface interaction energies available to date. In this progress report, we highlight some of our most recent findings (see Publications for a complete list of publications funded by this effort).

We report[16] the first calorimetric measurement of the heat of reaction for the dissociative adsorption of H_2O on the NiO(111)-2x2 surface as a detailed function of coverage, which provides an experimental measure of the heat of formation of the resulting surface hydroxyl groups. Using density functional theory (DFT) calculations, we have identified the initial and final states of the NiO(111) surface that agree with the measured energetics and the surface symmetry. Using the experiment as benchmark, we compare the performance of different GGA+U and hybrid functionals for identified structures. This work provides an important benchmark for validating computational estimates of adsorption energies on NiO adding to our previous work on alkaline-earth metal oxide surfaces (MgO, CaO, SrO, BaO)[8] as well as transition metal surfaces.[11]

We have developed a novel catalyst,[18] $SrIrO_3/IrO_x$, which is stable in acidic electrolyte for over 30 hours of operation and exhibits higher intrinsic activity than any known OER catalysts previously reported in alkaline or acidic electrolyte. We have also used density functional theory (DFT) calculations and materials characterization techniques to investigate potential active sites contributing to the extremely high activity.

Supported ultrathin oxide films are well-defined systems for which we can test the accuracy of DFT. We used a large combination of supports and ultrathin oxide films to investigate trends in stability through a descriptor-based analysis.[17] Since the modelled films are bound to the support exclusively through metal-metal bonds, we find that the adsorption energy of the oxide-constituting metal atom can be used as a descriptor for the film-support interaction. The film-support lattice mismatch and the effect of simulation supercell size is studied in detail for two systems: single layer TiO and FeO supported oxides. A correction scheme to account for the lattice mismatch leads to stronger correlation between formation energy of the oxide and the descriptor.

We have studied the relationship between the atomic-scale structure of Co-oxide nanoislands supported on Au by using a combination of atom-resolved scanning tunneling microscopy, X-ray photoelectron and absorption spectroscopies and density functional theory calculations.[10] We revealed that conversion from Co^{2+} to Co^{3+} occurs by a facile incorporation of oxygen at the interface between the nanoisland and Au, changing the islands from a Co-O-bilayer to an O-Co-O trilayer. The O-Co-O trilayer islands have the structure of a single layer of, proposed to be the active phase for the oxygen evolution reaction. Currently, we are studying dissociation of H_2O on these nanoislands.

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15. Y. Hikita, K. Nishio, L. C. Seitz, P. Chakthranont, T. Tachikawa, T. F. Jaramillo, H. Y. Hwang, *Band Edge Engineering of Oxide Photoanodes for Photoelectrochemical Water Splitting: Integration of Subsurface Dipoles with Atomic-Scale Control*, Submitted (2015).
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18. L. C. Seitz, C. Dickens, K. Nishio, Y. Hikita, A. Vojvodic, H. Y. Hwang, J. K. Nørskov, T. F. Jaramillo, *A Highly Active and Stable* $SrIrO_3/IrO_x$ *Catalyst for the Oxygen Evolution Reaction*, In preparation (2016).

Data Mining and Analytics for Predictive Synthesis, Accelerating Realization of Advanced Materials

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Keywords: Predictive synthesis, machine learning, natural language processing, first principles, text extraction

Project Scope

Progress in accelerated materials design has moved the bottleneck in materials development toward the synthesis of novel compounds; the process is gated by trial and error synthesis techniques. Accordingly, our project seeks to build predictive tools via natural language processing, algorithm development, and first principles validation so that targeted compounds can be synthesized more rapidly, with an initial focus on the solid state synthesis of energy storage materials. We hypothesize that comprehensive data mining of the experimental literature will enable us to identify ways to synthesize novel compounds. The success of the project will be measured by robustness of text extraction and recipe prediction.

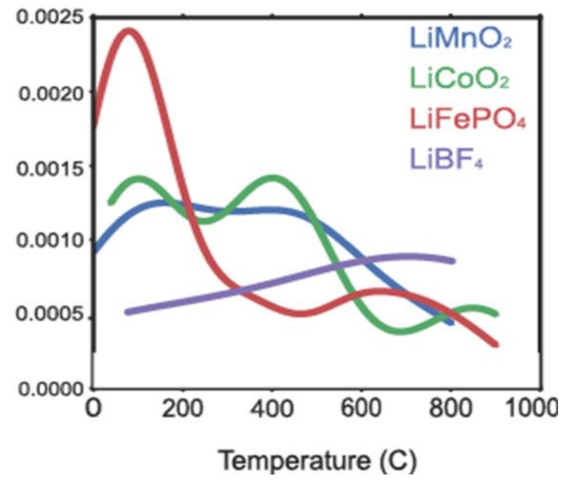

Figure. Demonstration of data mining automatically extracted from ~1400 papers, plotting the frequency of heating temperature as a function of electrode chemistry.

Relevance to MGI

Several recent reports have identified materials synthesis as a significant challenge to realizing an accelerated design process (see DOE Basic Energy Sciences Advisory Committee report). Our solution to this challenge leverages and integrates the existing body of experimental knowledge with modern predictive *ab-initio* tools and data extraction methods, ultimately allowing for the rapid suggestion of ways to synthesize new compounds. Our work will iteratively feedback between defining ontologies to extract synthesis methods from published experimental literature, mining past recipes for patterns, and correlating these recipes with first principles computed structural and thermochemical quantities. This data mining effort will produce prospective synthesis routes for novel compounds. We will then return to the experimental realm to test proposed recipes and further refine the domain knowledge of machine learned synthesis algorithms.

Technical Progress

We propose building a database of synthesis recipes from historic and current peer-reviewed literature, including developing the infrastructure and methods to make this information fully available to the research community as well as extensible to future publications. We have begun by extracting synthesis recipes using natural language processing from the vast set of literature on materials synthesis (focusing on journal articles). We have developed a software pipeline, implemented in Python, which automatically retrieves journal articles from publishers and applies rule-based text extraction for operations and entities. Our current efforts leverage text and data mining agreements with several publishers, including Elsevier and Springer. We currently extract from approximately fifty thousand full texts. Through our initial work we have learned that the operation lexicon for solid state materials, the actions that describe how to make a compound, has proven finite. Therefore, direct-matching via 'dictionaries' of known operations has worked well.

Future Plans

This project is in its early stages so significant work remains. The next step in text extraction is to apply machine learning approaches to improve our precision and recall. We will organize our extracted information into a structured database to be disseminated to the materials community by integration with online materials databases. Outside experts will have opportunities for input and error correction (further detail below). We will then mine this database using a novel combination of machine learning tools from the materials informatics community as well as natural language parsing tools (as the database contains semantic as well as quantitative information). Our goal is to mine these solid state recipes for patterns that can inform existing materials synthesis efforts and eventually generate potentially viable synthesis routes for new materials. Early efforts include simple machine learning approaches such as logistic regression and support vector machine classification. We will then leverage first principles calculations to relate patterns to *ab-initio* computed thermochemical data.

Broader impact

To broaden the impact of our research we plan to make our results, graphical models, and source code, publicly available enabling further scientific research, and third-party enhancements. Not only will this provide the infrastructure to enable more rapid advances in materials development, but also, it will enable the application of text extraction as a generalized tool for scientific progress in other applications and fields of study. One major educational objective of this research is to enable the use of the database by non-software experts through both online tutorials and in-person workshops. The online tutorials will teach the basic knowledge required to use online tools and functionalities while the workshops will help students/researchers make use of the database. We will also develop case studies and teaching units that can be used to couple skill development in computer programming with the use of engineering to solve societal problems. We will first pilot these efforts through the course work of the PIs and then globally through the Open Courseware Initiative at MIT, a free and accessible web-based publication of course content. In addition, we plan to run “hackathon” style activities to increase involvement of women and under-represented groups in programming activities developed through the research. This project lends itself to these efforts because of the modular and applied nature of the programming tasks.

Data Management and Open Access

Our research databases contain full-text journal articles, which are not intended for the public. Therefore, we have setup a multi-server hardware format to interface with outside groups. In this way, relevant, allowable data will be cloned from the internal database server to an open server. A Representational State Transfer protocol will be employed to allow for maximum compatibility. By integrating an API with the Materials Project (materialsproject.org), for example, we are able to distribute our results and receive live feedback from the Materials Project’s user base. Additional API integrations with other groups will allow for similar growth strategies in our effective user base. This high scale, human driven error-checking will accelerate the learning process for our predictive algorithms. Software development will be made available through an open access license, added by MIT’s Technology Licensing Office. Dissemination of publications and documentation can also be provided through MIT’s open access efforts at http://dspace.mit.edu/.

Accelerating Materials Discovery & Development

The objective of our research is to build predictive tools for materials synthesis so that targeted compounds can be synthesized in a matter of days rather than months or years. A significant amount of materials development time is spent on developing synthesis routes to create and optimize novel compounds. Shortening the duration of materials synthesis would lead to more rapid iteration between materials design efforts and their testing, thereby accelerating materials discovery and spurring efforts towards novel, high risk materials design concepts. The database we develop through this effort could have prospects for commercialization as there are synergistic efforts currently undertaking entrepreneurial ventures, although the right business model is needed for these to be viable opportunities.

Design of Novel Sodium Superionic Conductors using Integrated High-throughput First Principles Calculations, Data Mining and Experiments

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Keywords: sodium superionic conductor; first principles diffusion; pulsed electric current sintering; interface engineering; multivariate time series analysis

Project Scope

The aim of this project is to design and optimize novel sodium superionic conductors using a data driven approach that tightly integrates high-throughput first principles modeling, data mining, synthesis and characterization, and interfacial engineering. Our target is to develop materials that have Na^+ conductivity in excess of 1 mS cm^{-1} at room temperature, with either intrinsic stability against typical 4.5V cathodes and anodes, or forming a stable ionic conducting solid-electrolyte interphase (SEI).

Relevance to MGI

This undertaking would require significant advancements on several fronts: (i) the development of robust computational frameworks to manage long-running first principles transport simulations; (ii) the design of an efficient database schema for the storage of truly "big materials data" arising from these simulations; (iii) the innovative application of multivariate time series machine learning techniques to extract scientific insights and trends; (iv) the use of advanced methods to synthesize and characterize candidate sodium superionic conductors; and (v) the model-based engineering of interfaces to mediate interfacial bottlenecks and enhance Na^+ conductivity.

Technical Progress

We carried out a first-principles investigation to identify doping strategies to further enhance the Na^+ conductivity of cubic Na_3PS_4 (c-Na_3PS_4), a highly promising sodium SE.[1,2] Ab initio molecular dynamics simulations (AIMD) calculations show that the introduction of Na^+ excess interstitials is the key to achieving reasonable Na^+ conductivities. We predict that 6.25% Si-doped c- Na_3PS_4 has the Na^+ conductivity of 1.66 mS/cm (Figure 1), which is in excellent agreement with previous experiment results[2] (0.74 mS/cm). Remarkably, we find that Sn doping at the same concentration yields a much higher predicted Na+ conductivity of 10.7 mS/cm, though with a slightly higher dopant formation energy (publication 1). Based on the computational results, we attempted to synthesize and characterize Na_3PS_4 using ball milling Na_2S and P_2S_5 in a 75:25 molar-ratio in a ZrO_2 jar with 5mm ZrO_2 balls at 370 rpm for 20 hours. This was followed by heat treatment at 270°C and 420°C for 2 hours to yield cubic and tetragonal phases, respectively. Figure 2 shows the XRD patterns of the cubic and tetragonal Na_3PS_4. From AC impedance measurements, the room temperature conductivity of cubic-Na_3PS_4 was 0.2 mS/cm. Further work on the doping c-Na_3PS_4 is being carried out.

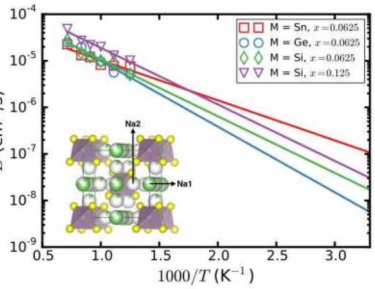

Figure 1: Computed ionic conductivity of doped Na_3PS_4

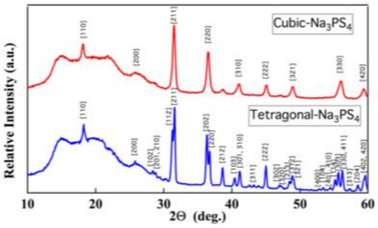

Figure 2: XRD pattern of Na_3PS_4

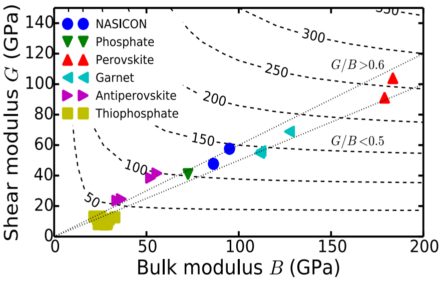

Figure 3: Mechanical properties of SEs.

We also investigated the mechanical properties and aqueous stability of widely known SEs from first principles calculations. The mechanical properties of the SEs have a profound influence on the fabrication and performance of all solid-state batteries. We find that the anion species and structural framework are found to have significant influence on the elastic properties (Figure 3). The relative elastic moduli of the various classes of SEs follow the order thiophosphate < antiperovskite < phosphate < NASICON < garnet < perovskite. Within the same framework structure, we observe that Na SEs are softer than their Li analogues (publication 2). Building on the approach proposed by Persson et. al.,[3] we also developed a quantitative free-energy measure to compare the relative aqueous stability of different SEs. We find the oxides to be more stable than the sulfides and halides in aqueous environments, but there is a wide variation in the relative aqueous stability even within the same anion chemistry.

Future Plans

In the future, we are considering the following steps (a) synthesizing the computationally predicted doped c-Na_3PS_4 and other predicted novel SEs; (b) extending the doping strategy to other known chemistries to improve ionic conductivity; (c) exploring other chemical spaces to identify materials with desired phase stability, topology and electrochemical stability; and (d) using data mining techniques to understand correlated diffusion mechanisms and identifying structure-property relationships.

Broader impact

We have already identified several chemistries and successfully developed optimization strategies to improve their ionic conductivity. The superionic conductors identified and synthesized in this DMREF will lead to safer, higher energy density storage based on all-solid state Na-ion batteries. PI Ong has developed a new course on “Quantum mechanical modeling of materials and nanostructures (NANO266)” for which the course materials are publicly available.

Data Management and Open Access

A web-based app has been developed that provides access to all the computational results carried under this project. The app will be made public once the project is completed. A Superionic Conductor Database has been setup that will integrate all computed and experimental data arising from this DMREF. All experimental data generated will conform to typical data formats used widely in academia and industry. The HT computational frameworks and materials analysis in this DMREF are being continuously made open source as add-ons to the open source Python Materials Genomics (pymatgen) materials analysis library (http://www.pymatgen.org) as well as other libraries.

Accelerating Materials Discovery & Development

The application of high-throughput first principles screening has allowed us to rapidly identify the most promising novel chemistries and doping strategies (e.g., Sn-doped c-Na_3PS_4), which are now the subject of focused experimental synthesis and characterization efforts. Indeed, we expect our multi-property optimization approach (e.g., phase stability, mechanical strength, electrochemical and aqueous stability, and ionic conductivity) to yield significant dividends in accelerating the development of practical materials that have real-world application potential, as opposed to the typical approach of focusing on a single property.

Through this initiative, we hope to identify, synthesize and characterize a wide variety of superionic conductor SEs that can be used in different applications.

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1. Zhu, Z.; Chu, I.-H.; Deng, Z.; Ong, S. P. Role of Na^+ Interstitials and Dopants in Enhancing the Na^+ Conductivity of the Cubic Na_3PS_4 Superionic Conductor. Chem. Mater. 2015, 27 (24), 8318–8325.
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Thin Film Biofabrication for Integrated Bio-electronics

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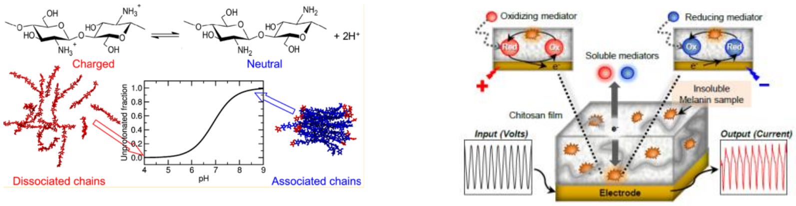
Keywords: Bioelectronics, Biofabrication, Polysaccharides, Self Assembly, Synthetic Biology.

Project Scope

Our broad goal is to integrate the advances in biology to materials fabrication. We envision that biology will underpin many of the important materials advances in the 21st century just as physics and chemistry provided the underpinning sciences for the 20th century materials. Our "biofabrication" efforts are particularly focused on:

(a) Stimuli-responsive self-assembling biological polymers (especially polysaccharides);
(b) Experimental methods to fabricate and characterize materials for bio-device communication; and
(c) Synthetic biology to enable precisely engineered molecular components (proteins) and bacteria with tailored properties.

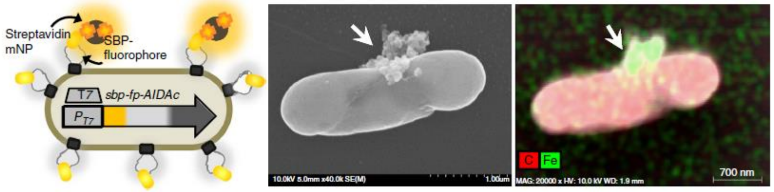
Our specific application is the integration of biological components into electronic circuitry.



(a) Chitosan self-assembly (modeling) (*JACS* **137**, 13024 (2015)

(b) Reverse engineering of materials (*Sci. Rep.* **5**, 18447 (2015)

(c) Synthetic biology to create bacterial-nanocomponent biohybrid materials (*Nat. Comm.* **6**, 8500 (2015)



Biofabricating integrated bio-electronics requires;
(a) molecular-level understanding of self-assembly,
(b) novel experimental characterization methods, and
(c) synthetic biology to create viable nanobio hybrids.

Relevance to MGI

As illustrated by the above Figure, there are three aspects of this project relevant to MGI. First, this project applies molecular modeling to understand how stimuli-responsive self-assembling polysaccharides can be induced to form complex structures with tailored functional properties. Modeling is being complemented by iterative experimental projects being undertaken by teams of international collaborators. Second, this project is developing novel experimental methods for fabrication (e.g., enzymatic methods) and for the rapid, quantitative characterization of soft materials (e.g., by reverse engineering). Currently, we are using medically-relevant problems (e.g., drug-materials interactions) as test beds for the development of these experimental methods. Finally, synthetic biology is providing unprecedented opportunities to integrate viable components into materials. Current efforts focus on coupling biology's chemically-based information processing modalities with device-compatible modalities (e.g., electrical and magnetic) to allow integrated bio-device communication and actuation.

Technical Progress

(a) Modeling studies indicate that stimuli-responsive polysaccharide self-assembly results from strong non-covalent associations and this indicates that the structure and properties of the resulting hydrogel significantly depend on how the triggering stimuli are imposed. (Morrow et al., 2015) This theoretical work is being used to guide experimental efforts aimed at tailoring electrical input stimuli to generate hydrogels with complex structures and properties.

(b) Experimental work demonstrated the biofabrication of a simple molecular communication device capable of (i) receiving and responding to molecular signals *from* the environment, and (ii) generating and transmitting a molecular signal *to* the environment. (Liu et al. 2015) Further experimental work is adapting reverse engineering methodologies for the rapid and quantitative characterization of materials' redox characteristics. (Kim et al. 2015)

(c) Synthetic biology methods were used to create viable components capable of transducing molecular inputs into electrical outputs. (Tschirhart et al. 2015) Also, bacterial constructs were generated that are capable of amplified and binned responses to molecular cues. (Terrell et al. 2015)

Future Plans

(a) Continue integrating molecular modeling with experimental characterization methods to understand how self-assembly can be controlled to tailor hydrogel structure and properties.

(b) Continue to develop materials fabrication and materials characterization methods for molecular and redox based communication.

(c) Continue to employ synthetic biology to create systems capable of bridging bio-device communication.

Broader impact (Optional for DOE grants/FWPs)

There are three broader impacts of this work. First, the modeling efforts serve as a guide for our international collaborators to generate self-assembling bio-based materials. These collaborations provide opportunities for our students to work with researchers from diverse backgrounds and to participate in international projects. Second, reverse engineering methodologies developed in this project are being adapted by the National Institutes of Standards and Technology (NIST) as part of their National Biotherapeutics Resource Center. NIST's goal is to create standard methods capable of generating simple, rapid and quantitative signatures of biosimilars. Third, the molecular communication research is integrated with federal stakeholders at the US Food and Drug Administration (through the Maryland Center for Excellence in Regulatory Science and Innovation) and the US Army (through the US Army Research Laboratory).

Data Management and Open Access

The work is disseminated by publication in peer-reviewed journals.

Accelerating Materials Discovery & Development

Modeling is expected to accelerate materials fabrication by reducing the need for empirical, time-consuming experimentation. Electrochemically-based reverse engineering methods are expected to provide simple, rapid and quantitative means to monitor and control materials properties. Synthetic biology provides transformative opportunities to create materials with important biological functionalities (e.g., for molecular recognition, decision making and actuation).

Publications

Review

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SCAN Meta-GGA: An Accurate, Efficient, and Soundly-Based Density Functional for the Materials Genome Initiative?

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Keywords: density functional, exchange-correlation energy, bonding, van der Waals interaction

Project Scope and Relevance to MGI

MGI aims to design useful new materials on the computer. High throughput materials searches, large unit cells, or molecular dynamics computations require an accurate and computationally efficient method. Standard semilocal density functionals (local density approximation, generalized gradient approximation, and meta-GGA) are widely used because they are computationally efficient, but need to achieve higher accuracy and reliability for ground-state energy differences and structures in normally-correlated materials. Our goal is to design a semilocal functional that is more accurate and reliable by building in more physics.

Technical Progress

On the 50th anniversary of Kohn-Sham density functional theory, we [1] have proposed a new computationally-efficient and usefully-accurate meta-generalized gradient approximation for the exchange-correlation energy of a many-electron ground state. The SCAN functional is strongly constrained, satisfying all seventeen known exact constraints that a meta-GGA can (including a new tight lower bound [2] on the exchange energy). It is also appropriately normed, i.e., exact or nearly exact for systems where a meta-GGA can be (such as slowly-varying densities and the densities of atoms in the limit of large atomic number). SCAN often performs like (or better than) a hybrid functional [3], without the empiricism and extra computational cost of a hybrid. Without being fitted to any bound system, SCAN usefully describes covalent, ionic, metallic, and weak (hydrogen or van der Waals) bonds [3]. Within a generalized Kohn-Sham scheme, SCAN yields band gaps that are better than those of GGA but not as accurate as those of standard hybrids. For stretched bonds, of course, SCAN requires a self-interaction correction and a long-range van der Waals correction [4]. [Supported by NSF (DMR-1305135) and by DOE Basic Energy Sciences (DE-SC0012575, Energy Frontier Research Center "Center for the Computational Design of Functional Layered Materials").].

Future Plans

We will develop a Perdew-Zunger-like self-interaction correction to SCAN by making a judicious use of localized orbitals. SCAN+SIC could improve the description of strong correlation.

Publications

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A Combined Experiment and Simulation Approach to the Design of New Bulk Metallic Glasses

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Co-Principal Investigator, Izabela Szlufarska, Department of Materials Science and Engineering, University of Wisconsin-Madison, szlufarska@wisc.edu
Co-Principal Investigator, Paul M. Voyles, Department of Materials Science and Engineering, University of Wisconsin-Madison, voyles@wisc.edu.

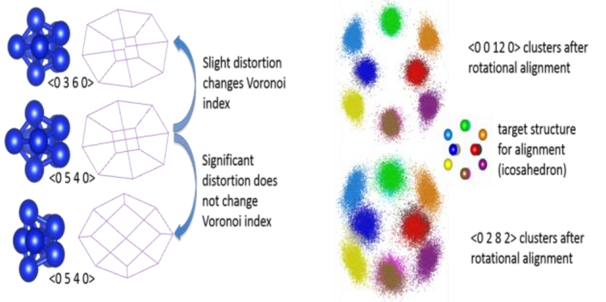
Keywords: Bulk Metallic Glass Design, Nucleation Kinetics, Glass Structure, Liquid Dynamics

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

During the current project period the coupling of experiment and simulation has progressed on two fronts. The MD simulations with accurate embedded atom method potentials have been able to reproduce the results from the analysis of nucleation measurements (thermodynamics and transport). A genetic algorithm optimizer is being developed to determine the optimal structure of an amorphous system given the simultaneous constraints of experimental and computed energy data. 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.



To determine ways to characterize glass structure and predict glass properties we are applying machine learning methods. Commonly used Voronoi indices are sensitive to some small distortions but insensitive to other large distortions. A new real-space structural descriptor based on point-pattern matching overcomes. Nearest-neighbor clusters are analyzed via machine learning after removing rotational and translational degrees of freedom.

Technical Progress

For aluminum based glasses the kinetics that yields the extremely high product number density during primary crystallization is not well understood. Perepezko has developed a novel technique based upon fast scanning calorimetry (Flash DSC) to measure the delay time, τ for nucleation and found that Cu doping in Al-Y-Fe MG has a large effect on τ. Since τ is directly related to the interface transport kinetics governing nuclei development, it is clear that the Cu substitution has a large effect on atomic transport. This new insight will guide our efforts to achieve bulk glass formation by inhibiting interface transport.

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.

Voyles and Morgan have worked with postdoc Min Yu to develop 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 using scanning transmission electron microscopy (STEM) data and an embedded atom method potential [3]. We 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. In addition, the population of grains and thus the fraction of grain boundary atoms increases. Predicted equilibration between FCC Al crystal and the glassy matrix agrees very well with Al-Sm metastable phase diagram. 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. With the trivial rotational and translation degrees of freedom removed, we can calculate a meaningful "structural distance" between two clusters, or a cluster and a prototype. For example, comparison of model clusters to a perfect icosahedron generates an "icosahedralness" score. The set of all distances between pairs of model clusters is amenable to machine learning clustering algorithms, enabling us to learn structural prototypes from a model automatically, without human bias.

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-Sm metallic glasses. Al-rich structures are already available, Sm-rich structures will follow in the next year. Both 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, leading to bulkier Al-based glasses. 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 in the process by developing FEM data analysis software for release to the broader community of scientists as both a software tool and online application on the MaterialHub (materialshub.org). That software has been adopted by researchers at the University of Muenster and the Bhabha Atomic Research Center. Undergraduates are involved in FEM software development and machine learning work. Machine learning activities have helped initiated our *Informatics Skunkworks*, a group dedicated to the 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.

We presented a live demo of atomic-resolution imaging using the U. Wisconsin Titan STEM, the primary experimental microscope for this project, at the 2015 UW Engineering Expo. The goal was to use the “wow!” factor of direct visualization of atoms, the basic building blocks of matter, to engage the interest of the general public in science and engineering. The demo was attended by ~60 small groups of between 5 and 30 students or members of the general public over the course of the two and half day event, for an estimated total attendance of ~400 people.

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. Once bulk Al glasses are available it will 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.

Publications

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Discovering Insulating Topological Insulators (DITI)

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Keywords: Topological insulators; defect properties; bulk-boundary correspondence; advanced synthesis.

Abstract

Topological insulators (TIs) represent a new paradigm for both fundamental condensed matter physics as well as future microelectronics technologies. Success in applications relies most fundamentally on design and discovery of highly insulating bulk materials displaying band inversion (due to spin-orbit coupling [SOC] or other topological entanglements) that enable room temperature operation of electronic and spintronic devices. The design loop is closed by characterization and demonstration of device type properties.

Project Scope

The goal of this interactive, interdisciplinary DITI team is to design, synthesize, characterize, and provide device proof-of-concept of new bulk-insulating materials with topological character and bandgaps of useful size. Target systems include oxides of heavy transition metals as well as untouched *s-p* materials, with the former being addressed with advanced exchange-correlation functionals, including one unique to this project. On the sample end, this project will use and extend the unique *Materials Advancement Portal (MAP)* hosted at UCSC, which maintains a catalog of samples that MAP members are curating.

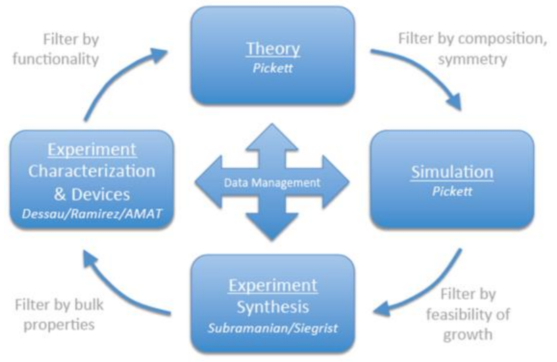

Figure. DITI synergies. *Designing Insulating Topological Insulators* requires integration of theory and simulation with synthesis (powder and single crystal) and transport characterization (especially to analyze bulk electrical [insulating] behavior, and characterization with ARPES to establish topological character. Every activity has feedback to each of the others.

Relevance to MGI

DITI focuses on little explored and newly designed materials classes based initially on selected examples from the experience of team members (AR,TS,MS) and the literature. Initial activities include skutterudites, double perovskites, and members of the Zintl family. Simulation of several members of the chosen classes (WP) provides prototypes for synthesis (MS,TS) and structural, transport, and thermodynamic characterization (AR,TS,MS), including sub-kelvin studies. These results feed back to simulation at each step, while promising samples are studied by ARPES (DS) to evaluate topological character. Rapid feedback from synthesis to simulation is essential for steady progress. Biweekly Skype session keep team members informed and focused, and make students an integral part of the team. Proof of principle device properties (AR) are shared with industry (C.-P. Chang, *http://appliedmaterials.com*) for feedback from the device production and marketing end.

Technical Progress

Many of the compounds that incorporate both the lattice symmetry required for “TI-ness” and strong correlations involve Ir. Work to date has focused on the interplay between the different valence states of Ir and the local structural and chemical environment within the solid solution series derived from the Brownmillerite structure. Samples of $Ba_2In_{2-x}Ir_xO_{5+\delta}$ ($x = 0 – 1.4, 2$) were synthesized and structural, magnetic, and charge transport properties measured. With increasing Ir content, three transitions in the room temperature structure were observed: orthorhombic to tetragonal to cubic to a monoclinic distortion of a hexagonal $BaTiO_3$ structure. Neutron diffraction shows $Ba_2In_{1.6}Ir_{0.4}O_{5.4}$ to be cubic and Ba_2InIrO_6 to be monoclinic, the latter contrary to previously published XRD refinements. Magnetization measurements show Curie-Weiss behavior for $x = 0.2 – 0.6$, which arises from near 50:50 ratio of Ir(V) and Ir(VI). *To our knowledge, this is the first time Ir(VI) has been stabilized with standard solid state methods under ambient conditions.* The electrical resistivity is semiconducting for all compounds studied, and decreases with increasing Ir content suggesting the proximity to a metal-insulator transition.

Future Plans

Future work will explore other Ir-contain structures such as the pyrochlore lattice and substitutional variants in order to delineate structural and valence stability ranges. Work is also planned to initiate complementary studies incorporating the 5*d* cations W, Os, and Re. Simulations will include s-p Zintl materials.

Broader impact

Graduate and undergraduate students (through REU and paid internships) working on this project will interact closely with group members, forming strong near-peer mentor relationships and participating in all aspects of the research enterprise from planning to publication. Both undergraduate and graduate students will gain interaction with industrial partners. We have engaged with Applied Materials, which has an interest in developing future talent and is committed to hosting students at their facility in Santa Clara. Student professional development will also be enhanced through ongoing interactions and internship opportunities with national laboratory collaborators. Siegrist's laboratory is situated within NHMFL, Dessau is a major user at national and international synchrotron facilities, and Pickett has collaborators at LANL, LLNL, and ANL who may provide interaction and internship visits with students supported by this project. While DITI involves researchers who have already started collaborating, we will use the tools available on the project and MAP websites to manage data, share best practices, and potentially enlarge the collaboration beyond the PIs on the project.

Data Management and Open Access

Pickett is updating his web site, which will include a shared workspace, UC-located, web site to share results within the team, for discussion across institutions, and for availability of other researchers. DITI plans to partner with the Materials Project to archive computational data in an organized, retrievable manner. DITI will use, and continue to manage, the Materials Advancement Portal (http://materials.soe.ucsc.edu/home) established in 2013 (AR). This site provides opportunities for new approaches to sample management and sharing.

Accelerating Materials Discovery & Development

Our DITI project incorporates all pivotal areas to discover, develop, and deploy TIs: theory and simulation (WP), synthesis (MS,TS), characterization (xray: MS,TS; transport and thermodynamic: AP; ARPES: DS); basic device concepts and manufacturing (AP, *Applied Materials*). This DITI project has the potential, through interaction with *Applied Materials*, to accelerate the development of next generation microelectronics, leading to greater technical expertise for U. S. customers and increased U. S. economic competitiveness. We believe MAP has the potential to transform the nature of collaborations where samples and data need to be shared.

Publications: this is a new project

Materials with predetermined nanostructures via the computational design and solution assembly of peptides

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Keywords: peptide, self-assembly, predetermined nanostructure

Project Scope

DNA origami is established as a nanomaterials field with computer prediction allowing design of proper base pairing to build targeted structures. However, the building of designed, new structure with peptides and proteins is severely limited and currently relies on the manipulation of natural proteins and biomimicry. This severe limitation of new nanostructures is directly attributed to the complexity of interactions between peptidic/protein molecules (as opposed to the more straightforward base pairing interactions of DNA) and the larger number of molecules possible with natural amino acids (not even considering non-natural amino acids). This project is developing and applying computational tools to predict molecules required to produce predetermined, non-natural nanostructure.

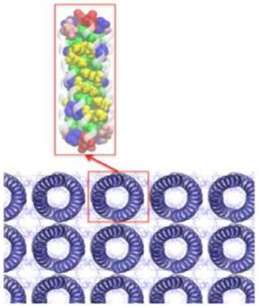

Figure 1. Schematic of tetrameric helical peptide bundles that pack together during solution assembly to form desired, predetermined two-dimensional lattice. Theory predicts the peptide molecules required to produce the predicted bundles and consequent nanomaterial.

Relevance to MGI

Recent, interesting efforts in peptide/protein self-assembly rely on intuition/empirical rules for peptide assembly into nanomaterials or the computational alteration of natural proteins. This project does not rely on empiricism or alteration of natural protein structures for new, designed nanostructure. A single peptide bundle motif (i.e. coiled-coil) is designed strictly through computation and subsequently the alteration of only the bundle exterior chemistry produces four different, de novo designed nanomaterials. This is a major step towards the design of materials with predetermined nanostructure that have the robust processiblity of peptides but are not subject to the vagaries of natural protein structure, expression and purification. Additionally, length scales defined (few nm) are approaching those required for the building of hybrid inorganic/organic materials with function normally associated with hard condensed matter physics (semiconducting heterostructures, plasmonic materials, and topological insulators). The experimental results are revealing success in theoretical prediction of desired nanostructures with subtle differences observed in some cases. These results are now being compared computationally with originally designed nanomaterials to determine why experimentally observed nanostructures were observed as opposed to the originally designed sequences.

Technical Progress

Four classes of homotetrameric (i.e. single peptide that forms a bundle with four molecules total in the bundle) coiled coil bundles were experimentally explored after theoretical prediction of molecules required to build the desired, designed nanostructures. Nanomaterials defined by two-dimensional lattice symmetry of bundle packing were chosen to build by predicted interbundle assembly: P_{222}, P_{622}, P_{422}. Additionally, tetrameric bundles were also designed to produce only soluble bundles with no regular lattice structure. Computational methods were developed and refined in order to produce several molecule candidates for each class of assembly. The molecular synthesis, solution assembly, and characterization of these first classes of predicted molecules have supported the proposed, overall effort. Importantly, to date, all molecules predicted to make a lattice have all been experimentally observed to form the predicted lattice or a lattice with very similar characteristics. Additionally, all molecules designed to make a bundle but not to form an interbundle lattice have, in fact, formed bundles with no regular lattice superstructure. It would have been impossible to empirically define peptides to assemble in such a hierarchical mechanism (to first assemble into tetrameric peptide bundles that then, in turn, assemble together to form a particle lattice symmetry in two-dimensions). However, the theoretical prediction of molecules required for predetermined nanostructure makes the production of desired nanomaterials robust and, with future work, preferably routine. The frequent, routine interaction of the experimental researchers with the theory group has been, and will be, crucial for future success. Monthly, in person meetings are providing much feedback in both directions. Currently, the theory group is comparing the observed structures with those predicted to determine why some predicted molecules have yielded slightly different structure than predicted. Additionally, the theory group is exploring designed nanostructures with different amino acids replaced with non-natural amino acids, where covalent chemistry can be carried out on the peptide bundles after nanostructure assembly.

Future Plans

Now that we've established a successful process for nanostructure prediction, molecular synthesis, solution assembly and nanostructure characterization with a feedback loop to the theory effort, we have several pathways going forward to be explored. We are using the nanostructures already created as templates for inorganic phase growth/assembly. With the exact display of peptides in two-dimensions, we are exploring placement of inorganic nanoparticles at desired positions on assemblies through display of specific chemical functionalities from the peptide termini. This allows the adsorption or growth of inorganic particles at specific points on the two-dimensional sheet to lead towards potential functionality. Additionally, we are using covalent chemistry to make the assemblies permanent as well as to define hierarchical steps of assembly. Namely, post assembly into two-dimensional, predicted sheets, we will use covalent chemistry from the sheets to grow materials in three dimensions with the sheet as a template with a specific symmetry.

Broader impact (Optional for DOE grants/FWPs)

The PI, co-PIs and students who are involved in this work have demonstrated a significant commitment to education and outreach. They serve as mentors and educators to a diverse population, and have been involved in activities that are expected to motivate and inform future generations of scientists. An example is the work with the ASM teachers camp at UD every year during which high school STEM teachers learn about materials science and new aspects of science and engineering to teach their own students. Exposure to new areas of materials science such as MGI-based efforts and the use of biomolecules as synthetic materials hopefully will lead new students to exciting careers in materials sciences (and STEM fields, in general).

Data Management and Open Access

Computer codes are currently under development but are being structured so as to facilitate their use in a wide variety of potential applications. Data is being collected, annotated, and stored in manner suitable for use by a variety of researchers.

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Discovery, Development and Deployment of High Temperature Coating – Substrate Systems

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Keywords: multilayers, superlattice intrinsic stacking faults, Co-Al-W, oxides

Project Scope

The goal of this project is to develop new computational and experimental approaches that accelerate the design of multilayered systems for extreme high temperature thermomechanical environments. Multicomponent, multiphase substrates based on the emerging Co-Al-W system are a primary focus. New computational tools deployed include (1) a self-consistent framework for alloy design that rigorously couples first principles calculations and multicomponent thermodynamics, (2) a high throughput thermomechanical code for exploration of the design space for multilayers and (3) a particle-based dynamic code parallelized with GPUs that addresses the challenging problem of designing failure resistant interfaces. These computational codes have guided the experimental program, which has identified new high strength alloy compositions and robust coatings.

Relevance to MGI

To narrow the design space and minimize expensive and time consuming synthesis processes, the new computational tools (above) have been developed, refined and employed to study several generations of high strength substrate alloys, protective oxides and environmentally resistant outer layers. These tools have guided the experiments conducted on single crystal substrates and multilayer metallic / intermetallic / ceramic systems.

Technical Progress

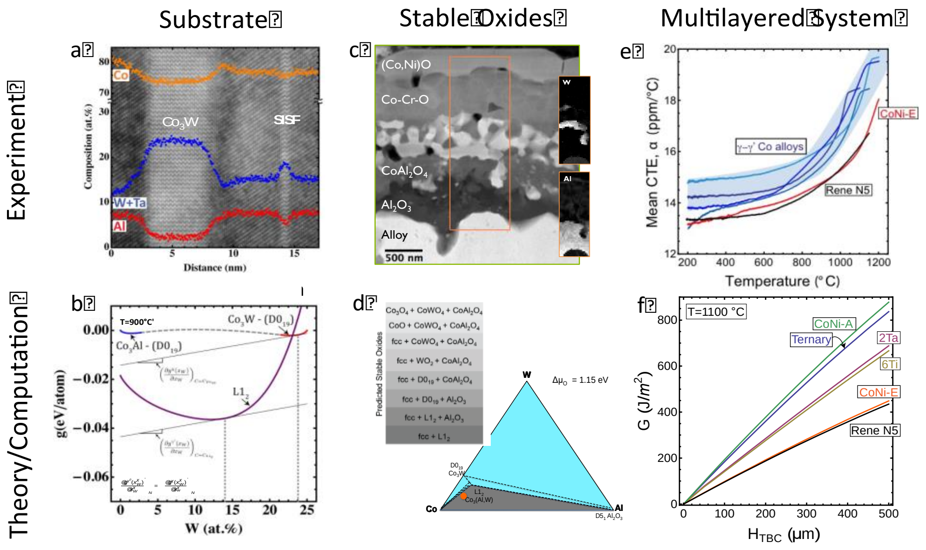

Figure 1 - (a) HAADF-STEM image of a fcc-Co + $L1_2$ + DO_{19} Co-Al-W-Ta alloy showing W enrichment and and Al depletion at the SISF (which has local DO_{19} atomic stacking), (b) first principles, analysis of the driving force for segregation at the SISF showing that W enrichment is strongly favored, (c) stable oxides observed during oxidation, (d) first principles calculations of stable oxide layers as a function of chemical potential of oxygen, (e) experimental data on coefficients of thermal expansion (CTE) for experimental cobalt alloys and (f) the driving force (G, energy release rate) for failure along the substrate interface during cooling from 1100˚C as a function of the thickness, H, of a ceramic thermal barrier layer thickness.

Fundamental requirements for robust high temperature multilayered systems include a substrate with high resistance of the to plastic deformation beyond 75% of melting temperature and multiple outer layers with good adherence and resistance to aggressive chemical and thermal environments. In single crystal substrates comprised of fcc-Co strengthened with the $Co_3(Al,W)$ intermetallic $L1_2$ phase, electron microscopy studies reveal very unusual modes of deformation that involve the formation of superlattice intrinsic stacking faults (SISFs), Fig. 1a, formed as a result of $L1_2$ precipitate shearing. HAADF-STEM studies reveal compositional fluctuations in the vicinity of these faults, Fig. 1a. A computational infrastructure that combines first principles techniques based on density functional theory and statistical mechanics has, for the first time, been used to quantitatively assess the thermodynamic driving force for Suzuki segregation at stacking faults, Fig. 1(b); the important implications of segregation for mechanical properties have been studied in detail. The load-bearing metallic substrate typically requires intrinsic oxidation resistance as well as an intermediate intermetallic layer for chemical protection and an outer ceramic layer for thermal protection. Fig. 1c shows the series of oxide layers that form during oxidation of a Co-Ni-Al-Cr-Ta-W alloy. Given the complexity of the oxide layers, the first principles infrastructure has been employed to calculate the stable oxides in a comparable Co-Al-W ternary alloy (Fig 1d) as a function of oxygen chemical potential. The driving forces (G, energy release rate) for coating failure (via delamination at the substrate interface) in multilayered systems for each of the experimental alloys containing a CoNiCrAlY intermetallic interlayer and a yttria-stabilized zirconia thermal barrier top coat of varying thickness, H, have been studied with a high throughput code for assessment of the thermomechanical performance, Fig. 1f. Large differences in the CTEs of the experimental alloys are the source of the variations in energy release rates, Fig. 1e, with the implication that relatively thin ceramic coatings are likely to be required to minimize the driving forces for delamination.

Future Plans

Ongoing combinatorial experimental and theoretical studies are aimed at identifying systems where α-Al_20_3 is thermodynamically stable at elevated temperatures. The first principles and statistical mechanics framework is being employed to study diffusion mechanisms and to study the thermodynamic stability of the $L1_2$ phase at finite temperatures. Single crystal substrates with low driving forces for SISF segregation (hypothesized to have high strength) are being synthesized for experimental studies. The particle-based dynamic code has been parallelized with GPUs and will be fully validated and compared to finite element predictions and employed to analyzed experimental results from our newly developed femtosecond laser-based interfacial toughness probe.

Broader impacts

There have been several student research exchanges between UCSB and the Univ of Erlangen and the Ruhr Univ of Bochum. UCSB has hosted three summer schools/workshops, on 3D Materials Science and Big Data (2013, 2015) and Integrated Computational Materials Science & Engineering (2014). All DMREF students attended GE-UCSB workshops that were held at GE Global Research in 2013 and 2014 and at GE Aviation in 2015.

Data Management and Open Access

The high throughput multilayer code is programmed in Mathematica and is available for all platforms as a part of a textbook being authored by Begley and at http://www.engineering.ucsb.edu/~begley/LayerSlayer.html. The first principles and statistical mechanics alloy design code will be open source and available at GitHub. Thermodynamic data generated in the program is now available in the Pandat / Computherm Co alloy database. All other experimental data has been or will be published in archival journals.

Accelerating Materials Discovery & Development

The computational tools have narrowed the design space and substantially accelerated the design of both substrates and multilayered systems and these tools have been transferred to several aerospace companies. This program is a GOALI program with General Electric, who has contributed substantial resources to this project and maintains an active internal program on these new Co-base alloys. Since our initial work on these systems, new programs have been initiated in the UK (Rolls Royce, Imperial College), Germany (Bochum and Erlangen), Japan (Daido, Kyoto, Tohoku) and China (USTB, CAS) and the US (Air Force Research Laboratory, Northwestern, NIST).

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Center for Accelerating Materials Modeling (CAMM) from SNS Data.

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Website: http://camm.ornl.gov
Keywords: neutron scattering, refinement of force fields, molecular dynamics, local dynamics

Project Scope

Neutron scattering enables simultaneous measurement of structural and dynamic properties of materials from the atomic scale (0.1 nm, 0.1ps) to the mesoscale (1um, 1us). These ranges are remarkably complementary to current capabilities of computational modeling, and the simplicity of the scattering cross section allows the straight-forward prediction of neutron scattering data from atomic trajectories in a computer model. Accelerating the rate of scientific discovery relies on the integration of modeling into all aspects of the neutron scattering experimental chain. This integration would enable refinement of model parameters (such as force fields) and allow models and experimental results to be compared in near real time.

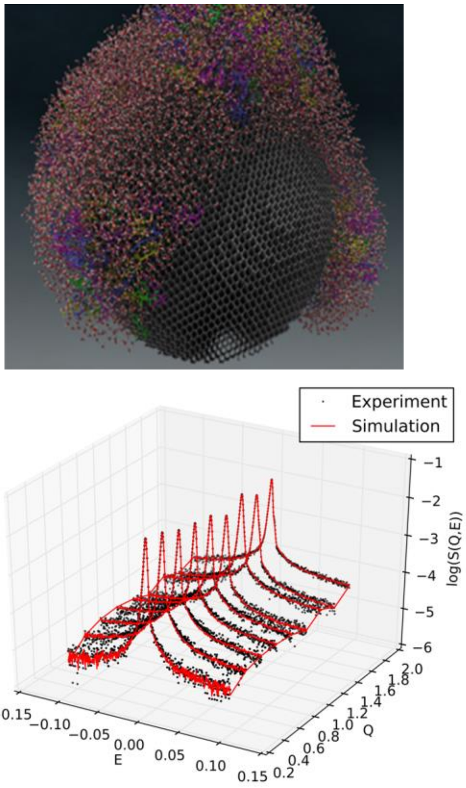

Figure. Top panel shows simulation of hydrated RNA on nano-diamond. Bottom panel shows comparison of simulated and measured quasi-elastic neutron scattering. Experiment was carried out on the BASIS instrument at the Spallation Neutron Source.

Relevance to MGI

The ability to correlate the atomic, nano- and mesoscale-structure with physical properties (e.g., mechanical, chemical, electrical) and functionality is critical to the rational design of the next generation of energy materials. Neutron Scattering provides unique insight into the structure and dynamics of over a wide range of important length and time scales and it does so materials in a fashion that does not substantially damage or modify the materials. CAMM is providing model parameter refinement tools based on neutron data as well as real time materials simulation capabilities enabled through leadership computing and advanced data analytics. This capability enables improving the predictive capability of materials models based on validation with neutron data as well as facilitating planning for targeted neutron scattering experiments based on model predictions (e.g., theory and simulation guided experiments).

Technical Progress

The Center for Accelerating Materials Modeling (CAMM) has the over-arching goal to drive the science-based development of software tools to link neutron scattering and computer modeling. CAMM has supported three thrust areas. In the area of phonon simulations, the focus this FY was on phonon anharmonicities in SnSe and $FeSb_2$. In case of SnSe, DFT calculations were performed to study the effect of pressure on the phase stability of the system. These simulations confirmed experimental observations and indicate a strong anharmonicity of the transverse optical modes [3]. In the case of $FeSb_2$, new inelastic neutron scattering measurements were carried out on the HYSPEC instrument at the SNS and HB3 at HFIR. Preliminary analysis shows an anomalous temperature dependence of the energy of some phonon modes and the team is working on explaining these observations using DFT. This work used the CAMM supported code *SimPhonies*. CAMM has developed a workflow to refine potential parameters of a specific model based on neutron scattering data. In the soft matter thrust, we demonstrated these tools on simulations of nano-diamond + RNA + water. We leveraged developments of the new Pegasus workflow system to seamlessly run the required simulations on supercomputing resources. In the third and newest focus area of CAMM, we are developing the dynamic pair density function (DPDF) approach. DPDF goes beyond simply focusing on the dispersion of excitations and utilizes all the data collected on the spectrometers at SNS. Initial work focused on understanding dynamics in super fluid helium and heavy water. In the related software development, a first prototype data reduction for DPDF was implemented in the data reduction framework *Mantid* used at the Spallation Neutron Source (SNS). Future impact is dependent on the adoption of CAMM developed tools by the wider scientific community. CAMM has engaged with several ‘friendly’ users to develop and test CAMM developed tools in close collaboration. Efforts on making our software tools more accessible have continue as part of CAMM, including the development of tutorials and a first hands-on workshop for the force field refinement workflow held in October as part of the HFIR and SNS Users Meeting.

Future Plans

During this FY, CAMM will focus on the development of the DPDF method and in particular continue to integrate the data processing into the current experimental workflows on the SNS spectrometers. Additionally, we will develop tools to calculate the DPDF from models to allow quantitative comparison. In the other thrusts, the aim of work this FY is on the continued improvement of the CAMM workflow and related software tools as well as growing the user base for these tools through partnering with friendly users, developing more detailed documentation and holding additional tutorials. We will also develop a strategic plan for future CAMM activities that are synergistic with current and upcoming funded projects.

Data Management and Open Access

Documentation, tutorials and codes related to the CAMM refinement workflow are publically accessible through the website http://camm.ornl.gov. Users of the SNS and HFIR facilities have access to the facilities analysis infrastructure which has the CAMM framework installed. CAMM is also working closely with the Compute and Data Environment for Science (CADES) project at Oak Ridge National Laboratory to provide data access and citation in the future.

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High-Throughput Mapping of Functional Dielectric/Metallic Heterostructures

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Keywords: perovskite oxide superlattices, electronic properties, off-axis sputter deposition, density functional theory, interface effects

Project Scope

The principal objective is to map the structure and properties of three selected broad families of metallic-dielectric perovskite superlattices through an integrated theoretical-experimental approach. This combines first-principles calculations, construction of first-principles-based models, development of a guided-sampling high-throughput first-principles approach, and experimental synthesis and characterization of selected systems. Success is measured by the identification, synthesis and characterization of individual systems with targeted functional properties or unusual and distinctive behavior that validate the map and will potentially be suitable for technological applications.

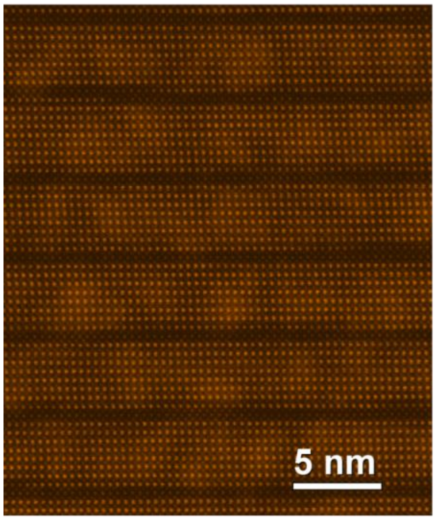

Figure. HR-STEM image of a $PbTiO_3/SrRuO_3$ superlattice grown in Dawber's laboratory.

Relevance to MGI

The team includes all the necessary capabilities for first-principles computation, modeling, synthesis and characterization of metallic-dielectric perovskite oxide superlattices, with a long track record of previous collaboration. The models are tested both for their ability to reproduce first-principles data and for their ability to predict and interpret the results of experiments. Dawber's enhanced thin film growth capabilities allow growth of superlattices specifically selected to test model predictions, allowing iterative improvement of the models as needed; one example of this iteration in the current project is the synthesis of specific $PbTiO_3/BaTiO_3$ superlattices predicted by the model to have the highest piezoelectric coefficients.

Technical Progress

Significant progress in the modeling of enhanced piezoresponse has been made by focusing on modeling the relationship of the superlattice IR active phonons to the phonons of the constituent compounds; a theoretical paper presenting this phonon analysis is in preparation while complementary experimental efforts to study electromechanical response, structural distortions and IR characteristics in $PbTiO_3$/$BaTiO_3$ superlattices are underway.

Experimentally, through comparison with $PbTiO_3$/$SrRuO_3$ superlattices and $PbTiO_3$/$SrTiO_3$ superlattices, both with symmetric top and bottom electrodes, we have determined, through electrical measurements and TEM analysis, that in addition to intrinsic compositional inversion symmetry breaking and effects due to oxygen vacancy ordering, asymmetries in the roughness of particular interfaces may play an important role in asymmetrizing the polarization response of our systems. Therefore, in addition to the ongoing first principles investigation of the preferred sites for oxygen vacancies in these systems by Divilov and Fernandez-Serra, and modelling their dynamics by Chandra, we have investigated the effect of asymmetrically abrupt interfaces to compliment the experimental insights gained from the experiments. Our aim is to be able to separate and quantify the multiple effects that lead to asymmetry so that they can be precisely controlled.

The results of our first principles investigation of the prototypical metallic-dielectric superlattice $SrCrO_3$/$SrTiO_3$ have been published and efforts are underway to fabricate high quality examples of this superlattice in the new deposition system in Dawber’s laboratory. These samples will enable magneto-transport measurements in Du’s laboratory and resonant x-ray scattering experiments at NSLS-II at BNL.

Building on the method for determining ground-state and low-energy structures of superlattices that we developed early in the project, we are currently constructing a database of low energy structures of superlattice constituents.

Future Plans

On the experimental side, fabrication efforts will focus on $PbTiO_3$/$BaTiO_3$, $PbTiO_3$/$SrRuO_3$, $SrCrO_3$/$SrTiO_3$ and $SrCoO_3$/$SrTiO_3$ with characterization chiefly via electrical transport, atomic force microcopy, X-ray diffraction and transmission electron microscopy. A combined experimental and theoretical effort to quantify and control the multiple sources of asymmetry in ferroelectric superlattices will be a major focus in the coming year.

On the theoretical side, we will complete the design of the constituent compounds database and add information for more compounds, and work on the development of first principles models for the structure, electronic states, and properties of metallic-dielectric superlattices. We will then refine the models to make quantitative predictions of band gaps and features of the bandstructure and phonons relevant to thermoelectric performance.

Broader impact

Excellent integration of theory and experiment, a key element of the Materials Genome Initiative, has been achieved by the establishment of regular electronic interactions among the participants at Rutgers and SBU. A biweekly time slot is reserved for a joint Skype teleconference, which takes place unless interrupted by travel of team members. There is a constant feedback mechanism to ensure that all efforts are framed in the context of how the results of theory and experiment can be related to each other. As an example, the experimental procedure used to characterize polarization offsets was revised to provide quantities more directly obtainable from DFT calculations, and in the other direction, simulations are performed based on experimental information, such as the sharpness of interfaces as revealed by TEM measurements. The theorists use this opportunity to ask experimentalists for data details, additional characterization and synthesis of additional samples, while the experimentalists ask for theoretical analysis, interpretation and guidance. Hands-on experience in theory-experiment integration is gained by all students, both experimentalists and theorists, as they all participate in the regular Skype meetings with PIs and Co-PIs and are required regularly to present their results for discussion.

Data Management and Open Access

The superlattice structure determination scripts have been made available to the community on a website constructed by Zhou [1]. Bonini is working with emerging software tools for storing and accessing results of first-principles calculations (AflowLib, Materials Project and AIIDA), to design our constituent-compounds database as an overlay. This will allow us to share the first-principles results with other users of the software and will provide a prototype for constructing special-purpose databases that are widely accessible.

Accelerating Materials Discovery & Development

Two aspects of our recent work may help accelerate materials discovery and development. Firstly, our new understanding of what drives enhanced piezoresponse in ferroelectric superlattices; we already using this for new examples and assessing their feasibility of fabrication. Second, we aim to quantify the significance of different aspects of non-ideality in producing a bias in the electrical response of ferroelectric superlattices. Having this information will clarify in which areas of a fabrication process it is critical to maintain high control and which areas there is more tolerance, so that the process can be effectively scaled up.

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Publications

Please include a list of all publications supported by this award. (If number of publications is greater than 10, please list only the 10 most relevant.) These papers must include an acknowledgment to the award. Manuscripts that have been submitted may be included. Do not include ‘manuscripts in preparation’. If you have not already done so, please forward electronic copies of these publications to the appropriate program manager listed below.

1. Y. Zhou and K.M. Rabe . *Determination of ground-state and low-energy structures of perovskite superlattices from first principles.* Physical Review B, **89**, 214108 (2015).
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Search for Magneto-Electronic Complex Fluoride-based Interfaces with Novel Properties.

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Keywords: oxyfluorides, multiferroics, density functional theory, molecular beam epitaxy, scanning probe microscopy

Project Scope

Complex fluoride thin films and heterostructures are studied synergistic computational and experimental methods with the goal of obtaining materials with larger magnetoelectric couplings. In complex fluorides, the origin of multiferroic properties (A-site displacement for perovskites) together with the larger electronegativity of fluorine can result in enhanced magnetoelectric effects in comparison with oxide perovskites. The computational work employs first-principles techniques□to determine the most likely structures to have large magnetoelectric responses. These fluoride materials are synthesized using molecular beam epitaxy. Experimental characterization of the structural, dielectric, and magnetic properties are carried out and the results are compared to the theoretical findings.

Relevance to MGI

Our synergistic computational/ experimental collaboration searches for interfaces and new thin film materials based on complex fluoride compounds with unique electronic, magnetic, and magnetoelectric properties. The computational component suggests new materials and interfaces likely to have strong magnetoelectric properties, and the experimental component attempts to grow them using MBE and to characterize them to determine the physical properties. The computational and experimental efforts quantitatively determine the structural parameters that could modulate the magnetoelectric properties, such as strain, symmetry breaking, electrostatic coupling, frustration, and charge transfer (Figure 1). This will lead to a development in the design and implementation of new materials into electronic devices that are more power efficient and faster than current technology The computational design strategy will be shared with the scientific community by developing user-friendly software that uses DFT as the basis as the electronic structure characterization. This software will allow users to create various interfaces by considering different crystallographic orientations with minimal lattice mismatch using a graphical representation.

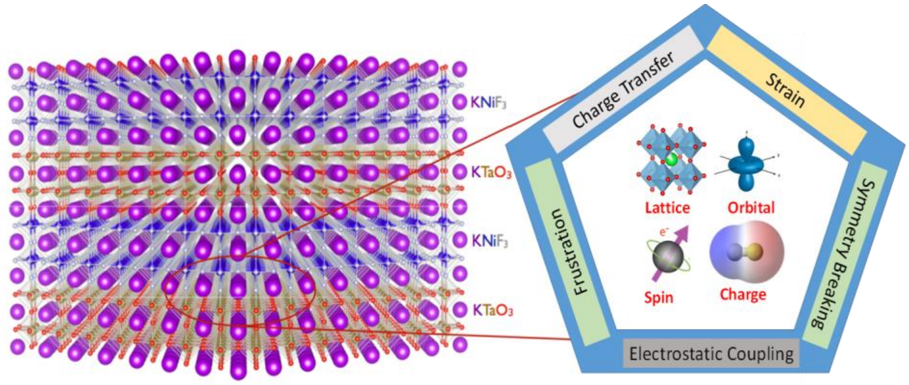

Figure 1. Physical phenomena (e.g., charge transfer, strain, symmetry breaking, electrostatic coupling, frustration) that may lead to multifunctional properties as a result of new lattice, orbital, spin, and charge orderings found in oxides/oxides interfaces and expected in mixed oxyfluorides oxide/fluoride ($KTaO_3$ and $KNiF_3$ in the figure) interfaces. Diagram based on Zubki *et al.* [1].

Technical Progress

As a first approach, we studied the effect of the epitaxial strain on the structural, electronic, and magnetic properties in the fluoride perovskite $NaMnF_3$ using density functional theory. 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 a non-linear piezoelectric response as a function of epitaxial strain was found. The latter effect is completely different from findings reported in oxide perovskites [2]. Additionally, an out-of-plane polarization was observed, in contrast to oxide perovskites, where the ferroelectric polarization tends to be in-plane. A cooperative FE ordering between Na and Mn sites was found for compressive strain against a pure *A*-site geometrically driven ferroelectricity with tensile, orthorhombic ac-strain [3]. Magnetic ordering reveals a non-collinear ground state with a $G_zA_xF_y$ magnetic representation. A non-linear magnetoelectric coupling was also found in this material under the strained $Pna2_1$ ground state crystal phase. This is the first perovskite-fluoride where non-linear piezoelectric and magnetoelectric responses co-exist.

Using the computational results as guidance, we have grown $NaMnF_3$ thin films on $SrTiO_3$ (001) substrates and metallic $SrRuO_3$ layers grown on $SrTiO_3$, the latter in order to use bottom contacts for ferroelectric and magnetoelectric measurements (Figure 2). We have indeed found that this compound is multiferroic, with simultaneous magnetic and ferroelectric orders. Piezoelectric force microscopy indicates that the material is ferroelectric at room temperature, while antiferromagnetic/weak ferromagnetic order is induced below 70 K. Magnetoelectric coupling has not been definitively proven yet, however, and will require further improvement of sample quality to test this further.

Moving forward, we have analyzed by means of first-principles calculations the electronic and structural properties of oxyfluorides heterostructures. $(KTaO_3)_n/(KMF_3)_l$ with M = Zn and Ni, where superlattices with alternating *p*- and *n*-type interfaces were considered, as shown in Figure 1. We found that the orbital levels symmetry at the interfaces is strongly dependent of the O–M–F coordination. The polar catastrophe phenomenon also takes place in the oxyfluoride interfaces as previously reported in similar oxide interfaces. Unexpectedly, we found that fewer number of layers is needed in order to achieve the insulator-to-metal transition in comparison to, for example, $SrTiO_3/LaAlO_3$ [4]. The magnetic structure keeps the *G*-type AFM ordering as in the bulk compound. Surprisingly, we observed a large k^3-Rashba type splitting 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 [5]. We are now focused on the multiferroic behavior of the $LaScO_3/NaMnF_3$ system, where our preliminary results show a stable multiferroic behavior. From the experimental point of view, we are planning on growing the $LaScO_3/NaMnF_3$ system first, since we have recently developed our MBE technique for growth of $NaMnF_3$.

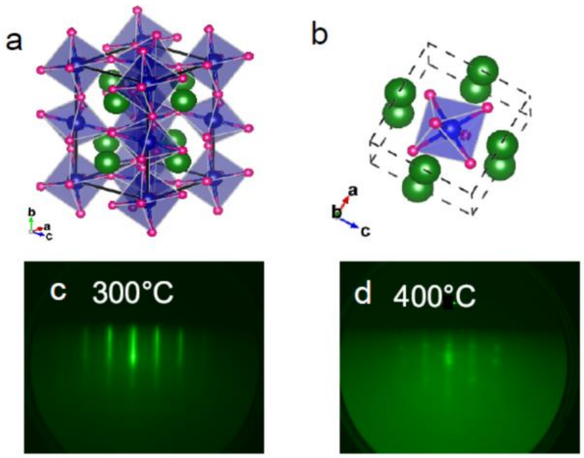

Figure 2. (a) Sketch of $NaMnF_3$ orthorhombic unit cell with MnF_6 octahedra outlined. (b) View along the b-axis growth direction. (c,d) RHEED patterns from samples grown at two temperatures on $SrTiO_3$, with the 300 °C sample showing superior structural quality.

Finally, we have grown and characterized $BaCoF_4$ multiferroic thin films. The properties of the MBE-grown samples, especially their weak ferromagnetism, was explained by our first-principles calculations which demonstrated that a uniaxial strain caused by the interaction with the substrate was responsible for the effect. This is the first time that this compound has been demonstrated to be multiferroic since its discovery in 1970, and the first time that it has been observed to be a weak ferromagnet in thin film form.

Future Plans

From the theoretical point of view, we will continue the characterization of the proposed interfaces, in particular one where antiferrodistortive (AFD) rotations distortions and magnetism can be coupled, as it is the base of $LaScO_3$/$NaMnF_3$. Other interafaces will be also considered, by attempting different fluorides and oxides with the smallest lattice mismatch, but also taking into account the effects of strain that occur in real interfaces. From the experimental side of the project, we will continue with the optimization of the growth of $NaMnF_3$ thin films. In parallel, we will focus on the growth of the oxide layer as well so as to grow the oxide/fluoride heterostructures.

Broader impact (Optional for DOE grants/FWPs)

Three graduate students, one undergraduate student, one postdoc, and a research professor are involved in the project. We have monthly joint group meetings where students and postdocs discuss all aspects of the project, theoretical, computational, and experimental. This research experience, where students are aware of all aspects of the project, will enable project participants to become successful scientists in the future.

Data Management and Open Access

We are developing our web site that will distribute software and materials parameters that could be used by students and other interested parties everywhere to simulate and fabricate similar thin films and heterostructures with interesting magnetoelectric properties.

Accelerating Materials Discovery & Development

We have successfully demonstrated that the compound $NaMnF_3$ is indeed multiferroic. The experimental confirmation was a result of the suggestion of the computational work of the project. This is a specific example of the success of the project because the participating experimentalists would not have necessarily grown this compound, since there are many other possible alternatives. The computational work was able to demonstrate that other variations of the compound (e.g., different elements) were not necessarily multiferroic.

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An Integrated Multiscale Modeling and Experimental Approach to Design Fouling-resistant Membranes

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Keywords: Water purification, Antifouling, membrane design, multiscale modeling

Project Scope

Membrane fouling is one of the most important and challenging problems in membrane science. The proposed multidisciplinary research effort will advance the basic science associated with membrane fouling during the purification of impaired waters. Fouling propensity of a membrane depends greatly on its surface properties such as chemistry and morphology. The goal of this collaborative research and education program is to develop the multiscale mathematical framework to predict fouling behavior on the surfaces of membranes with different geometric patterns and chemical coatings. To achieve this goal, investigations will examine the roles of pattern geometry and feature sizes, surface chemistry, foulant type, and operating conditions on membrane fouling.

Relevance to MGI

In this research program, comprehensive studies involving iterative feedback between computational modeling and experimental measurements will be performed to test two main hypotheses: 1) targeted combinations of geometric and chemical patterns on a membrane surface will significantly reduce membrane fouling, and 2) experimentally-trained multiscale computational models will accelerate the discovery of novel geometric and chemical surface modifications that significantly reduce membrane fouling. This effort will i) produce a mathematical framework and corresponding models to identify the physical mechanisms and geometric features controlling mass and momentum transfer through and over micro- and nano-patterned membranes, ii) provide a deep understanding of how foulants and energy fluxes are controlled and regulated by complex topologies, and iii) elucidate how the macroscopic behavior of filtration flow rates and reactive transport processes are coupled with phenomena at the micro- and nano-scale. This work will be transformational because delivering an experimentally-validated computational framework will enable rapid screening of many membrane surface modifications to short-list the most promising ones for further testing, and it will lead to a leapfrog improvement in membrane filtration technologies.

Future Plans

The main tasks of our research program fit into the structure: Fabricate, Characterize, Test, Train Models, and Simulate Novel Membrane Designs.

Fabricate: Create thin-film polyamide nanofiltration and reverse osmosis membranes with well-defined submicron surface patterns using nanoimprint lithography.

Characterize: Evaluate the fabricated patterned membranes by using appropriate experimental techniques for visualization of surface patterns; analyzing the surface chemistry; determining the grafting densities; evaluating surface hydrophobicity; and determining the surface charge.

Test: Evaluate the performance of the new membranes through constant flux, cross flow filtration measurements on as-received membranes, patterned membranes, and chemically-modified patterned membranes.

Train Models: Multiscale dynamics of transport processes over patterned membranes: Across-scale coupling: Use homogenization theory and upscaling techniques to formulate physics-based (bottom-up and top-down) coupling conditions to link scales from the nanometer to the meter and create a predictive multiscale framework. Level I of multiscale modeling: Lab Scale Modeling: Develop predictive understanding of the entire membrane performance, i.e. fouling resistance, membrane flux, pressure drop. Level II of multiscale modeling: Mesoscale Modeling: Develop predictive understanding of the clogging and/or antifoulant dynamics at the pattern scale. Level III of multiscale modeling: Molecular Modeling: Develop predictive understanding of particle/surface interactions, screening effects due to crowding, and structure of the deposited foulant using MD simulations.

Simulate Novel Designs: Utilize the models developed and trained in the preceding tasks, but with geometries that have not yet been tested. Evaluate a variety of geometrical patterns and chemical coatings to determine the designs that are most likely to improve upon their predecessors.

Broader impact

The proposed research addresses a grand challenge facing society today - how to make clean water available to a growing population at low cost. Membranes used in water treatment processes are exposed to feed waters containing organic, inorganic, and biological species, which leads to fouling and loss of membrane productivity over time. Since performance loss due to fouling is one of the largest costs associated with membrane processes in water treatment, discovery of new surface treatments that limit fouling would have significant economic and societal impacts. The ability to predict fouling properties of new membrane surfaces *in silico* will accelerate the discovery of novel membrane designs and decrease the time from lab-to-market.

This research program will provide a multidisciplinary environment for training graduate and undergraduate researchers. New communication platforms such as Zoom video conferencing will be used to deliver virtual science demonstrations and laboratory tours to elementary school students. Virtual and interactive conferences will be held bi-annually to educate a broad audience about membrane science, water purification and materials engineering. Potential technology users will be invited to these online conferences to increase likelihood for implementing new membrane innovations and realizing societal benefits.

Data Management and Open Access

Any software and source codes developed in this work will be made available to the open source community via the Github web-based software development and version control repository. The software will be distributed using the LGPL open source license. While the open source external components are accessible to all users through the components' websites, we will make the best effort according to the components' license to maintain the relevant versions of them on our location for convenient purposes.

Accelerating Materials Discovery & Development

The grand vision of this project aligns with the Materials Genome Initiative: 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. 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 outlined in the current project. Entrepreneurial activities (such as I-corps or SBIR) are planned for the third and fourth year of the project.

Closing the Loop to Make the World's Strongest Ferromagnetic Ferroelectric

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Keywords: Complex oxides by design, ferroelectric, ferromagnet, multiferroic, molecular-beam epitaxy.

Project Scope

The physics behind this discovery makes use of spin-lattice coupling as an additional parameter to influence the soft mode of an insulator on the verge of a ferroelectric transition. Appropriate materials for this (1) have a ground state that in the absence of strain is antiferromagnetic and paraelectric, (2) are on the brink of a ferroelectric transition, and (3) exhibit large spin-lattice coupling manifested by a significant decrease in permittivity as the material is cooled through its Néel temperature. $EuTiO_3$ meets these criteria and by straining it we have achieved the world's strongest ferromagnetic ferroelectric.

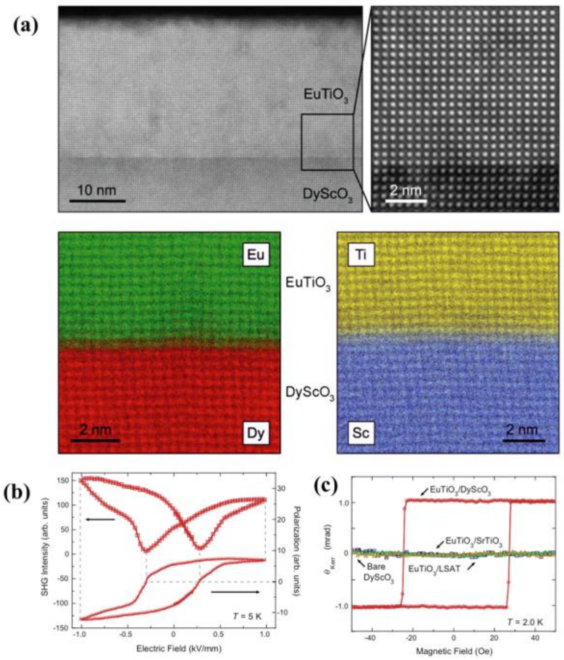

Figure. (a) Elemental maps of europium and dysprosium observed by STEM-EELS on a 22-nm-thick commensurate $EuTiO_3/DyScO_3$ film, confirming an abrupt $EuTiO_3/DyScO_3$ interface with the correct oxidation states. Observation of (b) ferroelectricity by second harmonic generation and (c) ferromagnetism by magneto-optical Kerr effect in this same strained $EuTiO_3$ grown on (110) $DyScO_3$, confirming predictions that under sufficient biaxial strain, $EuTiO_3$ becomes simultaneously ferromagnetic and ferroelectric. Control samples with zero ($EuTiO_3/SrTiO_3$) or opposite ($EuTiO_3$/LSAT) strain are consistent with theoretical predictions for $EuTiO_3$.

Relevance to MGI

Strained $EuTiO_3$ is a prime example in which theory led the way to a remarkable strain-enabled discovery. The idea behind this new route to ferroelectric ferromagnets is that appropriate magnetically ordered insulators that are neither ferroelectric nor ferromagnetic, of which there are many, can be transmuted into ferroelectric ferromagnets. Fennie and Rabe predicted[1] that $EuTiO_3$, a normally boring paraelectric and antiferromagnetic insulator (in its unstrained bulk state), could be transformed using strain into the strongest known multiferroic with a spontaneous polarization and spontaneous magnetization each 100× superior to the reigning multiferroic it displaced, $Ni_3B_7O_{13}I$.

Although testing this prediction seems straightforward, the groups who first tested it ran into an unforeseen complication: no matter what substrate they deposited $EuTiO_3$ on, it was ferromagnetic. With its identical lattice constant (both are 3.905 Å at room temperature), $SrTiO_3$ is an obvious substrate for the growth of unstrained epitaxial $EuTiO_3$ films. Surprisingly, as-grown $EuTiO_3$ thin films synthesized by pulsed-laser deposition (PLD) on (001) $SrTiO_3$ substrates exhibit expanded out-of-plane spacings (0.4% to 2% longer than bulk $EuTiO_3$) and are ferromagnetic with a Curie temperature of about 5 K. In contrast, unstrained, stoichiometric $EuTiO_3$ thin films grown by MBE on (001) $SrTiO_3$ have the same lattice constant as bulk $EuTiO_3$ and are antiferromagnetic.[2]

Technical Progress

One possible explanation is that the ferromagnetism observed in epitaxial $EuTiO_3$ films prepared by PLD on $SrTiO_3$ arises from extrinsic effects, masking the intrinsic properties of $EuTiO_3$ thin films. Extrinsic effects are known to occur in many thin films, particularly for deposition methods involving energetic species, which can induce defects. Another factor favoring extrinsic defects is the relatively low growth temperatures common for oxide thin-film growth, enabling defects to be frozen in. For example, some epitaxial $SrTiO_3$ films grown on $SrTiO_3$ substrates by PLD have been reported to be ferroelectric in striking contrast to the intrinsic nature of unstrained $SrTiO_3$, which is not ferroelectric at any temperature. Homoepitaxial $SrTiO_3$ films grown by PLD are also known to exhibit lattice spacings that deviate significantly from the $SrTiO_3$ substrates on which they are grown, although bulk $SrTiO_{3-\delta}$ (in either single crystal or polycrystalline form) exhibits negligible variation in its cubic lattice constant up to the $SrTiO_{2.5}$ limit of the perovskite $SrTiO_{3-\delta}$ structure. The sensitivity of $EuTiO_3$ that made it an appropriate material to transmute via strain into a multiferroic also makes it quite sensitive to defects. To overcome this issue and examine the intrinsic effect of strain on $EuTiO_3$, a more delicate deposition technique was needed.

Seeing that MBE can produce $EuTiO_3$ films with intrinsic properties in their unstrained state,[2] MBE was used to test Fennie and Rabe's strained $EuTiO_3$ predictions.[1] Commensurate $EuTiO_3$ films were grown on three substrates: (001) LSAT, (001) $SrTiO_3$, and (110) $DyScO_3$ to impart –0.9%, 0%, and +1.1% biaxial strain, respectively. The samples were studied by scanning transmission electron microscopy with electron energy loss spectroscopy (STEM-EELS) to assess the oxidation state of the film constituents and the abruptness of the interface between the film and substrate with atomic resolution and chemical specificity. After closing the loop to optimize the structural and magnetic properties of unstrained $EuTiO_3$, grown on $SrTiO_3$, strained $EuTiO_3$ films were prepared using these optimized conditions. Experimental measurements utilizing second harmonic generation (SHG) and magneto-optic Kerr effect (MOKE) confirmed that the $EuTiO_3$ grown on (110) $DyScO_3$ was simultaneously ferroelectric and ferromagnetic, while on the other substrates it was not, in agreement with theory[1] and resulting in the strongest multiferroic material known today.[3]

Future Plans

Another exciting prediction that remains to be verified is that an electric field on the order of 10^5 V/cm can be used to turn on ferromagnetism in $EuTiO_3$ when it is poised on the verge of such a phase transition via strain.[1] We recently showed that through the application of an electric field, the antiferromagnetic ground state of $EuTiO_3$, strained to be close to where it would have a ferromagnetic ground state (but still on the antiferromagnetic side), can be electrically tuned to the verge of the ferromagnetic state.[4] Seeing that the design rules developed by Fennie and Rabe are valid,[1] Lee and Rabe went on to predict an even higher temperature ferroelectric ferromagnet in strained $SrMnO_3$.[5] This exciting prediction awaits experimental confirmation.

Accelerating Materials Discovery & Development

Straining $EuTiO_3$ has unearthed a powerful way to create multiferroics. Prior research focused on starting with materials that were ferroelectric and trying to introduce magnetic ordering into them, or starting with magnetically ordered materials and trying to introduce ferroelectricity into them. The beauty of $EuTiO_3$ is that its starting point, the ground state of unstrained $EuTiO_3$, is neither. Although this example has a very low magnetic ordering temperature (5 K), importantly it is an existence proof that materials with hidden ground states that are amazing multiferroics can arise from materials with relatively boring ground states. Because there are so many materials that in their ground state are paraelectric and antiferromagnetic insulators, this example also underlines the importance of theory in guiding experiment to multiferroics with improved properties.

Turning on magnetism in a material by applying an electric field to it remains an open challenge. Such an important milestone would be a key advance to the field of multiferroics, both scientifically and technologically.

Electronics has flourished because of the ability to route voltages with ease and on extremely small scales. If magnetism could be similarly controlled and routed, it would impact memory devices, spin valves, and many other spintronics devices and make numerous hybrid devices possible.

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Acknowledgments

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High-Throughput Simulations and Experiments to Develop Metallic Glasses

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Keywords: Metallic Glasses; Nanocalorimetry; High-throughput; Data-Mining;

Project Scope

The primary goal of this project is to develop novel bulk metallic glasses (BMGs) based on high-throughput computing, materials synthesis, and characterization. To this end, new theoretical approaches are being developed in order to make predictions and aid the experimental synthesis and characterization of these materials. Advanced experimental techniques are being tailored for this specific approach. A successful conclusion of this project will yield better understanding of the underlying physics of metallic glass formation, generate publically available databases containing both theoretical and experimental data, and develop novel materials of industrial interest.

Relevance to MGI

One of the main hindrances to the development of new BMGs is the enormous time and monetary cost of exploring the many possible compositions. In order to tackle this challenge, we are developing a suite of high-throughput experimental and theoretical techniques. Based on preliminary experimental data and physical insight, a novel theoretical approach is being developed to predict the glass forming ability of metallic alloy systems. This approach combines physical insight and data mining techniques applied to a very extensive database containing thermodynamic data obtained from DFT simulations. On the experimental side, 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.

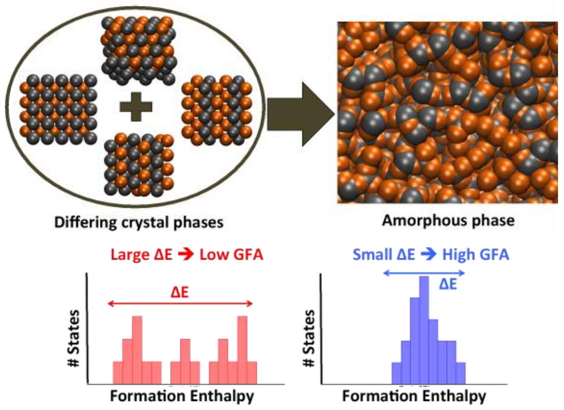

Figure. Schematic illustration of our concept. The existence of multiple distinct phases, presenting dissimilar structure but similar formation enthalpy, frustrates crystallization and leads to glass formation.

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

In the first stage of the project, the team concentrated on two model systems: CuZr, a well-known good glass former; and NiZr, a known weak glass former. These systems were used in order to provide a proof of our proposed mechanism. The approach consisted of looking for specific compositions that presented a large number of different phases with distinct structures, but with formation enthalpy close to the ground state. Our ansatz is that the presence of such phases will frustrate the crystallization process, leading to glass formation. Based on the information contained in our database and on a simple theoretical model, we produced maps that predicted the glass forming regions. These predictions were compared with measurements made on samples produced in the glass forming region and its vicinity, ultimately confirming the strength of our model. These results are discussed in depth in a recently submitted paper (see *Publications*).

Having proved the effectiveness of our model, our recent efforts have been concentrated on the development of a robust descriptor for determining the glass forming ability (GFA) of different alloy systems at multiple compositions. The goal is to obtain a fast, high-throughput code that is able to run through a large number of different alloy systems, generating GFA spectra and singling out the most promising materials. This code is being directly integrated with our existing AFLOW framework and is run in conjunction with the AFLOWLIB database. Our concept has been translated into a set of mathematical expressions that combine structural and thermodynamic data into a single descriptor. Experimental data has been used to select and refine these expressions. As a result, we have obtained a code capable of computing GFA versus composition plots for any binary alloy system present in our database. The code is fast, able to accurately screen more than one hundred different alloy systems per day. A paper reporting this approach is in preparation and should be submitted within the next few months.

Future Plans

The code we have developed is very accurate in predicting GFA peak positions. However, there is room for improvement in the prediction of peak heights. In order to achieve this goal, we plan on utilizing experimental data on the thickness of metallic glass samples produced. We also plan on extending and generalizing the code for the quantitative descriptor to work for multicomponent systems, which will massively increase the number of potential compositions available in which to find new glass forming materials. Working on multicomponent systems creates the need for additional calculations to expand the AFLOWLIB thermodynamic database, and we are working to develop new structural prototypes to use for these systems. We plan to focus these efforts on aluminum-based metallic glasses, a technologically highly desirable system which to date has proven difficult to develop.

Broader impact (Optional for DOE grants/FWPs)

This project has been supporting two postdocs and a graduate student across the three different teams, providing them with extensive training. This process leads 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 AFLOWLIB and Materials Atlas Project databases. Codes written to make the theoretical predictions are going to be released as a part of the AFLOW framework in the future. Ultimately, we aim on producing novel BMGs with promising properties, which can become available to the broader society in the form of commercial products.

Data Management and Open Access

Preliminary data produced in this joint effort has been made available through two distinct databases, the AFLOWLIB database (http://aflowlib.org/) and the Materials Atlas Project database (http://www.materialsatlasproject.org/). Both databases are ever-expanding and can act as platforms for the dissemination of multiple projects.

Accelerating Materials Discovery & Development

The primary aim of this project is to develop new techniques and approaches for materials design, particularly for the development of metallic glasses. We are investing considerable effort in creating novel tools for both high-throughput computational screening and high-throughput synthesis and characterization of novel BMGs. Computational analysis of existing databases allows us to rapidly and efficiently screen large numbers of potential systems, in order to identify promising candidate materials for high-throughput synthesis. The close collaboration between theory and experiment facilitated by the MGI allows for continuous feedback to improve both approaches. The combination of high-throughput computational and experimental approaches will allow us to develop new design rules which will accelerate the search for technologically promising materials. This will enable the development of BMGs based on inexpensive constituent elements, thus overcoming a current major barrier to the commercialization of these materials.

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Acoustically Transformative Materials

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Keywords: Polymers, Elastomers, Molecular Design, Stimuli-responsive, Acoustics, Shapeshifting

Project Scope

The goal is to create novel class of materials that can be activated, actuated, and navigated remotely using sound waves in a programmable and time-resolved manner. Theoretical predictions will guide synthesis of polymer architectures possessing superior elasticity and distinct acoustic response. Particularly challenging is the feedback between the material-dependent acoustic characteristics and acoustically-triggered changes of materials properties. By understanding these correlations, we will develop stimuli-responsive materials that would not only respond to sound by changing their physical properties (density, shear modulus, and shape), but also actively manage acoustic performances, such as tunable phononic band gaps and sound attenuation.

Relevance to MGI

The materials design (*Matyjaszewski*) has been driven by theoretical predictions (*Rubinstein*) and experimental verifications (*Sheiko*). Scaling analysis and computer simulation of polymeric networks constructed of ring- and brush-like macromolecules suggested that these architectures allow for extraordinary broad range of elasticity, strength, and toughness that are not available in conventional polymer systems. Initial series of synthetic and physical experiments corroborated these predictions and provided feedback to the theoretical group. In addition to the scaling predictions, the next round of theoretical studies developed accurate guidelines for the synthetic design in terms of specific chemical parameters (degree of polymerization, branching density, and crosslinking density). This study has culminated with the synthesis of solvent-free elastomers which display an unprecedented combination of low modulus (~100 Pa), high strain at break (~1000%), and extraordinary elasticity, i.e. properties on par with designer gels. In the next step, we will study interaction of sound waves with the designer materials to explore different activation mechanisms that shift density, modulus, and shape. These studies will provide additional feedbacks to theory and validate adjustments in molecular design.

We have corroborated the entanglement plateau modulus of bottlebrush melts decreases with N_{sc} as $G_e \sim N_{sc}^{-3/2}$ which allows pushing the modulus of solvent-free elastomers down to 100 Pa. For polymer rings, we predict that the storage modulus varies as $\sim M^{-1}$, where M is the number of monomers between crosslinks. Upon extension, the ring elastomers exhibit non-linear stress-strain behavior due to sequential unfolding of hierarchic loops. These adaptive polymer matrixes will enable actuation of acoustically responsive fillers that carry multiple functions when exposed to ultrasound: They will expand, dissociate, and assemble to generate, enhance, and modulate acoustic signal.

Technical Progress

The scaling analysis predicts that dense bottlebrush macromolecules shall display the lowest possible entanglement modulus and a relatively high extensibility as $\frac{G_{e,DB}}{G_{e,linear}} \cong \left(\frac{v}{b^2 l}\frac{n_g}{n_{sc}}\right)^{3/2}$ and $\frac{\lambda_{DB}}{\lambda_{linear}} \cong \frac{b^2 l}{v}$ where $G_{e,linear}$ and λ_{linear} are the entanglement modulus and maximum extensibility of linear polymer melts and elastomers of the same chemical composition, and n_g^{-1} – grafting density and n_{sc} – degree of polymerization (DP) of the side chains. In addition to the scaling predictions, this theory also provides accurate guidelines for the chemical structure of brush-like polymers. For example, it predicts that poly(n-butyl acrylate) bottlebrushes with the following molecular parameters ($n_g = 1.75 \pm 0.14, n_{sc} < 130, v = 0.2\, nm^3, l = 0.25\, nm, b = 1.8\, nm$) will allow for a decrease in modulus down to $G_{e,DB}/G_{e,linear} \cong 10^{-4}$ and an increase of extendibility as $\lambda_{DB}/\lambda_{linear} \cong 4$. This suggests that solvent-free elastomers can be synthesized with moduli 10^2-10^5 Pa, matching that of polymer gels and soft biological tissues, but with superior deformability compared to conventional hydrogels.

To verify the theoretical predictions we have prepared well-defined cylindrical brushes with an extraordinary long backbone, controlled grafting density, and systematically varied degree of polymerization of the side chains. We have synthesized a series of five poly(n-butyl acrylate) (pBA) bottlebrushes with particularly long backbones ($n_{bb} \cong 2{,}040$), high grafting densities ($n_g^{-1} \cong 0.6$), and systematically varied degrees of polymerization (DP) of side chains ($n_{sc} = 6, 17, 23, 34,$ and 130) utilizing the atom-transfer radical polymerization (ATRP) technique. Given the architectural complexity and large size of bottlebrushes, multiple characterization techniques have been employed to independently measure n_{bb}, n_{sc}, and n_g^{-1}.

We have verified the theoretical predictions and provided quantitative evidences for (i) disentanglement of brush-like polymers in melt, (ii) ultra-soft elastomers with a modulus on par with hydrogels, and (iii) acoustic activation of microbubble expansion inside ultra-soft elastomers. Our experimental studies have corroborated both the scaling relation $G_e \sim n_{sc}^{-3/2}$ and present a new lowest possible magnitude of the entanglement modulus as $G_e = 178 \pm 15\, Pa$, which sets a lower boundary for elastic modulus of polymer elastomers. In agreement with this prediction, we have prepared a series of solvent-free pDMS networks that display a steady decrease of shear modulus down to 520 Pa with decreasing crosslinking density, which is ca. 400 times softer than $G_{e,lin} \cong 200\, kPa$ of linear PDMS melts.

Concurrently, we have synthesized stimuli-responsive microcapsules of 0.1–10 μm in diameter that demonstrate controlled expansion under ultrasound heating, which results in drastic changes in modulus and density of a composite material. By controlling the chemical composition of the microcapsule core, we can control both the onset temperature of expansion within a range of 80-150 °C and the expansion ratio within a range V/V_0=1-30. Ultra-soft elastomers filled with these microcapsules demonstrate consistent variations of the shear modulus depending the volume fractions of the microcapsules as a function of temperature. Pulse high-intensity focused ultrasound (HIFU) have been applied to initiate shape transformations and acoustic lithography for these unique composite materials. We have quantified the effect of acoustic pressure, pulse length, and frequency on sample temperature and shape alteration as a function of time.

Future Plans

We will explore potential for practical applications of acoustically actuated objects. (i) We will design composites that will switch shape and volume in a programmable fashion both in space and in time. These acoustically-triggered shapeshifting may be vital for promoting self-healing of cracks and permeation of particles through obstructions. (ii) We will explore intriguing opportunities for sono-lithography and non-invasive surgery, where object's shape can be altered locally in a sequential order. (iii) We will design tunable phononic band-gap materials, and study modulation of the acoustic properties by controlling spatial arrangement, individual dimensions, and mechanical properties of expandable microcapsules.

Broader impact

This project provides with an extraordinary opportunity to develop a *new direction in materials design* wherein fundamental changes in materials properties are activated by sound waves that concurrently shift acoustic, optical, and geometric characteristics of macroscopic objects. The interdisciplinary nature of the project will ensure maximum opportunity for (i) integrating science and education through interdisciplinary training of junior researchers, (ii) enhancing diversity by broadening participation of underrepresented groups, and (iii) fostering infrastructure for collaborative research. A team of four students receive first-hand experience in (i) synthesis of complex and well-defined architectures by controlled radical polymerization, (ii) theory and computer simulation of brush-like polymer melts and netwqorks, and (iii) acoustic properties of stimuli-responsive polymers. Especially productive was the joint work of synthetic and theoretical students on the design of bottlebrush elastomers. Another sub-team is focused on the design and properties of composite materials for acoustic applications.

Data Management and Open Access

We collect all primary data produced under this award as well as the associated metadata that describes the experimental setup, synthetic procedures, theoretical models, and methods for data analysis. All primary data, including synthetic protocols and chemical structures, will be made publically available by the time of publication or the end of the funding period via journal articles, reports to NSF, and data archives at UNC and CMU. In addition, we disseminate the results via the webpages of the UNC and CMU groups. Other research products, such as instrumentation, data sets, and software are shared upon request. Sharing unpublished data with our peers is vital for future collaborations. Preliminary data, paper drafts, work plans, communications with colleagues, and physical samples are not included in this plan. Also excluded are invention disclosures, commercial information, materials necessary to be held confidential until they are published, or any information protected under law.

Accelerating Materials Discovery & Development

A new class of materials has been developed as a result of a close collaboration between the theoretical, synthetic, and physical groups. Close feedback loops between different project tasks are particularly vital given the synthetic complexity and hierarchic nature of bottlebrush network architectures. However, organizing and managing such collaboration is very challenging due to the intrinsic limitations of theoretical predictions and experimental verifications, which lead to multiple feedback loops and iterations until a consistent structure-property correlation is established. Even though this slows down the publication process, the MGI approach made it possible to publish two key papers in Nature Materials and Advanced Materials. A patent application has been submitted as well.

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Nanoporous Materials Genome: Methods and Software to Optimize Gas Storage, Separation, and Catalysis

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Keywords: Porous Materials • High-throughput screening • Electronic structure methods • Molecular simulation • Validation experiments

Project Scope

The Nanoporous Materials Genome Center (NMGC) discovers and explores microporous and mesoporous materials, including **metal-organic frameworks** (MOFs), **zeolites**, and **porous polymer networks** (PPNs). These materials find use as storage and separation media and catalysts in many energy-relevant processes and their next-generation computational design offers a high-payoff opportunity. Towards that end, the NMGC (i) develops state-of-the-art predictive theories (from high-level electronic structure methods to validated molecular mechanics force fields), predictive modeling tools, applets, databases, and web-based repositories., and (ii) employs them to increase the pace of materials discovery and to understand the fundamentals of interactions and mechanisms that govern performance of nanoporous materials.

Relevance to MGI

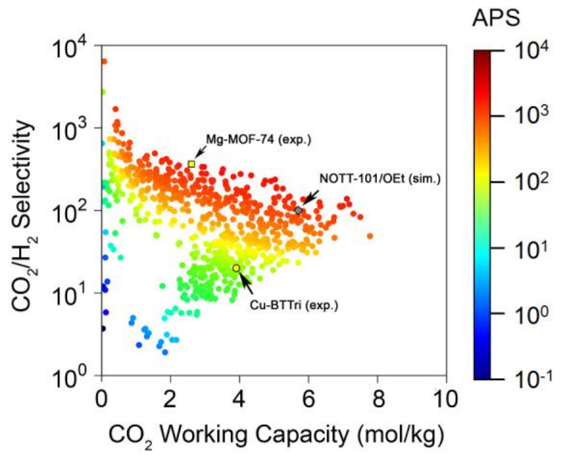
The goals of the NMGC are advanced by a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups with experience in Monte Carlo and molecular dynamics simulations, electronic structure calculations, scientific computation, and applied mathematics. The majority of the completed and on-going projects benefit from iterative feedback where computational modeling is instrumental for understanding the function of specific nanoporous materials or for discovering materials with optimal properties for subsequent synthesis, characterization, and validation.

Technical Progress

The NMGC research efforts have already led to more than 70 publications. In this presentation, we highlight the key achievements of selected application projects, a software tool, and a database/web tool that are central to the goals of the NMGC: (i) discovery of MOFs for pre-combustion CO_2/H_2 separation (see Figure), (ii) discovery of zeolites for sweetening of highly sour natural gas, (iii) discovery of the NU-1000 MOF for the selective hydrolysis of organophosphonate chemical warfare agents, (iv) discovery of a MOF that catalysis the ethane-to-ethanol conversion via a high-spin iron(iv)-oxo intermediate, (v) a Python tool for the computation of mixture adsorption isotherms, and (vi) the Nanoporous Materials Explorer.

Future Plans

The NMGC team will continue its collaborative endeavors to discover nanoporous materials with optimal gas storage, separation, and catalytic abilities and to use an integrated computational/experimental approach for unraveling structure/chemistry/function relationships.



CO_2/H_2 Separation: A genetic algorithm for efficiently identifying top-performing MOFs was developed and applied to pre-combustion CO_2/H_2 separation (APS = Adsorbent Performance Score) Available experimental data points and a target MOF in the optimal region for selectivity and working capacity are labeled. Validation experiments support the computational prediction.

Broader impact, Data Management and Open Access

In collaboration with the Materials Project, the NMGC has developed the *Nanoporous Materials Explorer* [https://materialsproject.org/wiki/index.php/Nanoporous_Materials_Explorer]. This openly accessible web-based tool aids materials discovery and also serves as repository for computational and experimental data generated by the NMGC. NMGC researchers have created a database of computation-ready experimental (CoRE) MOF structures [http://gregchung.github.io/CoRE-MOFs/] and developed a Python tool for the computation of mixture adsorption isotherms using data from unary isotherms and the ideal adsorbed solution theory [https://github.com/CorySimon/pyIAST]. The collaborative NMGC activities have also strengthened the training of a large number of postdoctoral associates and of graduate, undergraduate, and high school students.

Accelerating Materials Discovery & Development

Conventional approaches aimed at discovery and development of nanoporous materials for storage, separation, and catalysis applications are hampered by the large number of already synthesized zeolites and MOFs, the much larger number of hypothetical zeolite and MOF structures, and the large number of potential applications, i.e., it would be impossible to synthesis a significant fraction of these materials and to characterize their performance for a variety of applications. The MGI approach employed by the NMGC allows one to explore thousands of materials for a plethora of applications in a relatively short time frame. NMGC research has led to the discovery of zeolites for extraction of ethanol from aqueous solution (Patent Application PCT/US15/41566), for hydrocarbon dewaxing (Patent Application PCT/US15/41544), and for sweetening of highly sour natural gas mixtures (Provisional Patent Application 62235870), and of MOFs for Kr/Xe and CO2/H2 separation and for ethane-to-ethanol conversion.

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Simulation-Driven Design of Highly Efficient MOF/Nanoparticle Hybrid Catalyst Materials

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Keywords: Catalysis, regioselectivity, oxidation, hydrogenation, metal-organic framework

Project Scope

This project seeks to exploit recent advances in synthesizing nanoporous materials via a true building-block approach to conceive, synthesize, characterize, and test new heterogeneous catalysts that exhibit enzyme-like control in demanding chemical transformations. Catalytically active metal nanoparticles are encapsulated within metal-organic framework (MOF) crystals. MOFs are nanoporous materials synthesized in a building-block approach from metal nodes and organic linkers. Enshrouding metal nanoparticles within MOFs prevents their agglomeration and allows control over reactant access to their surfaces. In this project, molecular-level modeling is used to guide the selection and synthesis of appropriate metal surfaces and MOF channels for two important classes of reactions: oxidation and hydrogenation. The objectives of this project are 1) to develop new ways of synthesizing heterogeneous catalyst materials with structural control ranging from the atomic level to the particle level and 2) to demonstrate how new levels of synthetic control, combined with predictive molecular-level modeling, can drastically decrease the development time of new catalytic materials.

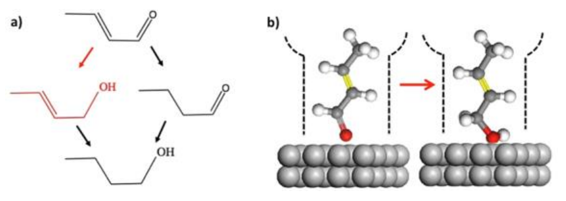

Figure. a) Hydrogenation of crotonaldehyde (top) to crotyl alcohol (red), an unsaturated alcohol, is the desired reaction. Normally, however, hydrogenation leads to the saturated alcohol or aldehyde (black). b) In a sterically constrained reaction path, the α-β unsaturated bond (yellow) is inaccessible, suggesting a strategy for regioselective catalysis to the desired unsaturated alcohol.

Relevance to MGI

The building-block approach to MOF synthesis and the accompanying possibility for the synthesis of an almost unlimited number of materials clearly create exciting possibilities for catalysis, as well as other applications such as chemical separations, gas storage, sensing, and drug delivery. But it also creates the following challenge: how does one identify the most promising structures, among the millions of possibilities, for a particular application? In this project, we have developed computational tools to generate millions of MOFs on the computer and computationally predict their properties to find the right materials with the right properties for hybrid MOF/nanoparticle catalysts. This computational approach will greatly accelerate the rate at which we can discover and develop new materials for catalysis, as well as other applications of nanoporous materials.

Technical Progress

We have synthesized metal nanoparticles and enshrouded them with a coating of a MOF, predominantly focusing on Pt and Au nanoparticles that are encapsulated in ZIF-8 and UiO-66. We performed size and regioselective hydrogenation of alkenes and alkynes using a Pt@ZIF-8 composite. Large substrates such as cis-cyclooctene and cis-cyclohexene, which are larger than the aperture of ZIF-8 (3.4 Å), go unreacted while linear alkenes and alkynes were hydrogenated with approximately 60% conversion. Additional regioselective hydrogenation experiments involving Pt@ZIF-8 focused on the comparative reactivity of 1-hexene versus trans-3-hexene. The encapsulated particles catalyzed the 1-hexene reaction but were completely inactive toward 3-hexene. In addition, trans-1,3-hexadiene was used to confirm the regioselectivity using a single molecule with two reactive sites (the double bonds). Using nm Pt nanoparticles encapsulated in ZIF-8 under 1 bar hydrogen, we achieved 60% conversion of 1,3-hexadiene to 3-hexene with approximately 95% selectivity after 24 hours.

We encapsulated Au nanoparticles within ZIF-8 crystallites and demonstrated hydrogenation of crotonaldehyde to crotyl alcohol with 90-95% selectivity (see the Figure). After the reaction, TEM showed that the Au nanoparticles were stabilized against sintering under reaction conditions. The selectivity toward crotyl alcohol is among the highest reported in the literature for Au-nanoparticle-based catalysts. We are currently using a combination of IR spectroscopy of adsorbed CO and DFT calculations to elucidate the atomic structure of the MOF/NP interface.

To help choose the best NP compositions, we introduced a conceptually simple and computationally efficient DFT approach to model reactions under the steric constraints provided by NP@MOF composites. The adsorption of reactants, intermediates, and products associated with oxidation of n-butane to 1-butanol (and 2-butanol) on clean and oxygen-covered palladium surfaces was investigated with (and without) the constraints of a pore. Reaction energies were calculated, and we found that the thermodynamic favorability of the intermediate reactions is affected by the presence of steric constraints, oxygen coverage, and the exposed crystal surface of the metal. Based on these results, a Pd(111) surface with 0.25 ML oxygen coverage and steric constraints (provided by a suitable MOF) seems promising to favor the desired sequence of reactions that would lead to the conversion of n-butane to 1-butanol. We have also modeled the pathway for butane oxidation on an oxygen-covered $Ag_3Pd(111)$ surface. We calculated the thermodynamics and kinetics for 15 possible reactions at up to 5 different oxygen coverages. The results suggest that the optimal catalyst should avoid formation of butoxy, and instead favor butane direct conversion to butanol or butane activation to butyl and OH*. Based on this work, we are developing a microkinetic model, which will be used for rational catalyst design for this reaction by considering other allows such as Cu_3Pd and PdZn.

Using an automated topologically-based crystal generator developed as part of this project, we have created 13,515 MOFs and evaluated their properties via molecular simulation. We characterized their pore size distributions, surface areas, pore volumes, and some adsorption properties. Since our automated approach is topologically-guided, we were able to create MOFs with a diverse range of topologies. We identified an isoreticular series of MOFs based on a rare topology. Only one MOF was found in the literature with this topology to date. With a collaborator, we synthesized four members of the isoreticular series and demonstrated their porosity via gas adsorption measurements.

Future Plans

We are applying our DFT approach to find top-performing metal nanoparticles for regioselective oxidation of n-butane. Microkinetic modeling will play an important role in this screening. Top materials will be synthesized, characterized, and tested for catalytic performance. Characterization of NP/MOF interfaces includes an iterative modeling and experimental feedback.

Broader impact

This project supports the training of 3 graduate students, 2 post-docs, and 1 undergraduate student. The team is highly interdisciplinary and includes both experimentalists and modelers. The lead PI gave 8 invited talks during the past year (universities in the US and Korea, ACS meeting, NIST, Pacifichem). All of these talks focused on high-throughput computational screening of materials. In addition, while not explicitly part of this project, he chaired the 2015 conference on Foundations of Molecular Modeling and Simulation (FOMMS). The theme of the conference was “Molecular Modeling and the Materials Genome.” 172 people, including 79 students, attended the FOMMS conference, which included invited talks and a workshop devoted explicitly to MGI topics.

Data Management and Open Access

The database of MOFs will be made publicly available. We already make our molecular simulation codes Music and RASPA publicly accessible. Our DFT approach for modeling reaction under steric constraints can be readily adopted by anyone with access to the popular VASP code. Indeed, one motivation in our development was that the method be easy for others to adopt (no special software needed).

Accelerating Materials Discovery & Development

Given that there are over 5000 existing MOFs and that metal nanoparticles can be created with a wide range of compositions, there are a very large number of NP@MOF catalyst materials that could be tested for regioselective reactions, such as oxidation of n-butane to 1-butanol. Computational screening and insights from computation are, thus, essential to accelerating the discovery of top-performing materials. A major portion of this project has focused on developing synthetic and computational tools for this task. Oxidation of n-butane to 1-butanol is an extremely challenging reaction; if a good catalyst is discovered, there should be significant industrial interest. Several of the PIs are involved with a start-up company, NuMat Technologies (founded before this project began), focused on development of MOFs for gas storage. NuMat's expertise, for example in material scale-up, could facilitate commercialization of new materials discovered in this project.

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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)

Relevance to MGI

Knowledge about fundamental properties of metal dichalcogenide materials is readily available, yet in order to serve as the foundation for the design of manufacturable optoelectronic devices, a much broader range of properties need to be available and tested. These include growth conditions, phase diagrams and surface interactions. For instance, $MoTe_2$ is a transition metal dichalcogenide material that has attracted much attention as 2D semiconductor, yet we find that under typical growth conditions it attains a metallic phase T' at the single layer limit and not the semiconducting 2H phase known at room temperatures. This provides both a challenge and an opportunity: *in-situ* growth of single-layer films of $MoTe_2$ into functional devices needs to include a guided transition towards the semiconducting room-temperature phase as a processing step, yet lateral semiconductor/metal transitions can be part of a compositionally-homogeneous single layer film, if ways are found to stabilize locally one phase over the other.

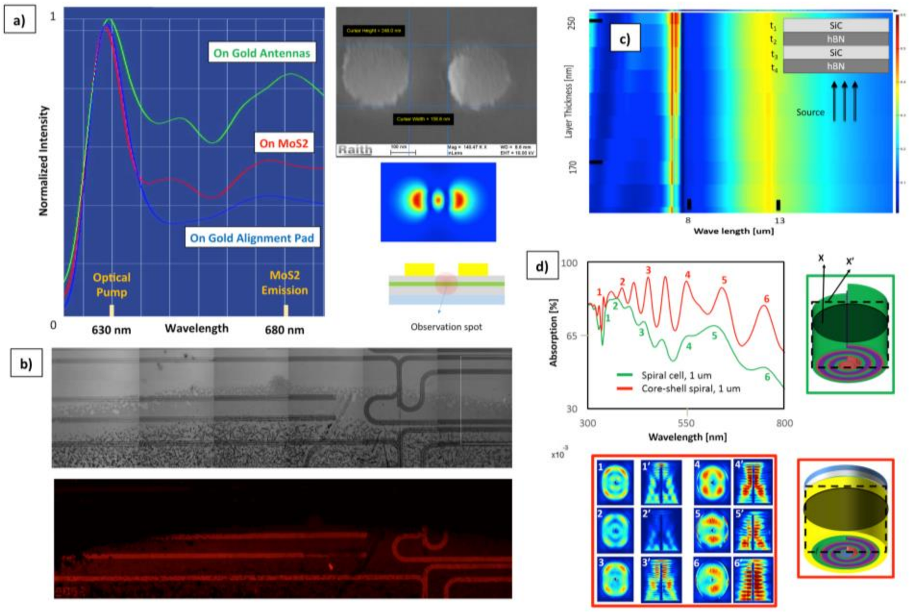

Figure 1. Update of Sorger's effort. a) Emission enhancement of dimer-based TMDs grown by Bartels. Lower left: numerically validated field enhancement. b) PL from TMD films grown (Bartels) on Silicon-Nitride waveguides on insulator. c) Layered materials for thermal radiation control. d) Layered spiral cell structure for broadband 90% photo absorption[1]. Comparison with a metal (electrical PV contact) cladded design enables a nanocavity for strong light-matter-interactions.

Technical Progress

Due to space constrains, the Sorger update is summarized in the caption of Figure 1. Furthermore, we investigated structural phase transitions by design in monolayer alloys (Reed). Mo- and W-dichalcogenides are unusual two-dimensional materials because they exhibit several different monolayer crystal structures with strongly differing electronic properties. This intriguing yet poorly understood feature may support monolayer phase engineering, phase change memory and other applications. However, knowledge of the relevant phase boundaries and how to engineer them is lacking. Here we find that alloyed $MoTe_2$–WTe_2 monolayers support structural phase transitions, with transition temperatures tunable over a large range from 0 to 933 K.[2] We develop cluster expansion models fitted to DFT calculations of microscopic alloy configurations and compute phase diagrams using Monte Carlo methods and mean field theory. We map temperature–composition phase diagrams of alloys between pure $MoTe_2$ and pure WTe_2, and benchmark our methods to analogous experiments on bulk materials. We are also developing algorithms to identify the spectrum of materials that are potentially isolatable as 2D materials. So far, we have identified over 500 candidate 2D materials, obtained estimated bandgaps and symmetries for these materials. Moreover, we investigated direct growth of MoS_2 onto the 128°YX-cut of $LiNbO_3$ permits acousto-electric spectroscopy on the TMD overlayer as validated by the hybrid device assembled in this work (Bartels).[3] This finding opens many new avenues of research[5]: while our hybrid device relied on metal contacts to the TMD film so as to validate congruence between electric transport and SAW-based conductivity measurements, subsequent experiments may dispense with the contacts, thereby allowing entirely contact-free transport measurements on TMD films. Moreover, the tight coupling of the TMD film to the underlying substrate as being indicated by the blueshift of the PL signal suggests that not only acousto-electric but also acousto-mechanic spectroscopy on TMD films may be possible. In such experiments, the SAW exerts tensile or compressive strain allowing measurement of the coupling of the dynamic deformation to the electronic degrees of freedom of the TMD material. Spin and charge excitations in recently discovered TMD-based quantum dots could also be controlled dynamically by SAW-driven deformation potential coupling and Stark effect. The rigid connection of the TMD layer to the $LiNbO_3$ is crucial for such acousto-mechanically driven approaches, since it ensures close coupling of the SAW to the film. We also highlight that our device fabrication used exclusively scalable techniques avoiding transfer or exfoliation steps. This paves the road towards the incorporation of TMD films as, for example, optically active elements, into conventional and inexpensive $LiNbO_3$-based SAW devices of a type similar to those currently used, for example, as frequency filters in cell phones. As a consequence, we foresee that the fundamental device concept introduced in this article will attain widespread application both in the fundamental study of the properties of TMD films and in the technological

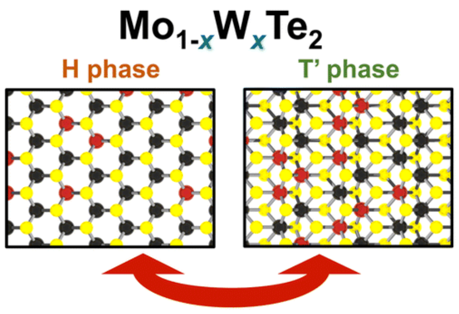

Figure 2. Alloyed $MoTe_2$–WTe_2 monolayers support structural phase transitions over a large temperature range from 0 to 933 K [3].

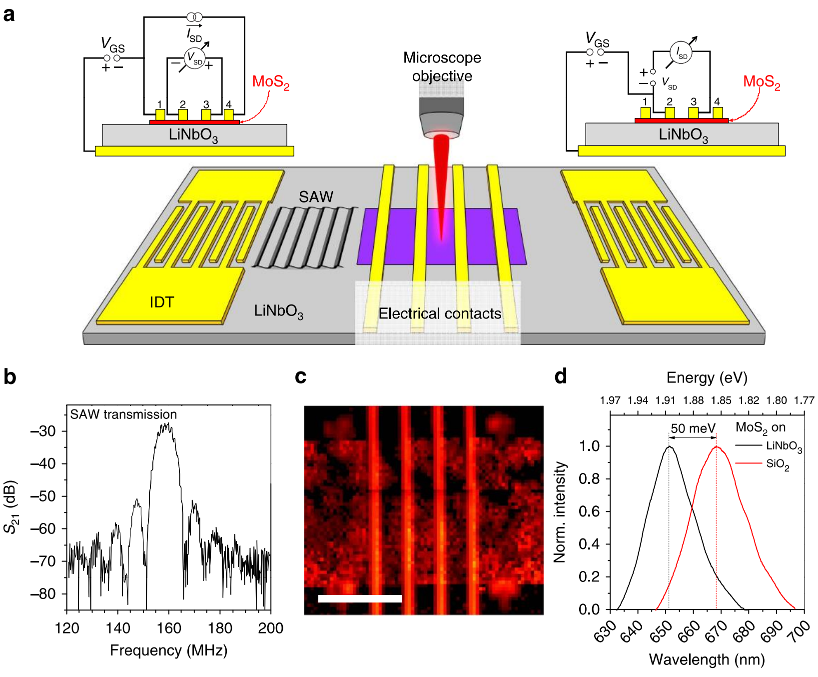

Figure 3. Acousto-electric-mechanic spectroscopy of 2D material films[3].

realm where optically active thin, inorganic and durable films are desired: our SAW device remained functional for 9 months in air withstanding multiple intermittent thermal cycles of heating to temperatures as high as >450 K and cooling to as low as <10 K in vacuum in the meantime. Measurements on different TMD materials show promising initial results and will be reported on once completed.

Future Plans

We are developing a database for all potential 2D materials and their basic properties that will be published. On the device side, future efforts include the completion of monomer/dimer PL enhancements using MoS_2, experimentally comparing the same properties for all known TMDs towards establishing the first absolute reference of quantum efficiency for these materials, conducting lifetime tests to probe the Purcell facture directly, demonstrate the first 2D-materila plasmon laser. Bartels fabricated $MoWSe_2$ films in the hope of tuning the transition temperature as described by Reed, and Raman spectra were obtained (not shown). Ongoing efforts focusing decoding the relative fractions for W and Mo since the T structures are not the same, thus making it difficult to identify the respective material.[4]

Broader impact

Broadly and band-gap tunable, *in-situ* on silicon growable, atomically thin light sources and sensors can have a transformative impact on optoelectronics and on-chip integration schemes of devices. Furthermore, the incorporation of an accredited Hispanic Serving Institution (UCR) provides impact through human resource development and integration of minority individuals. The PI being in Washington DC, enables an outreach arm to Congress for STEM education and R&D in the US. In combination with interdisciplinary interaction (PIs are from 3 different departments), development of two untenured faculty and a proven pathway to educational outreach, this project is well aligned with NSF's broader impact goals.

Data Management and Open Access

Data is being shared with the public in classical ways. In addition, we plan to establish an online database for 2D materials to facilitate the acceleration of 2D materials developments by other researchers.

Accelerating Materials Discovery & Development

Commercialization opportunities exist for 2D-based materials or material systems arising from a) their unique properties, and b) the ability to custom engineer their properties. PI Sorger, for instance, filed a provisional patent on rolling a multi stack of 2D materials to form a strong optical absorber for photo-conversion technologies whilst only requiring two electrical contacts for solar-cell carrier extraction. Furthermore, he requested funds for an NSF I-Corps on "Utilizing atomically layered 2D materials for heat-management of coatings". Here, the atomically layered materials of this DMREF will be explored for radiation management towards heat dissipation; we envision an aerosol or coating for power carrying transmission line or building cooling of dessert areas.

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Developing design rules for enhancing charge mobility in conjugated polymers

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Keywords: Conjugated copolymers, polarons, coherence, charge-modulation spectroscopy

Project Scope

The focus of this project is to understand the nature of charged carriers (polarons) in high-performance conjugated copolymer films with the goal of developing a set of design rules for optimizing charge mobility. The essential idea is to determine the polaron's coherence function from its polarization-resolved mid-IR absorption spectrum and relate the anisotropic coherence lengths to the crystalline structure and film morphology. Various model donor-acceptor polymers whose electronic and structural properties are precisely controlled will be synthesized and characterized via X-ray diffraction and charge-modulation spectroscopy to develop and test molecular and assembly design rules for high mobility.

Relevance to MGI

Our team's activities are centered around a theoretical treatment developed by the Spano group[1], which allows one to evaluate *quantitatively* the degree of delocalization of charge carriers in conjugated polymers. The theory will be applied to polymers made *ad hoc* by the Luscombe group, which specializes in synthesizing extremely well-defined model polymers (e.g. 100% regio-chemistry control, extremely low dispersity).[2, 3] The Salleo group will use advanced structural characterization techniques, involving synchrotron-based X-ray scattering[4], as well as charge modulation spectroscopy (CMS) to close the loop on correlating molecular and crystalline structure to carrier delocalization and transport. By introducing different types of disorder in the theory, we will be able to determine what structural features minimize the effect of disorder on delocalization, thereby making polymers resilient to disorder. An example of how disorder leads to localization, and how the latter can be detected by a profound change in the mid-IR spectrum is provided in Figure 1. The example here pertains to the homopolymer poly(3-hexylthiophene) (P3HT) but much of the team's effort will be devoted to applications involving donor/acceptor copolymers which show the greatest promise for applications such as solar cells.

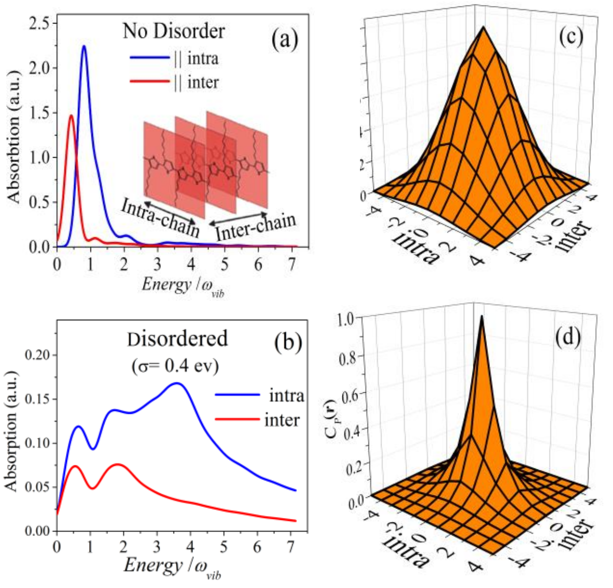

Figure 1: Calculated mid-IR spectra for the electric field polarized along the polymer axis (intra-chain) and along the stacking axis (inter-chain) for 6x6 P3HT π-stacks with no disorder in (a) and with site disorder in (b). The associated coherence functions are shown in (c) and (d). Here ω_{vib} = 0.17 eV.

Technical Progress

Thus far the code developed by Spano and coworkers[1] has been vectorized and implemented on a high-performance computer cluster at Temple University. This has enabled calculations on much larger aggregate sizes than previously realized. The 6 × 6 homopolymer π-stacks featured in Figure 1 are but one example. We have further shown analytically how the total oscillator strengths of the polarized mid-IR absorption bands depend on polaron coherence and are currently executing large-scale simulations of mixed and segregated copolymer π-stacks with various forms of disorder. On the characterization end we have increased the signal-to-noise of the CMS measurements by improving test device quality and optimizing the spectrometer set-up. We are also working on extracting absolute extinction coefficients from our measurements. Finally, important steps have been achieved with respect to synthesis of low band-gap alternating copolymers. Specifically, one of goals is to synthesize monodisperse model alternating copolymers such as those portrayed in Figure 2. To this end, new catalysts must be designed. We have begun to synthesize bimetallic Ni catalysts,[5] which are more active than conventional catalysts used for the controlled polymerization of homopolymers,[2] so that a controlled polymerization can be maintained even for large monomers.

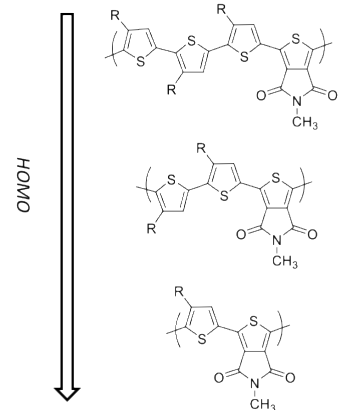

Figure 2: Proposed D/A polymer series in which polymer HOMO level is varied with increasing acceptor content.

Future Plans

The primary tasks for future work involve the development and testing of rational design rules for creating high mobility organic semiconductors in order to accelerate materials towards the marketplace. Our theory, which takes into account the many complicating factors of the physics of charge transport in organic semiconductors (such as the anisotropy of structural disorder and strong electron-phonon coupling), has already identified spectral signatures with which to measure the degree of delocalization of charges, but needs to be further advanced in order to more thoroughly appreciate how the anisotropic polaron coherence lengths (and hence mobilities) can be optimized for various forms of disorder. In order to test theoretical predications, conjugated copolymers based on electron-rich thiophene and electron-deficient bithiazole units will be synthesized *ad hoc* and analyzed experimentally using X-ray diffraction for structural characterization, infra-red spectroscopy to characterize charge delocalization, and charge transport measurements to characterize mobility. In order to isolate intrachain from interchain information we will need in-plane aligned films. Alignment can be obtained by applying shear during deposition or using dip-coating. Our ultimate plan is to link specific features of the molecular structure and of the short-range microstructure to the degree of delocalization of the charges along the polymer and stacking axes. If successful, the proposed research will provide the organic electronics community with a method to experimentally and theoretically evaluate materials for high-performance organic semiconductors quickly and efficiently. Moreover, it will also provide the first measurements of the anisotropic coherence lengths of polarons in conjugated polymers using steady-state infra-red absorption spectroscopy thereby providing fundamental insights into what governs delocalization and trapping.

Broader impact

Organic semiconductors have the potential to impact many areas of electronics, from photovoltaics to lighting, all the way to bioelectronics. A pervasive penetration of this material's family into the marketplace is predicted with applications including transistors for RFID tags, all-organic display backplanes and "wearable" sensors for healthcare applications. All these devices rely exclusively on the transport of charges. Higher carrier mobilities will increase the competitiveness of organic semiconductors and ultimately help realize fully flexible, low-cost and sustainable electronics. Intervening at the materials design stage, which is where the proposed work fits, creates a huge boost to materials development as it provides a guide to chemists' intuition and greatly accelerates the design-to-market cycle by eliminating early in the design phase materials that are not promising.

With respect to education, the results obtained will be incorporated in classes in organic electronics taught by Luscombe and Salleo. Spano will use the research proposed as a springboard for the development of a new class at Temple on organic semiconductors. The PIs will build together an interdisciplinary module encompassing advanced theory, synthesis and characterization to be taught at all three Universities. In addition the PIs will build a set of online videos, which will be made publicly available, as well as a short course to describe how to "design", make and characterize an organic semiconductor. The target audience will be advanced undergraduates in the sciences and engineering. The mode of these online videos will be based on ScreenCasts, which have received significant positive reviews.

Data Management and Open Access

Results of the research activity will be shared with other researchers and students within a reasonable time frame in order to conform to the NSF policy on dissemination and sharing of research results. The public release of data will be at the earliest reasonable time. As soon as the computational data, characterization data or mobility data are extracted from the proposed activity, the results will be accessible through publications, seminars, and dissemination via the web. The research activity findings will be presented in local, national, and international conferences. The outcome of the research findings will be published in journal papers, which will be made available through the PIs' websites or through personal communication by e-mail with the PIs. The Ph.D. theses resulting from this research will be published and made accessible to the public**.**

Accelerating Materials Discovery & Development

Helping design high-mobility materials can impact all applications of organic semiconductors, from solar cells to light-emitting diodes and transistors. We expect that the methods developed, both theoretical and experimental, can be broadly used by the community thereby providing rapid screening approaches for new materials. The integrated MGI approach allows one to design and test such design rules for materials optimization in a manner which would not be possible with the full integration of theory, synthesis and characterization.

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Computationally Driven Targeting of Advanced Thermoelectric Materials

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Keywords: Thermoelectrics, electronic structure, transport properties

Project Scope

This project seeks to accelerate the discovery of new *classes* of thermoelectric (TE) materials and guide their subsequent optimization by combining theory, experiment and high-throughput computations. To this end, we are (i) developing a computational approach and infrastructure for TE materials search, (ii) validating this approach through experimental measurements, and (iii) applying this approach in a high-throughput format to a broad range of known, crystalline materials. The resulting database of experimental, computational and structural results is analyzed to reveal material design strategies and is open to the community.

Relevance to MGI

Development of TE search and optimization strategies requires an iterative feedback loop between synthesis and characterization on one end, and theory and computations 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 have overcome this challenge by adopting a strategy where experimental results are integrated into a semi-empirical model that is built off of ground-state electronic structure calculations. This approach has been applied to 10,000s of compounds due to its computational speed. We are now faced with the opposite challenge, where computational prediction is more rapid than experimental validation. A two-pronged, orthogonal approach is adopted to close the loop wherein (i) the efficacy of the approach is tested across a broad range of chemistries/structures, and (ii) new classes of high performance materials that emerge from the search are experimentally assessed. Furthermore, the application and adaptation of modern statistical and data mining techniques to our set of computed materials properties will offer a route toward understanding and modeling chemical trends in transport properties across large chemical spaces.

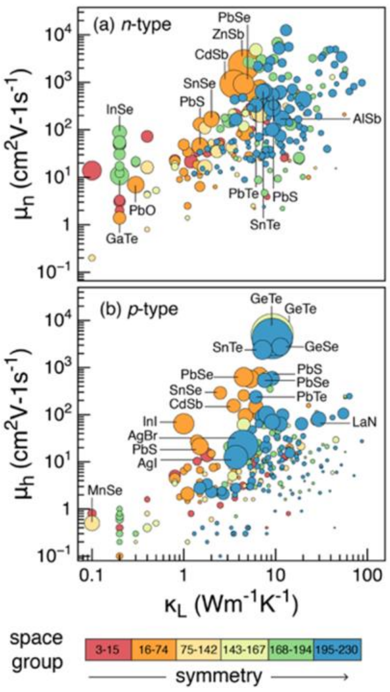

Fig. 287 binary A_1B_1 compositions (1500 structures): calculated mobility vs. lattice thermal conductivity, bubble radius (β), and color (space group). Cubic (blue) and orthorhombic (orange) crystals dominate large β materials[2].

Technical Progress

To address the challenges associated with direct computations of charge carrier mobility (μ) and lattice thermal conductivity (κ_L), we combined classic scattering theory, a large body of experimental data and electronic structure calculations. Together these enabled the development of semi-empirical models that include only the quantities that are readily available from standard density functional theory calculations. Separation of the intrinsic materials properties that contribute to the TE figure of merit (zT) yielded the quality factor $\beta \sim \mu\, m_{\mathrm{DOS}}^{3/2}\, \kappa_L^{-1}$, with m_{DOS} being the charge carrier DOS effective mass. The computationally accessible descriptor β was found to correctly identify known TE materials and enabled high throughput screening for new candidates across 10,000s of compounds with structural complexity in excess of 50 atoms per unit cell.[1] The lattice thermal conductivity model has recently been experimentally validated and refined across a wide variety of pnictides, chalcogenides, and halides with diverse structural chemistry. Detailed investigations of specific structural classes with promising β have allowed further refinement of the model accuracy within these classes.

This β–driven□□□□roach has been applied to the discovery of new structure-property relations and potential candidates in specific chemistries. Utilizing our β–parameter we explained the predominance of the simple binary A_1B_1 chemistry among known TE materials. We evaluated the thermoelectric performance of 518 A_1B_1 compounds, including all of their known polymorphs (~1500 structures) and found that the good TE performance in this chemistry originates from low valent ions in combination with cubic and orthorhombic crystal structures, which primarily offers favorable *p*-type charge transport.[2] Based on these results, we have initiated a study to assess if low valent ions can lead to good TE performance across different stoichiometries. A new metric for alloy scattering has been developed to facilitate the selection of alloying species and validated against experiment.[3] We continue to expand TEDesignLab.org, implementing a suite of interactive web-based visualization tools for high-dimensional data that will enable users to mine the raw data and unearth new structure-property relations.[4] These efforts have been incorporated into a book chapter of the new version of the CRC handbook.[5]

Future Plans

Dopability is a critical design requirement and computational strategies for assessing dopability need to be developed. As prediction of κ_L has been refined experimentally, we will focus on refining μ and dopability. The impact of unpaired spins and their spatial arrangement on the calculation of μ□□□□□□□ has begun to be explored. We will also grow TEDesignLab.org to include customized data mining functionalities and comparison between theory and experiment. Such advanced functionalities seek to turn the website into a true laboratory that allows the public and scientific community to explore material property trends in the context of TE materials.

Broader impact

The team is engaged in a suite of activities to foster the MGI spirit. We have given 15 invited talks and colloquia on this work in the last two years. The semi-empirical approach we have developed to overcome high throughput issues with scattering of electrons and phonons are expected to be valuable throughout thermal and electronic materials (e.g., power electronics, transparent conductors, LEDs, PV absorbers). The integration of material science and data mining is being integrated 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 topics within this project.

Data Management and Open Access

Open access to the computational and experimental data, corresponding data analysis functionalities, and computer codes is core to this project. Through the www.tedesignlab.org website, users can import and export both computational and experimental data about specific or a subset of TE materials, search for materials with certain properties, and visualize materials properties. We continue to integrate various data analysis functionalities into the web interface as well as the codes developed to compute, analyze and/or mine the data.

Accelerating Materials Discovery & Development

In the absence of an MGI approach, the traditional process for thermoelectric discovery is based on chemical intuition and experimental testing. This approach takes approximately 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 here are expected to significantly reduce the number of experimental efforts that have negative results by providing an initial screening of potential performance.

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Facilitating the Development of Modular Data Models in Materials Science

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Website: https://mgi.nist.gov/facilitating-development-modular-data-models-materials-science
Keywords: data repository; structured data; database; automated capture, workshops

Project Scope

The Materials Data Curation System (MDCS) has the potential to accelerate interoperable data exchange within materials science and engineering. This platform is designed to enable the typical PI to easily capture and disseminate diverse datasets with sufficient domain-specific metadata. In order to use the MDCS, the user must compose a data model, which is a comprehensive description of the structure of metadata, data, and files under consideration, within their unique project. This NIST MGI project aims to convene experts with the goal of developing foundational data types and domain-specific data models to address common modeling, synthesis and measurement techniques.

Relevance to MGI

NIST is specifically charged with establishing essential data exchange protocols and the means to ensure the quality of materials data and models. This project seeks to help the PI adopt the MDCS, which is one possible mechanism for interoperable data exchange with sufficient metadata.

Technical Progress

Early work has focused on hosting workshops for early adopters of MDCS software. Both general and domain specific workshops have been held with the goals of: (1) developing foundational data types (2) developing domain-specific data models (3) educating scientists in the use of MDCS software, and (4) obtaining feedback for revisions to MDCS software. With a focus on automated capture, outputs are being integrated into existing research projects including the NIST Interatomic Potentials Repository and High-Throughput Experimental Materials Science.

Future Plans

Significant progress has been made in the development of foundational data types and domain-specific data models, which can be reused in the MDCS for common modeling, synthesis and measurement techniques. The focus of future work is on making these data models discoverable and accessible to the MDCS user base. As a short-term measure, data models will be exchanged on a GitHub community organization. However, a repository tailored to discovery and reuse of data models would be more effective. This project is currently scoping requirements for a data model repository and requirements for direct integration with MDCS software.

Data Management and Open Access

While it is very easy to upload a file into a repository, additional metadata is required for discovery, additional metadata is required for reuse, and if large scale high-throughput reuse of data is to be achieved, community-developed data standards are needed. These additional requirements could place additional burden on the scientist. The focus of this project is to reduce this burden.

Accelerating Materials Discovery & Development

This project seeks to demonstrate automated capture, as well as improve interoperability of materials data and metadata. Complementary to projects such as NIST Materials Resource Registry, this project will help accelerate the access and reuse of data, which will then accelerate new methods and metrologies based on data-intensive materials discovery and development.

Discovery of Design Rules for High Hydroxide Transport in Polymer Architectures

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Co-Principal Investigator: Stephen J. Paddison, Department of Chemical and Biomolecular Engineering, University of Tennessee Knoxville, spaddison@utk.edu.

Keywords: Hydroxide ion transport, membrane architecture, materials modeling, *ab initio* molecular dynamics, dissipative particle dynamics, polymer synthesis.

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 including the use of less expensive membranes, cell hardware, and catalysts. At present, however, there is little understanding of the relationship between polymer architecture, morphology, and hydroxide transport rates and mechanisms in AEMs. In this project, a joint theoretical-experimental team will leverage computational modeling and simulation, applied mathematics, polymer synthesis, and materials characterization in a tight feedback loop in order to elucidate these connections at the molecular level and produce new strategies for designing AEMs with high hydroxide conductivity. Currently, over 100 different anion exchange membrane candidate structures have been proposed in the literature, but there is no consensus in the community as to the most desirable pathways forward. This project will seek to clarify promising approaches to achieving membranes with high hydroxide transport that will form the building blocks of next-generation electrochemical devices.

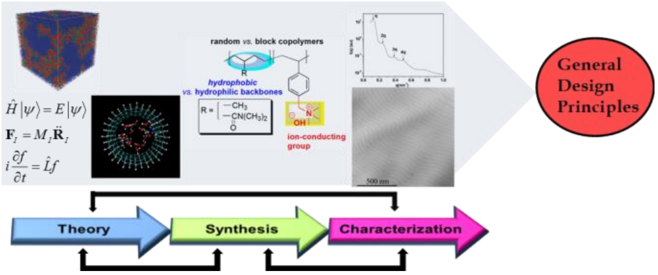

Figure 1. Integrated approach to elucidate the relationships of polymer structure–hydroxide ion transport property in AEMs.

Relevance to MGI

The MGI envisions an integrated and interdisciplinary approach to materials discovery and design, which the present project embodies through an interplay between theoretical and experimental efforts. In particular, the experimental protocol consists of synthesis and characterization of polymer structures with different backbones, tethering groups, terminal ionic groups, and the study of their effects on morphology, water distribution, and hydroxide diffusivity. The theory and simulation protocol consists of first principles molecular dynamics simulations of hydroxide solvation and diffusion in model aqueous AEM channels decorated with different tethering groups and coarse-grained simulations aimed at elucidating the connections between backbone composition and morphology. Such calculations will produce a molecular level understanding that will help guide specific polymer synthesis and characterization studies. The experimental feedback will, in turn, help refine the theoretical and computational models through structures that are approachable using current synthetic tools. Through this feedback loop, we will generate design rules for 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 and (ii) analyzing and folding in AEM property data in the existing literature. Of particular importance in this work is the search through a large library of possible structures in order to promote descriptors of high performance materials and to disseminate new design strategies to the community.

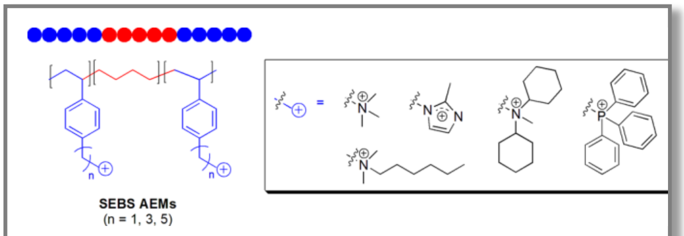

Figure 2. Terminal cation structures that will be investigated for AEMs based on SEBS polymer.

Technical Progress

- A first phase of materials synthesis has focused on precursor AEM polymers: polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene) (SEBS) is functionalized with alkyl bromide of different tether lengths.
- Poly(phenylene oxide)-based AEMs have been synthesized with different side chain tether chemistries using a modular approach. This library of different side chain materials with a single backbone will help to understand near-cation effects on hydroxide diffusion.
- Structural models of aqueous AEM channels using carbon nanotubes and graphene sheets (cylindrical and slab geometries) have been generated and functionalized with various cation and tethering group chemistries for *ab initio* molecular dynamics studies of hydroxide diffusion in different chemical environments.
- The various AEMs being synthesized in this project have been partitioned into 'beads' or particles, each consisting of the chemical groups and constituents of the polymers, for the purposes of undertaking coarse grained dissipative particle dynamics (DPD) simulations. Interaction parameters for these beads are being derived from ab initio electronic structure calculations based on hybrid density functional theory.

Future Plans

- Ab initio molecular dynamics calculations will be carried out (**Tuckerman**) for the structures described above in order to study the effect of cation and tethering group chemistry, length, and size on hydroxide solvation and diffusion in the model geometries. This information will be used to guide the synthetic studies described below. We aim to identify specific chemical environments that enhance hydroxide by promoting both vehicular and Grotthuss type diffusion synergistically.
- In the materials synthesis effort (**Bae**), once an optimal tether length and chemistry is achieved (n in Figure 2), the terminal cation structure will be modified with different substituent sizes in order to study the effects of the cation structure on AEM properties. Next, AEMs with different degrees of hydrophilicity and rigidity in polymer backbones will be prepared for an investigation of their influence on hydroxide ion conductivity. The results will be used to refine the theoretical models described in the preceding paragraph.
- Common themes in the AEM literature are currently being examined by **Hickner** to find common threads for high-performance materials. Additionally, a descriptor of hydroxide transport is being developed that can help to sort out the most promising themes in the many AEMs that have already been reported.
- DPD simulations (**Paddison**) will be undertaken using the LAMPS program on large molecular systems (> 10^7 atoms) of the various AEMs synthesized by the team in order to elucidate relative differences in the polymer morphology as a function of head group, backbone and tether chemistry, and length. We aim to identify morphologies that will facilitate high rates of hydroxide ion diffusion.

Broader impact

After thorough investigation of the structure-property relationships of AEMs, we will classify the experimental and computational results based on 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 will, therefore, apply our structure-property correlations to the available AEM literature data, classify them according to our derived materials design rules. Ultimately, we will write a comprehensive review or account article 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 will be shared at an AEM symposium session at a professional society meeting and all software tools used in this project will be available as open source packages. Cross-training of students through close collaboration within the team and their research progress will be highlighted via publications and presentations at scientific meetings. In addition, students working on this project will have 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 will be 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 that will be learned from this fundamental research project will help to develop better performing AEMs in the future and guide the community to develop common descriptors for characterizing high-performance membranes.

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Center for Next Generation of Materials by Design EFRC

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Website: cngmd-efrc.org
Keywords: nitride, perovskite, metastability, polymorph, solar

Project Scope

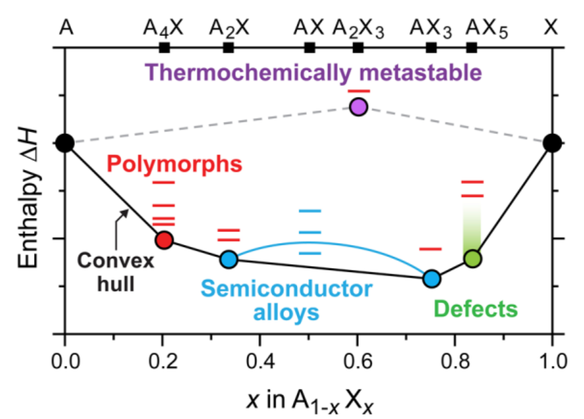
Our overall objective is to discover and synthesize novel functional materials in a predictive manner through multiple-property search, incorporation of metastable materials into predictive design, and the development of theory to guide materials synthesis. Our main goal is to develop a systematic methodology to incorporate and actively design for functional metastability. Another aim is to develop a theory-driven approach to guide the synthesis of new materials by coupling theory and state-of-the-art *in-situ* characterization to probe materials growth pathways. We focus on ***inorganic semiconductor materials*** with ***desired optoelectronic properties*** for solar energy conversion and related technologies.

Relevance to MGI

The CNGMD EFRC is specifically designed to address several critical scientific gaps that must be overcome for computational materials design to be a robust tool for the discovery of new functional materials—namely 1) ***multiple-property design***, 2) ***accuracy and relevance***, 3) ***metastability***, and 4) ***synthesizability***. Our goals map directly to these gaps:

1. Design and discover new energy-relevant materials with targeted functionalities by integrating theory, high-throughput computation, synthesis, and characterization.
2. Develop foundational theoretical, synthesis, and characterization tools.
3. Incorporate functional metastable materials and establish ranges for materials metastability.
4. Develop a systematic theory-driven approach to guide the synthesis of new materials.
5. Promote and disseminate the Next Generation of Materials by Design to the broader materials science community.

Our approach integrates detailed high-throughput experimental studies and advanced *in-situ* characterization methods with a computational design environment involving high throughput as well as detailed theoretical studies along with data mining. We have developed a number of experimental tools to rapidly synthesize and characterize new materials, including combinatorial methods. In parallel, we are developing theory tools including neural network approaches. We are also developing and employing *in-situ* characterization methods at SLAC, including *in*-situ XRD during annealing or solution synthesis.



Four classes of metastable materials (shown in color) targeted for theory-driven discovery and synthesis in the CNGMD EFRC.

Technical Progress

We have made significant progress against our goals through five highly collaborative, integrated projects. In the ***Perovskite-Inspired Search*** project, we used calculations and data-mining as well as experimental studies to understand the defining material properties that distinguish the methylammonium lead halide perovskites for photovoltaic applications [1]. We identified 9 potential classes of promising materials and initiated studies on bismuth-based systems [2,3]. High throughput calculations in the ***Ternary Pncitides Search*** project identified a number of new nitride materials—both binaries and ternaries. We are also studying tin nitrides [4] where we have discovered new metastable systems and are exploring specific ternary systems.

To develop the fundamental understanding of metastability needed for incorporation into materials by design, we are investigating four classes of metastability relevant to inorganic semiconductors for energy applications, which are illustrated in the Figure above showing the convex hull for a simple binary system: **1) *polymorphs*, 2) *semiconductor alloys*** with positive mixing enthalpy including heterostructural alloys, **3) *defects*** where local non-equilibrium effects can alter properties, and **4) *thermochemically metastable*** materials that are thermodynamically unstable compared to their constituent elements. The ***Polymorphs*** project takes a multipronged approach using theory and experiment to predict, synthesize and study Mn, V and Ti oxides—all of which exhibit a rich set of structures that are very relevant to a range of technological applications. We are employing solution-phase, including electrodeposition [5], and vapor-phase synthesis methods along with *in*-situ characterization at SLAC to understand the synthetic pathways that access different polymorph structures. Theoretical work is mapping the thermodynamics of these systems and providing information on bulk and surface energetics under reaction conditions. We also developed a new approach to screen/sample structural space named the Polymorph Sampler and have applied it to some binary oxides. In the ***Chalcogenide Alloys Project***, we are predicting alloy phase diagrams from first principles calculations and have shown that qualitatively new features emerge in heterostructural alloys when compared to conventional isostructural alloys [6]. Thin-film growth and characterization has validated the predictive character of the calculated phase diagram. In the ***Defect Phase Diagram*** project we are using theory to understand vacancies and doping for Ga_2O_3. Dopant activation with Sn was studied by X-ray absorption spectroscopy [7].

Data Management and Open Access

A publically accessible computational materials database, *NREL MAtDB*, (www.materials.nrel.gov) has been launched. This database focuses on optoelectronic properties of semiconductors and is comprised of calculated properties for about 20,000 crystalline ordered materials at the DFT level (atomic structure and total energy) and multiple properties at the GW level for 250 semiconducting and insulating materials (mostly oxides, chalcogenides, and nitrides). We are collaborating with the *Materials Project* to pipeline vetted data to specific applications including new ones under development.

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Designing, Understanding and Functionalizing Novel Superconductors and Magnetic Derivatives

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Keywords: Unconventional Superconductors, Relevant Magnetic Phases, Materials Design, Neutron and Muon measurements, Nano-device transport studies

Project Scope

The present project aims to make breakthroughs in understanding and designing novel superconductors, magnetic semiconductors and other magnetic derivatives, which can lead to materials with higher transition temperatures and devices with novel functionalities. Five PI's specializing in neutron scattering (Dai) and muon spin relaxation (Uemura) as advanced magnetic probes, synthesis and transport of bulk and nano-scale systems (Ni Ni and Kim), and theory and computational material design (Kotliar), form a strong research team to characterize high-quality specimens with multiple probes and electric field-effect doping, and to interpret the results and propose new materials design using advanced computational models.

Relevance to MGI

Examples of chronological developments of research are shown below, with *future plans* shown by *Itallic*.

Case 1: A new iron based superconductor (Ca,La)$FeAs_2$: Materials prediction by theory [Kotliar] >> Single crystal synthesis [Ni] >> transport, magnetic (MuSR) characterization [Ni, Uemura] >> ARPES [Ni] >> comparison with band calculation with DMFT [Kotliar] >> paper submitted 2015

Case 2: Nematic spin correlations in $Ba(Fe,Ni)_2As_2$: Single-crystal synthesis [Dai] >> Neutron scattering in uniaxial pressure [Dai] >> MuSR in uniaxial pressure [Uemura, Dai] >> Moment size derivation from neutron and muon [Dai, Uemura] >> Moment size theory calculation to compare with experiments [Kotliar] >> *paper*

Case 3: New Doped Ferromagnetic Semiconductor (DMS) $(Ba,K)(Zn,Mn)_2As_2$: Theoretical proposal by Jungwirth >> synthesis of new material (Jin, IOP) [Uemura] >> MuSR [Uemura] >> papers >> (A) single crystals >> *exfoliation, encapsulation and electro-gating* [Kim] >> *functional device;* (B) *composition optimization by calculation* >> *materials design*

Case 4: Mott transition system $(Sr,La)_2IrO_4$: Specimens (Ramesh, Berkeley) >> Nano-scale device and transport [Kim] >> paper >> MuSR [Uemura]

Case 5: Mott transition system *RE*NiO_3 and V_2O_3: Specimens (Alonso, Kageyama) >> MuSR [Uemura] >> theory [Kotliar] >> paper >> *inelastic neutron scattering* >> *nano-device and transport* >> *materials design.*

Technical Progress

(A) Fe based superconductors (IBS): $Ca_{1-x}La_xFeAs_2$ (CaLa112) shows the record bulk Tc up to 42 K among nonoxide IBS's. The 112 systems were predicted theoretically by Kotliar, and later synthesized by several groups including that of the PI Ni. The breaking of C4 rotational symmetry even at room temperature makes it unique among all IBS's. The comparison of this CaLa112 with the other IBS systems will enable us to distill the important information on inducing high Tc. Collaborative studies of Uemura and Ni revealed that $Ca_{0.73}La_{0.27}FeAs_2$ is the "parent" antiferromagnetic compound. Kotliar and Ni showed that $Ca_{0.73}La_{0.27}FeAs_2$ has metallic Zig-zag As chains. The comparison of this material with the prototype 122 IBS is fruitful. It is interesting to note that $Ca_{0.73}La_{0.27}FeAs_2$ is apparently electron over-doped, unlike parent compounds of other IBS which are semi-metals with equal hole and electron carriers. A closer look into the ARPES data suggests that a reasonable Fermi surface nesting exists in this electron-over doped material while the DMFT calculations indicate the Fermi surface nesting is enhanced when it is hole doped. This sheds light on the important role of both Fermi surface nesting and exchange interaction in magnetism of this system. Recently PI Ni found that (Fe,Co) substitutions also lead to superconductivity of the 112 system, with Tc up to 20 K, as shown by the phase diagram (Fig. 1) obtained by transport, magnetization (Ni) and MuSR (Uemura) measurements. Dai, Uemura and Kotliar are collaborating to study nematic spin correlations in $Ba(Fe,Ni)_2As_2$ in uniaxial pressure (see Case 2) using a newly developed pressure cell for neutron and muon studies, and DMFT calculations for the Fe moment size.

(B) Mott transition systems: The present project also covers non-superconducting Mott transition system, In nano-structured devices of thin film $(Sr,La)_2IrO_4$, Kim studied electro field effect by gating. Even for large change of chemical potential, the system remains insulating. Crossover from negative to positive magnetoresistance was found at T = 80 K (Fig. 2). Uemura and Kim are examining bulk specimens of $(Sr,La)_2IrO_4$, and found gradual temperature evolution of the volume fractions of magnetically ordered regions (Fig. 3). MuSR studies of Uemura also revealed that in quantum tuning of V_2O_3 with hydrostatic pressure (Fig. 4) and in *RE*NiO_3 (*RE*=rare earth) with RE element substitutions, static magnetic order of Mott insulator state is destroyed by reduction of ordered volume fraction without change of local ordered moment size, in first-order quantum transition around quantum critical point (see Fig. 5). Kotliar is collaborating in interpreting these results. This work can be extended to inelastic neutron scattering (Dai, Uemura) and electrolyte gating (Kim) to study electronic structures near the boundary of Mott AF insulator and paramagnetic metal, together with the input from Kotliar's calculations.

Future Plans

Recently PI Kim developed a new method to exfoliate cleavable materials and encapsulate with hexagonal Boron Nitride. This new technology works very well for studying not only graphene but also other correlated electron systems. In addition to continuing above-mentioned studies on bulk specimens, the present project seeks formation of nano-structured specimens of unconventional superconductors, DMS systems, and non-superconducting Mott transition systems, and study various transport and magneto-transport properties. Encapsulated nano-scale specimens often result in ultra-clean transport with minimum impurity scattering effect, allowing reliable comparisons of the results with theoretical calculations.

Broader impact (Optional for DOE grants/FWPs)

As an effort for broader impact, PI Uemura and Dai are organizing a graduate lecture series "Frontiers of Condensed Matter Physics (FCMP)", connecting classrooms of Columbia, Rice and U. Oregon Eugene via simulcast broadcasting of lectures given by leading CMP physicists. Inviting about 30 lecturers and 50 graduate students enrolled in the lecture course, the present project organized FCMP Workshop in May 2015 at TRIUMF in Vancouver. All the DMREF PI's participated as lecturers. Using muon beam delivered exclusively for training purposes, a 3-day course was organized for hands-on training of 36 grad students on MuSR experiments. This activity was very successful and popular among participants.

Data Management and Open Access

MuSR and neutron data are made public through web sites of research facilities. Upon publication of results, codes for computational studies will be made available through the Kotliar group at Rutgers.

Accelerating Materials Discovery & Development

Establishment of the 112 FeAs systems and discovery and development of new DMS systems isostructural to FeAs superconductors are very good examples of materials design initially proposed by theories and computations and followed by actual synthesis. Without computational predictions, these materials could never been found.

Publications

Four collaborative papers are currently under review. For individual DMREF papers, see annual reports.

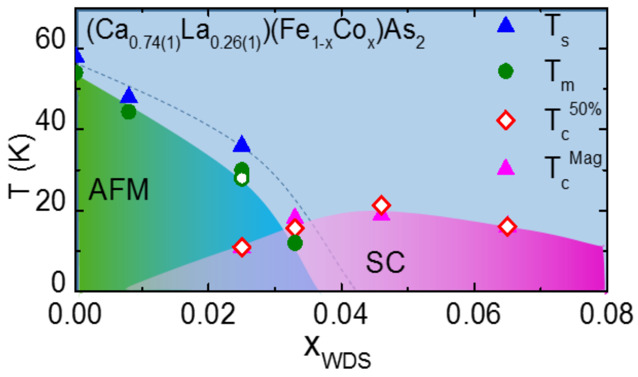

Fig. 1: Phase diagram of the 112 FeAs superconductor (Ca,La)FeAs tuned with (Fe,Co) substituutions. Ts, Tm, Tc represent structural, magnetic and superconducting transition temperatures. Work of Ni and Uemura after computational proposal by Kotliar.

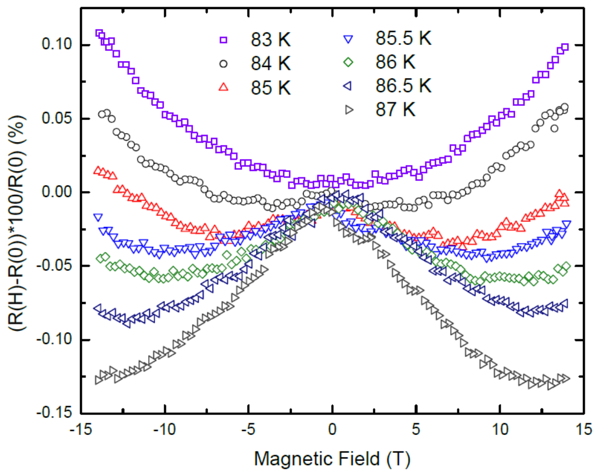

Fig. 2: Magneto resistance (MR) right around the MR sign change for the electron doped $La_{0.1}Sr_{1.9}IrO_4$ thin film measured by Kim with a nano-fabricated specimens for electrolyte gating.

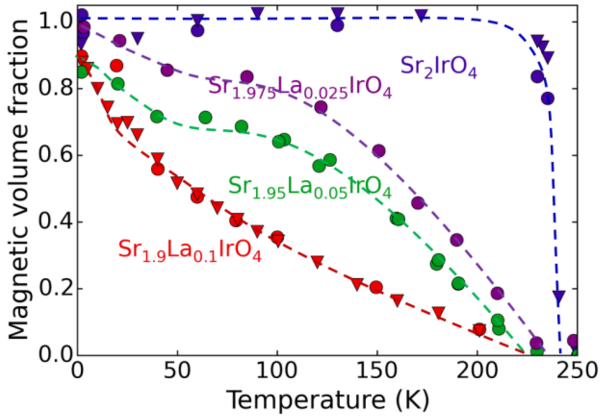

Fig. 3: MuSR results of the volume fraction of the regions with static antiferromagnetic order in $(Sr,La)_2IrO_4$ by Uemura and Kim

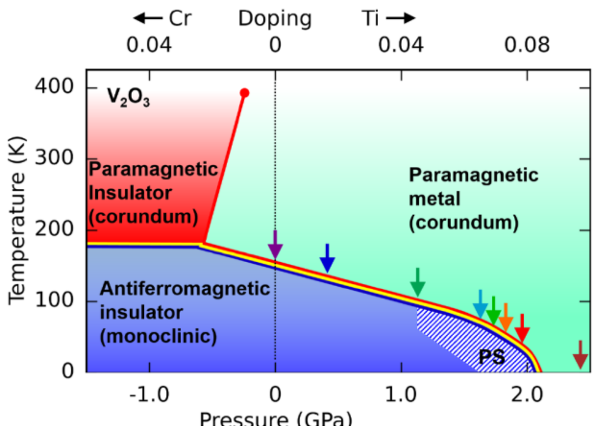

Fig. 4: Phase diagram of a Mott transition system V_2O_3 with hydrostatic pressure and (Cr,V) or (Ti,V) substitutions.

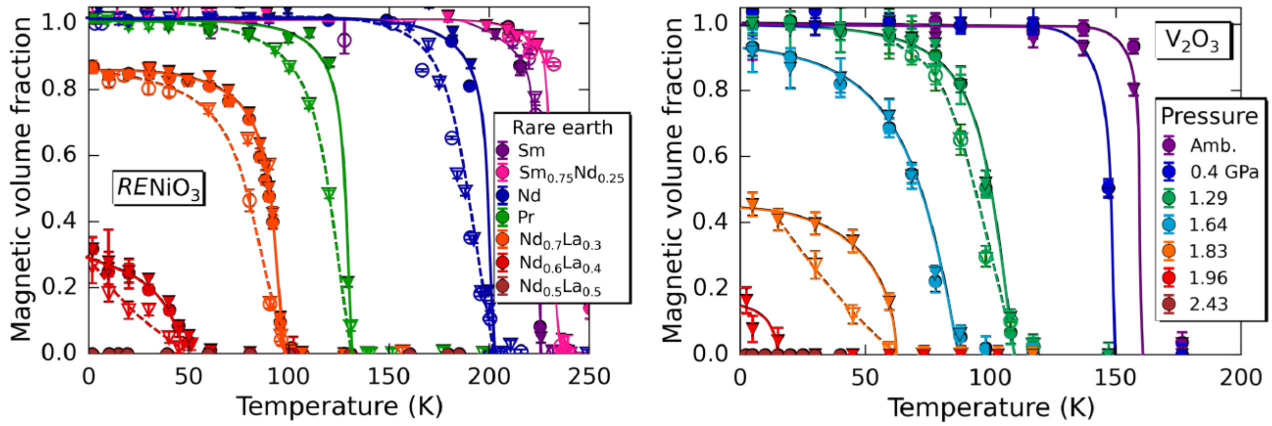

Fig. 5: MuSR results of the volume fraction of the regions with static magnetic order in *RE*NiO_3 (*RE*= rare earth) in ambient pressure and in V_2O_3 with hydrostatic pressure, showing first order transition (Uemura).

Design and fabrication of wide-band-gap nitride-based alloys.

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Keywords: Wide-band-gap nitrides, UV light emitters, density functional theory, molecular beam epitaxy, deep level optical spectroscopy

Project Scope

The nitride semiconductors are driving solid-state lighting and will have a similar impact on power electronics. High-quality alloys with larger band gaps are required to push optoelectronics into the UV and to enable higher voltage transistors. Computational theory, in tight collaboration with growth and characterization, is used to accelerate the development of AlN, Al-rich AlGaN and InAlN alloys, and BAlN by exploring suitable alloy compositions and heterostructures. A methodology for calculating capture cross sections is being developed to enable comparison with deep-level transient spectroscopy (DLTS) and deep-level optical spectroscopy (DLOS). The goal is to bring the materials quality up to device level.

Relevance to MGI

We aim to accelerate the development of technologically important wide-band-gap nitrides through close interaction between simulation, growth, and characterization, focusing on two areas: point defects and heterostructures. Point defects act as compensating centers, may lead to degradation, and can lower the operating efficiency of optoelectronic devices and high-voltage transistors. We perform first-principles calculations of defect formation energies, charge state transition levels and capture cross sections in order to identify candidate point defects in nitrides that can act as efficient channels for recombination [1]. Layers are grown by molecular beam epitaxy (MBE) and extensively characterized, including by DLTS and DLOS. The computational results enable identification of the observed point defects, which provides guidance for subsequent growth runs. Another area of investigation is band offsets and polarization fields in high-Al content and BN-containing heterostructures.

Technical Progress

$In_xAl_{1-x}N$ is an important nitride alloy as the constituents have the extreme band gaps of the wurtzite-structure nitrides: 6.0 eV for AlN and 0.65 eV for InN. $In_xAl_{1-x}N$ with $x \approx 0.18$ is lattice matched to GaN, thus providing a stress-free barrier for transistors. Higher In contents offer the potential for polarization-matched structures between InAlN and GaN. To understand the growth of InAlN, we have developed a full plasma-assisted MBE growth

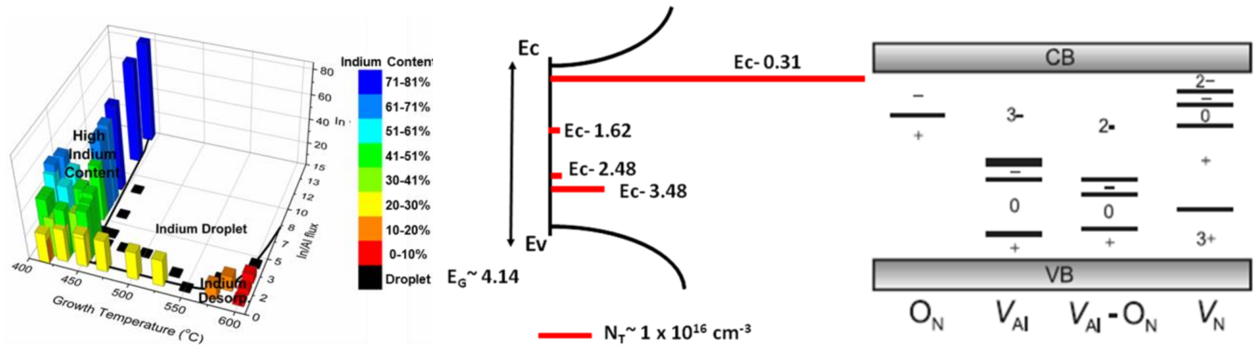

Figure: Growth, characterization and defect identification in InAlN. (a) InAlN growth diagram as a bar plot with indium content. (b) Summary of DLTS/DLOS-detected band-gap states in lattice-matched AlInN layers grown on GaN substrates. (c) Charge-state transition levels for defects in AlN obtained from hybrid density functional theory.

diagram for InAlN (see Figure). Three distinct growth regimes are identified: the indium droplet regime, high indium content regime, and the indium desorption regime. DLTS/DLOS measurements for an AlInN layer lattice matched to GaN reveal a spectrum of band-gap states. We are in the process of identifying the origin of the defects by comparing with defect levels calculated using density functional theory (DFT) with a hybrid functional.

Computational results for defects have also been compared with DLOS/DLTS studies of an $Al_xGa_{1-x}N$ compositional series to elucidate properties of deep level defects as a function of Al composition and band gap. Capture kinetic studies were also performed to determine the trap distributions. The structures were grown using ammonia-based MBE consisting of 100 nm *n*-type $Al_xGa_{1-x}N$ on top of 100 nm *n*-type GaN at x = 6%, 10% and 15%. In all samples, DLTS revealed a dominant electron trap with an activation energy that increases with increasing Al content: Ec- 0.61 eV, 0.73 and 0.78 eV for x = 0%, 6% and 10%, respectively with concentrations roughly in the range of ~ mid 10^{15} cm-3. This level appears to track the change in AlGaN electron affinity across the same composition range, suggestive of a vacuum-referenced binding energy behavior for this defect.

Another goal is to identify suitable donors for high-Al-content alloys that do not suffer from *DX*-center formation. The computations have shown sulphur to be the most promising donor impurity, and this is being experimentally tested.

Future Plans

On the computational side, we will continue the development of the methodology to calculate capture cross sections. We will also perform additional calculations for point defects and complexes in AlN as well as AlN-based alloys. We will study band structure, band offsets, and bowing in AlInN and BAlN, and also build an understanding of *n*-type doping and the potential for *p*-type doping in these alloys.

Regarding MBE growth, we will grow high-quality AlN by MBE and perform Si and C doping of AlN. Low-In AlInN/AlN will be grown for DLOS. We will investigate alternate intentional donors in AlN, as suggested by theory. For boron alloying into III nitrides, we have completed design and construction of a boron gas source system. BBr_3 was selected as a B source reagent for $B_xAl_{1-x}N$ growth studies and $B_xGa_{1-x}N$. The first growths will be performed in January 2016.

DLTS and DLOS studies will explore the capture barrier and kinetics on AlInN traps in the upper part of the band gap to investigate *DX*-center-like properties as a function of growth conditions and alloy compositions, Mapping of defects in AlGaN will continue in alloys with increasing Al concentration, up to the pure AlN end point.

Broader impact

Six graduate students are being trained as part of the project. Close interactions are stimulated by monthly teleconferences in which progress, collaborative efforts, and sample exchanges will be discussed.

Research from the project was already included in presentations and posters presented at the UCSB “Year of Light Symposium” on October 8, 2015, a public event that included talks by UCSB Nobel Prize laureates Herbert Kroemer, Alan Heeger, and Shuji Nakamura, as well as Steve Chu. Almost 1000 people, many from the general public, attended this event.

Data Management and Open Access

The first-principles calculations carried out for this project generate data on crystal structures, atomic configurations and wavefunctions of defects and impurities, and standard files associated with the electronic structure codes employed (mainly VASP). Input and output files from calculations will be uploaded to The NoMaD (http://NoMaD-Repository.eu/), a widely used facility serving the materials and computational physics communities.

Accelerating Materials Discovery & Development

Earlier experience in the field of nitride semiconductors has shown that pushing for materials development in the absence of a fundamental understanding of the factors that impact materials quality leads to problems down the line, when problems are encountered that cannot be surmounted simply by a trial-and-error approach. For the development of the wide-band-gap nitrides, our goal is to address the essential understanding from the start and thereby enable ultimately faster progress. Our project aims to have a strong impact on technology: the development of compact UV light sources impacts a wide range of technologies, including photolithography, optical data storage, detection of hazardous particles, water or air purification, and sterilization. High-power electronics can lead to tremendous energy savings in power conversion.

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Integrated Computational Framework for Designing Dynamically Controlled Alloy-oxide Heterostructures

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Keywords: Multi-scale, dynamically evolving heterostructures, oxidation

Project Scope

A major objective of this project is the development of an infrastructure that integrates first-principles multi-scale computation with precise experimental characterization to predict the evolution of complex multi-phase structures. Such tools are crucial for the design of protective coatings, targeted microstructures for catalysis and electrochemical energy storage devices. We are developing this infrastructure in the context of the measurement and prediction of thermodynamic and kinetic properties of oxidation processes in model Ti-Al alloys. Experiment serves to benchmark, validate and iteratively improve multiscale descriptions that bridge first-principles statistical mechanical methods with phase field models and level set methods.

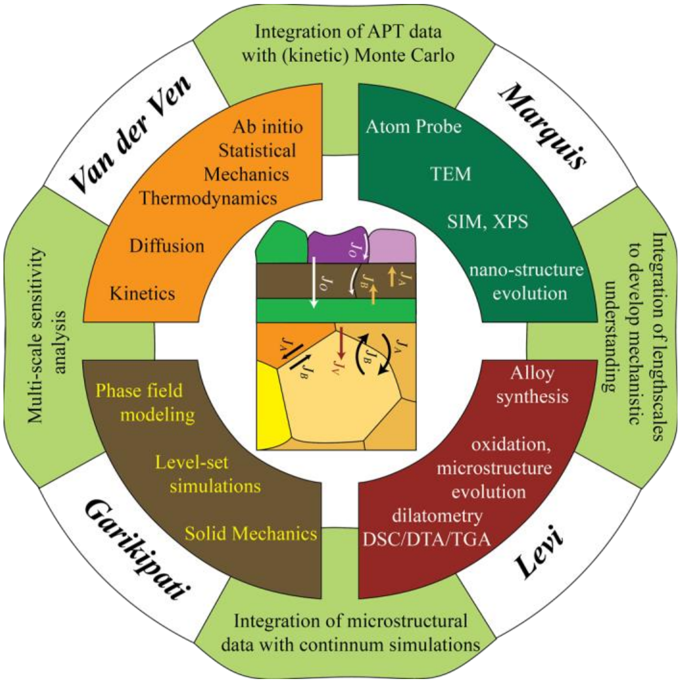


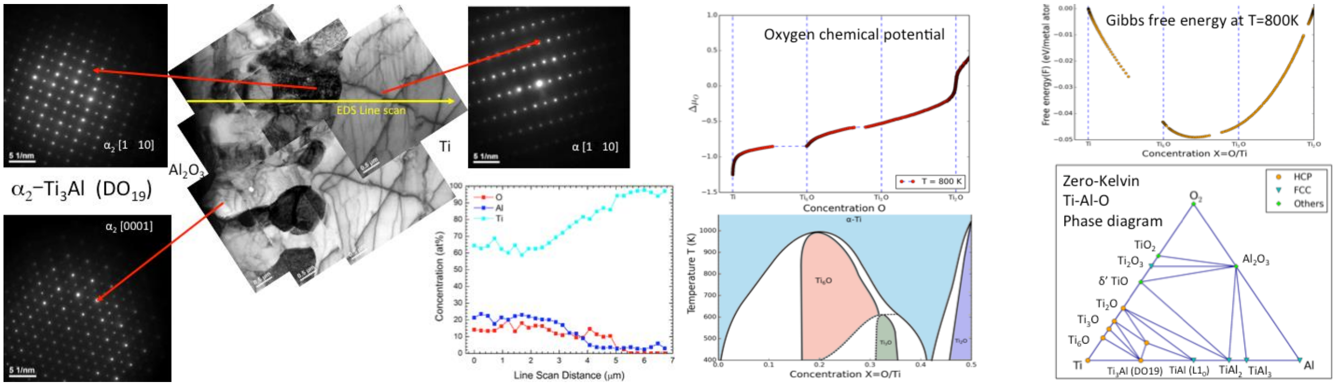
Figure 1: The prediction of the dynamic evolution of a multi-phase system, as during the oxidation of an alloy, requires a multi-scale approach that links first-principles statistical mechanics with continuum methods. An iterative coupling with experiment will lead to the establishment of a robust and rigorous theory of non-equilibrium processes as occur during oxidation, the synthesis of complex microstructures for catalysis and the working of electrochemical energy storage devices.

Relevance to MGI

Even the most advanced first-principles statistical mechanical methods rely on a variety of approximations that are difficult to avoid. Experiment will remain crucial, not only to identify unsuspected behavior and phenomena, but also to parameterize constitutive thermodynamic, kinetic and mechanical properties. Our aim is to integrate first-principles methods with experiment to leverage the strengths of both to their fullest. To this end, we are developing tools to iteratively refine thermodynamic and kinetic descriptions to make them quantitatively consistent with experimental measurements. These tools will prove invaluable in the design of new materials having targeted properties under realistic environmental boundary conditions.

Technical Progress

As a model system we are studying the oxidation of Ti-Al alloys. While this alloy is of tremendous technological relevance as a structural material in jet engines, it is especially interesting from a fundamental point of view in that it exhibits a wide range of thermodynamic, mechanical and kinetic behavior under oxidizing conditions. A remarkable property of Ti-Al alloys is its ability to dissolve oxygen to concentrations as high as 33%. The Ti-Al-O ternary exhibits a rich variety of thermodynamically stable phases. Experimental studies were devoted to characterizing and understanding the evolution of diffusion couples in the Ti-Al-O ternary. These experiments are providing crucial information about thermodynamic phase stability and about the kinetic mechanisms with which phases evolve due to Ti, Al and oxygen diffusion. The experimental studies were complemented with a comprehensive first-principles statistical mechanics study of finite temperature phase stability. These calculations have not only clarified complex order-disorder reactions as well as metastabilities, but have led to the prediction of the stability of new compounds in the Ti-O binary. The calculated thermodynamic properties, including free energies, chemical potentials and elastic moduli are being used as input in continuum simulations of diffusion and phase evolution using phase-field models and the level set method. While the Ti-Al-O ternary contains many phases that share a common underlying parent crystal structure, making a description of phase evolution among them possible with a phase field method, other phases have crystal structures that differ substantially, requiring methods that can treat sharp interfaces. To this end, we have developed a variationally based treatment of sharp interface motion in an elastic, multiphase solid. Experiment is also proving invaluable in providing detailed information at varying length scales about the nature of sharp interfaces and grain boundaries needed for level set approaches.



Future Plans

Experimental and computational studies of the thermodynamic and kinetic properties of the Ti-Al-O ternary system will continue with the objective of developing computational tools that link first-principles statistical mechanics methods with continuum phase field and level set approaches and that integrate these tools with atom probe tomography (ATP) and electron microscopy measurements. Sensitivity analysis approaches will be developed to aid the iterative refinements of calculated thermodynamic and kinetic data with experiment.

Broader impact (Optional for DOE grants/FWPs)

A major outcome of this work will be the formulation and implementation of a methodology and computational/experimental infrastructure that rapidly characterizes, elucidates and enables the design of heterostructures as relevant to oxidation, corrosion, catalysis and electrochemical energy storage.

Data Management and Open Access

Software developed within this program is being made publically available (e.g. CASM https://github.com/prisms-center/CASMcode). Software is also being developed to generate data in standard data base formats consistent with repositories that will be made accessible to the public (e.g. the DOE funded PRISMS materials commons repository at the University of Michigan).

Accelerating Materials Discovery & Development

The tools being developed to integrate experiment with first-principles computation will enable the rapid development of thermodynamic and kinetic descriptions of new chemistries, crucial for materials design.

Enhanced functionalities in 5d transition-metal compounds from large spin-orbit coupling

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Keywords: 5d compounds, spin-orbit coupling, layered chalcogenides, $IrTe_2$.

Project Scope

The physics and chemistry of 5d transition-metal compounds is distinguished by strong spin-orbit coupling, which can have a dramatic effect on materials properties. The focus of this DMREF project is to improve our scientific understanding of materials containing 5d elements and harness their unusual properties to develop new functional materials. Our goals include (i) achieving large magnetocrystalline anisotropy in crystals with mixed 3d and 5d transition-metal ions; (ii) finding new topological insulators and materials with other novel topological band structures; (iii) demonstrating unusual superconducting states; and (iv) developing materials with giant magnetoelectric, multiferroic, or magneto-optic effects.

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, especially regarding the interplay between competing interactions that give rise to functional behavior.

Technical Progress

Our activity has been broad, with 20 papers published and 4 submitted since the start of this program. Here we briefly describe the highlights of the most recent year of our program.

We have extended previous work on $IrTe_2$ by studying domain dynamics and evolution using first principles methods and experimental techniques, both ARPES [2,3] and variable-temperature STM [3,10], to elucidate the charge-ordering dimerization transition in $IrTe_2$. We also revealed complex domain structures having a topological nature in Fe-intercalated TaS_2 [1].

We theoretically proposed a new class of $J_{eff} = 1/2$ insulators in metal hexafluoro-iridates and rhodates, in which the octahedral cages surrounding the transition metals are relatively isolated, leading to relatively flat bands and novel behaviors [4] (see figure at right).

We have followed the lattice vibrational modes of Ni_3TeO_6 through its temperature- and field-driven magnetic phase transitions using optical methods, and theoretically clarified the nature of the responsible spin-phonon couplings [6]; measured and computed the changes in *d*-to-*d* and interband optical responses at these transitions

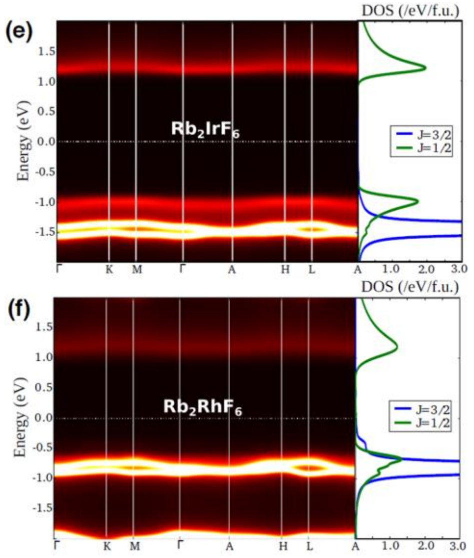

Figure. *Theoretically predicted spectral function and density of states of* Rb_2IrF_6 *and* Rb_2RhF_6*, new* J_{eff}*=1/2 compounds.*

[9]; and discovered and theoretically interpreted new high-field magnetic transitions in this material [5].

We have theoretically studied the rare-earth pyrochlore iridates $R_2Ir_2O_7$ using dynamical mean field theory (DMFT), showing that we correctly reproduce the qualitative pattern of metal-insulator transitions [8]. Unfortunately, we conclude that topological states will be difficult to stabilize in this class of compounds.

We constructed, characterized, and calculated the properties of "inverse topological insulator" heterostructures by combining topological insulator Bi_2Se_3 with normal insulator In_2Se_3 [7].

Future Plans

We will investigate 3d-5d mixed compounds with chemical formula $A_3BB'O_6$ (where A=Ca, Sr, B=Co, Ni, Cu, Zn and B, B' are 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 within a single 1D chain, and weak and switchable interchain interaction. We will perform a DMFT calculation for several compounds and estimate magnetic anisotropy from these calculations identifying most promising candidates. We will also study the Ruddlesden-Popper series, as for example the mixed system of La_2CuO_4 (S=1/2 Mott insulator) and Sr_2IrO_4 (J_{eff} = 1/2 Mott insulator). Their magnetic properties and the possible presence of superconductivity in doped systems will be studied. We will explore the possibility of multiferroicity in perovskite R_2CoIrO_6 and R_2NiIrO_6 (R=rare earths), and theoretically 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 both theoretically and experimentally. We will synthesize and investigate heterostructures between topological insulators and transition-metal dichalcogenides. We will extend our spectroscopic work on $IrTe_2$ to $AuTe_2$, where anionic effects take on an increased importance. We will initiate exploratory spectroscopic measurements of 1T-TaS_2, $Fe_{1/4}TaS_2$, and $Fe_{1/3}TaS_3$ to reveal the signatures of the chiral and antiphase domain walls. We will initiate exploratory spectroscopic work to uncover the properties of the novel improper ferroelectric $Fe_2Mo_3O_8$.

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: the 2013 and 2015 *Telluride Workshops on Spin-Orbit Coupling in 4- and 5d-Containing Materials*, and the *2014 Gordon Research Conference on Multiferroic and Magnetoelectric Materials*. We also proposed and obtained approval for a Focus Topic session on "Strongly spin-orbit coupled materials" through the Division of Materials Physics. This new focus topic was very successfully initiated at the 2015 March APS Meeting in San Antonio, TX, which is expected to continue in coming years, adding up to a long-term impact, and will be an important ongoing venue for the participation of students and young researchers.

Data Management and Open Access

Our full publication list (24 papers), 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/.

Accelerating Materials Discovery and Development

The MGI approach of our DMREF project allowed us to swiftly identify the fundamental mechanism (dimerization of 5d elements) of emergent complexity (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.

Ten Most Recent DMREF-Supported Publications

[1] Y. Horibe, J. Yang, Y.-H. Cho, X. Luo, S. B. Kim, Y. S. Oh, F.-T. Huang, T. Asada, M. Tanimura, D. Jeong, and S.-W. Cheong, “Color theorems, chiral domain topology, and magnetic properties of Fe_xTaS_2,” *J. of the Amer. Chem. Soc.* 136, 8368–8373 (2014).

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[5] J. W. Kim, S. Artyukhin, E. Mun, M. Jaime, N. Harrison, A. Hansen, J. Yang, Y. Oh, D. Vanderbilt, V. Zapf, and S.-W. Cheong, “Successive magnetic field-induced transitions and colossal magnetoelectric effect in Ni_3TeO_6,” *Phys. Rev. Lett.* 115, 137201 (2015).

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[8] H. Zhang, K. Haule, and D. Vanderbilt, “Metal-insulator transition and topological properties of pyrochlore iridates,” *Phys. Rev. Lett.* submitted.

[9] M. O. Yokosuk, A. al Wahish, S. Artyukhin, K. O’Neal, D. Mazumdar, P. Chen, J. Yang, Y. S. Oh, S. A. McGill, K. Haule, S.-W. Cheong, D. Vanderbilt, and J. Musfeldt, “Magnetoelectric coupling through the spin flop transition in Ni_3TeO_6,” *Phys. Rev. Lett.* submitted.

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MAterials Genome Innovation for Computational Software (MAGICS)

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David J. Singh, *University of Missouri-Columbia*

Keywords

Computational synthesis; layered two-dimensional functional materials; validation using ultrafast X-ray laser experiments; scalable and extensible software.

Project Scope

MAGICS Center is about computational synthesis, layered two-dimensional functional materials, validation using ultra-fast X-ray laser experiments and distribution of **open-source software, validated simulation and experimental data to the materials science community.**

Relevance to MGI

Functional layered materials (LMs) will dominate nanomaterials science in this century. The attractiveness of LMs lies not only in their outstanding properties, but also in the possibility of tuning these properties in desired ways. Electronic, optical, magnetic, and chemical characteristics can be tuned by inducing defects or dopants in LMs or by interaction with

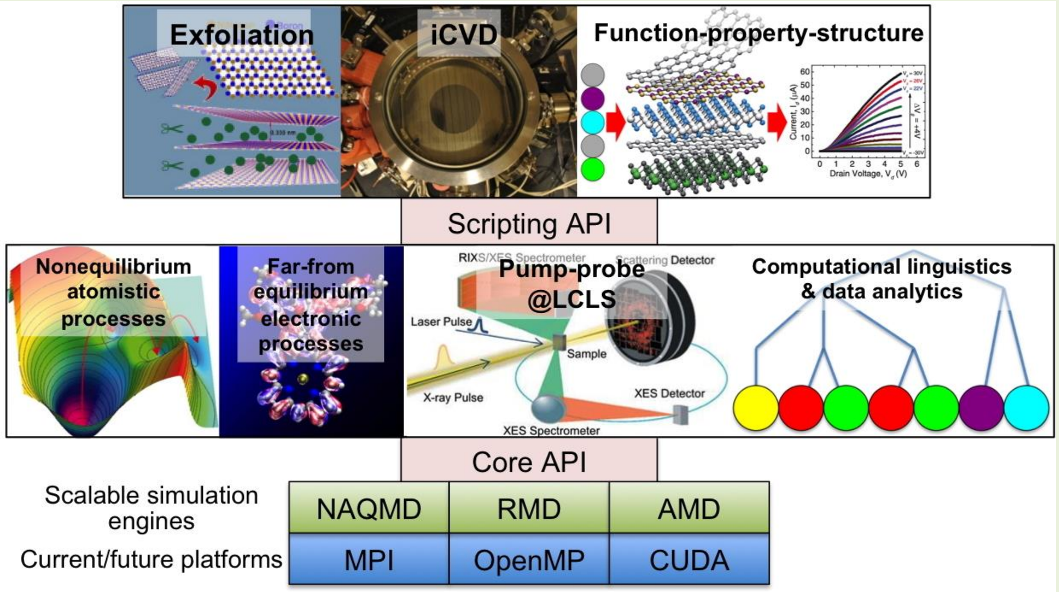

Figure: Layered materials genome: Computational software for the synthesis and characterizations of stacked functional LMs. iCVD–initiated chemical vapor deposition; API–Application programming interface; LCLS–Linac Coherent Light Source; NAQMD–non-adiabatic quantum molecular dynamics; RMD–reactive molecular dynamics; AMD–accelerated molecular dynamics; MPI–Message passing interface; OpenMP–Open multi-processing; CUDA–Compute unified device architecture.

external materials such as small molecules or by building van der Waals heterostructures with various LMs. Another attractive possibility is the introduction of multiple properties on different locations of a single nanosheet, which may lead to a completely new method of device fabrication and architectures.

Technical Progress

This is a newly funded Computational Materials Sciences Project from the Office Basic Energy Sciences, Office of Science, Department of Energy.

Future Plans

We will develop and deliver first-principles based computational synthesis software. The software will aid the synthesis of stacked LMs by chemical vapor deposition (CVD), exfoliation and intercalation. The software will provide function-property-structure relationships in LMs functionalized by initiated CVD process, and will be sufficiently general to help synthesis and characterization of other functional nanomaterials. ***The software suite will include plug-ins for a wide range of properties and processes*** including band structures and carrier effective masses, oscillator strengths and optical absorption/emission spectra, dielectric function, electric carrier mobility and radiative recombination time, excitonic properties, electrical conductivity, heat and mass transport, and various methods for free energy calculation.

The software will play a particularly important role in the analysis of ultrafast X-ray laser experiments on LMs at Stanford's LCLS. Function-property-structure relationships in stacked LMs span a wide range of length and time scales. Catalysis, plasmonics, charge separation and charge recombination, multielectronic excitation and exciton formation in LMs can best be studied through a joint experimental-computational study. Experimentally, we will use THz, optical and UV pumps and X-ray techniques at LCLS to study electronic and phononic processes. In conjunction, we will perform quantum simulations that can describe nonadiabatic processes to interpret pump-probe experiments at LCLS.

Data Management and Open Access

The software will ***run on all platforms from desktops to petascale and evolving exascale architectures***. We will build ***fault resiliency*** in the software to autonomously bypass unexpected failures on multimillion core architectures. The open-source software, simulation and experimental data from ultra fast X-ray laser used for validation will be distributed to the materials science community through the ***Materials Project*** at Lawrence Berkeley National Lab.

Accelerating Materials Discovery & Development

MAGICS Center will accelerate materials discovery and development by creating a new class of computational materials software for validated computational materials synthesis prior to the actual experimental synthesis of advanced materials. It is expected that MAGICS will decrease the cost and accelerate materials discovery and development time by 2X to 10X.

The Center software will be ***scalable*** and ***extensible***, featuring synthesis and characterization modules, community-developed new plug-ins, and ***high throughput and time-to-solution algorithms***.

Accelerated Development of Next Generation Ti Alloys by ICMSE Exploitation of Non-Conventional Transformation Pathways

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Keywords: Ultrafine microstructure, Texture-free, Spinodal, Pseudo-spinodal, Heterogeneous nucleation

Project Scope

This DMREF program builds on our discovery of non-conventional transformation pathways (DMR1309270) to design new Ti-alloys with ultrafine $\alpha + \beta$ microstructures. The scope is to *accelerate* the realization and utilization of the *new transformation pathways* and revolutionary alloy design concepts in the development of next generation Ti-alloys, by integrating multi-scale computational modeling and simulation with critical experimental characterization involving combinatorial approaches based on rapid prototyping. Ultrafine and uniform microstructures with little or no micro-texture are expected from the new transformation pathways and substantially improved properties, e.g., an excellent combination of strength and ductility and high temperature microstructural stability, are anticipated.

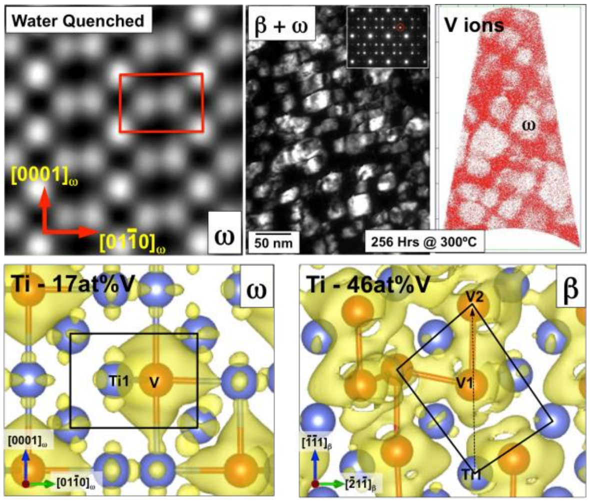

Figure 1. *Top*: Structural and compositional characterization of ω precipitates in a Ti-20at%V alloy using HAADF-STEM, dark-field TEM and APT; *Bottom*: DFT calculations showing the valence electron distribution in ω and β phases.

Relevance to MGI

Using available CALPHAD free-energy databases for the α and β phases in low misfit Ti-Mo and Ti-Mo-Al, and high-misfit Ti-V alloys, detailed Gibb Free-energy vs composition profiles first predicted for different temperatures. Past efforts included Phase-field simulations for Ti-Mo and Ti-Mo-Al alloy to predict microstructure evolution along precursory-spinodal and pseudo-spinodal transformation pathways. These efforts will be replicated for model Ti-V. Ab initio calculations at temperatures comparable to experimental conditions, and high temperature synchrotron experiment are being/will be carried out to validate CALPHAD predictions and SEM/TEM/APT characterizations are being carried out to validate the microstructures as function of time-temperature and alloy composition predicted by the phase-field simulations. The new data will be integrated into the CALPHAD database, initiating the next iteration of the integrated program till fast prototyping.

Technical Progress

(a) *Formation and evolution of ω precipitates in a high-misfit β-stabilized Ti alloy*

Our prior efforts have largely focused on ω phase formation and its role on fine scale α precipitation in β-stabilized Ti alloys with a low β/ω misfit, such as Ti-Mo and Ti-5553. This year we have expanded the scope of our investigation into probing non-conventional transformation pathways in high-misfit Ti alloys. Firstly, the evolution of ω □□□□□□□□□□□□ during isothermal annealing of a model Ti-20at%V alloy has been examined by combining conventional TEM (including aberration corrected HAADF-STEM) and atom probe tomography (Fig.1-*top*). These experimental results have been rationalized based on DFT calculations focused towards investigating the nature of bonding in the ω and β phases (Fig.1- *bottom*). Insights obtained by coupling these experimental and atomistic modeling results will be used to develop a detailed physical understanding (involving structural, compositional and interatomic bonding) of the evolution ω precipitates in high misfit β-stabilized Ti alloys. These studies will also serve as inputs for additional phase field modeling. Furthermore, these studies will lay the foundations for the future investigation of the role of cuboidal ω precipitates on subsequent α □□□□□□□□□□ion in high β/ω misfit Ti alloys via a non-classical mehcanism□

(b) Examination of phase separation in binary Ti-Mo alloys using cluster expansion method – UNT Efforts

We are conducting a systematic study of phase separation tendency in Ti-Mo and Ti-Nb systems using UNiversal CLuster Expansion (UNCLE) method (Lerch et al.) Accurate VASP based ab-initio calculations of a relatively small number of Ti-Mo supercells were used to determine the effective cluster interactions. We have performed ground state searches and applied genetic algorithms to explore Ti-Mo configuration space for α, β, and ω phases. The binary ground state diagram for Ti-Mo system has created from DFT parameterized UNCLE calculations. Using our derived effective cluster interactions, we mapped the ab-initio results onto a simpler Hamiltonian and carried out large-scale Systems with up to fifty thousand atoms in the system to study phase separation tendency in Ti-Mo system. We investigated phase separation in Ti-Mo system with 5, 10, 15, 20, and 25 atomic% Mo by performing Monte Carlo (MC) simulations wherein a wide temperature range (5000 to 100K) was scanned via a simulated annealing method. Figure 2 shows MC simulated annealing profiles for 95%Ti-5%Mo and 75%Ti-25%Mo systems. Preliminary analysis indicates increasing phase separation tendency at higher Mo concentration. We are currently examining the results to understand the structure of the new phase.

(c) Fundamental understanding of the inter-granular nucleation mechanism

In order to obtain ultrafine and uniform $\alpha + \beta$ microstructures with little or no micro-texture in Ti-alloys, a fundamental understanding of the interplay between inter-granular and intra-granular heterogeneous nucleation of α phase is essential. For intergranular α nucleation at prior β grain boundaries (GBs), we have focused on: a) determining how grain boundary parameters, i.e., misorientation and GB plane inclination, contribute to variant selection of GB α and the subsequent development of coarse colony microstructures into grain interior with strong transformation texture in Ti-5553; b) Determining the properties of a critical nucleus (including size, shape and activation energy) at GBs as a function of grain boundary energy, interfacial energy, relative orientation between the low-energy facet of the nucleus and the grain boundary at different degrees of undercooling by employing a fully variational approach based on the multi-phase-field theory and NEB saddle-point searching algorithm.

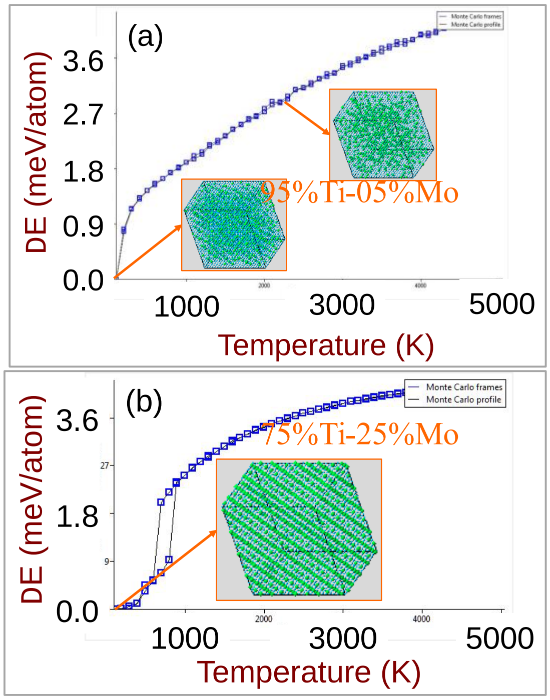

Figure 2. Simulated annealing profiles from our Monte Carlo runs are shown. The heating and cooling curves for 25%Mo system shows a characteristic hysteresis indicating of a transition, which corresponds to a phase separation.

Future Plans (To be modified based on sections “b” and “c” above)

(a) Investigation in the presence of additional precursor phases and the possibility of phase separation in binary Ti-Nb, Ti-V and Ti-Cr alloys

- So far, the presence of miscibility gaps in Ti-alloys have been largely surmised based on limited experimental investigations coupled with solution thermodynamic modeling of phase diagrams. Using a combinatorial approach, involving compositionally graded alloys deposited via laser additive processing, we will probe in detail the possible presence of miscibility gaps in these binary alloys. We will employ the high-resolution characterization techniques listed earlier, and additionally carry out *high temperature high-energy x-ray diffraction experiments at appropriate synchrotron* facilities, such as the Advanced Photon Source (APS) at Argonne National

Laboratory. The eventual goal is to use precursor phase separation in the β matrix, if present, to engineer fine-scale α precipitates.

- Our recent efforts have shown the presence of an additional precursor orthorhombic phases in several Ti alloys , e.g. O'' in Ti-5553 and O' Ti-Nb-Zr. A systematic and quantitative study of the individual and combined influence of chemical and structural non-uniformities generated in the β-matrix due to precursory ω precipitation, precursory spinodal decomposition and newly identified phases such as O' and O'' on the intra-granular nucleation mechanism of α phase and the subsequent development of fine-scale microstructure. The NEB method and multi-phase field theory developed for the study of inter-granular α nucleation mechanism will be extended to determine the properties of a critical nucleus.

(b) Characterization of the mechanical properties of different microstructures

While the principal emphasis of the proposed program is to discover and exploit novel non-classical transformation pathways in Ti alloys, the eventual goal is to engineer microstructures that exhibit a reasonable combination of strength and ductility. Therefore, as part of this program, a preliminary evaluation of mechanical properties via tensile testing and subsequent characterization of the deformation mechanisms will be carried out. In additional to providing fundamental insights into the deformation mechanisms of these novel microstructures, our approach will allow us to identify favorable microstructures and, hopefully, point towards promising future pathways for microstructural modification.

Broader Impact

The proposed program will directly prepare graduate students to immediately contribute to the success of ICMSE in industry. Additionally, the proposed training programs for researchers involved in materials development will afford a rapid uptake of the new methodology, resulting in very much increased effectiveness of our materials technologists. The computational tools and testing/verification data sets (fitted atomic potentials, amended thermodynamic functions, free energy surfaces, activation energy profile and configurations, generalized stacking fault energy surfaces, elastic constants, etc.) will be made freely available to industry and general public.

Data Management and Open Access

To coordinate and manage data for the entire project, we will use web-based tool DMP Online (http://dmponline.dcc.ac.uk/), where we will build and edit a customized plan complying to NSF requirements. The atomic potentials developed will be archived at the NIST Interatomic Potentials Repository Project for other researchers to access and download. An instructional module will be uploaded at the NSF funded NanoHub portal at Purdue University. We are committed to making the computational tools and testing & verification data sets freely available to research community.

Accelerating Materials Discovery & Development

Presently under development.

Publications

1. Y. Zheng, R.E.A. Williams, J.M. Sosa, Y. Wang, R. Banerjee, and H.L. Fraser, "The indirect influence of the omega phase on the degree of refinement of the alpha phase in metastable beta titanium alloys", *Acta Mater.*, **103**, 165 (2016).
2. Y. Zheng, R.E.A. Williams, J.M. Sosa, Y. Wang, R. Banerjee, and H.L. Fraser, "The role of omega phase on the non-classical precipitation of the alpha phase in metastable beta titanium alloys", *Scripta Mater.*, **111**, 81 (2016).
3. Y. Zheng, R.E.A. Williams, D. Wang, R. Shi, S. Nag, P. Kami, R. Banerjee, Y. Wang, H.L. Fraser, "Role of Omega Phase in the Formation of Extremely Refined Alpha Precipitates in Titanium Alloys", *Acta Materialia*, **103**, 850-858 (2016).
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Emergent Functionalities at the Epitaxial Interfaces of Correlated and Spin-Orbit Materials

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Keywords: epitaxial interface, strain, proximity effects, superconductivity, topological materials

Project Scope

This project combines analytic and predictive computational theory with experimental epitaxial growth and atomic scale characterization to investigate the physical phenomena of thin materials on the order of one to a few unit cells that have enhanced functionalities emerging from the interplay of strain, proximity to the substrate, correlations, and spin-orbit interactions.

Relevance to MGI

Density functional theory (DFT) calculations provide the basic structural and electronic properties for model systems, allow the systematic variation of structural and composition parameters, and provide the basis and crucial interactions for many-body models of phenomena such as superconductivity. In the half-Heusler materials, collaboration between Agterberg and Weinert has led to a new *j=3/2* Cooper pairing theory. In the Fe-based superconductors, DFT calculations (Weinert) in conjunction with photoemission experiments have demonstrated the importance of spin-orbit coupling and magnetic correlations in these systems. The calculated electronic structure for different magnetic configurations (e.g., checkerboard vs. collinear antiferromagnetic) differ significantly (as found for $FeTe_{0.5}Se_{0.5}$). The resultant bands are being used as inputs to models of the superconductivity and magnetism (Agterberg). Broken inversion symmetry has been discovered (Agterberg & Weinert) to lead to a spin vortex phase (Fig. (a)). Materials of candidate systems, such as the FeSe single and bilayer films, are synthesized using molecular beam epitaxy, and characterized in situ by atomic-resolution scanning tunneling microscopy/spectroscopy (Li). Comparisons of the predictions of the calculations (Weinert & Agterberg) to the experimental observations (Li) are used to validate the structural models used, as well as indicating features that must be explained by the theory. These activities demonstrate the iterative feedback loop between project components, which has enhanced project outcomes, particularly in the two main thrusts in half-Heusler materials and FeSe superconductors discussed below.

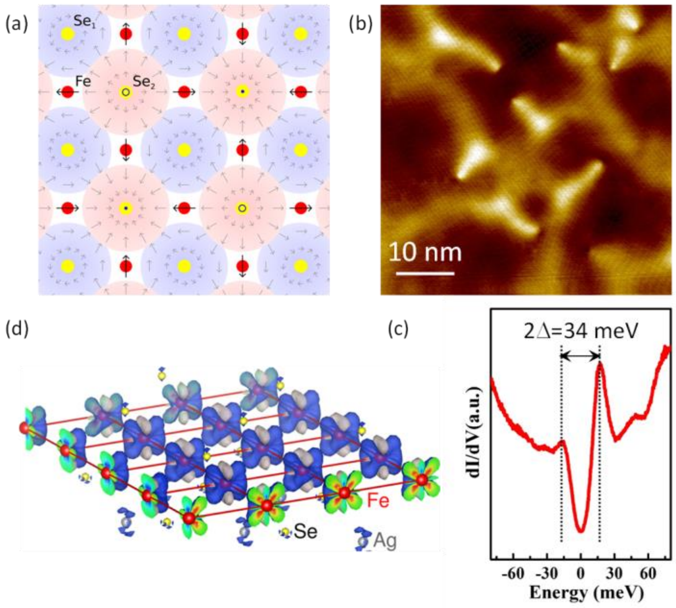

Figure (a) Spin vortex lattice phase of FeSe stabilized by broken inversion symmetry. (b) STM image of bilayer FeSe grown on $SrTiO_3$ (001) substrate showing the interfacial defects. (c) Tunneling spectrum of an intercalated impurity on bilayer FeSe showing the opening of a 17 meV local gap. (d) Isosurfaces (0.006 e^-/a_B^3) corresponding to gain (blue) and loss (gray) of valence density in the stripe magnetic phase of an FeSe bilayer due to Ag intercalation arising from states within 0.5 eV of the Fermi level.

Technical Progress

Spin-orbit and superconductivity in Half-Heusler materials: The half-Heusler materials YPtBi and LuPtBi have recently been proposed to be topological materials due to a large spin-orbit interaction that leads to band inversion. Subsequently, both these materials have been observed to be superconducting and the resulting superconducting state cannot be explained by a standard BCS theory. We have developed a model of the superconducting state (Agterberg) that emphasizes the electronic structure found by density functional theory (Weinert). We have shown that pairing occurs between $j=3/2$ fermion states that are created through spin-orbit coupling, which leads to qualitative differences from the conventional theory of pairing between $j=1/2$ states. In particular, in addition to the usual singlet and triplet states, Cooper pairs with quintet or septet total angular momentum are possible. Purely on-site interactions can generate s-wave quintet time-reversal symmetry breaking states with topologically nontrivial point or line nodes. Furthermore, due to the broken inversion symmetry in these materials, the usual s-wave singlet state can mix with a p-wave septet state, again with topologically stable line-nodes. Such a p-wave septet state is not permitted for usual $j=1/2$ pairing, which indicates that the usual s-wave singlet will not have any unusual properties. These findings lay the foundation for understanding the unconventional superconductivity of the half-Heuslers and point to novel physics in materials with $j=3/2$ states stemming from strong spin-orbit coupling.

Interplay of magnetism, spin-orbit, and superconductivity in FeSe: Building on the theoretical (Weinert) and photoemission results showing the importance of magnetic correlations and spin-orbit in the $FeTe_{0.5}Se_{0.5}$ system, we have investigated the interplay of magnetism, spin-orbit, and superconductivity of FeSe on substrates, in particular $SrTiO_3$. The calculated electronic structure for different magnetic configurations (e.g., checkerboard vs. collinear antiferromagnetic) differ significantly (as found for $FeTe_{0.5}Se_{0.5}$). The bands, including symmetries information, have been used as inputs to models of the superconductivity (Agterberg). The results indicate that in the 2D FeSe materials, spin-orbit coupling together with broken inversion symmetry (arising from proximity to the substrate) changes the usual single-Q collinear antiferromagnetic stripe phase into a double-Q non-collinear spin vortex phase as shown in Figure (a). This phase has no zero-energy spin-waves and is therefore robust against the fluctuations that lead to the Mermin-Wagner theorem.

Local gap opening at intercalated impurities in FeSe bilayer: Li has grown epitaxial single and bilayer FeSe films on Nb-doped $SrTiO_3(001)$ substrate (Fig. (b)). In situ tunneling spectroscopy measurements show that while the single layer films are superconducting with a much enhanced gap of ~20 meV, the bilayer is metallic. Upon doping with Ag impurities, however, local gaps that are tied to the Fermi level are observed (Fig. (c)). DFT calculations (Weinert), while ruling out a simple impurity/defect explanation of the gap, indicate local modifications of the electronic structure around the Fermi level, including a change in the local antiferromagnetic ordering from stripe to checkerboard and an increase in the number of Fe *d* electrons (Fig. (d)). These measurements and DFT calculations suggest that the local electronic changes could lead to an effective attractive Hubbard U Ag-FeSe cluster, allowing the formation of local Cooper pairs (Agterberg).

Future Plans

A major thrust will be to further investigate FeSe on substrates. Already, calculations and experiments have pointed out the importance of the short-range magnetic correlations, defects, and spin orbit coupling in modifying the electronic structure. This information is being incorporated into models of the superconducting state with particular emphasis on the broken inversion symmetry. In addition, an understanding of the origin and consequences of the attractive U local pairing interaction for impurity (e.g., Ag) clusters will be developed.

Development of DFT methods to deal with constraints, the first-principles determination of Hubbard U parameters (as needed to treat correlated systems), and more robust approaches to calculating the spin-orbit/magnetic effect important in these materials will continue and will be made available in *flair*.

Experimental work will focus on intercalated impurities in few layer FeSe films, aiming to further determine the origin of local pairing and superconductivity as part of the iterative feedback loop of synthesis, characterization, and theoretical modeling.

Broader impact

In addition to the participation of graduate students and postdocs in this project, undergraduates are also extensively involved. Jacob Dood, a Physics major, has been working with graduate students in Li group since spring 2015 focusing on constructing an in situ four-probe system to measure the superconducting transition temperature of the single layer FeSe films. An undergraduate from the University of Chicago, Drew Melchert, spent the summer (through September) of 2014 working with Agterberg and Weinert on an extension of a model of superconductivity based on pair density waves that resulted in him being a co-author on a paper published in Physical Review B.

As a result of long term collaboration between Weinert and Prof. Kohji Nakamura's group in Mie University in Japan, a formal exchange program was signed in summer 2015 to facilitate graduate student exchanges and co-advising of thesis research. This program is poised to enhance the educational experience for both US and Japanese graduate students in the material discovery advocated by MGI. A number of Japanese graduate students have visited UWM, with the latest (Kenji Nawa) currently still at UWM working with Weinert. As a featured speaker at the 18th Asian Workshop on First-Principles Electronic Structure Calculations (Nov. 9-11, 2015, Tokyo) and at the International Meeting on First-Principles Calculations (Nov. 20, 2015, Osaka), both of which targeted graduate students and post-docs, Weinert has advocated the MGI approach to materials discovery.

Data Management and Open Access

An implementation of the Full-potential Linearized Augmented Plane Wave (FLAPW), flair, is actively being developed by the PI and an international group of collaborators, and is also being used by a number of other researchers worldwide. Much of the development is focused on approaches to allow more direct comparisons to various experimental probes, particularly spectroscopies. Some of these analysis tools have been ported and are available for other electronic structure codes, including vasp and Quantum Espresso.

Accelerating Materials Discovery & Development

The interactive feedback loop of synthesis, characterization, and theoretical modeling advocated by the MGI initiative has allowed the rapid development of synthesis of topological and superconducting materials with enhanced properties, and opened up new avenues of collaborative research (for example in the half-heuslers with University of Maryland, photoemission studies of FeSeTe with Brookhaven National Lab, and FeSe with Oak Ridge National Lab, University of Wisconsin-Madison, and University of Colorado). These advances would likely not have occurred without the MGI approach.

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Merging DFT with DMRG via wavelet coarse graining

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Website: http://dft.uci.edu/DMRGDFT.php
Keywords: Density Functional Theory, Density Matrix Renormalization Group, Machine Learning, Wavelets, Basis set

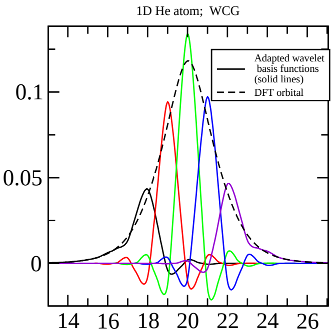
Project Scope

This project aims to produce new approaches to electronic structure calculations of strongly correlated systems, where standard DFT calculations often fail or are limited. Previously, a 1D mimic of 3D reality was created using the power of DMRG to do large calculations in 1D. The focus is on reaching the thermodynamic limit for strongly correlated systems. Several fundamental aspects of DFT were discovered using this. There are currently two main thrusts: Use of wavelet coarse graining of DFT calculations to make much larger systems accessible to accurate quantum solvers (such as QMC), and use of machine learning to find the exact exchange-correlation functional of DFT in strongly correlated systems.

Relevance to MGI

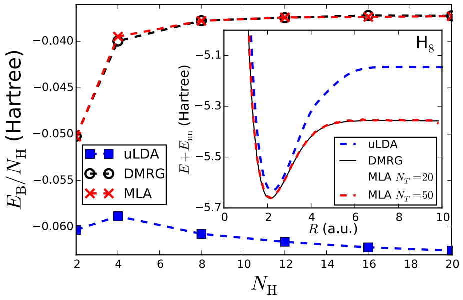
The backbone of all computational materials databases used in MGI is DFT calculations, which typically fail for moderate to strongly-correlated systems. Strongly correlated molecules and solids require treatments beyond current DFT methods, but such methods, such as coupled cluster or the density matrix renormalization group, have computation times that grow rapidly with the size of the basis, limiting the size of the system that is accessible. Our projects are aimed at greatly reducing these computational costs. Validation of our methods is straightforward at present, as we can solve large 1D systems to chemical accuracy using DMRG, adapted to ab-initio Hamiltonians. This 1D laboratory greatly reduces coding/testing time for our new methodologies, especially when we extrapolate to the thermodynamic limit needed for materials calculations. Once they have proven successful in 1D, they will be implemented and tested in 3D. All codes and methods are made publically available through the iTensor library.

Technical Progress



Wavelet coarse graining: Wavelet bases have been used in electronic structure for some time. The usual focus is fast DFT for very large systems, and the basis is not adapted to the problem at hand—in fact, the number of basis functions tends to be very large. Here we have focused on the opposite end of the spectrum of electronic structure, high accuracy for strongly correlated systems. Our goal is to generate the smallest local orthogonal basis complete enough to give chemical accuracy. The locality, smoothness, and orthogonality of some Daubechies-type wavelet bases make them a natural starting point. In our approach, called Wavelet Coarse Graining (WCG), we adapt a standard wavelet transform for a specific molecule or solid. For example, a nuclear cusp requires dozens or hundreds of unadapted wavelets to be represented precisely; but by adapting the transformation so that the large-scale functions include the cusp, we only need one or a few functions. Our adaptation is based on occupied orbitals from a density functional calculation, although Hartree-Fock or even a minimal Gaussian basis set could serve as well. The adaptation is required to reproduce these occupied orbitals exactly, but it automatically builds in additional degrees of freedom to allow electronic correlation and minimize the effect of errors in the DFT input. *The figure shows WCG on a 1D Helium atom with an exponential interaction[2]. LDA gives a single occupied Kohn-Sham orbital (dashed curve). WCG uses the LDA orbital to produce five orthogonal basis functions (solid lines). The basis functions are weighted by their coefficient in the (exact) expansion of the DFT orbital. An exact diagonalization using only these five basis functions reproduces the exact 1D Helium energy to within 1 mH*. Our adaptation procedure is based on a quantum circuit representation of wavelet transforms, where the transform is described by a minimal set of angles. The circuit-angle representation automatically builds in orthgonality, allowing unconstrained fitting. The final result is a basis defined on a coarse grid, plus associated finite Hamiltonian, which can then be treated with a sophisticated correlation method, such as DMRG.

Machine learning: The Burke group had already established, with simple models, that it is possible to learn the non-interacting kinetic energy as a density functional from examples. This allows self-consistent orbital-free DFT calculations with the ML functional, once subtleties related to inaccurate functional derivatives are overcome. Now, since we have essentially exact solutions to the interacting problem via DMRG, we use ML to find the interacting functional (including the exact exchange-correlation energy). Moreover, we are applying a partitioning scheme that allows us to learn the functional for a periodic lattice from a sequence of accurate calculations on finite clusters.



The figure shows binding energies evaluated by machine learned functionals. DMRG and unrestricted LDA results are presented as comparison. Inset: binding curve of H_8. The machine learning approximation (MLA) quickly converges to the correct curve as the amount of training data increases.

Future Plans

With regards to wavelet coarse graining, we are nearing the completion of several tests in the one-dimensional laboratory that will test the limitations of the algorithm described above. Knowing how crude the initial wavefunction is allowed to be while still yielding chemical accuracy in the quantum calculations, finding the most efficient wavelets possible, and testing the speed and convergence of the resulting basis are all current investigations. We hope to achieve chemical accuracy with as few as two basis function per electron. Applying the results to real systems is a focus but not expected to be a major hurdle. Wavelets in three dimensions are a cross product of one dimensional wavelets. Solving systems with exact methods that are computationally difficult using other basis functions will also be investigated.

Once we have shown our ML functional can predict the thermodynamic limit of both ‘metals’ and ‘insulators’ in 1D, we will begin its implementation in a realistic 3D code. Initial tests will check that the ML formalism, trained on PBE data, can reproduce PBE results. After that, we will apply some more accurate method, such as quantum Monte Carlo, to train on more accurate energies, and test our method for systems where PBE fails.

Broader Impacts

Given that success would enable much larger accurate electronic structure calculations for strongly correlated systems that are currently possible, this would have enormous impact. The instant dissemination via the infrastructure being put in place in MGI would mean almost immediate impact on real-world manufacturing processes.

Data Management and Open Access

All the DMRG and WCG routines are being made available publically at the website, itensor.org. ITensor—Intelligent Tensor—is a C++ library for implementing tensor product wavefunction calculations. It is efficient and flexible enough to be used for research-level simulations. The ML methods are all standard techniques of kernel ridge regression, which are widely known and publically available.

Accelerating Materials Discovery & Development

Reductions in cost and increases in computational efficiency are the principle goals of the two projects listed here, but they are achieved in different ways for each. Yet, both focuses compliment each other. Constructing a basis of wavelet functions offers an intriguing possibility to use exact methods on a coarse basis to obtain the same results as a full calculation on a finer basis. The truncation of the number of basis functions by an order of magnitude speeds up the computation by an impressive amount. We look forward to testing our method and finding how far this technology can be pushed. Machine learning the exact density functional for the thermodynamic limit of materials simulations, including strongly correlated materials, could greatly increase the utility of the MGI.

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Engineering Organic Glasses

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Keywords: Glass, anisotropic packing, molecular orientation, stability, crystallization

Project Scope

Glasses are remarkable materials with liquid-like spatial uniformity and crystal-like strength, making them ideal for many applications. Traditional liquid-cooled glasses often suffer the shortcomings of structural relaxation and shrinkage over time. Furthermore, they are usually isotropic. By physical vapor deposition (PVD), the team aims to produce high-density, high-stability glasses with active control over molecular orientation and packing. Simulations reveal the mechanism by which these remarkable materials are produced and propose molecular and process space to explore. Polymer additives are used to stabilize organic glasses against crystallization and fracture. Highly stable glasses with controlled molecular packing are useful for organic electronics, drug delivery, and bio-preservation, and expand the range of materials available for designing new products with advanced applications.

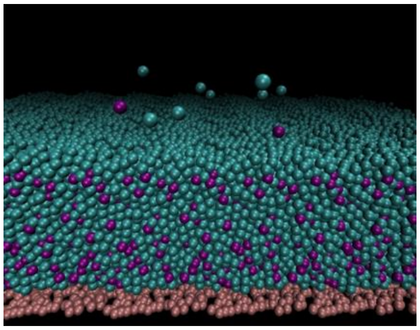

Figure 1. Creating ultra-stable glasses by computer simulations, in which vapor molecules are gradually deposited into the free interface of a growing film.

Relevance to MGI. The collaborative environment created by the MGI has produced results that would be difficult to achieve by single labs working alone. To date the team has published 14 papers, 9 of which have two or all PIs as co-authors. Of the remaining 5, three resulted from collaborations with labs outside this group. These close collaborations mean that experiment and theory happen simultaneously, not sequentially. Our key findings (published in *Nat. Mater.* and *PNAS*) integrate experiment and theory in one seamless package. These efforts directly benefitted from the iterative feedback loop that is the hallmark of the MGI.

Technical Progress

Stable Glasses by PVD with Control over Molecular Orientation. Recent experiments indicate that PVD glasses can be much more stable than traditional liquid-cooled glasses and might correspond to equilibrium states that could hitherto be reached only by glasses aged for thousands of years. We created ultrastable glasses by computer simulation that mimics PVD (Fig. 1). These stable glasses have the properties expected for the equilibrium supercooled liquid, and optimal stability is attained on deposition at the Kauzmann temperature.[1,2] This methodology has been applied to the PVD of real molecules, including polymers.[5] In general, PVD glasses can be so much denser and kinetically more stable than liquid-cooled glasses that to reach the same levels, ordinary glasses must be aged for thousands of years.

A fruitful interaction between experiment and theory revealed the mechanism by which PVD creates glasses that have preferred and tunable molecular orientations.[12,13] We apply a high-throughput scheme to investigate the effect of the substrate temperature ($T_{Substrate}$) on glasses of organic semiconductors. We find that molecular orientation in these glasses is continuously tunable and controlled by $T_{Substrate}/T_g$, where T_g is the glass transition temperature (Fig. 2). All molecules tested can produce highly anisotropic glasses, with similar dependence of

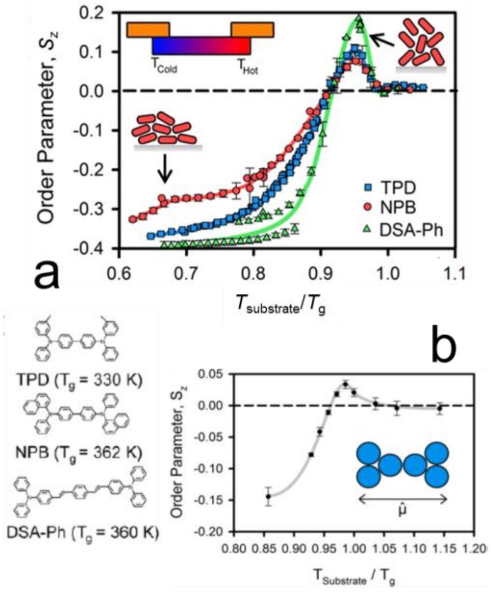

Figure 2. (a) Molecular orientation in PVD glasses can be controlled by the substrate temperature. Molecular orientation can increase the efficiency of organic electronics such as OLEDs. (b) Computer simulations reproduce the experimental trends and explain the result in terms of preferred orientation at the surface of the equilibrium liquid and the ability to reach local equilibrium at a given substrate temperature.

molecular orientation on substrate temperature. Simulations reproduce the experimental trends and explain molecular orientation in the deposited glasses in terms of surface properties of the equilibrium liquid. These results provide an avenue for performance optimization of active layers in organic electronics.

For molecules able to form liquid crystals, the tunable range for molecular packing in PVD glasses increases substantially (Fig. 3).[14] For itraconazole, orientational order of the PVD glass has a similar trend as seen for the TPD family of molecules (Fig. 2), but *the effect is substantially larger*. At a high substrate temperature, itraconazole attains a much larger S_z (by a factor of 3) than DSA-Ph, the non-LC molecule that shows the largest vertical alignment effect. In addition to the orientational order, the PVD glass exhibits smectic order with tunable layer spacing as detected by WAXS and GIWAXS. The greater tunable range of structural order achieved here is a consequence of the generic effect of vapor-depositing elongated molecules and the self-assembly power of LC molecules. This result suggests new opportunities for controlling molecular packing in glasses.

Understanding and Controlling Crystallization in Molecular Glasses. Fast crystal growth abruptly can emerge as molecular liquids are cooled to become glasses. This Glass-to-Crystal (GC) mode can cause crystallization rates 10^4 times faster than predicted by standard models and threaten the stability of amorphous materials. We studied this phenomenon in 12 systems,[6] including two that are structurally homologous and dynamically similar to the model glassformer *ortho*-terphenyl (OTP).[7] While the 12 systems differ greatly with growth rates spanning 10^4 times, the general condition for GC growth is that liquid diffusion be slow relative to crystal growth according to $D/u < 7$ pm. This condition suggests that the phenomenon is a solid-state process terminated by fluidity. GC growth must solidify several molecular layers before rearrangement by diffusion. The most recent work of the team shows the importance of fracture and surface mobility in the crystallization of molecular glasses.[10]

Low-concentration polymers can improve the properties of organic glasses, in particular, stability against crystallization[3] and fracture.[7] Doping the organic glass nifedipine (NIF) with 1 wt % polymer has no effect on the T_g of host molecules, but substantially alters the rate of crystal growth. The crystal growth rate varies exponentially with polymer concentration, in analogy with the polymer effect on solvent mobility. The ability to inhibit crystal growth is not ordered by the strength of host-polymer hydrogen bonds, but correlates with the polymer's T_g, suggesting that the mobility of polymer chains controls their inhibition of crystal growth.

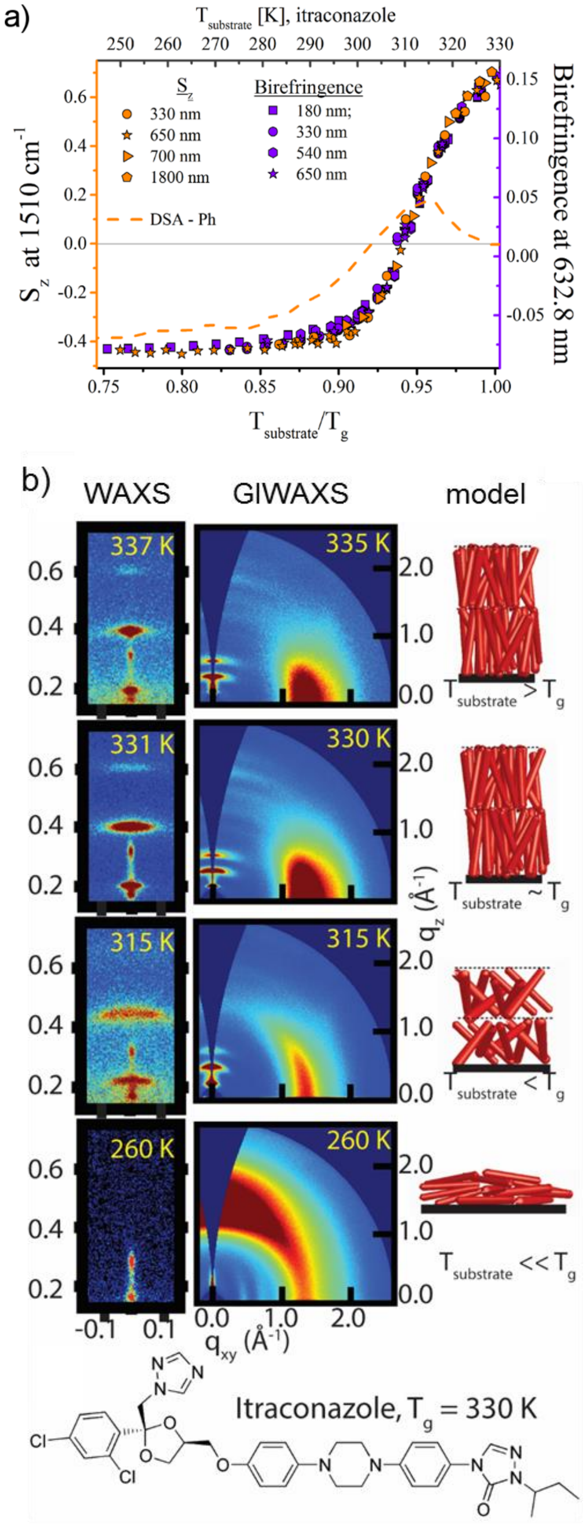

Figure 3. (a) Effect of $T_{substrate}$ on S_z and birefringence of PVD itraconazole. The effect is much larger than observed with non-LC molecule DSA-Ph. (b) WAXS and GIWAXS data of PVD itraconazole and proposed structural models.

Future Plans. (1) PVD of a wide range of LC molecules (rod-like and discotic) to test the generality of preliminary results (Fig. 3). (2) PVD of azobenzenes in the presence of optical fields to control molecular conformation in molecular glasses. (3) PVD of polar molecules to produce glasses with polar order.

Broader impact. The project has involved 12 graduate students, 3 postdocs, and 3 undergraduates. They worked in a highly interdisciplinary environment. Some have graduated to become independent researchers and educators. Personnel supported by this grant worked with UW-Madison's Pre-college Enrichment Opportunity Program for Learning Excellence (PEOPLE), which has a proven record of increasing the enrollment of minority and low-income high school students to colleges and universities. This program provides experiences that help students to become scientifically literate citizens and encourages them to consider careers in science and engineering.

This MGI project and others based in UW-Madison are publicized in the website "Wisconsin Materials Institute: Gateway to Collaborative, High-impact Materials Science Development" (http://materials.wisc.edu/faculty-research/mgi-projects-at-uw-madison/). The cover photo is Figure 1. The caption reads "A computer simulation of a physical vapor deposition (PVD) process. This process assists researchers in developing high-density, high-stability glass by controlling molecular orientation. The goal is to develop molecular glass that overcomes the shortcomings of traditional glass. Resulting new glass have applications in drug delivery, bio-preservation and organic electronics." Yu was an instructor for a workshop organized by the UW-Madison Extension Service in May, 2015, titled "Amorphous Pharmaceuticals". This continuing-education workshop was attended by 15 industrial scientists, and used materials drawn directly from the research results of this project.

Data Management and Open Access. The results of this work have been published in visible and widely accessible journals, and disseminated in presentations by the PIs and their coworkers in major scientific meetings, including MRS, APS, ACS, and AAPS. A special symposium was organized in the 2015 MRS titled "Amorphous molecular solids and ultra-stable glasses" to showcase the research conducted under the support of this grant.

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Design Knowledge Base of Low-Modulus Titanium Alloys for Biomedical Applications

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Keywords: Ti-Mo-Nb-Ta-Zr, Elasticity, Diffusivity, Thermodynamics, Biomedical

Project Scope

This project aims to establish a fundamental knowledge base to enable accelerated design of low-modulus Ti alloys for biomedical prosthetic devices, i.e., alloys with elastic modulus matching that of bone (20-30 GPa). An effective approach integrating high-throughput computational predictions and high-throughput experimental validations will be employed to establish CALPHAD-type digital databases of elasticity, diffusivity, and thermodynamics in the Ti-Mo-Nb-Ta-Zr system. The established databases will be used to accelerate the design of new alloying and processing concepts of low-modulus Ti alloys for biomedical applications.

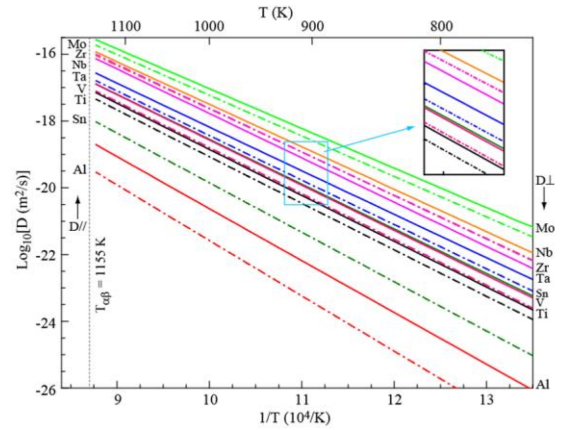

Figure 1. Predicted dilute diffusion coefficients D for alloying elements X in hcp Ti. Dashed lines // c-axis, and solid lines ⊥ c-axis.

Relevance to MGI

The project team embodied the three elements of the MGI Materials Innovation Infrastructure: *Computational Tools* (high-throughput first-principles calculations and CALPHAD modeling), *Experimental Tools* (high-throughput diffusion multiple and Laser Engineered Net Shaping (LENS) processed gradient composition samples), and *Digital Data* (facile establishment of digital databases of elasticity, thermodynamics, and diffusivity for the Ti-Mo-Nb-Ta-Zr system). The knowledgebase will accelerate the design of low-modulus Ti alloys.

Technical Progress

The technical progress is made in establishing digital databases of all three key properties through both computational and experimental tools:

1. *Diffusion coefficients of alloying elements in the Ti-Mo-Nb-Ta-Zr system*: The dilute diffusion coefficients of seven alloying elements in hcp Ti are obtained using a 8-frequency model and first-principles calculations [1] as shown in **Figure 1** (manuscript in preparation). Both dilute/impurity and chemical diffusion coefficients (across the entire single-phase compositions) of Ti-X and Zr-X (X=Mo,Nb,Ta,Zr) systems at 3 temperatures are obtained from high-throughput diffusion multiples and a new *forward-simulation* diffusivity extraction procedure (manuscript in final preparation). The Ti-Zr example is shown in **Figure 2**. The newly developed *forward-simulation* procedure enables, for the first time, reliable evaluation of dilute/impurity diffusion coefficients from regular diffusion couples without using isotopes, which is very significant since the laborious isotope experiments are rarely performed nowadays to obtain the essential dilute/impurity data for diffusivity/mobility database establishment. **Figure 3** shows excellent agreement of the data obtained from the current work with literature isotope data.

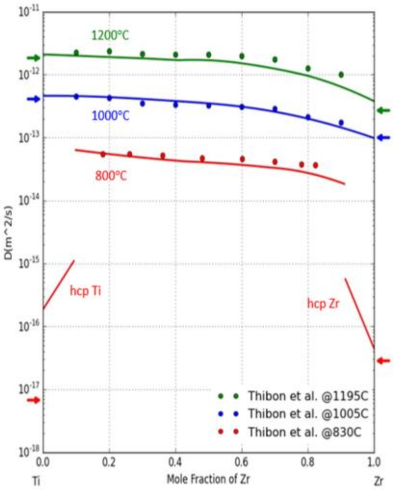

Figure 2. Experimentally obtained diffusion coefficients (lines) from diffusion multiples in comparison with literature data (points) of the Ti-Zr binary system.

2. *Elastic properties of the Ti-Mo-Nb-Ta-Zr system*: Elastic constants and Young's modulus of the bcc-phase in the Ti-X and Ti-X-Y (X and Y are alloying elements) systems were obtained using an efficient first-principles strain-stress method [2]. **Figure 4** shows the first-principles predicted Young's moduli for the Ti-X alloys, indicating the possibility to design biomedical Ti alloys with elastic modulus matching that of bone (20-30 GPa) (manuscript to be submitted soon). Experimental validation of the computational predictions is in progress using localized measurements of elastic constants from both diffusion multiples and LENS processed gradient composition samples (Several binary Ti alloys were also made using arc melting for validation)
3. *Thermodynamic (CALPHAD) modeling of the Ti-Mo-Nb-Ta-Zr system*: Three ternary phase diagrams of the Ti-Mo-Zr, Ti-Ta-Zr, and Ta-Nb-Zr systems have been obtained from diffusion-multiple experiment and provided to Penn State for CALPHAD modeling. The CALPHAD approach [3] uses data from first-principles calculations and experiments in the literature and results from the present work. Modeling of the binary Ti-X and ternary Ti-X-Y systems is in good progress. As an example, **Figure 5** shows the calculated Ti-Mo-Ta phase diagram. More phase equilibria data will be obtained from diffusion multiples to serve as input data to CALPHAD modeling and as validation.

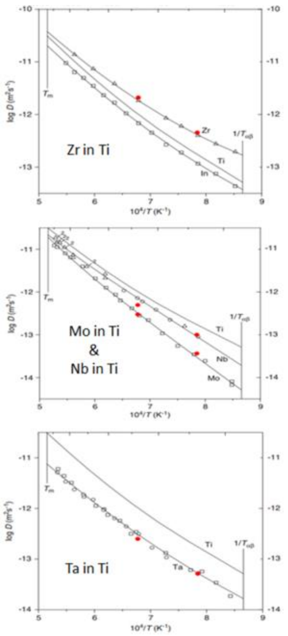

Figure 3. Comparison of the dilute/impurity diffusion coefficients obtained from diffusion multiples using a forward-simulation procedure (red dots) with literature results using isotope experiments.

Future Plans

We will continue to perform computations and experimental measurements on elasticity, diffusivity, and thermodynamics in the Ti-Mo-Nb-Ta-Zr system to complete the digital databases on these three key properties for the design of low-modulus, biocompatible Ti alloys. Ongoing work on experimental measurements of elastic constants and phase diagrams will be completed by 2016. Methodology to predict diffusion coefficients of bcc Ti alloys that are unstable at zero Kelvin will be examined. After completion of the elastic properties of Ti-X binary systems, the elastic properties in Ti-X-Y ternary alloys will be performed. A thermodynamic database for the Ti-Mo-Nb-Ta-Zr system will be built based on input from first-principles calculations, current experimental measurements as well as literature data.

More cross-validation and integration of computational and experimental results will be performed. Validation of predicted low-modulus alloys will finally be performed using arc-melted Ti alloy samples. Several manuscripts will be submitted for publication to summarize and distribute the results and data to the materials community.

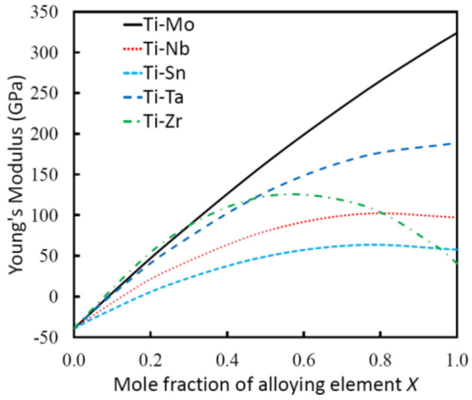

Figure 4. Predicted Young's moduli of Ti-X binary alloys from first-principles calculations.

Broader impact

Biocompatible Ti alloys with low elastic modulus are considered to be one of the best options for prosthetic implants. The ability to tailor the composition and microstructure to design alloys to meet specific property requirements is the goal of MGI in general and the purpose of this study in particular. The biocompatible, low modulus Ti alloys are a perfect test bed for MGI since on the one hand their complexity requires the use of all the tool sets of MGI, but on the other hand they are sufficiently "simple" for the tools to make a real difference in alloy development. The timely design and insertion of high-performance materials are critical to the global competitiveness of US manufacturing as well as minimization of the negative impact to the environment. This NSF program is educating next-generation materials scientists and engineers who will master both advanced computational and experimental approaches with cross-disciplinary knowledge of materials to better serve society. Three graduate students are trained in the spirit of MGI. The research and education of the proposed study will also help usher in a new paradigm of materials research and innovation where materials design is conducted by up-front simulations followed by key validation experiments in contrast to the current approach that is heavily based on experimental iterations followed by mechanistic characterization / explanations. The students and researchers are constantly been asked to think about both experimental and computational work and how to integrate them.

Data Management and Open Access

Data and samples to be generated in the research section of this project will be placed into two categories – physical samples and records of sample and simulation characteristics. Physical samples will consist of diffusion multiples, LENS processed Ti alloy gradient samples, and Ti alloys made using arc melting for property validation. Records will include digital files of simulation, characterization, and performance results, along with both digital and hand-written lab notebook records of procedures and practices used. Calculations using Density Functional Theory (DFT) will be performed to gain insight into elastic, thermodynamic and diffusion properties of stable and unstable phases. Output will be electronic files and plots. The data sets are generally in binary or ASCII format readable by common data analysis and/or graphical analysis programs (e.g., Microsoft Excel, SigmaPlot, Origin). The PI's and co-PI's laboratories are open to sharing results in any form with interested parties upon request. The results of the work are/will be archived in peer-reviewed publications that will include much of the metadata resulting from the work. Deposition of the data and metadata into the NIST Materials Data Depository is planned.

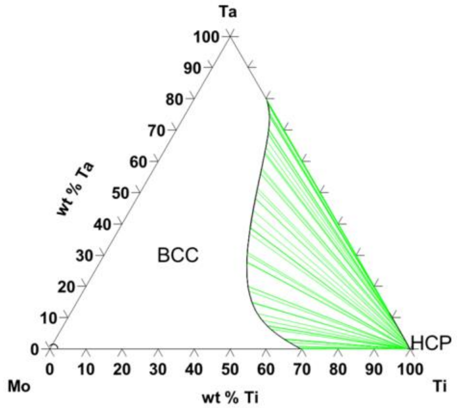

Figure 5. The Ti-Ta-Mo phase diagram at 600 °C modeled using the CALPHAD approach.

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Publications

The following manuscripts were partially or wholly supported by this award.

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6. A. J. Wang, M. Z. He, R. Zhang, Y. Du, D. L. Chen, B. B. Fan, S. L. Shang, and Z. K. Liu, "*Mechanical properties and spinodal decomposition of* $Ti_xAl_{1-x-y}Zr_yN$ *coatings*", Phys. Lett. **A 379**, 2037 (2015).
7. Z. Chen and J.-C. Zhao, "*Experimental determination of impurity and interdiffusion coefficients in Ti-X and Zr-X (X = Mo, Nb, Ta, Zr) binary systems using diffusion multiples*", in final preparation.

Theory-guided Experimental Search of New Classes of Designed Topological Insulators

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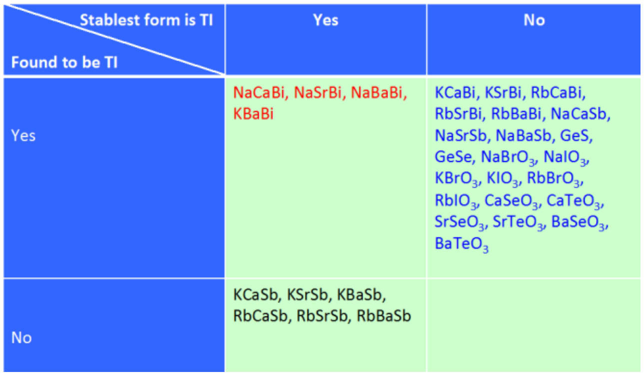
Investigators: Qihang Liu, Xiuwen Zhang, Justin Waugh, Xiaoqing Zhou, CU Boulder; Saicharan Aswartham, Xiangde Zhu and Jasminka Terzic, University of Kentucky.

Keywords: Topological insulators, Spin-polarization; ARPES; DFT; 'Inverse Design'.

Project Scope

We accelerate material development by using *Functionality-Directed material discovery* (also called 'Inverse Design') as follows (a) Develop a science-based "Design Principle" (DP) that reflects a target functionality (F) we are searching for (e.g., for F = topological insulation, DP = specific band inversions). (b) Search via DFT for the specific DP in groups of materials in assumes structures (c) Select those that best satisfy the DP and are thermodynamically stable according to DFT. (d) After narrowing down large pools of potential candidates, subject the "best of class" cases to synthesis and characterization of F. Iterations and feedback are used to refine the DP. In the current DMREF we focus on F = Topological insulation and F = Hidden spin polarization, and F = Rashba semiconductors.



Stablest form is TI / Found to be TI	Yes	No
Yes	NaCaBi, NaSrBi, NaBaBi, KBaBi	KCaBi, KSrBi, RbCaBi, RbSrBi, RbBaBi, NaCaSb, NaSrSb, NaBaSb, GeS, GeSe, $NaBrO_3$, $NaIO_3$, $KBrO_3$, KIO_3, $RbBrO_3$, $RbIO_3$, $CaSeO_3$, $CaTeO_3$, $SrSeO_3$, $SrTeO_3$, $BaSeO_3$, $BaTeO_3$
No	KCaSb, KSrSb, KBaSb, RbCaSb, RbSrSb, RbBaSb	

Figure. Predicted topological insulators in their stablest form (in red) or higher-energy structures (in blue). Related work: X. Zhang, L. B. Abdalla, Q. Liu and Alex Zunger, "Co-evaluation of topological properties and structural stability of ABO3 oxide compounds", In preparation.

Relevance to MGI

This project uses theory-directed screening of materials based on Functionality-Directed discovery as guided by Design Principles, a protocol that was adopted by MGI. Acceleration emerges from dual screening for functionality and stability + growability. We close the loop by iterative feedback between synthesis and properties measurement and theory.

Technical Progress

(1) Theoretical Discovery of new Topological Insulators that are thermodynamically viable**:** Via co-evaluation of TI-ness (via caculation of Z_2) and thermodynamic stability, we find: (a) A number of materials were theoretically predicted to be both stable and TI at the same time (NaCaBi, NaSrBi, NaBaBi, KBaBi,) whereas (b) others were predicted to be TI only in a high energy (non ground state) structures (e.g. KCaBi, RbCaBi, GeS, GeSe, $SrTeO_3$, $BaTeO_3$, see figure above). (c) Many (but not all) materials identified as Topological Insulators on the basis of calculation of band inversion are thermodynamically unstable in the structure S that makes them TI's. Some candidates that are not TI in their ground state (GeS, GeSe, $SrTeO_3$, and $BaTeO_3$) were passed on to our experimental team: synthesis: G. Cao, Kentucky and ARPES: D. Dessau CU) confirming the prediction (no TI). One compound predicted TI and Stable NaBaBi was synthesized by Cao but not characterized as yet. ***Emerging Conjecture:*** Multiple band inversions–associated with the destabilizing occupation of *anti bonding* conduction bands and emptying of bonding valence bands—may be contraindicated with thermodynamic stability if it occurs over significant volume of the Brillouin zone (work in preparation).

(2) Transforming common III-V and II-VI semiconductor compounds into topological heterostructures [5]: We show how a heterovalent superlattice made of common semiconductor building blocks can transform its non-TI components into a topological nanostructure, illustrated by III-V/II-VI superlattice InSb/CdTe. We reveal the relationship between the interfacial stability and the topological transition, finding a "window of opportunity" where both conditions can be optimized. The understanding gained from this study could significantly broaden the current, rather restricted repertoire of functionalities available from individual compounds by creating TI's from non-TI building blocks.

(3) Prediction of spin truncation in non-centrosymmetric semiconductors [6]: We show via first-principles calculations and multi-orbital k • p model that in ordinary materials having multi-orbital hybridization the interplay between spin and various atomic orbital angular momenta leads to two interesting spin effects: (i) the spin magnitude in each band is generally truncated below its maximal value of ±1; and (ii) Since different bands could experience different degrees of spin truncation, a net spin polarization could ensue for the pair of spin-split bands. Spin truncation arises fundamentally from the Spin-orbit induced hybridization of different azimuthal orbital momenta in each band; its dependence on the band index is reflected also in the orbital texture both in topological and non-topological systems.

(4) Polytypism in LaOBiS2-type compounds based on different stacking sequences [7]: $LaOBiS_2$-type materials were generally assumed to have a unique and specific crystallographic structure (with a space group P4/nmm). Using first-principles total energy and stability calculations we find that contrary to this view the three-dimensional structure of this important family of compounds represents instead a family of energetically closely spaced modifications differing, i.e., polytypes, by the layer sequences and orientations. Because the energy difference between the polytypes of $LaOBiS_2$ is relatively small (within several meV/f.u.), the experimentally synthesized crystal could be a mixing of these polytypes.

Future Plans

Plans center on accelerated experimental validation of theoretical predictions, including (i) The materials that are predicted to be stable and TI at the same time will be tested in experiments. (ii) More materials with the functionality of large 'hidden spin polarization' will be further explored by theory and then be synthesized and tested via spin-ARPES. (iii) Additional collaborations are formed with experimental groups interested to examine our prediction of spin truncation effect in BiTeI (item 3) and field-induced TI-ness in III-V/II-VI superlattices or quantum wells (item 2).

Broader impact

(i) This project will validate ***a general platform for discovery of functional materials,*** as described under "scope". Although we focus here on SOC enabled functionalities, the ideas behind this "inverse Design" have far broader implications for discovery many other technology-enabling materials with specialized functionalities. These are otherwise difficult to detect via trial and error or serendipity and include such as 'oxides for electronics' or 'super absorbers for renewable energy' or thermoelectrics. (ii) The specific subject matter dealt with in this DMREF is instrumental for training next generation workforce in materials research and for the education of students.

Data Management and Open Access

(i) The codes that analyze the first principles wave functions to obtain information of band inversions and topological invariant Z_2, will be opened for public access. (ii) The materials predicted in this study will be made publically accessible. (iii) The theoretical data is currently saved in Extreme Science and Engineering Discovery Environment (XSEDE), which will be transferred to publically accessible sources.

Publications credited to DMREF

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[5] Q. Liu, X. Zhang and A. Zunger, *Transforming common III-V and II-VI semiconductor compounds into topological heterostructures: The case of CdTe/InSb superlattices*, Submitted, under review (2015).
[6]. Q. Liu, X. Zhang, J. A. Waugh, D. S. Dessau and A. Zunger, *Truncation of spin polarization in semiconductors via spin-orbit induced orbital hybridization*, Submitted, under review (2015).
[7]. Q. Liu, X. Zhang and A. Zunger, *Polytypism in LaOBiS2-type compounds based on different three-dimensional stacking sequences of two-dimensional BiS2 layers*, Submitted, under review (2015).

Poster List

NSF/DOE Materials Genome Initiative
Principal Investigators' Meeting

Poster Session I

Monday, January 11, 2016

1. **Nicholas L. Abbott**, University of Wisconsin-Madison
   Chemoresponsive Liquid Crystals Based on Metal Ion-Ligand Coordination

2. **Douglas Adamson**, University of Connecticut
   Polymeric Composites and Foams Based on Two Dimensional Surfactants

3. **Rakesh Agrawal**, Purdue University
   Rapid Design of Earth Abundant Inorganic Materials for Future PVs

4. **John Allison**, University of Michigan
   Center for PRedictive Integrated Structural Materials Science (PRISMS)

5. **Raymundo Arróyave**, Texas A&M University
   Accelerating the Development of Phase-Transforming Heterogeneous Materials: Application to High Temperature Shape Memory Alloys

6. **David Baker**, University of Washington
   Integrating Theory, Computation and Experiment to Robustly Design Complex Protein-Based Nanomaterials

7. **Zhenan Bao**, Stanford University
   High-Throughput Morphology Prediction for Organic Solar Cells

8. **Mark Bathe**, Massachusetts Institute of Technology
   Computational Design Principles for Functional DNA-Based Materials

9. **Katia Bertoldi**, Harvard University
   Biologically Inspired Optimized Materials and Technologies Transformed by Evolutionary Rules (BIOMATTER)

10. **Kaushik Bhattacharya**, California Institute of Technology
    Designing Microstructure for Engineering Toughness

11. **Simon Billinge**, Columbia University
    Novel, Data Validated, Nanostructure Determination Methods for Accelerating Materials Discovery

12. **Geoff Brennecka**, Colorado School of Mines
    Computation of Undiscovered Piezoelectrics and Linked Experiments for Design

13. **Michael Brenner**, Harvard University
    Self Assembly with DNA-Labeled Colloidal Particles and DNA Nanostructures

14. **Donald Brenner**, North Carolina State University
    Designing of Material-Liquid-Nanoparticle Interfaces for Tribological Control

15. **William Butler**, University of Alabama
    First-Principles Based Design of Spintronic Materials and Devices

16. **Marie-Carme Calderer**, University of Minnesota – Twin Cities
Materials Engineering of Chromanic and Colloidal Liquid Crystals via Mathematical Modeling and Simulation

17. **R.W. Carpick**, University of Pennsylvania
High-Throughput Discovery, Development, and Demonstration of Material Systems to Enable Low-Power NEMS-Based Computation

18. **Michael Chabinyc**, University of California – Santa Barbara
Controlling Hierarchical Nanostructures in Conjugated Polymers

19. **Ravi Chandran**, University of Utah
Computational Design, Rapid Processing, and Characterization of Multiclass Materials from Ti-B-X Platform

20. **James Chelikowsky**, University of Texas at Austin
Design and Synthesis of Novel Magnetic Materials

21. **Hai-Ping Cheng**, University of Florida
Exploring Multi-functional Molecular Electronic Materials

22. **Peter Collins**, Iowa State University
Collaboration to Accelerate the Discovery of New Alloys for Additive Manufacturing

23. **Vincent Conticello**, Emory University
Helical Protein Assemblies by Design

24. **Michael Demkowicz**, Massachusetts Institute of Technology
Designing and Synthesizing Nano-metallic Materials that Resist Flow Localization under Mechanical Deformation

25. **Chang-Beom Eom**, University of Wisconsin – Madison
Multifunctional Interfacial Materials by Design

26. **Elif Ertekin**, University of Illinois, Urbana-Champaign
Discovery and Design of Ferromagnetic Inverse-Entropy Shape Memory Alloys by Quantum Mechanical Simulation and Experiment

27. **Amar Flood**, Indiana University
Multiscale Theory for Designing Hierarchical Organic Materials Formed by Self-Assembly

28. **David Ford**, University of Massachusetts
Synthesis of Colloidal Crystals Guided by Particle-Based Theory and Simulation

29. **Seth Fraden**, Brandeis University
Programmable Chemomechanical Materials

30. **Glenn H. Fredrickson**, University of California, Santa Barbara
Computationally Driven Discovery and Engineering of Multiblock Polymer Nanostructures Using Genetic Algorithms

31. **C.M. Friend**, Harvard University
High-Throughput Computation and Machine Learning for Understanding and Designing Catalysts

32. **Laura Gagliardi**, University of Minnesota
Inorganometallic Catalyst Design Center

33. **William Goddard**, California Institute of Technology
Multiscale Theory and Experiment in Search for and Synthesis of Novel Nanostructured Phases in BCN Systems

34. **Jeffrey Greeley**, Purdue University
Design of Multifunctional Catalytic Interfaces from First Principles

35. **Francois Gygi**, University of California, Davis
High-Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling

36. **Ronald Hedden**, Texas Tech University
Combinatorial Methods to Enable Rapid Prototyping of Polymeric Pervaporation Membranes for Bio-alcohol Recovery

37. **Hendrik Heinz**, University of Colorado, Boulder
Design and Testing of Nanoalloy Catalysts in 3D Atomic Resolution

38. **Clifford Henderson**, Georgia Institute of Technology
Rapid Design and Engineering of Materials Systems for Nanomanufacturing via Directed Self-Assembly

39. **Graeme Henkelman**, University of Texas, Austin
Toolkit to Characterize and Design Bi-functional Nanoparticle Catalysts

40. **John Herbert**, The Ohio State University
Fragment-Based Quantum Chemistry for Non-Covalent Interactions and Excitation Energy Transfer

41. **Andreas Heyden**, University of South Carolina, Columbia
Design and Discovery of Multimetallic Heterogeneous Catalysts for a Future Biorefining Industry

42. **Elizabeth Holm**, Carnegie Mellon University
Mechanics of Three-dimensional Carbon Nanotube Aerogels with Tunable Junctions

43. **Kendall N. Houk**, University of California, Los Angeles
Iterative Theoretical Morphology Prediction, Synthesis, and Characterization of Novel Donor Oligomer for Accelerated OPV Materials

44. **Robert Hull,** Rensselaer Polytechnic Institute
Real Time Control of Grain Growth in Metals

45. **Michael Janik**, Pennsylvania State University
Computationally Guided Design of Multicomponent Materials for Electrocatalytic Cascade Reactions

46. **Debdeep Jena**, Cornell University
Extreme Bandgap Semiconductors

47. **Jeremiah Johnson**, Massachusetts Institute of Technology
Analysis and Optimization of Polymer Networks for Emerging Applications

48. ***Peter Johnson**,* Brookhaven National Laboratory
Center for Emergent Superconductivity: Designing New Correlated Electron Systems

49. **Tresa Pollock,** University of California, Santa Barbara
Accelerating the Design and Synthesis of Multicomponent, Multiphase Metallic Single Crystals

50. **Yunzhi Wang**, The Ohio State University
Accelerated Development of Next Generation Ti Alloys by ICMSE Exploitation of Non-Conventional Transformation Pathways

51. **Thomas Proffen,** Oak Ridge National Laboratory
Accelerated Development of Next Generation Ti Alloys by ICMSE Exploitation of Non-Conventional Transformation Pathways

NSF/DOE Materials Genome Initiative
Principal Investigators' Meeting

Poster Session II

Tuesday, January 12, 2016

1. **Yung Joon Jung,** Northeastern University
   Engineering Strong, Highly Conductive Nanotube Fibers via Fusion

2. **Kathleen Kash**, Case Western Reserve University
   Heterovalent Ternary Nitride Semiconductors and Mixed Ternary-Binary Heterostructures

3. **Chandler Becker**, NIST
   The NIST Materials Resource Registry as a Platform to Improve Data Discoverability

4. **John Kieffer**, University of Michigan, Ann Arbor
   Simulation-Based Predictive Design of All-Organic Phosphorescent Light-Emitting Molecular Materials

5. **Paul R. C. Kent,** Oak Ridge National Laboratory
   Network for Ab Initio Many-Body Methods

6. **Stephen Klippenstein***,* Argonne National Laboratory
   An Ab Initio Transition-State-Theory-Based Master Equation Code for Elementary Kinetics

7. **Irena Knezevic,** University of Wisconsin, Madison
   Coupling Electrons, Phonons, and Photons for Nonequilibrium Transport Simulation

8. **Sanat Kumar,** Columbia University
   Modeling and Inverse Design of Anisotropic DNA-Mediated Colloidal Self-Assembly

9. **Robert Kohn**, New York University
   Adaptive Fine-Scale Structure Design: From Theory to Fabrication

10. **Enrique Lavernia**, University of California, Davis
    Engineering Strength and Toughness into HCP Metals Using Twin Meshes

11. **James Lewis**, West Virginia University
    Designing Tunable Au-Based Bimetallic Nanocatalysts

12. **Patrick Mather**, Syracuse University
    Laminated Elastomer Composites with Anisotropic Shape Memory

13. **Paul McEuen,** Cornell University
    Graphene Based Origami and Kirigami Metamaterials

14. **Efstathios Meletis**, University of Texas – Arlington
    Multiscale Design of Hard and High Temperature Resistant Coatings by Computation and Experiment.

15. **Thomas Miller**, California Institute of Technology
    Next-Generation Nanostructured Polymer Electrolytes by Molecular Design

16. **Michael Mills**, The Ohio State University
Mechanistic and Microstructure-Based Design Approach for Rapid Prototyping of Superalloys

17. **Tim Mueller**, Johns Hopkins University
Design of Nanoscale Alloy Catalysts from First Principles

18. **Sankar Nair**, Georgia Institute of Technology
Accelerating the Discovery and Development of Nanoporous 2D Materials (N2DMs) and Membranes for Advanced Separations

19. **Jens Nørskov**, SLAC National Accelerator Laboratory, Stanford University
Predictive Theory of Transition Metal Oxide Catalysis

20. **Elsa Olivetti**, Massachusetts Institute of Technology
Data Mining and Analytics for Predictive Synthesis, Accelerating Realization of Advanced Materials

21. **Shyue Ping Ong**, University of California, San Diego
Design of Novel Sodium Superionic Conductors using Integrated High-Throughput First Principles Calculations, Data Mining and Experiments

22. **Greg Payne,** University of Maryland
Thin Film Biofabrication for Integrated Bio-electronics

23. **John P. Perdew,** Temple University
SCAN+rVV10: A Promising Density Functional for Layered Materials

24. **John H. Perepezko,** University of Wisconsin, Madison
A Combined Experiment and Simulation Approach to the Design of New Bulk Metallic Glasses

25. **Warren Pickett**, University of California, Davis
Discovering Insulating Topological Insulators

26. **Darrin Pochan,** University of Delaware
Programmable Peptide-Based Hybrid Materials

27. **Karin Rabe**, Rutgers University
High-Throughput Mapping of Functional Dielectric/Metallic Heterostructures

28. **Aldo Humberto Romero**, West Virginia University
Search for Magneto-electronic Behavior in Complex Fluoride-based Interfaces

29. **Sapna Sarupria**, Clemson University
An Integrated Multiscale Modeling and Experimental Approach to Design Fouling-Resistant Membranes

30. **Darrell Schlom**, Cornell University
Closing the Loop to Make the World's Strongest Ferromagnetic Ferroelectric

31. **Jan Schroers**, Yale University
High-Throughput Simulations and Experiments to Develop Metallic Glasses

32. **Sergei Sheiko**, University of North Carolina, Chapel Hill
Acoustically Transformative Materials

33. **Joern Ilja Siepmann,** University of Minnesota
Nanoporous Materials Genome: Methods and Software to Optimize Gas Storage, Separation, and Catalysis

34. **Randall Snurr**, Northwestern University
Simulation-Driven Design of Highly Efficient MOF/Nanoparticle Hybrid Catalyst Materials

35. **Volker Sorger**, The George Washington University
Theory-Enabled Development of 2D Metal Dichalcogenides as Active Elements of On-Chip Silicon-Integrated Optical Communication

36. **Frank Spano**, Temple University
Developing Design Rules for Enhancing Mobility in Conjugated Polymers

37. **Eric Toberer,** Colorado School of Mines
Computationally Driven Targeting of Advanced Thermoelectric Materials

38. **Zachary Trautt**, NIST
Facilitating the Development of Modular Data Models in Materials Science

39. **Mark Tuckerman**, New York University
Development of Design Rules for High Hydroxide Transport in Polymer Architectures

40. **Yasutomo Uemura**, Columbia University
Designing, Understanding and Functionalizing Novel Superconductors and Magnetic Derivatives

41. **Chris Van de Walle**, University of California, Santa Barbara
Design and Fabrication of Wide-Band-Gap Nitride-Based Alloys

42. **Anton Van der Ven**, University of California, Santa Barbara
Integrated Computational Framework for Designing Dynamically Controlled Alloy-Oxide Heterostructures

43. **David Vanderbilt,** Rutgers University
Enhanced Functionalities in 5d Transition-Metal Compounds from Large Spin-Orbit Coupling

44. **Michael Weinert**, University of Wisconsin, Milwaukee
Emergent Functionalities at the Epitaxial Interfaces of Correlated and Spin-Orbit Materials

45. **Steven White**, University of California, Irvine
Speeding Up Strongly Correlated Calculations: Wavelet Coarse Graining and Machine-Learned Density Functionals

46. **Lian Yu**, University of Wisconsin, Madison
Engineering Organic Glasses

47. **Ji-Cheng Zhao**, The Ohio State University
Design Knowledge Base of Low-Modulus Titanium Alloys for Biomedical Applications

48. **Alex Zunger**, University of Colorado – Boulder
Theory-Guided Experiments in Search of Designed Topological Insulators and Band-Inverted Insulators

49. **William Tumas**, NREL
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