The background of the cover is filled with numerous spheres of varying sizes and colors. The colors include white, light blue, red, and cyan. Some spheres are solid, while others are partially colored or have small green and red dots on their surface. The spheres are arranged in a somewhat random, overlapping pattern, creating a sense of depth and complexity.

CHMaD

Center for Hierarchical Materials Design

YEAR IN REVIEW 2014

CHiMaD

Center for Hierarchical Materials Design

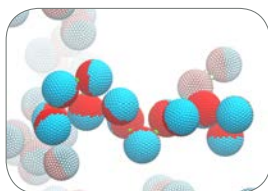
YEAR IN REVIEW

2014

Editor:

Emine Begum Gulsoy, Ph.D.

Associate Director, CHiMaD



ON THE COVER Self-assembly of colloids with anisotropic dielectric properties (red and blue surfaces), bound by charged nanoparticles (green). Depending on the solvent selected, the nanoparticles preferentially bind (electrostatically) to surfaces with either low or high dielectric constant, thus opening the possibility of generating solvent-dependent structures. From molecular dynamics simulations with fully resolved dielectric effects, performed by Huanxin Wu and Erik Luijten.

TABLE OF CONTENTS

| | |
|--|----|
| FOREWORD: A Message from the Directors | ii |
| MISSION AND VISION | 1 |
| RESEARCH | 2 |
| Data Mining | 2 |
| Polymer Matrix Materials..... | 6 |
| Low-Dimensional Nanoelectronic Materials..... | 12 |
| Precipitation-Strengthened Alloys..... | 18 |
| In-Situ Si-Composite Materials | 26 |
| Directed Self-Assembly of Block Copolymers Films for Lithographic Applications..... | 29 |
| Biomaterials..... | 38 |
| Organic Bulk Heterojunction Polymer Solar Cells..... | 43 |
| TOOL DEVELOPMENT | 50 |
| OUTREACH | 52 |
| HONORS AND AWARDS | 54 |
| PUBLICATIONS | 56 |
| CONTACTS | 57 |

FOREWORD



We are pleased to present the first annual report of the Center for Hierarchical Materials Design (CHiMaD), the National Institute for Standards and Technology (NIST) Center of Excellence in Advanced Materials. CHiMaD is focused on achieving the goals of the Materials Genome Initiative (MGI), set forth by President Obama and his administration. We are committed to achieving these goals through the development of broad research and outreach programs that involve participants from university, national laboratory and industry. Central to these programs are the many collaborative efforts that we have developed with NIST. It is these collaborative efforts that make our center unique, and which ensure that we shall attain the goals of the MGI on a national level.

CHiMaD is demonstrating the power and potential of bringing together data science, computational approaches and state-of-the-art experiments to design materials ranging from cobalt alloys for bearing applications to polymers for photovoltaics. The research effort compasses 35 principal investigators, 27 postdoctoral research fellows, 38 graduate students and four undergraduate students working on CHiMaD research projects. This report presents the objectives and accomplishments of our eight use-case groups, and multiple tool development efforts. The breadth of our portfolio allows us to interact with a broad spectrum of the industrial community, as well as to involve many NIST scientists. We are also working towards being a resource for the Nation through the sponsorship of workshops and summer schools. During this inaugural year we have already sponsored four workshops on topics from the development of CALPHAD protodata repositories to computational methods for coarse grain simulations of polymers. CHiMaD is also developing the computational and experimental tools needed for materials design and the Nation's materials research community.

As you will see from the following report, CHiMaD is off to a very fast start. Our first year has set a firm foundation for success in the future. We look forward to making the promise of the Materials Genome Initiative a reality.

Juan De Pablo, Gregory Olson, Peter Voorhees
Co-Directors, CHiMaD

MISSION AND VISION

MISSION *Accelerating materials discovery and commercialization by design and development of hierarchical methods and materials and enabling the complete integration of theory, computation and experimentation by building a strong community of current and future researchers.*

The Center for Hierarchical Materials Design (CHiMaD) is a NIST-sponsored center of excellence for advanced materials research that is focused on developing the next generation of computational tools, databases, and experimental techniques in order to enable the accelerated design of novel materials and their integration to industry, one of the primary goals of the Obama administration's Materials Genome Initiative (MGI).

This Chicago-based consortium includes Northwestern University (NU), University of Chicago (UChicago), Northwestern-Argonne Institute for Science and Engineering (NAISE) — a partnership between Northwestern University and Argonne National Laboratory (ANL) — and the Computational Institute (CI) — a partnership between University of Chicago and Argonne National Laboratory. The consortium is also partnered with Questek Innovations, a pioneering materials design company, ASM International and Fayetteville State University.

Designing novel materials of specific properties for a particular application requires simultaneously utilizing physical theory, advanced computational methods and models, materials properties databases and complex calculations. This approach stands in contrast to the traditional trial-and-error method of materials discovery. CHiMaD aims to focus this approach on the creation of novel "hierarchical materials" that exploit distinct structural details at various scales, from the atomic on up, to obtain enhanced properties. The Center's research focuses on both organic and inorganic advanced materials, in fields as diverse as self-assembled biomaterials, smart materials for self-assembled circuits, organic photovoltaic materials, advanced ceramics and metal alloys.

CHiMaD OBJECTIVES

- To *foster* hierarchical materials discovery, in accordance with the goals of MGI and NIST, by developing the next generation of computational tools, databases and experimental techniques
- To *connect* and *convene* the current experts and the next generation of scientists by advancing the multi-disciplinary and multi-sector communication through workshops, seminars, training opportunities and meetings
- To *provide* opportunities to transition new breakthroughs in advanced materials to industry
- To *adopt* a seamless integration of prediction, measurement and interpretation
- To *maintain* and *advance* the collective knowledge on material systems and methodologies
- To *serve*, together with NIST, as a national resource for verified codes and curated databases that will enable proliferation of a materials-by-design strategy and materials discovery through US industry partners
- To *build* on the established success in metal alloys systems to prove generality of the materials-by-design approach through application to both inorganic and organic advanced systems for both structural and multifunctional applications
- To *expand* the 3D and 4D characterization methods for hard materials design and to bring such methods to the forefront of soft materials design

DATA MINING

Alok Choudhary (co-lead)¹, Ankit Agrawal (co-lead)¹, Gregory B. Olson², Christopher Wolverton², Wei Chen³

¹Electrical Engineering and Computer Science, Northwestern University

²Materials Science and Engineering, Northwestern University

³Mechanical Engineering, Northwestern University

The CHiMaD data mining team is working towards making significant advances in data-driven informatics to accelerate materials discovery. In this era of big data, we are being bombarded with huge volumes of data from a variety of different sources (experiments, simulations) at unprecedented rates in practically all fields of science and engineering, and materials science is no exception. Advanced techniques for data-driven analytics are needed to analyze all this data in ways that can help extract meaningful information and knowledge from it, and thus contribute to accelerating materials discovery and the vision of Materials Genome Initiative. The diversity and expertise within the CHiMaD team provides unique opportunities for collaborations among materials scientists and computer scientists to realize this goal. This requires designing and developing specific analytics and data mining approaches for problems in materials science, and evaluating the resulting insights/discoveries via necessary experiments and simulations. The long-term vision is to work with NIST to enable data-to-discovery (or actionable insights) at unprecedented latency through summary statistics, query, reporting, analysis, bottom-up as well as hypothesis-driven discoveries and data mining on various heterogeneous and big databases that are complex, high dimensional, structured and semi-structured.

DESIGN GOALS

The primary goal for this reporting period was to identify important problems in materials science that can benefit from data-driven informatics, and kick-off collaboration(s) with domain scientists within the CHiMaD team. To this end, we have initiated three specific collaborations in materials informatics building on our prior work in the field. One of them aims to design an effective interface between data mining techniques and the CALPHAD methodology for materials genomic design, with an illustrative application of advanced steel design using NIMS steel data. Another collaboration aims to use machine learning to discover functional relationships between material properties and quantitative attributes derived from the composition of the material. It is built on our previous work on data-driven discovery of stable compounds, and we expect our technique to be applicable

to and capable of solving a broad variety of materials problems. Finally, the third collaboration uses machine learning to identify key microstructure descriptors from a vast array of candidates as potential microstructural design variables, which is an important research question in microstructure representation.

SIGNIFICANT ACCOMPLISHMENTS

A team of undergraduates in our special Murphy Scholar section of Freshman Design collaborated with **Agrawal, Choudhary, Olson**, and research associate Wei Xiong to initiate our research on the integration of a process-property database with a CALPHAD database for fusion of prior knowledge with data in the adaptation of data mining techniques.

In collaboration with **Agrawal, Choudhary, and Wolverton**, doctoral student Logan Ward has developed a new hierarchical modeling technique on DFT data that has been demonstrated to be very effective for the problem of band gap prediction from material composition.

In collaboration with **Chen and Choudhary**, doctoral students Hongyi Xu and Ruoqian Liu developed a machine learning based design representation method for designing heterogeneous microstructures. This work won the best paper award at the 40th ASME Design Automation Conference, 2014.

RESEARCH ACCOMPLISHMENTS

Integrating CALPHAD and data mining for advanced materials design

The CALPHAD (CALculation of PHase Diagrams) approach is currently considered as one of the most promising approaches for materials genomic design. The great advantage of the CALPHAD approach is model-prediction of a multi-component system based on self-consistent optimization. The developed CALPHAD database is easy to couple with other models in order to extend its capability of describing multi-scale phase behavior. Thanks to mature computational software, like Thermo-Calc, the development and applications of the CALPHAD approach have been greatly accelerated over the years. However, so far, there is no comprehensive research available integrating the CALPHAD and data mining methodologies for advanced materials design.

This work involving a collaboration of **Agrawal, Choudhary, Olson**, and research associate Wei Xiong, aims to design an effective interface between data mining techniques and the CALPHAD methodology for materials genomic design. The research studies are performed on the carbon steels with raw data sets obtained from experiments provided by NIMS (National Institute for Materials Science, Japan).

In Spring 2014, a team of undergraduates in our special Murphy Scholar section of Freshman Design collaborated with our team to initiate our research on the integration of a process-property database with a CALPHAD database for fusion of prior knowledge with data in the adaptation of data mining techniques for greater accuracy

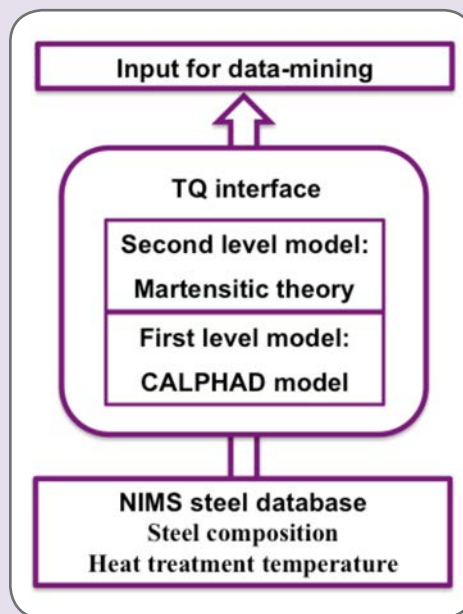


Figure 1. Flowchart for implementing theoretical models using CALPHAD database in data mining.

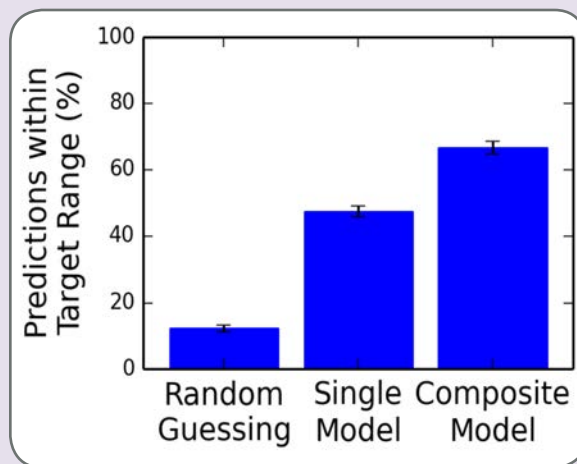


Figure 2. Performance of three different strategies to locate 30 compounds with a band gap energy between 0.9 and 1.7 eV out of a set of 2500 candidates from the ICSD. The first strategy is to randomly select a nonmetal-containing compound. The other two strategies are to use a model produced using the machine-learning-based method described in this work that was trained on the band gap energies of a distinct set of 22667 compounds from the ICSD to locate compounds with band gap energy within the desired range. The first of those two strategies uses a single model trained on all compounds in the training set, and the latter uses the composite predictions of a several models each trained on different groups of similar compounds. Error bars represent the 95% confidence interval.

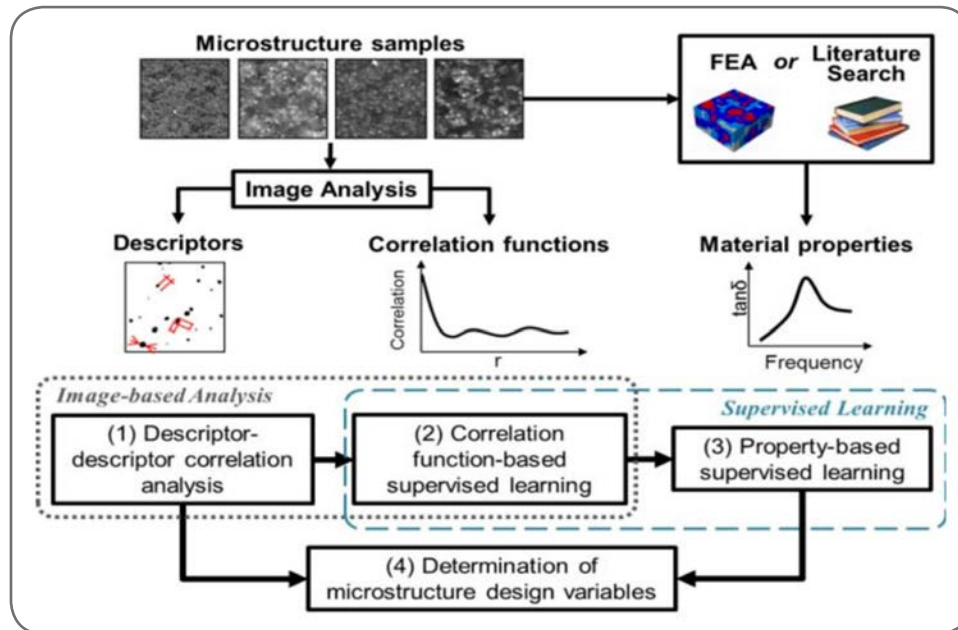


Figure 3. The framework of machine learning-based microstructure descriptor identification.

of process-structure-property correlation. Using a subset of the full process-property database, the team demonstrated stronger correlation for a subset of steels compared to previous data mining using the process-property data alone. Research associate Wei Xiong, who is a CALPHAD technology expert educated at the Royal Institute of Technology (KTH) in Sweden, coached the team.

After the student pilot project, Xiong continued the research developing a TCICP-based link to automate interaction of the Thermo-Calc CALPHAD software with the full process-property database and mining tools in collaboration with **Agrawal**. An interface is being built between the Thermo-Calc Gibbs energy module and the input database for data mining using TQ toolkit in the Thermo-Calc software package, which can read both experimental data and thermodynamic models from Thermo-Calc database, and further convert them into important physical properties using physical metallurgical models of steels. The flow chart of the constructed interface is shown in Figure 1. The resulting data would be analyzed by data mining techniques to mine process-structure-property (PSP) relationships.

General-Purpose Machine Learning Strategy for Predicting Properties of Inorganic Materials

In recent years, there has been significant focus towards using material property databases and combinatorial searches to accelerate materials discovery. One goal of modern

materials science is to use these datasets to create predictive models for material properties, which may be approached using machine learning. While previous approaches have been successful in predicting a single property of a single class of materials, no one has yet introduced a single method that is capable of producing predictive models capable of solving a broad variety of materials problems. In a collaboration among **Agrawal**, **Choudhary**, and **Wolverton**, doctoral student Logan Ward has developed such a method and applied it to a variety of material property databases, including ones containing crystalline and amorphous materials. The method works by using machine learning to discover functional relationships between material properties and quantitative attributes derived from the composition of the material. It employs a set of attributes broad enough to capture important chemical effects for multiple materials problems and introduce a hierarchical modeling strategy to enhance the accuracy of our models by partitioning the databases into subsets of similar materials. This new method can be used to learn novel design rules, predict the properties of yet-unstudied materials, and dramatically accelerate combinatorial searches. Figure 2 presents an illustrative application of the method for a simulated search for compounds suitable for use in a single-layer solar cell. In order to optimize efficiency, a candidate compound needs to at least have a band gap between 0.9 – 1.7 eV. Many other properties are necessary for a suitable solar cell material, but a

| Data Mining Group Researchers and Their Roles | | | |
|--|-------------------------|-----------------------------|--|
| Name | Position | Institution/ Affiliation | Project Title (PI) |
| Alok Choudhary | PI | NU/EECS | <i>Data Mining</i> |
| Ankit Agrawal | PI | NU/EECS | <i>Data Mining</i> |
| Gregory B. Olson | PI | NU/MSE | <i>Materials Design</i> |
| Christopher Wolverton | PI | NU/MSE | <i>DFT</i> |
| Wei Chen | PI | NU/ME | <i>Design Methods</i> |
| Wei Xiong | Postdoctoral Researcher | NU/MSE | <i>Materials Design (Olson)</i> |
| Logan Ward | Graduate student | NU/MSE | <i>DFT (Wolverton)</i> |
| Amar Krishna | Graduate student | NU/EECS | <i>Data Mining (Choudhary/Agrawal)</i> |
| Ruoqian Liu | Graduate student | NU/EECS | <i>Data Mining (Choudhary/Agrawal)</i> |

favorable band gap energy is a requirement. The ability to locate materials that are likely to have a desirable band gap can therefore act as an initial screen.

Machine Learning-based Design Representation Method for Designing Heterogeneous Microstructures

In designing microstructural materials systems, one of the key research questions is how to represent the microstructural design space quantitatively using a descriptor set that is sufficient yet small enough to be tractable. Existing approaches describe complex microstructures either using a small set of descriptors that lack sufficient level of details and require prior empirical identification and selection, or using generic high order microstructure functions of infinite dimensionality without explicit physical meanings. In a collaboration between **Chen** and **Choudhary**, doctoral students Hongyi Xu and Ruoqian Liu have developed a machine learning-based method (Figure 3) that solves this problem by effectively reducing the infinite dimension of the microstructure design space to a small set of descriptors without a significant information loss. With a large number of candidate microstructure descriptors collected from literature covering a wide range of microstructural material

systems, the method is able to perform 4-fold of functionalities: (1) eliminate redundant microstructure descriptors via image analyses, (2) identify key microstructure descriptors based on microstructure morphology, (3) identify key microstructure descriptors based on structure-property relationship, and (4) determine the final set of microstructure design variables. The benefits are demonstrated by an example of polymer nanocomposites optimization. The designs are compared using key microstructure descriptors versus using empirically chosen microstructure descriptors to validate the proposed method.

PUBLICATIONS

Xu, H., Liu, R., **Choudhary**, A., and **Chen**, W., "A Machine Learning-Based Design Representation Method for Designing Heterogeneous Microstructures", IDETC2014-34570, August 17-20, Buffalo, New York, 2014. Best Paper Award, 40th ASME Design Automation Conference. This work was not directly supported by CHiMaD, but reported as a research highlight, and laid the foundation for the PIs' collaboration within CHiMaD. ■

POLYMER MATRIX MATERIALS

L. Catherine Brinson (lead)^{1,2}, Wei Chen², Sinan Keten³, Erik Lijten^{1,4,5}, Juan de Pablo⁶

¹Department of Materials Science and Engineering, Northwestern University

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While polymer composites are lightweight and corrosion resistant with tailorable properties, their capabilities are vastly under-utilized due to lack of: 1) understanding of multiphase composite properties under small constituent changes, 2) ability to tailor electrical and mechanical properties simultaneously, and 3) durability predictions for long-term properties under use conditions. In this Use Case, we promote development of a “materials informatics initiative” including integrated databases, curation, visualization, and analysis tools to relate macroscale polymer composite behavior to chemical constituent and kinetic behavior, and linking these resources to further development of high-performance modeling and predictive tools.

We focus in this project on polymer nanocomposites initially, with long term vision for general composites. The key of multiphase polymer response is to understand the interaction of filler particles with the matrix material and to explore the physical properties of the interphase zone. This is accomplished both by experimental efforts and physics-based modeling using Molecular Dynamics and Monte Carlo simulations to predict interphase polymer response as a function of confinement, crosslinking density and monomer chemistry. At the same time, we are assembling the known data into a central resource, which will be used with supervised learning methods to identify overarching trends. Combining the physics based methodology with the curated experimental data will provide an unprecedented ability to develop new predictive models of composite behavior.

DESIGN GOALS

The ultimate goal for this project is to develop databases, models and tools to enable prediction of hierarchical composite behavior based on constituent components and processing.

The short-term goals of the use-case group are: (1) to design cellulose-polymer nanocomposites with optimized interphase behavior for high modulus/diffusion resistance; (2) to develop Databases/Models/tools to predict interphase properties as well as diffusion and elastic modulus of the system.

Specifically, areas of interest that will be investigated are as follows:

Experiments on local interphase properties: **Brinson** and Gilman (NIST) will be conducting mechanophore, aquaphore

and Atomic Force Microscopy (AFM) experiments on local polymer modulus in interphases.

Models for cellulose polymer nanocomposites: **De Pablo, Keten, Lijten**, Phelan (NIST), Douglas (NIST) will be collaborating to model fluorophores near an interface, predict partitioning of energies and interpret lifetime measurements. They will also be modeling mechanophores and investigating how much energy is required for the bonds to break. In addition, they will work on multi-scale modeling of effective properties such as modulus and diffusion as well as connecting and synergizing Molecular Dynamics, Monte Carlo and Self-Consistent Field models.

Data Structures and databases for poly-mers and composites: **Brinson** and **Chen** will continue building “NanoMine” data

resource for nanocomposites, while **de Pablo** will continue developing the “Polymer Design Database.” These data resources will then be integrated with each other as well as the large dataset resource Ian **Foster** is developing and larger NIST efforts.

SIGNIFICANT ACCOMPLISHMENTS

Brinson group, in collaboration with **Chen**, created the database system “NanoMine” for polymer nanocomposite material systems and developed associated relevant tools, e.g., Niblack local thresholding based TEM/SEM image binarization tool, set up an entry portal into NanoMine, and began to populate a few sample data sets. **Brinson**, in collaboration with Gilman (NIST), also performed local AFM experiments for interphase characterization of epoxy-CNC systems.

Chen group developed a machine learning-based method for identifying the key microstructure descriptors and collaborated with **Brinson** for the database system development.

Keten group studied the elastic properties of interfacial region between graphene and PMMA and predicted the local modulus gradient map, comparing to data from **Brinson**. The confinement of the polymer layer to nanoscale dimensions alters the mechanical response, giving rise to elastic properties that are a function of material geometry as well as bulk material properties. In collaboration with Phelan (NIST), this group is also developing models and algorithms for integration with COMSOFT Workbench.

Luijten group focused on the development of coarse-grained models based upon quantum-mechanical all-atom simulations, with an emphasis on the applicability of these models in self-assembly studies. In the first stage of this project, an all-atom model for linear polyethyleneimine has been developed based upon the CHARMM force field.

De Pablo group developed models to address the rheology of block copolymers and nanocomposites to obtain structure and dynamic information. These results will be connected to the data resources (Polymer Design Database developed and in beta testing) as well as to higher level nanocomposite property prediction schemas by **Keten** and Phelan.

RESEARCH ACCOMPLISHMENTS

The polymer matrix materials group has made significant progress, including experimental measurements of local interphase properties, atomistic, coarse-grained scale simulations, and creating of a platform for data structures and databases for polymers and composites. Below, we summarized the major research accomplishments.



Figure 1. The main page and data entry for the data system “NanoMine” for polymer nanocomposite.

Data Structures and Databases for Polymers and Composites

A significant barrier to understanding and predicting polymer nanocomposite properties is the difficulty of gathering and analyzing all the existing published data. Currently, each researcher must assemble their own limited set of comparison data sets from individual pdf files downloaded from journals, extracting information manually and often with many gaps of details. Huge strides can be made by creating a centralized repository of data which can then be investigated with simple to sophisticated data analysis tools. A significant effort was devoted to developing a novel data resource for polymer nanocomposite, called “NanoMine” (**Brinson, Chen, Zhao**). It leverages the Materials Data Curator (MDC) system developed at NIST with customized data structures for experimental and computational polymer nanocomposites data from both the literature and PIs’ labs. Detailed templates and material data structures (“schemas”) have been developed to account for processing, structure and property information of material systems. The schemas for “NanoMine” material data are set up and follow a systematic approach to group and categorize parameters so that the data entered to the database can be properly curated. For polymer nanocomposite data, processing, structure and property parameters are first divided into five sections, materials, sample processing, measurement methods, data/measured values, microstructure information. Each section contains some key parameters and designing/analysis tools. Figure 1 shows the main page and one data entry snippet. This data system will connect with Polymer Design Database (**de Pablo**) for multiphase polymers which is being developed as a computational tool to predict structural, thermodynamic and dynamic properties of functional polymers and block co-polymers, including phase association of nanoparticles in BCPs.

As a key component of the “NanoMine” system, the image binarization tool is critically needed to characterize the microstructure from TEM/SEM images. A new approach was developed by utilizing the Niblack local thresholding in conjunction with the assumption that the background information of each pixel is highly correlated with the gray-scale values of its neighbor pixels (**Brinson and Cheni**). This technique is an important pre-processing step before the statistical characterization of the materials’ microstructure. By adjusting the size of the neighborhood, we were able to

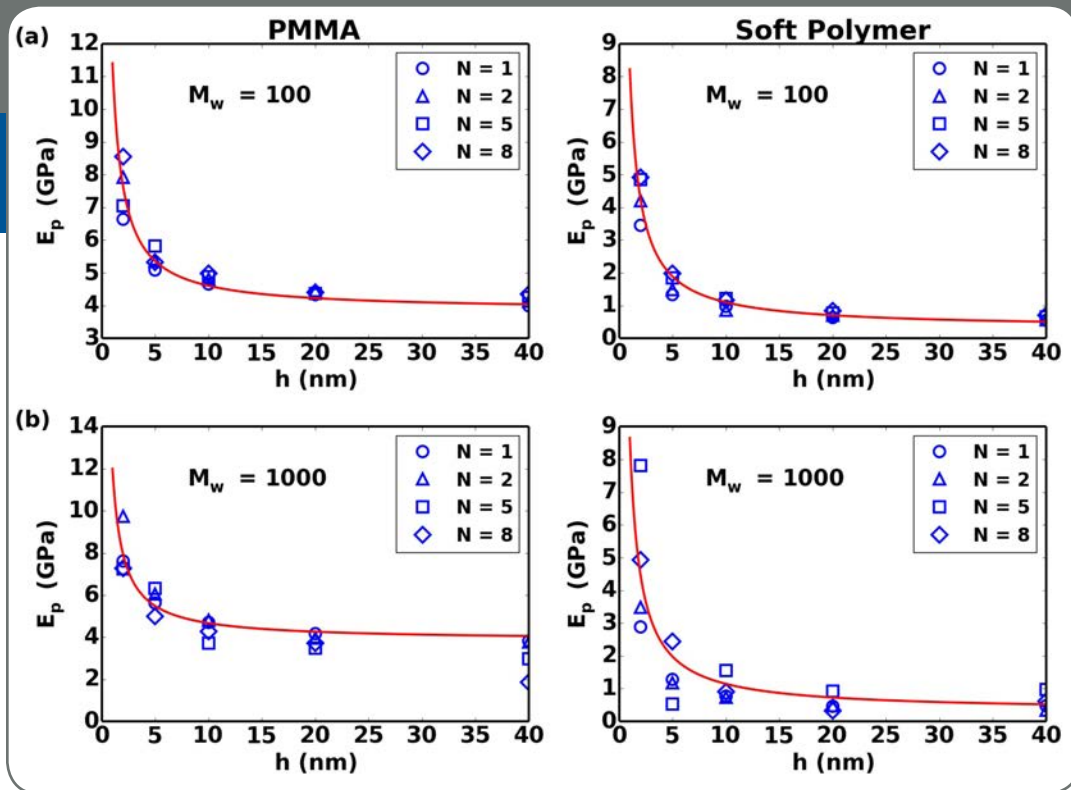


Figure 2. CGMD calculated and model predicted elastic modulus of confined polymer phase for PMMA and soft polymer (with reduced interchain interaction). M_w is the number of monomers per polymer chain, N is the number of graphene sheets in graphene phase, h is the thickness of confined polymer phase, E_p is the elastic modulus of confined polymer phase.

achieve better binarization results than the most commonly used methods.

To build the relationship between microstructure and physical properties, one needs to select and extract the most significant descriptors from a large variable pool. A machine learning-based method was developed for identifying the key microstructure descriptors from the vast array of candidates as potential microstructural design variables (Chen). With a large number of candidate microstructure descriptors collected from literature covering a wide range of microstructural material systems, our method is able to perform 4-fold of functionalities: (1) eliminate redundant microstructure descriptors via image analyses, (2) identify key microstructure descriptors based on microstructure morphology, (3) identify key microstructure descriptors based on structure-property relationship, and (4) determine the final set of microstructure design variables. The benefits are demonstrated by an example of polymer nanocomposites optimization. We compare designs using key microstructure descriptors versus using empirically-chosen microstructure descriptors to validate the proposed method. This work will also supplement the “NanoMine” development (Brinson) and be used in the generation of the models for the nanocomposites.

Experimental Measurements of the Local Mechanical Properties

The key of multiphase polymer response is to understand the interaction of filler particles with the matrix material and to explore the physical properties of the interphase zone. To

characterize the local mechanical properties of polymer thin films and polymer nanocomposites a technique has been developed using AFM indentations (Brinson, Cheng), wherein a spatial map of the gradient of the modulus near an interfaces is obtained. This has been demonstrated on both model nanocomposite systems (flat 1-d controlled systems) and in situ nanocomposites. The properties of the interphase will be used in the models (Keten, de Pablo, Lijten) for the nanoreinforcement-matrix properties.

Nanocellulose is chosen as the reinforcement for our Composites Use Case due to their in-

herent high modulus, surface area and tunable surface chemistry, plus their renewable nature. The Cellulose Nanocrystal (CNC) fibers can be extracted from multiple sources, including wood, bacteria, and tunicate, and exhibit a large range of variations in morphology which were examined by AFM, TEM and NMR. The CNC fibers were further treated by different processing methods, resulting in different surface functional groups and different surface energies. To form nanocomposite materials, the CNC fibers were blended with DGEBA epoxy resin (Diglycidyl Ether of Bisphenol A) using a high speed shear mixer, and then casted into a mold with Polyetheramine curing agent. Model composites were made by bilayer spin-coating of CNC and epoxy onto wafers. The spatial arrangement of CNC networks inside a polymer matrix were investigated by using Förster resonance energy transfer (FRET) method from NIST (Gilman), in which, the interface between CNC and polymer was labeled by fluorescence dye: 5-(4,6-dichlorotriazinyl)-aminofluorescein. Via this method, the dispersion, as well as the interfacial damaging of CNC fibers can be clearly revealed. The mechanical properties of interphase formed by CNC and epoxy are being determined via AFM nanomechanical mapping (Brinson).

Atomistic and Coarse-Grained Simulations

To address the difficulty of accurate prediction of composite properties, a multi-pronged approach has been taken, wherein several modeling approaches at different length scales have been explored and will be integrated and coupled with the database resources. These models all incorporate coarse graining in order to account for the length and

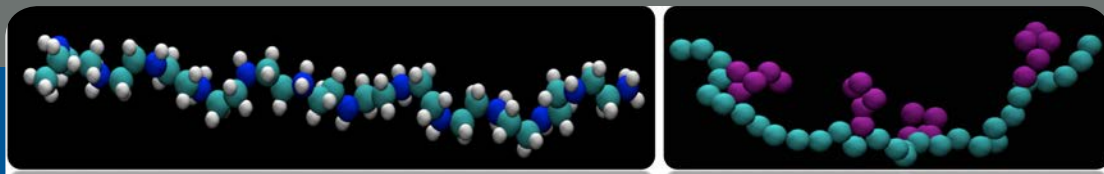


Figure 3. All-atom model for linear polyethyleneimine (PEI, left) mapped onto a coarse-grained model (right). The coarse-grained model will be employed in large-scale molecular dynamics simulations for the prediction of complexation phenomena and self-assembly involving PEI.

time-scales relevant for polymers and polymer-nanoparticle systems. At present, some efforts explicitly consider nanocellulose, while others address model polymers and block copolymer systems and integration of generic nanoparticles.

Numerous studies have shown that a large differential in elastic properties of hard and soft phases in cellulose nanocomposites helps in mitigating crack propagation. However, to date, measurements on the mechanical response of soft interphase layers in such systems and their size-dependent properties have been a source of controversy. We carried out predictive coarse-grained molecular dynamics (CGMD) simulations to address this issue by studying the mechanical properties of atomically layered nanocomposites (**Keten**). The research thus far has focused on model systems consisting of graphene and poly(methyl methacrylate) (PMMA) for which we have previously established experimentally validated CGMD potentials (Hsu et al. *J. Chem. Theo. and Comp*, 2014, Ruiz et al., *Carbon*, 2014). We show directly through simulations on model layer-by-layer graphene-polymer nanocomposites that the confinement of the polymer layer to nanoscale dimensions alters the mechanical response, giving rise to elastic properties that are a function of material geometry as well as bulk material properties. We propose a simple analytical model that quantitatively captures the effect from confinement on the elastic modulus of polymers. (Figure 2) We compare to AFM data from **Brinson's** group on CNT-PMMA systems. We are exploring methods to integrate the coarse graining method developed here into the COMSOFIT workbench.

The interfacial mechanics of cellulose nanocrystals (CNCs) where MD simulations were conducted on (110) and (200) CNCs surfaces interacting with PMMA and amorphous cellulose was also investigated by **Keten**. For hydrophobic material PMMA, interfacial adhesion energy does not vary significantly for different surfaces; while for the hydrophilic material amorphous cellulose, interfacial adhesion energy shows stark differences depending on surface chemistry. The analyses indicate that for the hydrophilic (110) surface, electrostatic interactions would contribute more to the interfacial interactions; and for hydrophobic (200) surface, Van der Waals interactions are dominant. These results pave the way for carrying out systematic MD calculations to tailor interfacial properties in nanocomposites to tune matrix properties and failure mechanisms. We will compare to data from the **Brinson** group.

Significant efforts have also been focused on the development of coarse-grained models based upon quantum-mechanical

all-atom simulations, with an emphasis on the applicability of these models in self-assembly studies (**Luijten**). As a model test case, we chose linear polyethyleneimine (l-PEI), a cationic polymer that has numerous applications and offers significant flexibility, as it can be functionalized with side groups and synthesized in other structures as well, notably dendritic (branched) structures (as shown in Figure 3). In the first stage of this project, we have generated an all-atom model for l-PEI based upon the CHARMM force field. This work has enabled us to make important improvements compared to existing models for the same polymer, notably in the potential-energy surface for the dihedrals. We are currently investigating the consequences of these refinements on the predicted conformations. We will compare to the data from **Brinson** and **Keten** groups.

A particularly important need in the general area of nanocomposites is to develop models capable of describing the linear and non-linear rheology on the basis of molecular models. A model has been developed by relying on a field-theoretic description of the polymeric matrix, a slip-spring description of entanglements, and an explicit representation of the nanoparticles embedded in the polymeric matrix (**de Pablo**). Preliminary results indicate that the model is able to describe the phase behavior of homopolymer nanocomposites, and that of diblock copolymer nanocomposites (see Figure 4). The predictions of the model for macromolecular and nanoparticle diffusion are consistent with experimentally observed trends, and work is now underway to characterize the rheology of the model under shear and elongational deformations. These results will be important in developing predictions of morphology and thus properties, and will be connected to the data resources under development (NanoMine and Polymer Design Database) as well as to higher level nanocomposite property prediction schemes (**Keten**, Phelan).

COLLABORATIONS

Collaboration with Materials Data Curator at NIST

**Collaborators: Alden Dima, Carelyn Campbell
Materials Science and Engineering Division, NIST**

Richard Zhao in **Brinson** group is working with Alden Dima and Carrie Campbell at NIST in using the Materials Data Curator (MDC) developed at NIST for polymer nanocomposite database. Detailed interactions on developing schemas for the data and needs for the MDC as it moves from alpha to beta testing.

Collaboration on Local Polymer Response

Collaborators: Jeff Gilman, Chelsea Davis
Materials Science and Engineering Division, NIST

Xu Cheng (**Brinson** group) is working with Jeff Gilman and Chelsea Davis at NIST on characterizing the local response of polymer near nanocellulose in epoxy. Samples have been exchanged and tested in both labs and Xu Cheng will visit NIST in late January with a longer visit planned later in the year.

Collaboration on Polymer Nanocomposite Databases

Collaborators: Linda Schadler
Materials Science and Engineering Rensselaer Polytechnic Institute (RPI)

Richard Zhao (**Brinson** group) is working together with Wei **Chen** at NU and Linda Schadler at RPI on creating and curating data on polymer nanocomposites and developing the first comprehensive database for polymer nanocomposites. The database is called “NanoMine”.

Collaboration on Machine Learning-based Method

Collaborators: Alok Choudhary
Department of Electrical Engineering and Computer Science, Northwestern University

Chen's group is work together with Ruoqian Liu (**Choudhary** group) and Alok **Choudhary** on the work of “A Machine Learning-based Design Representation Method for Designing Heterogeneous Microstructures”

Collaboration on Polymer Nanocomposite Databases

Collaborators: Irene Hassinger, Linda Schadler
Materials Science and Engineering, RPI

Xiaolin Li (**Chen** group) is collaborating with He Zhao (**Brinson** group) and **Brinson** at Northwestern and Irene Hassinger (Schadler group) and Linda Schadler at RPI on creating and curating data on polymer nanocomposites and developing the first comprehensive database for polymer nanocomposites.

Collaboration on the Development of Force Fields for Polymers in Self-assembly

Collaborator: Hai-Quan Mao
Materials Science and Engineering, Johns Hopkins University

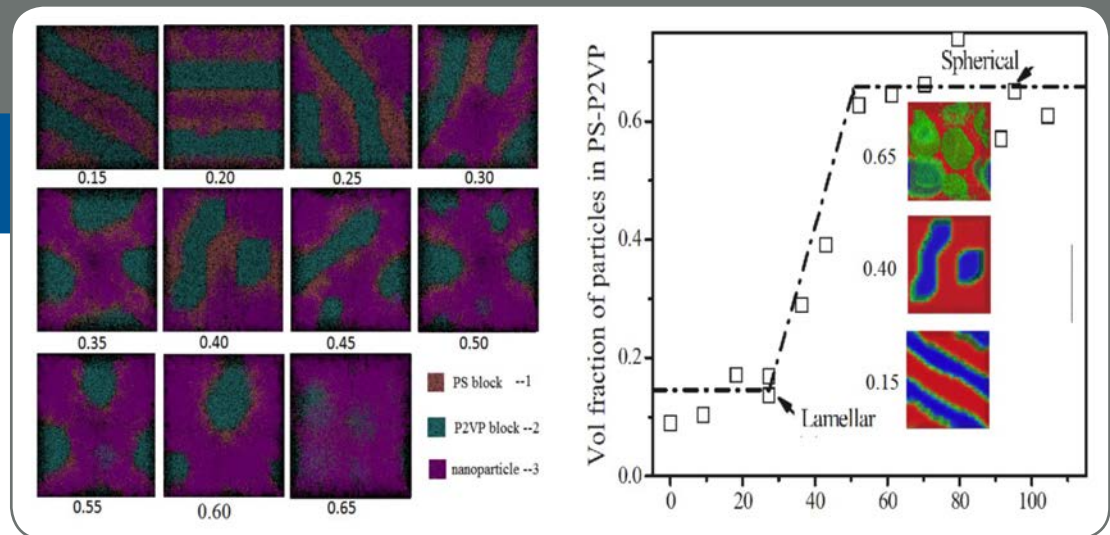


Figure 4. Representative configurations of block copolymer nanocomposite for different nanoparticle loadings. Nanoparticles induce a transition from a lamellar to a spherical phase, in agreement with experiments.

Luijten group has a long-standing collaboration with Prof. Mao's group (partly NIH-funded) on the study of self-assembled nanoparticles for gene delivery. We now have leveraged this collaboration to develop force fields for atomistic simulations of the copolymers involved in this self-assembly. These force fields, which are crucial for quantitative predictive capabilities for polymeric materials, will be tested directly against experimental results obtained in the Mao group, permitting iterative improvement of our models.

CHiMaD Student Zonghui Wei (Luijten) visited the Mao group at Johns Hopkins University for several days to ensure close collaboration between the two research groups. Prof. Mao visited Northwestern University. In addition, we have frequent communications by phone and via Skype.

PUBLICATIONS

Xu, H., Liu, R., **Choudhary**, A., and **Chen**, W., “A Machine Learning-Based Design Representation Method for Designing Heterogeneous Microstructures”, IDETC2014-34570, August 17-20, Buffalo, New York, 2014. Best Paper Award, 40th ASME Design Automation Conference.

DATABASES

NanoMine

System of interest: processing, structure and property parameters are first divided into five sections, materials, sample processing, measurement methods, data/measured values, microstructure information, where the Materials section includes the chemical component and basic properties of the matrix polymer and nano-phase filler. Sample Processing accounts for the procedure during sample preparation, especially the parameters in composite mixing that are important to morphology and subsequently properties of the composite materials. Detailed processing steps for thermoset and thermoplastic are included within respective modules for each type of polymers. Measurement Methods section contains information of the measurement equipment, such as SEM/TEM, DMTA and IR. Such information is the key to account for the conditions

Polymer Matrix Materials Group Researchers and Their Roles

| Name | Position | Institution/ Affiliation | Project Title (PI) |
|----------------------|------------------------------|-----------------------------|--|
| L. Catherine Brinson | PI | NU/MSE | <i>Database development for polymer nanocomposites and interphase property characterization</i> |
| Wei Chen | PI | NU/ME | <i>A Machine Learning-based Design Representation Method for Designing Heterogeneous Microstructures</i> |
| Juan de Pablo | PI | UC/IME | <i>Rheology models of BCPs and coposites; Polymer Design Database development</i> |
| Sinan Keten | PI | NU/CIVIL | <i>Modeling of interface and interphase phenomena in cellulose nanocomposites</i> |
| Erik Luijten | PI | NU/MSE | <i>Force-field-based Development of Effective Potentials for Polymeric Materials</i> |
| Zhiwei Cui | Research Assistant Professor | NU/ME | <i>Computational modeling of polymers and nanoparticles. Also coordinator for Use Case Group (Brinson)</i> |
| Marc Palmeri | Postdoctoral Researcher | NU/MSE | <i>Experimental analysis of polymer composites and nanocomposites (Brinson)</i> |
| Zequn Wang | Postdoctoral Researcher | NU/ME | <i>Hierarchical Materials Design Project (Chen)</i> |
| Chen Shao | Postdoctoral Researcher | NU/ME | <i>Study on mechanical properties of layer-by-layer nanocomposites (Keten)</i> |
| Richard (He) Zhao | Graduate Student | NU/ME | <i>Databases for Polymer Nanocomposites (Brinson)</i> |
| Xiaolin Li | Graduate Student | NU/ME | <i>Image binarization for dielectric polymer nanocomposites (Brinson)</i> |
| Xu Cheng | Graduate Student | NU/ME | <i>AFM for local mechanical properties of polymers in composites (Brinson)</i> |
| Xin Qin | Graduate Student | NU/ME | <i>Interfacial Mechanics of Cellulose Nanocrystals and Nanocomposites (Keten)</i> |
| Zonghui Wei | Graduate Student | NU/AP | <i>Development of effective force fields for polymers in self-assembly (Luijten)</i> |
| Yongrui Su | Graduate Student | UC/IME | <i>Rheology models of BCPs and composites (de Pablo)</i> |

where the property data are obtained. Measured Values section contains property data of the sample with each class of properties in individual module. Finally, the Microstructure section provides the micrograph images and morphology in terms of statistical descriptors.

Methodology: Literatures, Experiments, Finite Element Analysis

Distribution: Public

Link to beta version: <http://puma.mech.northwestern.edu:8001>

Collaborations: He Zhao, Xiaolin Li, L. Catherine **Brinson**, Wei **Chen**, Irene Hassinger (RPI), Linda Schadler (RPI)

Polymer Design Database

System of interest: Characteristic properties for design of polymer blends and copolymers for engineering applications, including DSA. The database is now being populated by resorting to automated techniques that extract target content from the literature. Human intervention is then required to verify relevance and accuracy of computer-generated entries. The database will be tested through a formal course, to be taught at the University of Chicago in

Spring 2015, with collaborators from NIST (Debra Audus and Jack Douglas). The database also includes a thermodynamic property prediction set of modules based on state-of-the-art molecular models.

Methodology: Theory and experiment

Distribution: Not released yet

Collaborations: Juan **de Pablo**, Ian **Foster**, Paul **Nealey**, and Heinrich **Jaeger**

Prediction of Phase Behavior of Polymers and Polyelectrolytes

Database and Simulation Software, this software is being developed jointly with the “Directed-Self Assembly of Block Copolymers Films for Lithographic Applications” use case group. Please refer to that Use Case for additional information.

System of interest: Polymer blends, polyelectrolytes, copolymers

Methodology: Computational and experimental

Distribution: Under development

Collaborations: Juan **de Pablo**, Ian **Foster**, Paul **Nealey**, Matthew **Tirrell**, Heinrich **Jaeger**, Jack Douglas, Carl Freed ■

LOW-DIMENSIONAL NANOELECTRONIC MATERIALS

Mark C. Hersam (lead), Lincoln J. Lauhon

Department of Materials Science and Engineering, Northwestern University

The Low-Dimensional Nanoelectronic Materials use-case group seeks to understand and realize p-type and n-type doping in the low-dimensional limit. Since low-dimensional nanoelectronic materials have exceptionally high surface area to volume ratios, doping can be realized via two qualitatively different pathways: conventional substitutional doping and surface chemical functionalization. Furthermore, contacts can be designed to selectively inject carriers into the conduction or valence band, thus providing effective n-type and p-type behavior, respectively. Experimental methods in this use-case group include charge transport measurements, optical spectroscopy (e.g., absorbance, photoluminescence, and Raman spectroscopy), and high-resolution microscopy (e.g., scanning probe microscopy, electron microscopy, and atom probe tomography). These experimental methods are complemented by an extensive suite of computational techniques including multi-scale modeling, molecular dynamics, density functional theory, and finite element methods. The interplay between experiment and computation accelerates the understanding and design of doped low-dimensional nanoelectronic materials and their heterostructures.

DESIGN GOALS

For the previous funding period, the Low-Dimensional Nanoelectronic Materials use-case group made significant progress towards two design goals:

(1) *Producing Low-Dimensional Semiconductors of Controlled Carrier Concentration.* Towards this end, **Lauhon** is advancing the synthesis of transition metal dichalcogenides with substitutional dopants and developing characterization methods that can correlate composition with electrical properties. For example, the stoichiometry of MoS₂ grown by chemical vapor deposition was analyzed by X-ray photoemission spectroscopy and electrical characterization. In addition, methods were developed to prepare and analyze two-dimensional semiconducting samples by atom probe tomography.

(2) *Developing p-n Heterojunctions Consisting of Low-Dimensional Semiconductors.* Of particular interest are p-n heterojunctions that allow gate-tunability over the carrier concentrations in both of the constituent materials. Towards this end, **Hersam** has realized wafer-scale p-n

heterojunction diodes using solution-processed p-type semiconducting single-walled carbon nanotubes (s-SWCNTs) and n-type amorphous indium gallium zinc oxide (a-IGZO) thin films via photolithographic and etching techniques. These p-n heterojunctions show highly reproducible anti-ambipolar charge transport with high on/off ratios and provide insight into the band alignment and charge distribution at the interface between doped low-dimensional semiconductors.

SIGNIFICANT ACCOMPLISHMENTS

(1) In a CHiMaD collaboration involving **Lincoln Lauhon** and **Mark Hersam**, the stoichiometry of MoS₂ grown by chemical vapor deposition was analyzed by X-ray photoemission spectroscopy and electrical characterization, revealing that variations in sulfur loading produced controlled variations in electrical properties. This work resulted in a collaborative publication in *ACS Nano* involving **Lauhon** and **Hersam**: I. S. Kim, V. K. Sangwan, D. Jariwala, J. D. Wood, S. Park, K.-S. Chen, F. Shi, F. Ruiz-Zepeda, A. Ponce, M.

The forward current at $V_G = 4$ V is low (~ 20 nA) but abruptly increases for intermediate V_G values and then falls to the instrumental noise floor (~ 10 pA) at $V_G = 0$ V. This behavior is also evident in the p-n heterojunction transfer plots (I - V_G) (Fig. 2c, green). This anti-ambipolar transfer plot shows one current maximum (on-state) in between two off-states at either extremes of the gate voltage range. The voltage dependence of the anti-ambipolar plot is approximately a superposition of the transfer plots of the p-type unipolar FETs in red and blue, respectively (Fig. 2c).

Due to screening from the ~ 20 nm thick a-IGZO, the junction itself is less modulated by the gate field compared to p-n heterojunctions based solely on two-dimensional materials, thus simplifying the charge transport mechanism and facilitating the realization of reproducible and spatially homogeneous characteristics. For example, Fig. 2b shows that the reverse saturation current possesses a relatively weak gate-dependence. In Fig. 2d, three-dimensional plots of current (I_D) as a function of V_G and forward bias voltage (V_D) illustrate that the charge transport is primarily a result of two semiconductors with opposite carrier types in series. Specifically, cross-sections along the V_D axis at $V_G > 2.2$ V (point of maximum current) resemble the output plots of s-SWCNT FETs under positive bias, whereas $V_G < 2.2$ V shows a saturating behavior that correlates with the output plots of a-IGZO FETs. These results were reported in collaborative publication in *Nano Letters* involving **Lauhon** and **Hersam**: D. Jariwala, V. K. Sangwan, J.-W. T. Seo, W. Xu, J. Smith, C. H. Kim, L. J. Lauhon, T. J. Marks, and M. C. Hersam, "Large-Area, Low-Voltage, Antiambipolar Heterojunctions from Solution-Processed Semiconductors," *Nano Letters*, 15, 416 (2015).

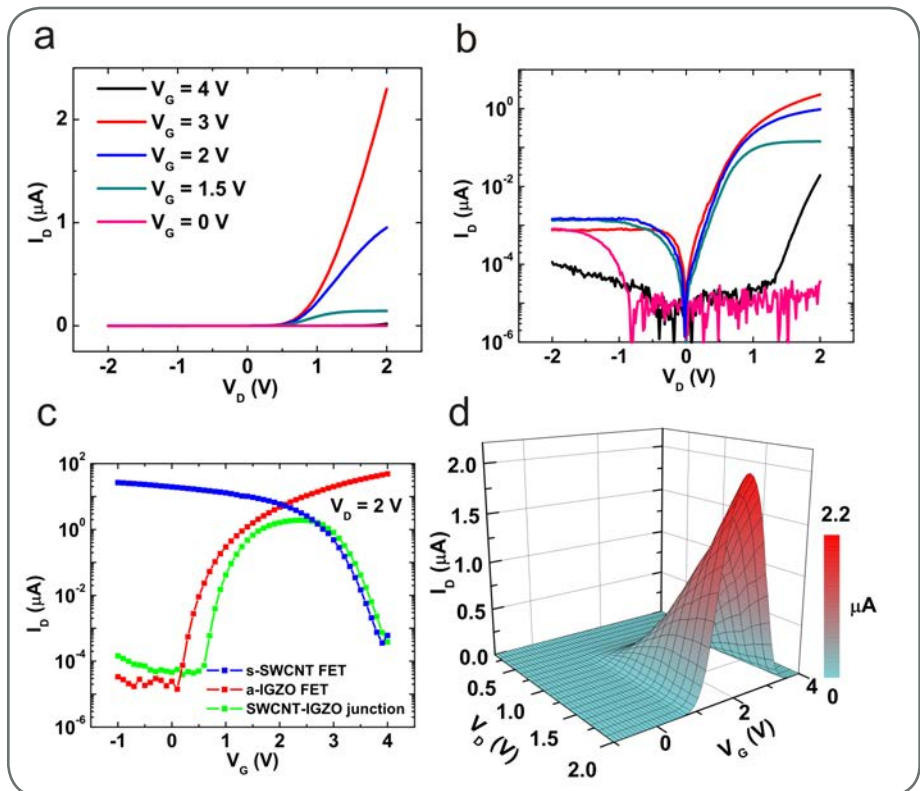


Figure 2. (a,b) Output characteristics of a s-SWCNT/a-IGZO p-n heterojunction at different gate voltages on a linear (a) and semi-log (b) y-axis. The weak gate modulation of the reverse saturation current magnitude can be seen in b. The plot colors in a and b represent the same gate voltage values as indicated in the legend of a. (c) Semi-log transfer characteristics of a p-type s-SWCNT FET (blue), n-type a-IGZO FET (red), and s-SWCNT/a-IGZO p-n heterojunction (green). (d) Three-dimensional representation of the anti-ambipolar transfer characteristics at varying drain biases. The grid lines running along the V_D axis represent the forward output characteristics at the indicated gate voltage (V_G).

COLLABORATIONS

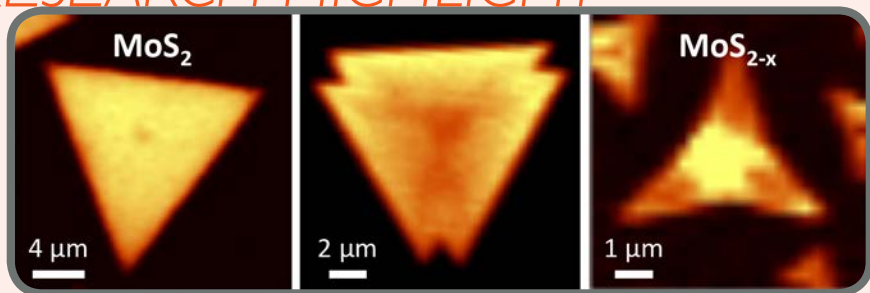
Chemical Vapor Transport Growth of Transition Metal Dichalcogenides

Collaborator: Albert Davydov

Materials Science and Engineering Division, NIST

The Davydov group is growing transition metal dichalcogenide (TMDC) crystals by chemical vapor transport (CVT) that will be characterized using atom probe tomography (APT). In Year 1, NbSe₂ bulk single crystals were grown and provided to Northwestern University. Davydov visited Northwestern University on Sept 18, 2014 to meet with **Lauhon**, **Hersam**, and **Voorhees** to discuss ongoing efforts and coordinate plans for Years 1 and 2. Davydov, **Hersam**, and **Lauhon** also conducted multiple teleconferences and e-mail exchanges during the year to define and coordinate the Low-Dimensional Nanoelectronic Materials use case group.

RESEARCH HIGHLIGHT



Chemical Vapor Deposition of MoS₂ Thin Films

Collaborators: Albert Davydov (see affiliation previous page),

James Maslar

Chemical Sciences Division, NIST

Davydov and Maslar have designed and built two chemical vapor deposition (CVD) reactors for large-scale growth of TMDC thin films to be shared with the NU team for compositional characterization (**Lauhon**) and device fabrication (**Hersam**). Davydov is focusing on chloride CVD chemistry for large-scale MoS₂ and related alloy thin film growth with controlled composition, doping, thickness, and microstructure. Maslar will employ a warm-wall, vertical-flow, single-wafer reactor that can be operated in atomic layer deposition (ALD) mode (with sequentially-injected precursors) or in CVD mode (with co-injected precursors). Different precursor chemistries are being investigated including organometallic compounds, metal carbonyls, metal halides, thiols, and elemental sources.

Device Fabrication and Transport Measurements on TMDC FETs

Collaborators: Albert Davydov (see affiliation previous page), Abhishek Motayed (Guest Researcher in the Davydov group)

Davydov is collaborating with both **Lauhon** and **Hersam** on fabricating field-effect transistor (FET) devices based on mono- to few-layer thin MoS₂ and related thin films. In year one, the NIST group tested transfer characteristics and low-frequency noise in single and multilayer MoS₂ FETs as a function of the active channel thickness. The

CONTROL OF STOICHIOMETRY OF CHEMICAL VAPOR DEPOSITION DERIVED MoS₂

In Soo Kim¹, Vinod K. Sangwan¹, Deep Jariwala¹, Joshua D. Wood¹, Spencer Park¹, Kan-Sheng Chen¹, Fengyuan Shi¹, Francisco Ruiz-Zepeda⁵, Arturo Ponce⁵, Miguel Jose-Yacamán⁵, Vinayak P. Dravid^{1,4}, Tobin J. Marks^{1,2}, Mark C. Hersam^{1,2,3*}, and Lincoln J. Lauhon^{1*}

¹Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208 USA

²Department of Chemistry, Northwestern University, Evanston, IL 60208 USA

³Department of Medicine, Northwestern University, Evanston, IL 60208 USA

⁴International Institute of Nanotechnology, Northwestern University, Evanston, IL 60208 USA

⁵Department of Physics and Astronomy, University of Texas at San Antonio, San Antonio, TX 78249 USA

SCIENTIFIC ACHIEVEMENT

The stoichiometry of MoS₂ grown by chemical vapor deposition was analyzed by X-ray photoemission spectroscopy, and controlled variations in stoichiometry were achieved by varying the sulfur loading. Analysis of the electrical properties of field effect transistors demonstrated improvements in device characteristics in sub-stoichiometric material. This surprising finding is consistent with the existence of a mobility edge; in materials with significant charge carrier scattering due to defects or interfaces, a minimum carrier concentration must be achieved to enable delocalized carrier transport.

SIGNIFICANCE

Semiconducting transition metal dichalcogenides are layered materials that can be made as thin as one monolayer, opening up new opportunities in electronic and photonic devices. Point defects such as sulfur vacancies providing additional charge carriers but also introduce scattering channels. Understanding and control over defects in these emerging materials is essential for their insertion into new devices and technologies.

CITATION INFORMATION

Kim et al, *ACS Nano* 8, 10551 (2014)

ACKNOWLEDGEMENTS

This work was supported by the Materials Research Science and Engineering Center (MRSEC) of Northwestern University (National Science Foundation Grant DMR-1121262), NSF PREM Grant DMR-0934218, the Office of Naval Research (Grant N00014-14-1-0669), the Keck Foundation, and the Center for Hierarchical Materials Design (US Department of Commerce, NIST 70NANB14H012). The microscopy work was supported by grants from the National Center for Research Resources (5 G12RR013646-12) and the National Institute on Minority Health and Health Disparities (G12MD007591) from the National Institutes of Health.

NIST and NU groups have positioned themselves to start sharing device structures for complimentary electrical and optoelectronic testing in year two. NIST's advanced double-channel system for temperature-dependent 1/f noise measurements with low instrumental background noise is well-suited to study the effect of non-stoichiometry and

Low Dimensional Use-Case Nanoelectronic Materials Group Researchers and Their Roles

| Name | Position | Institution/ Affiliation | Project Title |
|-------------------|------------------|-----------------------------|--|
| Lincoln J. Lauhon | PI | NU/MSE | <i>Substitutional doping and alloy formation in transition metal dichalcogenides</i> |
| Mark C. Hersam | PI | NU/MSE | <i>Low-dimensional semiconducting heterojunctions</i> |
| Xiaochen Ren | Graduate student | NU/MSE | <i>Substitutional doping and alloy formation in transition metal dichalcogenides</i> |
| Jung-Woo T. Seo | Graduate student | NU/MSE | <i>Low-dimensional semiconducting heterojunctions</i> |
| Hadallia Bergeron | Graduate student | NU/MSE | <i>Low-dimensional semiconducting heterojunctions</i> |

doping in MoS₂ and related TMDCs on the FET performance. Active material and device exchange between the NU and NIST groups for electrical testing and correlation to doping and other materials properties is planned for Year Two.

Low-Dimensional Nanoelectronic Materials Modeling Collaborators: Francesca Tavazza, Benjamin Burton, Project Leaders, and Arunima Singh, Guest Researcher, Materials Science and Engineering Division, NIST

Burton, with assistance from Singh, has initiated a first-principle modeling of phase diagrams for multicomponent TMDC systems, starting from the MoS₂-MoTe₂, MoS₂-MoSe₂, and MoSe₂-MoTe₂ pseudo-binary sections, as well as building the FPPS (First Principles Phase Stability) repository. To accurately treat a layered structure of TMDC compounds, van der Waals interlayer interactions were included into the DFT based ab-initio simulation. Since experimental phase diagrams for the above systems do not exist, the phase diagram simulation is the most critical step in developing guidance for designing TMDC alloys with the composition-defined band gap values. Preliminary simulation for the MoS₂-MoTe₂ system indicates formation of one ordered phase and two miscibility gaps, while the MoS₂-MoSe₂ system forms a continuous solid solution with no phase segregation.

In year two, the WSe₂-NbSe₂ and MoS₂-NbS₂ diagrams will be considered since niobium has been proven to act as an efficient p-dopant in both WSe₂ and MoS₂. The simulation at NIST will complement experimental efforts from **Lauhon**

for developing substitutional p- and n-doping in TMDC compounds and alloys.

In parallel, Tavazza and Singh have applied DFT theory to evaluate the effect of high-k dielectric oxide substrates on the electronic properties of ultra-thin TMDC layers (including possible doping effects). Initial simulation of MoS₂ mono- to three- layer films on sapphire has shown progressively weak interaction between MoS₂ and Al₂O₃ with increasing numbers of layers, while the n-doping effect due to charge transfer from the Al₂O₃ into the MoS₂ layer remains constant. The band gap and effective masses of MoS₂ are found to be unaffected by the underlying substrate. In year two, Tavazza and Singh will continue assessing the influence of sapphire on the electronic structure and transport properties of CVD-grown MoS₂ and related TMDC films. The ab-initio modeling will be correlated with experimental work of NU (**Lauhon, Hersam**) and NIST (Davydov, Motayed) on the corresponding TMDC/substrate heterostructures.

A long term goal for the above NIST/NU modeling effort is to develop an open-source tool for the high-throughput screening of suitable substrates for the growth and functionalization of 2D materials. While several 2D materials were produced experimentally, many more 2D materials with useful properties have been theoretically predicted. Their synthesis requires knowledge of substrates that can stabilize the 2D materials. Specific goals include: (i) perform high-throughput DFT based computational screening of suitable substrates for the synthesis of 2D materials, (ii) characterize the mechanical and electronic properties of 2D materials

adsorbed on substrates, and (iii) build a database of suitable substrates of 2D materials. Initially, a systematic and high-throughput substrate search for the following theoretically predicted but non-yet-synthesized experimentally 2D materials will be undertaken by **Tavazza** and **Singh**: three group-III monochalcogenides (AX, with A = In and X = S, Se, Te), twelve group IV-monochalcogenides (BX, with B = Ge, Sn, Pb and X = O, S, Se, Te), and twenty seven metal dichalcogenides (MX₂, M = Ti, V, Cr, Mn, Fe, Co, Ni, Ta, W and X = S, Se, Te). This computational screening will help in identifying likely and eliminating unlikely substrates, allowing for more efficient use of experimental resources and accelerating possible applications.

PUBLICATIONS

I. S. Kim, V. K. Sangwan, D. Jariwala, J. D. Wood, S. Park, K.-S. Chen, F. Shi, F. Ruiz-Zepeda, A. Ponce, M. Jose-Yacamán, V. P. Dravid, T. J. Marks, M. C. **Hersam**, and L. J. **Lauhon**, "Influence of Stoichiometry on the Optical and Electrical Properties of Chemical Vapor Deposition Derived MoS₂," *ACS Nano*, 8, 10551 (2014). Partial CHiMaD support.

D. Jariwala, V. K. Sangwan, J.-W. T. Seo, W. Xu, J. Smith, C. H. Kim, L. J. **Lauhon**, T. J. Marks, and M. C. **Hersam**, "Large-Area, Low-Voltage, Antiambipolar Heterojunctions from Solution-Processed Semiconductors," *Nano Letters*, 15, 416 (2015). Partial CHiMaD support.

TECHNOLOGY TRANSFER

Inventions Disclosed:

- System and method for anti-ambipolar heterojunctions from solution-processed semiconductors
- US Provisional Patent application filed on 1/9/15.
- Inventors: D. M. Jariwala, V. K. Sangwan, W. Xu, H. Kim, T. J. Marks, and M. C. **Hersam**
- This invention describes a method for forming large-area, anti-ambipolar p-n heterojunctions using solution-processed p-type semiconducting single-walled carbon nanotubes (s-SWCNTs) and n-type amorphous indium gallium zinc oxide (a-IGZO) thin films via photolithographic and etching techniques. ■

PRECIPITATION-STRENGTHENED ALLOYS

G. B. Olson (co-lead)¹, D. C. Dunand (co-lead)¹, D. N. Seidman¹, P. W. Voorhees¹, C. M. Wolverton¹, W.-K. Liu², A. Umantsev⁵, W. Chen², J. Sebastian⁴, D. Snyder⁴, W. W. Zhang⁴, J. Saal⁴, A. Choudhary³, A. Agrawal³, and M. Bedzyk¹

¹Department of Materials Science and Engineering, Northwestern University

²Department Mechanical Engineering, Northwestern University

³Department Electrical Engineering and Computer Science, Northwestern University

⁴QuesTek Innovations

⁵Department of Chemistry and Physics, Fayetteville State University

New capabilities in predictive design of precipitation-strengthened alloys are being applied to Co-based superalloys and high-performance Shape Memory Alloys, both employing low-misfit coherent aluminide precipitates closely analogous to the γ - γ' Ni-based superalloys. The Co-based alloys are of interest for both high-temperature creep and fatigue resistance in turbine applications, as well as ambient temperature wear-resistance applications such as aerospace bushings to replace Be-Cu alloys. The shape memory alloys are of high interest for device and actuation applications in medicine, aerospace and automotive sectors where ultrahigh-cycle fatigue is the primary limitation of current alloys; here, efficient precipitation strengthening can eliminate the accommodation slip associated with thermoelastic martensitic transformation, standing as the principal cause of cyclic instability.

DESIGN GOALS

Short-term goals for the Co alloys address ambient temperature applications, where the intrinsic low surface friction characteristics of Co-based alloys makes their precipitation strengthened variants of clear near-term interest as a replacement for Be-Cu aerospace bushing applications of current environmental concern. Long-term goals address high-temperature applications where metallic superalloys play a vital role in electrical power generating systems (gas and steam turbines) and jet engines. While achievement of the full set of properties necessary for these applications is an ambitious goal, the potential of the new family of Co-based superalloys to achieve the same strength levels of current Ni-based superalloys, but with a temperature capability

100-150 °C higher would enable a major advance in the fuel efficiency of gas turbines and jet engines.

In support of new capabilities in additive manufacturing by 3D printing, precipitation-strengthened superalloy research will also address process optimization in the 718+ Ni-based alloy being developed under the DARPA Open Manufacturing program in collaboration with Honeywell.

The breadth of planned databases for Shape Memory alloy design will support both the near-term optimization of high Pd alloys for medical applications favoring high radiopacity and low Ni content for biocompatibility, and the longer-term design of lower-cost high Zr alloys to meet the requirements

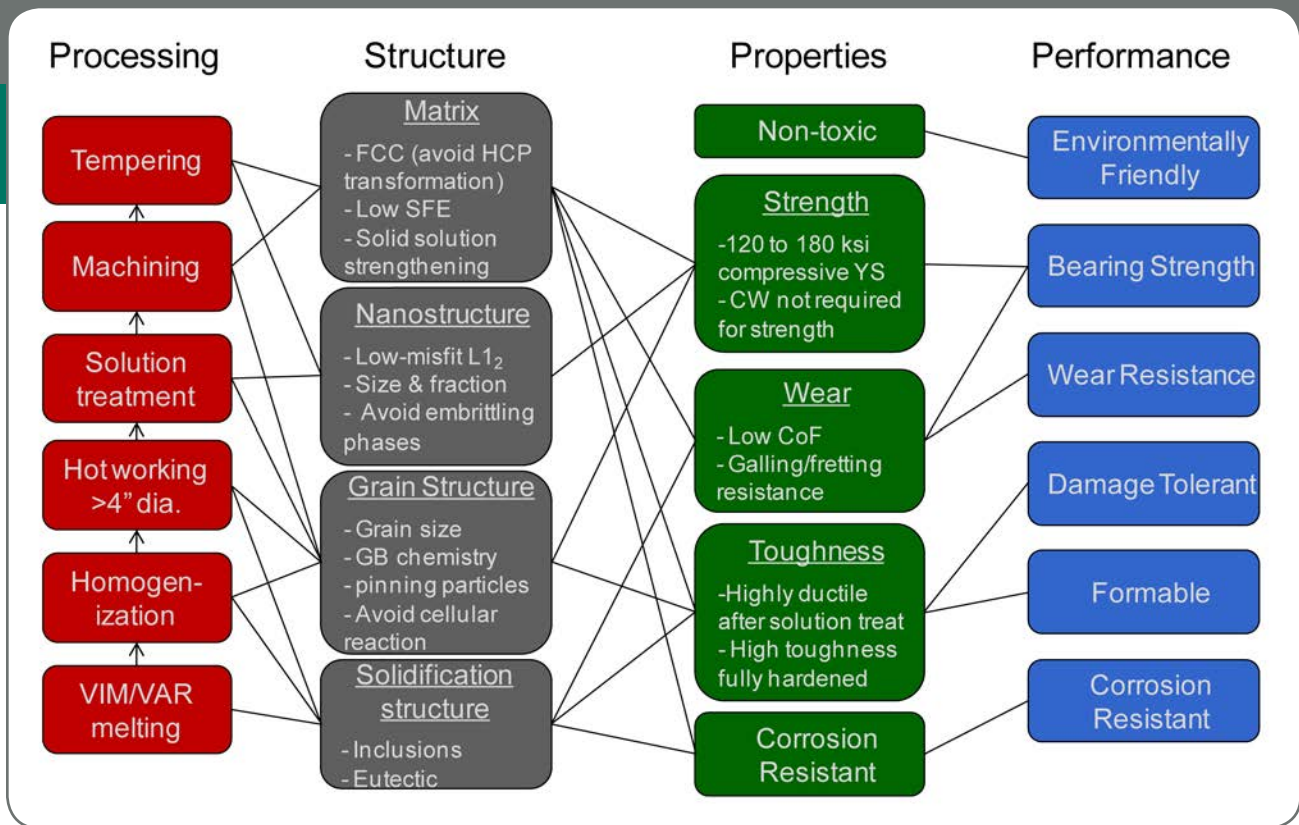


Figure 1: Hierarchical system structure of Co-based aerospace bushing alloy.

of aerospace and automotive actuators. This will allow the new class of cyclically-stable alloys to have broad technological impact.

SIGNIFICANT ACCOMPLISHMENTS

- QuesTek (**Olson, Sebastian, Snyder, Zhang, Saal**) has demonstrated a Co-based alloy for aerospace bushing applications meeting all primary property requirements in testing by Northrup Grumman. Database extensions to support further process optimization have been conducted, and alloy qualification test plans have been established.
- In a database workshop at NIST, plans were made for the pre-CALPHAD protodata repository to be hosted at NIST, and the metal alloy project was selected as the first to begin populating this database using a specified format.
- An undergraduate team in Northwestern University's Materials Design class (**Olson**) placed third in the 2014 ASM Design Competition. Their design of a multicomponent aluminide-strengthened shape memory alloy for medical applications employed our current CALPHAD databases to optimize mixed Pd-Zr aluminides for greater strengthening efficiency.
- A team of undergraduates in our special Murphy Scholar section of Freshman Design collaborated with **Olson, Choudhary** and **Agrawal** to initiate our research on the integration of a process-property

database with a CALPHAD database for fusion of prior knowledge with data in the adaptation of datamining techniques for greater accuracy of process-structure-property correlation. The team demonstrated stronger correlation compared to previous datamining using the process-property data alone.

RESEARCH ACCOMPLISHMENTS

Discussion at the Inaugural CHiMaD meeting established quantitative property objectives and system structures for both the Co-based alloys and Shape Memory Alloys. The hierarchical system structure for the near-term case of the Co-based aerospace bushing alloy is represented in Figure 1.

In support of fundamental data development for high-temperature Co alloys (**Dunand** and **Seidman**) arc melted alloy buttons of compositions (at.%) Co-7Al-8W-4Ti-1Ta-10Ni-0.15B and Co-7Al-8W-4Ti-1Ta-15Ni-0.15B, under argon atmosphere. The alloys were flipped and melted over ten times to ensure homogenization, then sectioned and vacuum encapsulated. The encapsulated samples were homogenized at 1300C for 24 hours in box furnace, water quenched, and aged at 1000C for 1000h in vacuum, in preparation for equilibrium studies

Activities at QuesTek (**Olson, Sebastian, Snyder, Zhang, Saal**) have centered on achieving higher yield strength in the bushing alloy of Figure 1 through simulation-driven thermal process optimization. In particular, aging treatment optimization has addressed more efficient precipitation strengthening and a reduction in the anneal time to peak strength

Refinement of Thermodynamic databases using new LEAP analysis of γ' particle evolution at 780 °C in NGCo-3A alloy

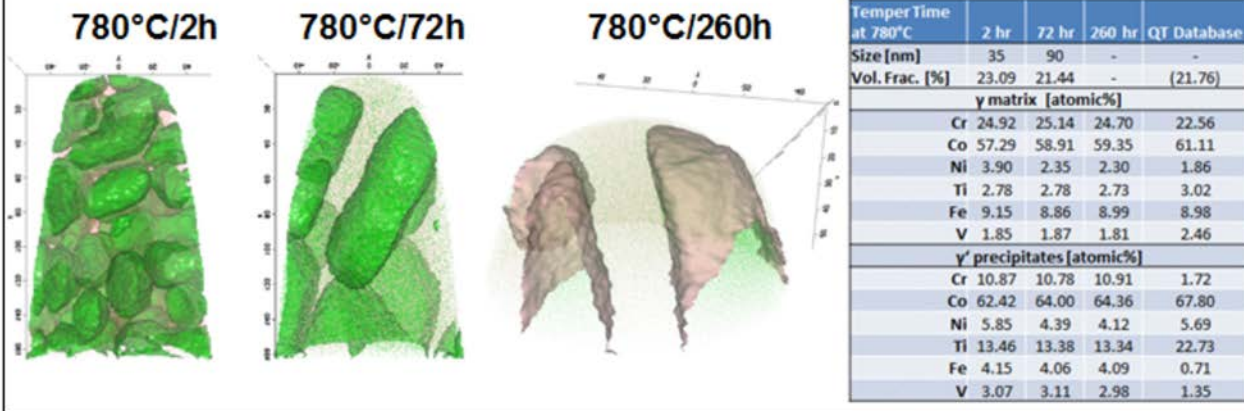


Figure 2: Experimental LEAP analyses of Co bushing alloy used to calibrate QuesTek's Co thermodynamic databases in preparation for PrecipiCalc simulations.

(previously ~70 hours). Higher precipitation strengthening is achieved through higher precipitate phase fractions and refined precipitate size. **Zhang** has extended QuesTek's Co thermodynamic and mobility databases with experimental and literature data, applied in the PrecipiCalc® software (now commercially available as TC-Prisma through ThermoCalc®) to simulate a range of aging treatments that target higher precipitate strengthening by these means.

As this tool is rooted in the kinetics of multicomponent precipitation theory, the key inputs to PrecipiCalc are thermodynamic and kinetic databases, which are fundamental databases that describe phase stability and transformation kinetics within multicomponent systems. Such databases were developed internally by QuesTek since no commercial databases are currently available for cobalt alloy systems. In support of the thermodynamic assessment, **Sebastian** and **Saal** analyzed LEAP atom probe tomography data at three distinct aging conditions at 780C: under-aged (2hr), peak aged (72hr) and over-aged (260hr). The LEAP reconstructions and corresponding phase compositions are presented in Figure 2.

For mobility database assessment, **Zhang** has collected available literature data for diffusivities in cobalt alloys. Using the refined databases, **Saal** and **Snyder** applied the PrecipiCalc precipitation simulator to model the effect of varying aging treatments on the predicted strength of the alloy. Figure 3 plots the predicted increase in strength during aging at various conditions. The condition highlighted by the blue star is that was applied to the current material shown to have a yield strength of 126 ksi. As represented in Figure 4, a two-step anneal process was then predicted to reduce the time to peak strength from ~70 hours to ~24 hours.

Two of the most promising modified heat treatment conditions were selected from this simulation study for tensile test validation in comparison with the previous standard isothermal treatment condition. The results confirm

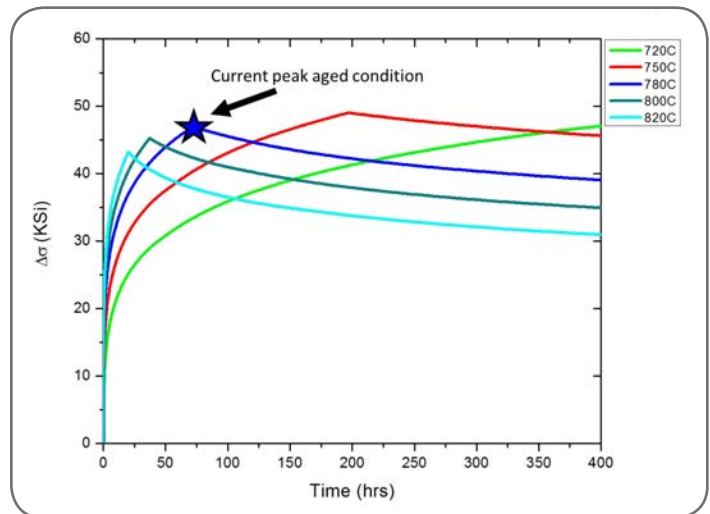


Figure 3: Calculated isothermal aging curves for the Co bushing alloy showing the predicted increment in yield strength due to precipitation of Co₃Ti during aging as a function aging time. Note: a yield strength increment of "0" is the as-solution treated strength in the absence of precipitation hardening.

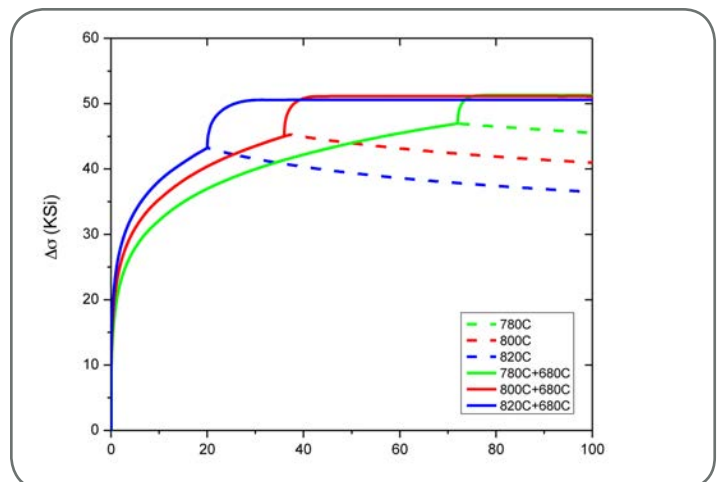


Figure 4: Calculated aging curves for Co alloy with a two-step anneal process, predicting a much reduced processing time with two-step treatment.

Nanodispersion-Strengthened Shape Memory Alloys

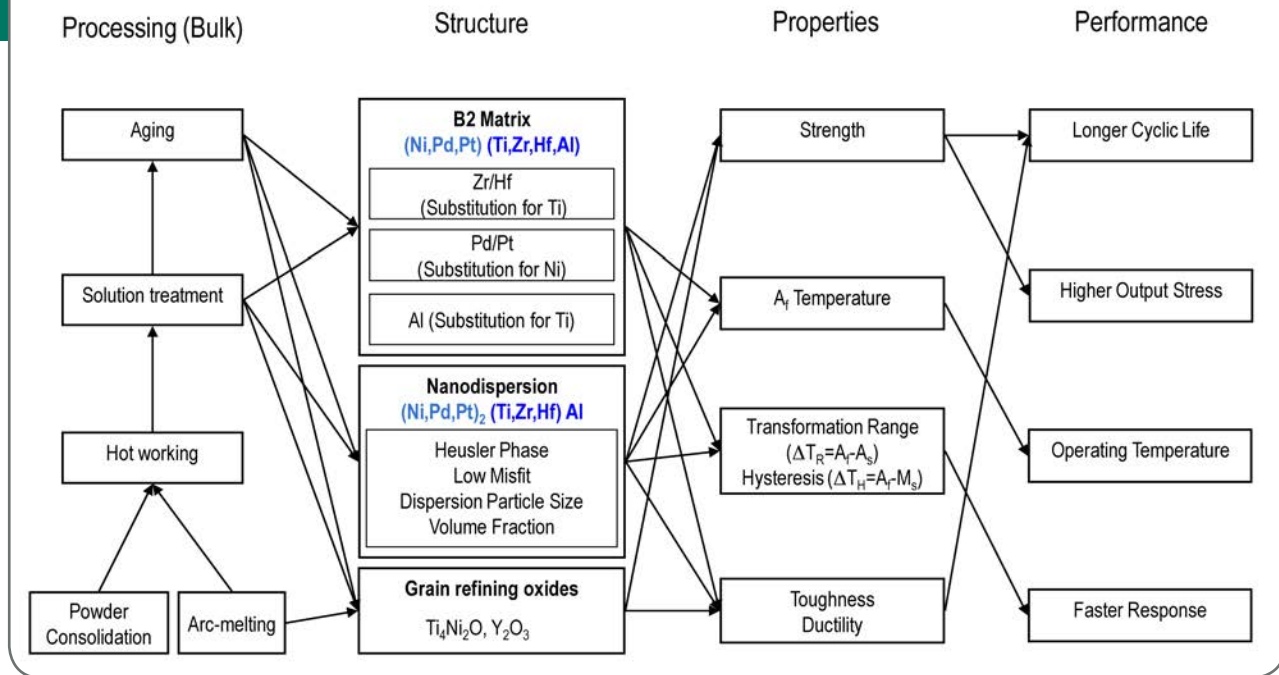


Figure 5. System structure of coherent aluminide nanodispersion-strengthened shape memory alloys for high fatigue performance.

predicted reduction in required aging time to achieve equivalent strength.

Higher yield strength is now being sought through Hall-Petch grain refinement strengthening. The current alloy prototype shows a relatively coarse grain size of 75 μm diameter, in association with a lower than specified carbon content. QuesTek has placed an order for an intermediate scale heat of the design composition for desired TiC-based grain refinement. Production of a 300-lb heat has been initiated at MetalWerks PMD (Aliquippa, PA) and is anticipated to complete in the first quarter of 2015.

Toward further enhancement of the AIM methodology for accelerated qualification of new materials using the Co bushing alloy as test case, QuesTek staff are collaborating with **Chen** to better codify the current AIM probabilistic minimum property forecasting method and quantify its uncertainty. In late 2014, a meeting was held at QuesTek to plan the research approach. All property distribution and corresponding simulation data were transferred from QuesTek to NU for the three previous demonstrations of the AIM method. A meeting with Northrup Grumman staff was also held at QuesTek in December to establish the qualification test plan for the Co bushing alloy and assess possible sources for its funding.

Discussions with **Wolverton** have established priorities for initial applications of high-throughput DFT methods to support CALPHAD database development. A database of solute-vacancy binding energies has been identified as of high

potential impact in design of high-temperature creep resistance. Co based and Ni based systems will be assessed in parallel to take advantage of the greater availability of validation information in Ni based systems.

An identified opportunity to leverage related activities in the new technology of additive manufacturing is the DARPA Open Manufacturing program where QuesTek collaborates with Honeywell in the accelerated process optimization and AIM process qualification of the 718+ Ni based superalloy. Under a Year 1 collaboration supporting this, QuesTek has supplied as-deposited material to Lyle Levine of NIST who has collected the raw data for a 4D tomographic study of microstress evolution at the current stress relief temperature, using the APS synchrotron at ANL. Preliminary analysis shows high promise for the desired quantification of underlying phenomena.

The general system structure for both near-term and long-term design of coherent aluminide nanodispersion-strengthened shape memory alloys for enhanced fatigue performance is represented in Figure 5. The doctoral research of Dana Frankel, supervised by **Olson**, has focused on the design of biocompatible, PdTi-base SMAs for biomedical applications. Phase relations, precipitation kinetics, transformation temperatures, and mechanical properties have been characterized in the $(\text{Pd,Ni,Fe})_{50}(\text{Ti,Zr,Al})_{50}$ system. Controlled precipitation of nanoscale, low-misfit, L_{21} Heusler aluminides provides excellent strengthening and resistance to accommodation slip, maintaining high levels of thermal and mechanical cyclic stability for improved

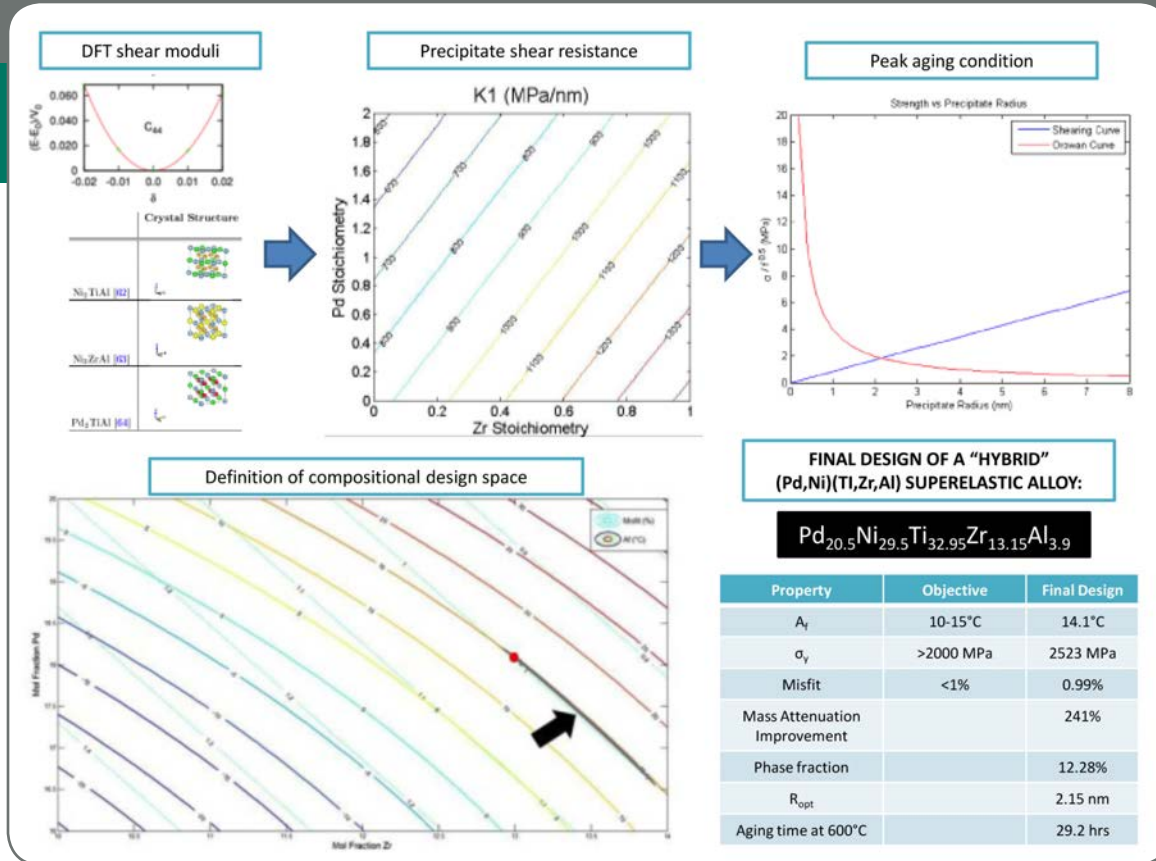


Figure 6. Graphical CALPHAD-based design of a multicomponent precipitation-strengthened shape memory alloy for fatigue-resistant medical devices.

fatigue life. Atom probe tomography (APT) has been employed to measure phase compositions and particle sizes, used to calibrate LSW models for coarsening kinetics and Gibbs-Thompson models for composition trajectories under unstable equilibrium. When combined with models for solid solution strengthening, precipitation strengthening, and transformation temperature, the predictive design of an optimally-strengthened superelastic alloy is demonstrated. Using Fe as an austenite stabilizer, a Ni-free (Pd,Fe)(Ti,Al) alloy with near-ambient transformation temperatures has been designed and characterized. The peak strengthened alloy, aged at 600°C for 3.5h to achieve a mean particle radius of 2.3nm, exhibits compressive transformation strains of 3% and extremely stable transformation behavior during thermal cycling.

While Pd is disadvantageous to strength, both DFT calculations and experimental data from the Ni(Ti,Zr,Al) system indicate that Zr is a highly effective strengthener. Frankel pursued this concept through coaching of an undergraduate team in Northwestern’s Materials Design class (**Olson**) in the Spring Quarter. Their graphical design, integrating DFT calculated shear constants of the Heusler phase, is represented in Figure 6. The team won 3rd prize in the 2014 ASM Undergraduate Design Competition. Dr. Shenyen Li of NIST also attended the design class as a CHiMaD Visiting Scholar, participating in a related project on a transformation plasticity alloy. Subsequent experimental validation of the SMA class project low-Ni, high strength “hybrid” (Pd,Ni)(Ti,Zr,Al)

alloy by Frankel confirmed enhanced room temperature hardness and near-zero values of interphase misfit during aging at 600°C. In the Fall Quarter, a team of graduate students in the ICME MS program (**Olson, Wolverton**) was organized under Frankel’s coaching to initiate follow-on research addressing the design of a high strength Ni-free (Pd,Fe)(Ti,Zr,Al) superelastic alloy.

While inhibition of accommodation slip through nanoscale dispersion strengthening is vital to cyclic stability, of equal importance is the control of nonmetallic inclusions (the bottom structure subsystem of Figure 5) which act as the potent fatigue nucleants determining minimum fatigue strength. **Liu** group has applied a finite element crystal plasticity modeling approach to quantify the effects of such nucleants on the fatigue properties of shape memory alloys, starting with the basic TiNi system. Studies have focused on fatigue nucleation at Ti(C,O) carbide and (Ti₄Ni₂O_x) oxide inclusions within single crystal grains of the B2 TiNi parent phase matrix. Analysis of several interacting inclusion clusters has shown that increasing the matrix strength by 50% results in a two order-of-magnitude increase in fatigue life, supporting the benefits of nano-dispersion strengthening. Further studies have modeled a stringer cluster of inclusions based on 3D focused ion beam tomographic reconstruction in collaboration with **Olson**. Preliminary results indicate that fatigue life is less sensitive to prior interfacial damage (from deformation processing) than to achievable variations in matrix strength. Moore has also served as an advisor to the ICME MS graduate student team who are applying his results to assess the combined effects of strengthening and inclusion control on SMA fatigue performance.

As an extension of the Phase Field model development effort led by **Voorhees, Liu** met with **Umantsev** of FSU to explore common elements of **Umantsev’s** Phase Field

2014 SRG Design Projects

- **ONR Cyberalloys** (Olson, Freeman)
 - CMD of **Fe & Ti** alloys for blast and fragment protection
- **DOE/GM Lightweighting Initiative** (Olson, Wolverton, Voorhees)
 - CMD of cast **aluminum** for cylinder heads
- **DOE/CAT Lightweighting Initiative** (Olson, Liu)
 - CMD of cast **steels** for crankshafts
- **ArcelorMittal AHSS** (Olson)
 - CMD of high-strength automotive Q&P **TRIP steels**
- **NIST/NIU MSAM Additive Manufacturing** (Olson, Liu, Cao)
 - CMD of **Fe & Ti** alloys for additive manufacturing
- **DARPA/Honeywell Open Manufacturing** (QuesTek)
 - ICME for SLM additive manufacturing of **Ni 718+**

Figure 7. SRG materials design projects.

microstructural modeling and **Liu's** nonlocal mechanics methods to establish a uniform strategy for fatigue modeling. An approach was determined to address the full scope of fatigue nucleation and crack growth based on the mesoscopic Fatimi-Socie damage parameter incorporating size-dependent gradient plasticity.

Northwestern University's SRG materials design consortium joined the CHiMaD organization, offering the leveraging opportunity of the CALPHAD-based metals design projects with topics and sponsors listed in Figure 7. These projects will help demonstrate the generality of the methods, tools, and database infrastructure of CHiMaD. The SRG Annual Meeting held each March at Northwestern will continue to serve as a review of CHiMaD metals activities offering interaction with a broader community.

In a database workshop at NIST April 28-29, organized by Carelyn Campbell (NIST), plans were made for the pre-CALPHAD protodata repository to be hosted at NIST, and the metal alloy project was selected as the first to begin populating this database using a specified DSpace format. A subsequent teleconference meeting of the Co alloy team led to the identification of highest priority alloying elements for thermodynamic and mobility database development. This then formed the basis for thin-film-based initial high-throughput experiment design by **Chung** and **Bedzyk** at Northwestern, to employ APS characterization facilities at ANL.

A team of undergraduates in our special Murphy Scholar section of Freshman Design collaborated with **Olson**, **Choudhary** and **Agrawal** to initiate our research on the integration of a process-property database with a CALPHAD database for fusion of prior knowledge with data in the adaptation of datamining techniques for greater accuracy of

Co Database Development

- Co-Al-W-Ni-Ti-Ta-Nb-B-Cr-Fe-V-Mn
 - Initial focus: Co-Al-W-Ni-Ti-Ta
 - 2nd focus: Nb-B
 - 3rd level focus: Cr-Fe-V-Mn (Bushing alloy applications?)

Co-Al-W (NIST/CHiMaD w/ThermoCalc (N. Dupin))
 Co-Ta-Ni (NIST)
 Co-Ti-Ni (*Cacciamani G*)
 Co-Ta-Ti (NIST/CHiMaD - use same Co-Ti as Co-Ni-Ti ?)
 Co-Al-Ni (Dupin thesis (1995))
 Co-Al-Ta
 Co-Al-Ti
 Co-W-Ni (Férrandez Guillermet (1988))
 Co-W-Ti
 Co-W-Ta

Figure 8. Alloy components for Co database development with priorities.

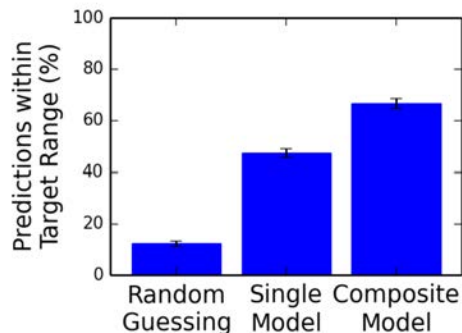


Figure 9. Performance of three different strategies to locate 30 compounds with a band gap energy between 0.9 and 1.7 eV out of a set of 2500 candidates from the ICSD. The first strategy is to randomly select a nonmetal-containing compound. The other two strategies are to use a model produced using the machine-learning-based method described in this work that was trained on the band gap energies of a distinct set of 22667 compounds from the ICSD to locate compounds with a band gap energy within the desired range. The first of those two strategies uses a single model trained on all compounds in the training set, and the latter uses the composite predictions of a several models each trained on different groups of similar compounds. Error bars represent the 95% confidence interval.

process-structure-property correlation. Using a subset of the full process-property database, the team demonstrated stronger correlation compared to previous datamining using the process-property data alone. The team was coached by Research Associate Wei Xiong, a CALPHAD technology expert educated at the Royal Institute of Technology (KTH) in Sweden. After the student pilot project, Xiong continued the research developing a TCIPC-based link to automate interaction of the ThermoCalc CALPHAD software with the full process-property database and mining tools in collaboration with **Agrawal**.

**Precipitation-Strengthened Alloys
Group Researchers and Their Roles**

| Name | Position | Institution/ Affiliation | Project Title (PI) |
|--------------------------|-------------------------|-----------------------------|--|
| Gregory B. Olson | PI | NU/MSE | <i>Materials Design</i> |
| David C. Dunand | PI | NU/MSE | <i>Co alloys</i> |
| David N. Seidman | PI | NU/MSE | <i>Co alloys</i> |
| Peter W. Voorhees | PI | NU/MSE | <i>Phase Field Methods</i> |
| Christopher M. Wolverton | PI | NU/MSE | <i>DFT</i> |
| Michael Bedzyk | PI | NU/MSE | <i>Rapid Assessment of Phase Relations</i> |
| Wing Kam Liu | PI | NU/ME | |
| Alexander Umantsev | PI | FSU/Chem | |
| Alok Choudhary | PI | NU/EECS | <i>Data Mining</i> |
| Ankit Agrawal | PI | NU/EECS | <i>Data Mining</i> |
| Jason Sebastian | PI | Questek | |
| David Snyder | PI | QuesTek | <i>AIM</i> |
| Weiwei Zhang | PI | Questek | <i>CALPHAD</i> |
| James Saal | PI | Questek | <i>AIM</i> |
| Shengyen Li | Postdoctoral Researcher | NIST | <i>Materials Design (Olson)</i> |
| Wei Xiong | Postdoctoral Researcher | NU/MSE | <i>Materials Design (Olson)</i> |
| Seyed Naghavi | Postdoctoral Reseracher | NU/MSE | <i>(Wolverton)</i> |
| Zequn Wang | Postdoctoral Researcher | NU/ME | <i>(Chen)</i> |
| Qinyuan Liu | Graduate Student | NU/MSE | <i>(Dunand, Seidman)</i> |
| Dana Frankel | Graduate Student | NU/MSE | <i>(Olson)</i> |
| John Moore | Graduate Student | NU/ME | <i>(Liu)</i> |
| Logan Ward | Graduate Student | NU/MSE | <i>(Wolverton)</i> |

In support of further fundamental database generation and datamining capabilities, doctoral student Logan Ward, supervised by **Wolverton**, has explored accelerated expansion of the Open Quantum Materials Database (OQMD – www.oqmd.org, @TheOQMD) which currently consists of DFT calculations of ~300,000 compounds taken from the Inorganic Crystal Structure Database (ICSD) as well as hypothetical prototype compounds. There are however a very large number (>100,000) entries in the Powder Diffraction File (PDF) for which compounds have been synthesized, diffraction data obtained, and yet a complete crystal structure solution is not available. To aid in the accelerated solution of these structures, the First-Principles Assisted Structure Solution (FPASS) method was previously developed [B. Meredig and C. Wolverton, “A Hybrid Computational-Experimental Approach for Crystal Structure Solution” *Nature*

Materials 12, 123 (2013).] The use of FPASS to solve crystal structures for a large number of compounds currently “unsolved” in the PDF will enable a much more complete high-throughput database. However, the previous implementation of FPASS was not user-friendly, and could only be used in a “case-by-case” basis. Logan and **Wolverton** have now developed software to automate the solution of crystal structures with the First-Principles Assisted Structure Solution (FPASS) method, and used these tools to validate the ability FPASS to solve a large number of “test cases” (i.e., cases for which the structural solution is known). A wide array of structure types, symmetries, and unit cell sizes was tested, and the automated version of FPASS found the correct structure in all 100 test cases. The results from this validation study have also been used to determine how to adjust algorithm parameters (e.g., genetic algorithm mutation

probabilities) to improve performance — a key step in the production of a tool intended to be used to solve the structures of large numbers of compounds. The automation tool-kit uses the Materials Interface software to perform FPASS, which has been made publically available [L. Ward, K. Michel, C. Wolverton, in preparation, 2015]. In recent months, use of FPASS has been initiated to determine the structures of unsolved entries from the Powder Diffraction File. To date, 10 solutions have passed all consistency checks.

In collaboration with **Agrawal** and **Choudhary**, Logan and **Wolverton** have explored a general-purpose machine learning strategy for predicting properties of inorganic materials. While previous approaches have been successful in predicting a single property of a single class of materials, they have introduced a single method that is capable of producing predictive models capable of solving a broad variety of materials problems, and applied it to a variety of material property databases, including ones containing crystalline and amorphous materials. The method uses machine learning to discover functional relationships between material properties and quantitative attributes derived from material composition. It employs a set of attributes broad enough to capture important chemical effects for multiple materials problems and introduces a hierarchical modeling strategy to enhance the accuracy of our models by partitioning the databases into subsets of similar materials. This new method can be used to learn novel design rules, predict the properties of yet-unstudied materials, and dramatically accelerate combinatorial searches.

COLLABORATIONS

Co-alloy Microanalytical Characterization

Collaborators: Eric Lass, Kil-Won Moon, Maureen Williams
Materials Science and Engineering Division, NIST

Dunand and **Seidman** research groups are collaborating with colleagues at NIST on the microanalysis of prototype Co-alloys

Co-alloy Database Development

Collaborators: Carelyn Campbell, Ursula Kattner
Materials Science and Engineering Division, NIST

This collaboration by Gregory **Olson** involves the sharing of pre-CALPHAD data for database development.

Stress relief dynamics in SLM 718+

Collaborator: Lyle Levine

Materials Science and Engineering Division, NIST

Gregory **Olson** is collaborating with Lyle Levine on APS synchrotron 4D tomographic measurement of a SLM 718+ alloy sample from DARPAOpen Manufacturing program on additive manufacturing.

Materials Design Class

Collaborator: Shenyen Li

Materials Science and Engineering Division, NIST

NIST post-doctoral researcher, Li, attended the Materials Design class, taught by **Olson** at Northwestern University throughout Spring Quarter 2014. ■

IN-SITU Si-COMPOSITE MATERIALS

Peter Voorhees (lead), Christopher Wolverton

Department of Materials Science and Engineering, Northwestern University

Using computations, verified databases, and experiments in collaboration with Dow Corning we shall design Si-based alloys that are both tough and melt castable. This will yield a composite that has many of the desirable characteristics of ceramics such as good wear resistance and excellent corrosion resistance, yet can be processed using industry standard casting approaches. A hallmark of this use-case group is the close interaction between Dow-Corning scientists in every aspect of this project. Through this close interaction the codes and databases that are developed are being transferred to industry. The databases will be assembled from open literature and commercially available sources and then concatenated into a CALPHAD databases. These databases will be available to the public.

DESIGN GOALS

The over-arching goal of the project is to the design of melt-castable ceramic materials, and to design high performance Si-based composite materials for structural applications. The focus of the use-case group is on Si-Cr-Ti-Co alloys. A major challenge with these materials is that the Si is a strong compound former. Since both Si, at room temperature, and Si compounds are brittle phases, the challenge is to design a polyphase microstructure that increases the toughness of the materials beyond that of the constituent phases. Thus, CALPHAD modeling is needed to choose the alloy compositions and predict the phases present for a given alloy composition. The required toughness of the composite can be attained through a fine spatial dispersion of one brittle phase in another. This polyphase mixture should have microstructural features sufficiently small, and thus interfacial area sufficiently high, to yield significant crack deflection. Such crack deflection is well known to yield a tough material using brittle component phases. The fine distribution

of the phases will be created via solidification of eutectic or near-eutectic alloys. Thus, models of the eutectic solidification process are needed to design the processing path and molds to yield these fine microstructures. Finally, since Si expands on freezing, it is necessary to choose alloy compositions that minimize solidification induced cracking. The goal is to produce to produce a castable-ceramic with a toughness in the 4-6 MPa m^{1/2} range.

SIGNIFICANT ACCOMPLISHMENTS

Central to the design of melt-castable Si-based ceramic materials is the ability to predict the phases that form for a given alloy composition, and the processing path needed to insure that these phases are present in the microstructure. To this end, Kattner and **Voorhees** are developing a publically available CALPHAD database for the Si-Cr-Ti-Co system using the density functional theory calculations of Skinner and **Wolverton** to fix the energy of the end members of the phase

diagram. Previous assessments have not used DFT data in their calculations and have relied on optimization of metastable structures with little to no experimental information, which may cause problems when extrapolating to multicomponent systems. In addition, the Wolverton Open Quantum Mechincal Database predicts a different CrSi_2 space group and prototype ($I4/mmm \text{ MoSi}_2$) than the experimental result ($P6422 \text{ CrSi}_2$), implying that the structure is entropically stabilized. Experimental information in the literature has been reassessed, and has resulted in the removal of the high temperature $\beta\text{-Cr}_5\text{Si}_3$ from the diagram due to the effect of C contamination. Using this information, the Si-rich corner of the ternary is shown in Figure 1. The new liquidus projection predicts a eutectic reaction of $L \rightarrow \text{CrSi}_2 + \text{CoSi}_2 + \text{Si}$ that is lower in Si content than the $\text{Si}+\text{CrSi}_2$ eutectic.

RESEARCH ACCOMPLISHMENTS

The systems design chart gives the overall design approach that we are employing see Figure 1. The objective of this chart is to show the interrelationship between processing, structure, properties, and performance.

In order to avoid cracking during solidification, the volume expansion on freezing should be as small as possible. This can be done by choosing an alloy composition that yields a volume of the liquid that is close or identical to the volume of the solid. However, during solidification the composition of the liquid changes due to solute segregation into the liquid. Thus, any calculation of the volume change on solidification must also consider the solidification path of the alloy. The key idea is to match the molar volumes of the liquid and solid near the end of solidification. So, design of an alloy that minimizes volume expansion induced cracking requires knowledge of how the molar volumes of the liquid can solid change with composition and temperature, as well as the solidification path that is given by the phase diagram. To address this goal we have created a molar volume database. The inputs to the database are from experiment and *ab initio* molecular dynamics (AIMD) for the liquid. The *ab initio* molecular dynamics calculations employ density functional theory calculations at each time step to determine the forces between atoms. The AIMD calculations were performed by Kwan Skinner (Dow Corning) and **Wolverton**. The densities from the AIMD calculations, and experimentally measured densities were interpolated using a classical CALPHAD method by **Voorhees**.

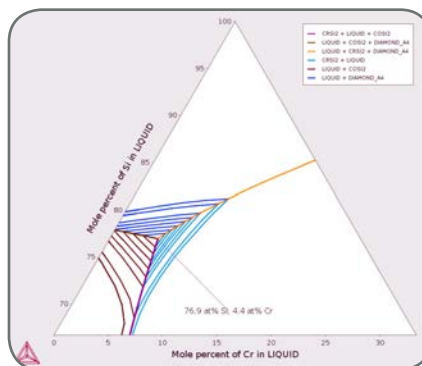


Figure 1. Isotherms on the liquidus surface of the recently reassessed Si-Co-Cr phase diagram showing the three-phase eutectic. The gold line is the Scheil solidification path.

The binary alloy systems Si-Cr, Si-Co, and Si-Ti have been reassessed using up-to-date experimental information coupled with DFT calculations for end member phases. In addition to the DFT data, the experimental data has been reassessed. This has resulted in the removal of the high temperature $\beta\text{-Cr}_5\text{Si}_3$ from the binary phase diagram. A recent study did not find the presence of this phase in the binary system and a study done on the Si-Cr-C system found this phase only in the presence of C^2 . The original study used graphite dyes and therefore, we presume the creation of $\beta\text{-Cr}_5\text{Si}_3$ is due to contamination and has not been included in our assessment. The integration of DFT in our assessment has also shown discrepancies between the experiments and first principle calculations. DFT predicts a different CrSi_2 space group and prototype ($I4/mmm \text{ MoSi}_2$) compared to the experimental ($P6422 \text{ CrSi}_2$). In addition, the low temperature $\alpha\text{Cr}_5\text{Si}_3$ and CrSi are also unstable, implying that these structures are all entropically stabilized.

With the newly optimized Si-Cr and Si-Co binaries, predictions of the ternary Si-Co-Cr system, are possible. In the Si-rich corner of the ternary, the liquidus projection predicts a eutectic reaction of $L \rightarrow \text{CrSi}_2 + \text{CoSi}_2 + \text{Si}$ that is lower in Si content than the $\text{Si}+\text{CrSi}_2$ eutectic (See Figure 1). This is beneficial, as it should reduce the amount of expansion in the last to freeze. Using a Scheil model, the solidification path could be predicted and an alloy composition could be selected to reduce the expansion as well as maintain eutectic structure (shown in gold). The alloys tested had significant reduction in cracking.

The need to understand and to predict the growth of eutectics has lead to the development of general theories for eutectic growth in binary alloys. Among them, the Jackson-Hunt theory establishes relations between the growth velocity, the eutectic spacing and the undercooling

**In-Situ Si-Composite Materials
Group Researchers and Their Roles**

| Name | Position | Institution/ Affiliation | Project Title (PI) |
|-----------------------|-------------------------|-----------------------------|---|
| Peter Voorhees | PI | NU/MSE | <i>In-Situ Si Composite Materials</i> |
| Christopher Wolverton | PI | NU/MSE | <i>In-Situ Si Composite Materials</i> |
| Oriane Senninger | Postdoctoral Researcher | NU/MSE | <i>In-Situ Si Composite Materials (Voorhees)</i> |
| Shiqiang Hao | Postdoctoral Researcher | NU/MSE | <i>In-Situ Si Composite Materials (Wolverton)</i> |
| Matthew Peters | Graduate Student | NU/MSE | <i>In-Situ Si Composite Materials (Voorhees)</i> |

(temperature of the solid/liquid interface compared to the eutectic temperature). These relations are the following $v = A_1 \Delta T^2, \lambda^2 v = A_2 \lambda \Delta T = A_3$ where A_1 and A_2 depend on the alloy diffusivity in the liquid, thermodynamic properties and interfacial energies at the solid/liquid interface, and A_3 depends only on the interfacial energies of the three interfaces in the eutectic. This model is an approximation, since the Si-CrSi₂ eutectic is a faceted eutectic.

Thus, through knowledge of these constants and the evolution of the solidification front during the casting process it is possible to predict the eutectic spacing that develops at a point in the casting and set the desired microstructure by choosing the alloy composition and processing conditions. However, it is difficult to measure quantities such as the diffusion coefficient. Skinner thus employed abinitio molecular dynamics to determine the intrinsic diffusion coefficients in a Si-Cr liquid. In addition to this information, it is also necessary to know the thermodynamic factor to predict the interdiffusion coefficient, which depends on the second derivative of the molar free energy of the liquid with respect to composition. We obtained this from the CALPHAD fit to the free energy of the liquid. By combining the predictions from density functional theory and CALPHAD free energies we determined a very difficult to measure liquid diffusivity, and hence reduce the range of uncertainty in the coefficients A_1 and A_2 . This leads to a more accurate prediction the development of the eutectic microstructure.

COLLABORATIONS

Collaboration on In-Situ Si Composite Materials

Collaborators: Vasgen Shamamian, Kwan Skinner, Andres Becerra, Lance Wu
Si-Alloys group, Dow Corning Corporation

The scientists from Dow Corning are deeply involved in the In-Site Si Composites project. Hence, the collaboration is in every aspect of the project and they are collaborating with everyone in the use-case group.

Collaboration on CALPHAD Assesment of Si-Alloys

Collaborators: Ursula Kattner^a, James Warren^{a,b}

^aMaterials Science and Engineering Division, NIST

^bMaterial Genomics, Material Measurement Lab, NIST ■

DIRECTED SELF-ASSEMBLY OF BLOCK COPOLYMERS FILMS FOR LITHOGRAPHIC APPLICATIONS

Paul Nealey (lead)¹, Juan de Pablo¹, Stephen Sibener², Luping Yu², Heinrich Jaeger², Ian Foster^{3,4}

¹Institute for Molecular Engineering, University of Chicago

²Department of Chemistry, University of Chicago

³Mathematics and Computer Science, Argonne National Laboratory

⁴Computation Institute, University of Chicago

Directed Self-Assembly (DSA) has the potential to revolutionize nanomanufacturing. The interest and exponential growth in research activity and expenditure is driven in the semiconductor industry by the prospect of manufacturing future generations of computer chips according to Moore's law, without having to invest billions in new fabrication facilities (i.e. based on extreme ultra violet lithography) that may or may not be able to meet the resolution requirements already being demonstrated by DSA. For hard drives, block copolymer lithography is the only known technology that is feasible to fabricate nanoimprint masters to manufacture bit patterned media at the required storage densities (at least greater than 2 Terabit/inch²). Finally, commercialization of DSA in nanomanufacturing is currently focused on block copolymers, but the general concepts and measurement tools, once established, are anticipated to be broadly applicable to other self-assembling materials and technologies.

DESIGN GOALS

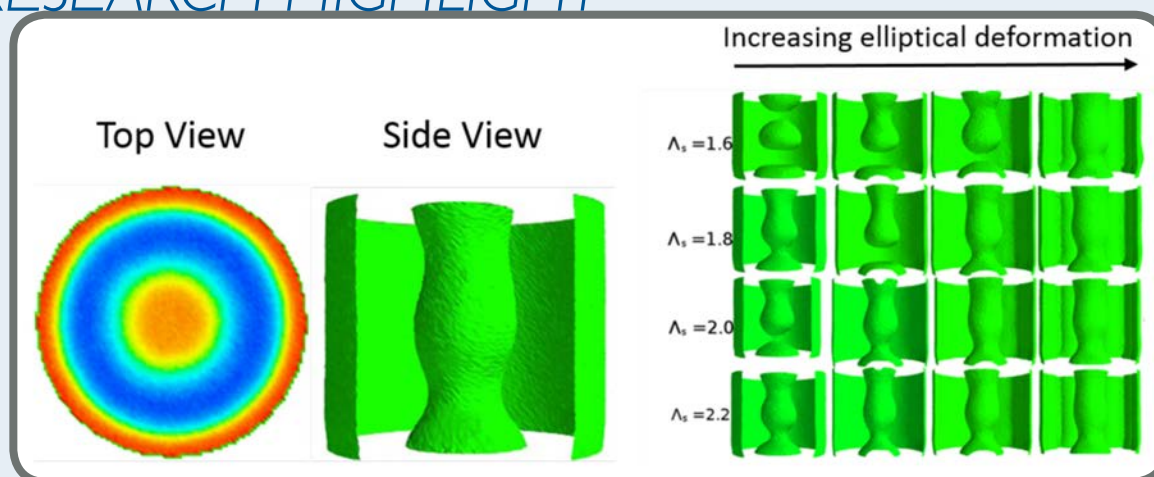
Here, we seek to lower the resolution limit, such that the DSA manufacturing processes can serve three to four future generations of products. We will rely on "Theoretically Informed Coarse Grained" (TICG) simulations, informed by atomistic simulations and experiments, coupled to evolutionary search strategies of material-pattern combinations, to design so-called high χ block copolymer systems capable of self-assembling into the sub 10 nm regime. We aim to identify a "champion" process flow and sub 10 nm DSA materials system employing the same strategy we used to develop the materials and processes used for generation 1 DSA, now implemented at IMEC, an international industrial consortium, HGST International, a leader in production of hard drives, and a host of other companies around the globe. We will advance our fundamental understanding of DSA and structure in the block copolymer films through a collaborative partnership between center researchers, NIST (Joseph Kline, Alex Liddle), and Argonne National Laboratory (ANL).

TICG simulations on Argonne's powerful computers, coupled to state-of-the art experimental characterization at Argonne's Advanced Photon Source, will capture the details of the three-dimensional structure of individual block copolymer domains, and the collective averages of three-dimensional structure and pattern perfection over large areas, all as a function of materials, processing and boundary conditions used in DSA. Experiments will include transmission electron microscopy and tomography, and resonant soft X-ray scattering (RSoXS) in transmission-tomography mode.

SIGNIFICANT ACCOMPLISHMENTS

- Resonant soft X-ray scattering of PS-b-PMMA DSA with different boundary conditions (**Nealey/de Pablo**)
- Resonant soft X-ray scattering of PS-b-P2VP DSA at C and N absorption edges (**Nealey/de Pablo**)
- Resonant soft X-ray scattering of multilayered DSA with top-and-bottom patterns (**Nealey/de Pablo**)

RESEARCH HIGHLIGHT



GRAPHOEPI TAXIAL ASSEMBLY OF CYLINDER FORMING BLOCK COPOLYMERS IN CYLINDRICAL HOLES

Brandon L. Peters¹, Ben Rathsack², Mark Somervell², Takeo Nakano³, Gerard Schmid⁴ and Juan J. de Pablo¹

¹Institute for Molecular Engineering, University of Chicago, Illinois 60637

²Clean Track Advanced Technology Group, Tokyo Electron America, Austin, Texas 78741

³Clean Track Advanced Technology Group, Tokyo Electron Limited, Minato-ku, Tokyo, Japan

⁴Strategic Lithography Technology, Global Foundries, Malta, New York 12020

SCIENTIFIC ACHIEVEMENT

Monte Carlo simulations were performed with block copolymers to explore the hole-shrink problem for lithographic applications. The commensurability of the natural periodicity of the block copolymer and the diameter of the hole is a key factor for creation of polymer cylinders that extend through the hole. When a system deviates from the ideal commensurability conditions, rational changes of the wall-polymer interactions, the hole geometry, or the composition of a blend with homopolymers are shown to provide viable strategies for formation of cylinders that extend through the hole and are useful for lithographic patterning.

SIGNIFICANCE

This research uses a Monte Carlo simulation to simulate experimentally relevant systems. Importantly, we demonstrate that by deforming circular holes into ellipses, it becomes possible to form full cylinders over a wider range of conditions than in perfectly cylindrical holes. We also find that homopolymer addition, at concentrations in the vicinity of 20%, increases the range of conditions over which full cylinders are observed. These results allow simulations to identify conditions and material combinations that will alleviate defects in experiments.

CITATION INFORMATION

Peters, B. L., Rathsack, B., Somervell, M., Nakano, T., Schmid, G., & de Pablo, J. J. (2014). Graphoepitaxial assembly of cylinder forming block copolymers in cylindrical holes. *Journal of Polymer Science Part B: Polymer Physics*. DOI: 10.1002/polb.23652

ACKNOWLEDGEMENTS

This work is supported by the Center for Hierarchical Materials Design (CHIMAD). Additional support from the Semiconductor Research Corporation for development of fast simulation codes is gratefully acknowledged.

- Three dimensional DSA using 2D chemical patterns (**Nealey/de Pablo**)
- In-situ membrane sample preparation for block copolymer DSA (**Nealey**)
- Intermediate X-ray Energy beamline commission at the Advanced Photon Source (**Nealey**)
- End-to-End Alignment of Gold Nanorods on Topographically Enhanced Cylinder-Forming Templates and their Surface Enhanced Raman Properties (**Sibener**)

- Particle Organization through Two Levels of Selectivity – Making the Most of Defects in Block Copolymers (**Sibener**)
- Dynamics of Block Copolymer Swelling by a Selective Solvent for the Spatially Resolved Molecular Deposition (**Sibener**)
- Evolutionary design of polymer brushes and triblock materials for sub-10nm DSA (**de Pablo/Nealey/Jaeger**)
- Coarse grained simulation of DSA for contact hole-shrinking (**de Pablo**)

RESEARCH ACCOMPLISHMENTS

Over the 2014-2015 funding period, **Nealey** group has developed membrane sample fabrication techniques through extensive collaboration with Argonne National Laboratory (ANL) and industrial collaborators such as IMEC and HGST that enable transmission characterization of the in-film structures of blockcopolymer DSA. Collaborating with Joseph Kline from NIST, the **Nealey** group performed RSoXS experiments on these membrane DSA samples at the Advanced Light Source (ALS) to characterize the in-film structure of block copolymer. Four examples are given below:

1) RSoXS of PS-b-PMMA DSA with different boundary conditions

DSA of perpendicularly oriented lamella-forming BCP is of great interest for semiconductor industry and it's important for the lamella structures to propagate all the way through the film. However, molecular simulation suggests the existence of in-film 3D morphologies even when the top surface is well-aligned, and the formation of such structures is highly influenced by the boundary condition. DSA samples with

different guiding stripe widths were prepared at IMEC using an all-track process previously developed by the Nealey group, a first in the industry. Preliminary results show that the lamella goes through the film at optimal guiding stripe width but U-shape structures were formed in-film at wider guiding stripes, similar to those predicted by molecular simulations from the **de Pablo** group.

2) RSoXS of PS-b-P2VP DSA at C and N absorption edges

PS-b-P2VP is a high χ system that can deliver smaller dimensions beyond the limit of PS-b-PMMA, and it's an important candidate for 2nd generation DSA materials. Through collaborations with ANL and HGST, DSA samples with different guiding stripe widths were prepared on SiN membrane by the **Nealey** group. The existence of nitrogen in P2VP block also enables us to leverage the element-specific contrast that's unique to soft X-ray to identify the two blocks. Scattering experiments were performed at the C edge as well as the N edge, which is the first of such study on BCP DSA.

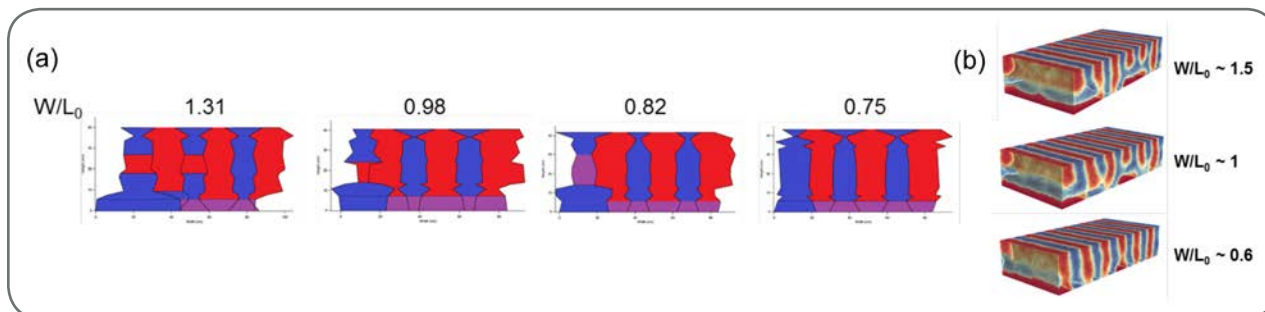


Figure 1. (a) Calculated in-film lamella structures by fitting scattering data of BCP DSA. (b) Molecular simulations for different guiding stripe widths show similar in-film structures.

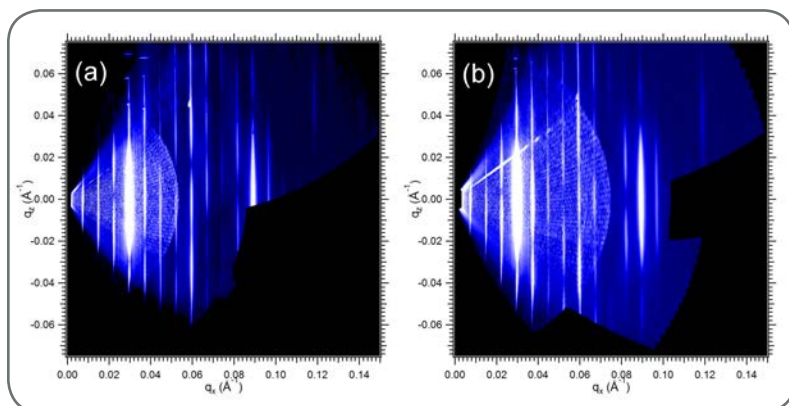


Figure 2. Qx-Qz scattering data of PS-b-P2VP lamella DSA at the C edge (a) and N edge (b) respectively.

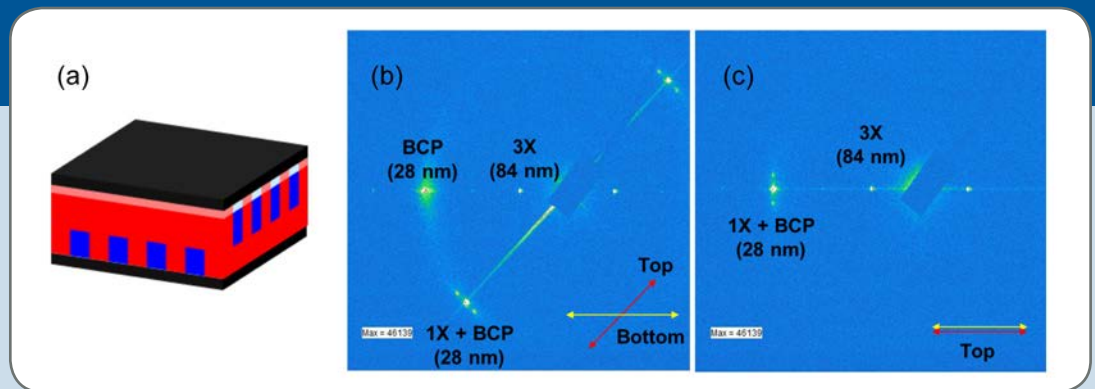


Figure 3. (a) Schematic of the lamella DSA with top and bottom patterns. (b)(c) Scattering pattern of the sample with pattern angle of 45° (b) and 0° (c) respectively.

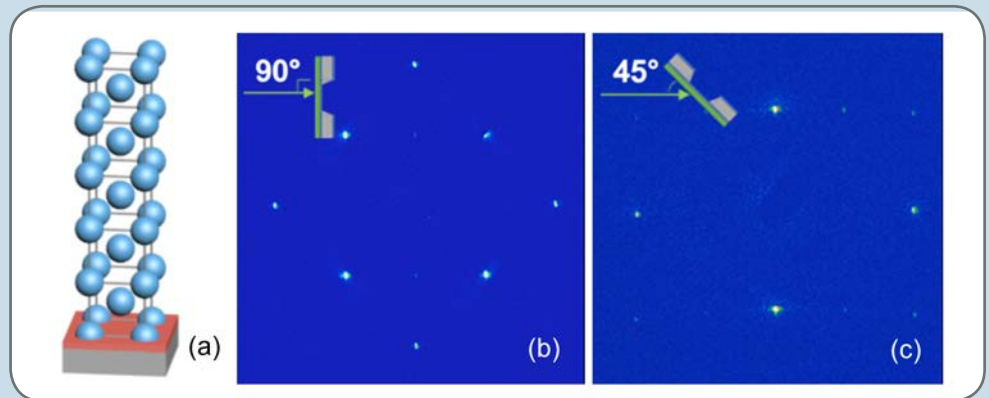


Figure 4. (a) Schematic showing 10 layers of spheres assembled on a 2D pattern that matches the BCC(001) plane. (b) (c) X-ray diffraction pattern of the BCC(001) assembly with incident angle of 90° (a) and 45° (b) respectively, perfectly matching crystallographic predictions.

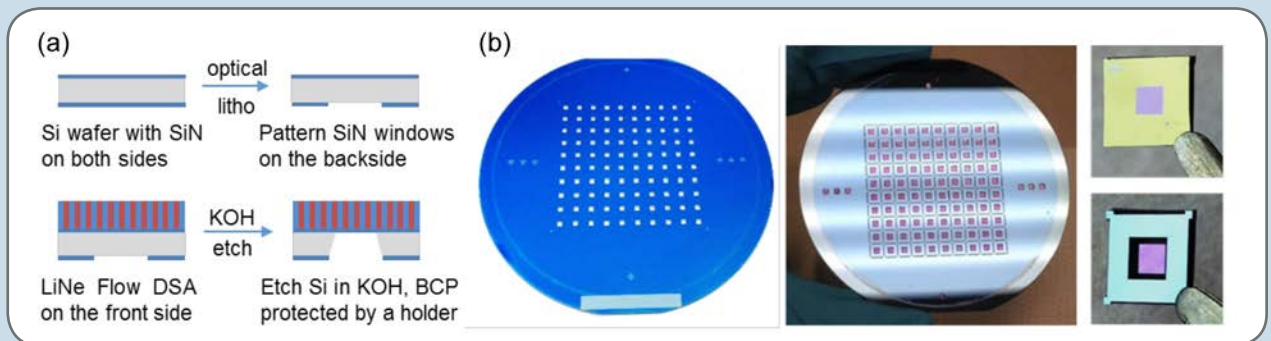


Figure 5. (a) Back etch process to prepare SiN membrane sample in-situ. (b) 4" wafers and individual membranes after back etch.

3) RSoXS of multilayered DSA with top-and-bottom patterns

DSA with guiding patterns on both top and bottom can direct the assembly in two directions; the resulting morphology at the interface is not clear. Techniques developed by the **Nealey** group to fabricate DSA patterns on membranes has made possible the transmission characterization of the entire film. Through molecular transfer printing, the top coat pattern was printed onto a patterned SiN membrane with different angles between the two patterns. Preliminary scattering results show two sets of peaks, suggesting DSA

along 2 directions. By fitting the scattering in both directions we will be able to delineate the interfacial morphology.

4) Three dimensional DSA using sphere-forming PS-b-PMMA

The **Nealey** group has developed strategies to extend the concept of DSA into 3D lattice systems by using a 2D chemical pattern to match one plane of the 3D lattice. These strategies are supported by simulations by the **de Pablo** group. DSA studies were done on sphere-forming PS-b-PMMA as a pilot system, which forms body-centered-cubic (BCC) lattice in the bulk. When the film thickness is commensurate

with plane spacing, DSA can be achieved through more than 10 layers of spheres on patterns matching BCC (001) geometry. The resulting structure is comparable to a single crystal, and soft X-ray diffraction-tomography was performed to understand the in-film lattice packing and the wobbling of spheres from their lattice points.

Enabling all the aforementioned transmission measurements, strategies have been developed by the **Nealey** group with Center for Nanoscale Materials at ANL to prepare membrane samples in-situ to avoid the unwanted artifacts inherent to conventional membrane preparation techniques. DSA was done on SiN coated wafers and in the final step back etched the Si to get SiN membranes. The polymer is protected by a specially designed holder and morphological details are thus perfectly preserved.

The **Nealey** group is also collaborating with the ANL to commission a new Intermediate X-ray Energy Beamline at Sector 29 of the Advanced Photon Source. The first beam was taken in the scattering chamber in late August 2014 and the instruments are going through final stages of characterization and calibration. The chamber hosts a seven-axis in-vacuum diffractometer with kappa geometry, which allows access to a larger area of reciprocal-space than standard two- and three-circle diffractometers typically found in RSoXS end-stations. With the diffractometer and analyzer fully operational, we are ready for the first RSoXS experiment, which is scheduled for February 2015.

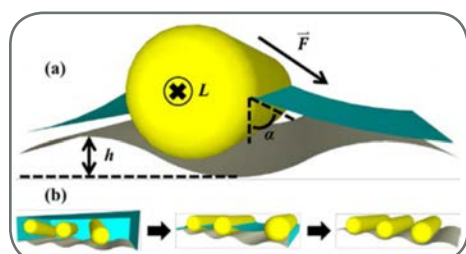


Figure 7. (a) Nanorods are drawn into registry with the corrugated polymer template with excellent (>97%) alignment (b) as the deposition solvent recedes

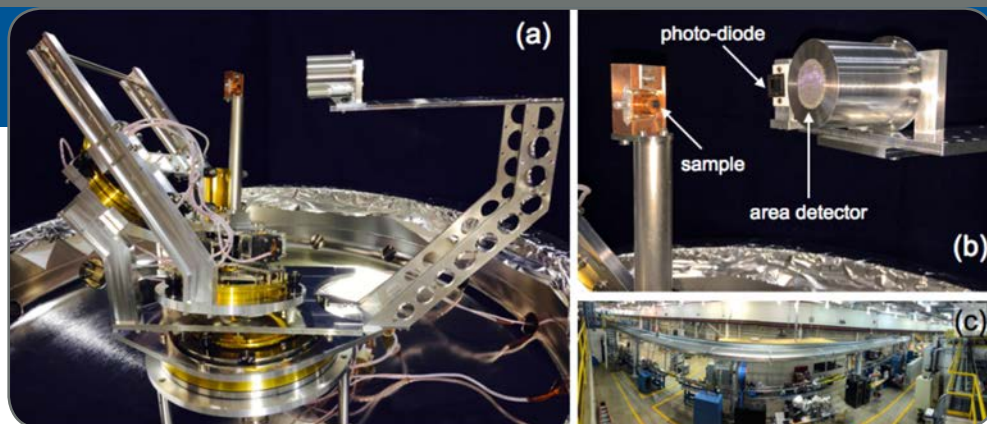


Figure 6. (a) The in-vacuum Kappa-diffractometer of the scattering end-station at 29ID. (b) Detailed view of the sample holder and the detectors. (c) Panoramic view of the Intermediate X-ray Energy Beamline at Sector 29 of the APS.

Over the 2014-2015 funding period, the **Sibener** group has been engaged in three projects concerning the directed self-assembly (DSA) of block copolymer (BCP) templates. These projects are unified by the common theme of using BCP substrates as a scaffold for the hierarchical organization and DSA of functional nanoparticles and molecules.

In the first of these projects, we aimed to produce end-to-end nanorod assemblies, due to the optimal field enhancement of end-to-end junctions. However, deposited nanorods naturally form side-by-side aggregates. To overcome these challenges, we have employed corrugated block copolymer templates for DSA of end-to-end nanorod arrays. Acetic acid vapor annealing was used to selectively swell and collapse the PMMA domains, producing a highly corrugated polymer template. Capillary forces draw deposited nanorods into the nanogrooves and enforce conformal alignment (>97%) with the groove (Figure 7). Prior alignment of polymer cylinders within lithographic channels enables global alignment of end-to-end nanorods (Figure 8). Our success in these goals has yielded SERS substrates with high sensitivity to incident laser polarization (Figure 9).

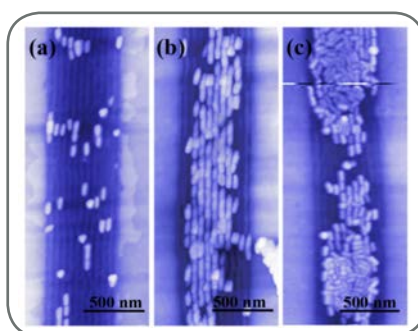


Figure 8. Hierarchical alignment of gold nanorods on pre-aligned DSA polymer scaffolds for a series of nanorod densities producing unprecedented end-to-end nanorod arrays. (a) 40 AuNRs/μm², (b) 160 AuNR/μm², and (c) >250 AuNRs/μm².

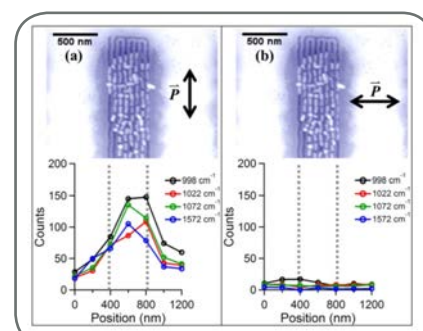


Figure 9. Novel SERS substrates show high sensitivity to the incident laser polarization. Benzenethiol SERS signals across the arrays with (a) parallel and (b) perpendicular incident laser polarizations

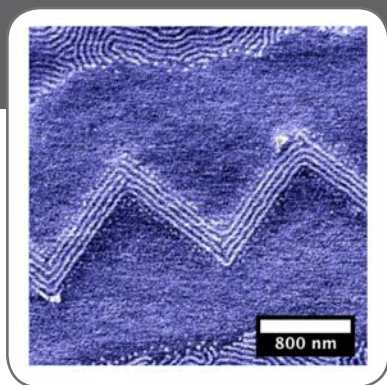


Figure 10. Conformal and continuous alignment of nanoconfined cylinders in kinked channels produces high strain energy grain boundaries

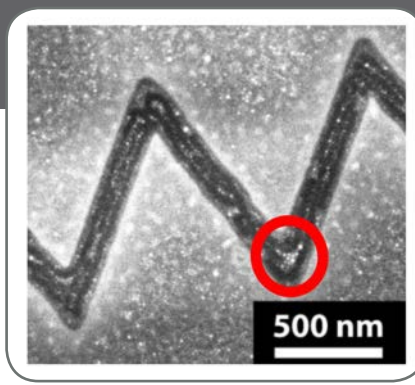


Figure 11. Engineered artificial grain boundaries enable highly precise localization of nanoparticles

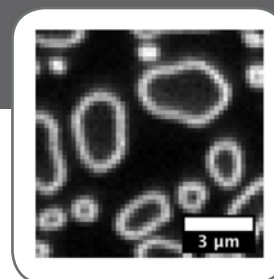


Figure 12. Fluorescence map of BODIPY incorporation demonstrates precise and selective molecular incorporation along the periphery of polymer islands

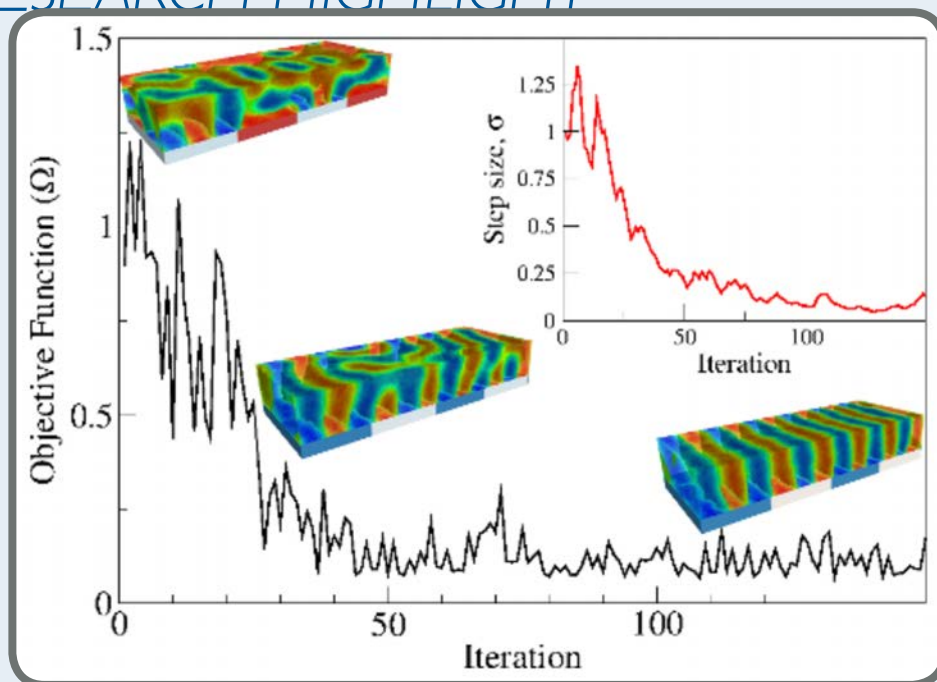
We have also investigated the use of artificial grain boundaries for the DSA of nanoparticle aggregates. Our approach involves two levels of control, (1) chemical selectivity and (2) defect selectivity, in order to direct the positions of nanoparticle additives. First, PS-capped nanoparticles are selectively incorporated into PS domains due to chemical compatibility. Next, particles aggregate along defect sites in the polymer matrix in order to relieve elastic strain. We can engineer defect locations by using the conformal alignment of nanoconfined cylinders within kinked (zigzag) channels to produce highly strained artificial grain boundaries (Figure 10). This hierarchical DSA approach has enabled the precise localization of nanoparticle defects at engineered defect sites (Figure 11).

Finally, in situ AFM of imaging block copolymer islands under a selective solvent allows direct observation of swelling front kinetics. These observations are relevant to understanding diffusion rates for emerging polymer-encapsulated drug delivery schemes. Moreover, by using the solvent as a carrier for small molecules, they may be incorporated into the polymer matrix. This spatially resolved incorporation has been observed for the fluorophore BODIPY (Figure 12). As this ongoing work continues, the use of DSA polymer templates will enable positional control over functional molecule gradients.

Using evolutionary strategies, **de Pablo**, in collaboration with **Jaeger** and **Nealey**, has demonstrated the use of evolutionary computation strategies for design of chemical patterns capable of self-assembling triblock copolymers into features with characteristic dimensions below 14 nm. Patterning at sub-10 nm is one of the design goals for our team, and the evolutionary work of our team, which currently places us below 14 nm, put us on a promising pathway to achieving

some of our long-term goals. In different work, **de Pablo** also demonstrated the use of DSA for hole-shrinking applications at length scales below 20 nm. That work was a collaboration with scientists and engineers from TEL and from Global Foundries. More specifically, the graphoepitaxial assembly of cylinder-forming block copolymers assembled into holes was investigated through theoretically informed coarse grained Monte Carlo simulations (TICG MC). The aim was to identify conditions leading to assembly of cylinders that span the entire thickness of the holes, thereby enabling applications in lithography. Three hole geometries were considered, including cylinders, elliptical cylinders, and capsule-shaped holes. Four distinct morphologies of cylinder-forming poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) block copolymers were observed in cylinders and elliptical holes, including cylinders, spheres, partial cylinders, and wall-bound cylinders. Additional morphologies were observed in capsule-shaped holes. PMMA cylinders that extend through the entire hole were found with PMMA-wetting surfaces; a weak wetting condition was needed on the bottom of the hole and a strong wetting condition was necessary on the sides of the hole. Simulations were also used to explore the morphologies that arise when holes are overfilled, or when PMMA homopolymers are added in blends with copolymers. We found that overfilling can alter considerably the morphological behavior of copolymers in cylinders and, for blends; we found that when the homopolymer concentration is >10%, the range of conditions for formation of PMMA cylinders that extend through the entire hole is increased. In general, results from simulations (TICG) were shown to be comparable to those of self-consistent (SCFT).

RESEARCH HIGHLIGHT



EVOLUTIONARY OPTIMIZATION OF DIRECTED SELF-ASSEMBLY OF TRIBLOCK COPOLYMERS OF CHEMICALLY PATTERNED SUBSTRATES

Gurdaman S. Khaira¹, Jian Qin¹, Grant P. Garner¹, Shisheng Xiong¹, Lei Wan², Ricardo Ruiz², Heinrich M. Jaeger³, Paul F. Nealey^{1,4}, and Juan J. de Pablo^{1,4}

¹Institute for Molecular Engineering, The University of Chicago, Chicago, IL 60637

²HGST, San Jose, CA 95135,

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⁴Argonne National Laboratory, Argonne, IL 60439

SCIENTIFIC ACHIEVEMENT

We used an evolutionary optimization method, coupled with molecular simulations, to predict the optimal chemical patterns for directed self-assembly of block polymers with density multiplication of lines and spaces. In contrast to blind search algorithms, the evolutionary approach is able to rapidly identify the optimal combination of pattern geometry, chemistry of the guiding stripes and chemistry of the background material. This work is the first to use computationally intensive, but realistic three-dimensional molecular simulations to address the inverse problem of design of guiding patterns for defect-free self-assembly of block copolymers in lithographic applications.

SIGNIFICANCE

Most practical applications of block copolymers rely on complex morphologies that are inherently non-equilibrium in nature. Designing a suitable guiding pattern for directed assembly into a sought after target represents one of the grand challenges for the use of block copolymers

in lithography. The guiding patterns need not have a one-to-one correspondence with a target morphology. Moreover, a large number of independent variables makes this inverse design problem intractable by trial-and-error. The method described in this work represents a “smart” strategy to efficiently search for an optimal combination of these system variables. From a user’s perspective, no-prior information on the sensitivity of a given parameter towards the final morphology is required. This approach is not limited to pattern or materials variables, but can also be extended to searches for optimal processing conditions, including annealing temperature, solvent evaporation rate, etc..

CITATION INFORMATION

Khaira, G. S., Qin J., Garner G. P., Xiong S., Wan L., Ruiz R., Jaeger H. M., Nealey P. F., and de Pablo J. J. “Evolutionary Optimization of Directed Self-Assembly of Triblock Copolymers on Chemically Patterned Substrates.” *ACS Macro Letters* 3, no. 8 (2014): 747-752..

ACKNOWLEDGEMENTS

This research work was performed under award 70NHN14H012 from the U.S. Department of Commerce, National Institute of Standards and Technology as part of the CHiMad. Additional support from the Semiconductor Research Corporation for the development of new processing strategies for sublithographic patterning is gratefully acknowledged. H.M.J acknowledges support from NSF CBET 1334426.

Directed Self-Assembly of Block Copolymers Films for Lithographic Applications

Group Researchers and Their Roles

| Name | Position | Institution/ Affiliation | Project Title (PI) |
|----------------------|-------------------------|-----------------------------|---|
| Paul Nealey | PI | UC/IME | |
| Juan de Pablo | PI | UC/IME | |
| Stephen Sibener | PI | UC/CHEM | |
| Luping Yu | PI | UC/CHEM | |
| Heinrich Jaeger | PI | UC/CHEM | |
| Ian Foster | PI | UC/CI | |
| Jiaxing Ren | Graduate Student | UC/IME | <i>RSoXS of block copolymer directed self-assembly (Nealey)</i> |
| Fanny Simoes | Postdoctoral Researcher | ANL/APS | <i>Intermediate Energy X-ray beamline setup (Nealey)</i> |
| John Colson | Postdoctoral Researcher | UC/IME | <i>Directed self-assembly of block copolymer polyelectrolytes (Nealey)</i> |
| Qianqian Tong | Graduate Student | UC/CHEM | <i>(Sibener)</i> |
| Jonathan Raybin | Graduate Student | UC/CHEM | <i>(Sibener)</i> |
| Hyung Ju Ryu | Postdoc | UC/CHEM | <i>(Sibener)</i> |
| Gurdaman Khaira | Student | UC/IME | <i>Evolutionary algorithms for materials design in DSA (DePablo)</i> |
| Brandon Peters | Graduate Student | UC/IME | <i>Directed self-assembly of copolymers (De Pablo)</i> |
| Grant Garner | Graduate Student | UC/IME | <i>Directed self assembly (De Pablo/Nealey)</i> |
| Roselyne Tchoua | Graduate Student | UC/CI | <i>Machine learning environment for automated creation of advanced databases (Foster)</i> |
| Katherine Oosterbaan | Undergraduate Student | UC/CHEM | <i>(Sibener)</i> |
| Michelle Chalupnik | Undergraduate Student | UC/CHEM | <i>(Sibener)</i> |
| Jay Prakadan | Undergraduate Student | UC/CHEM | <i>(Sibener)</i> |
| Mladen Rasic | Undergraduate Student | UC/CHEM | <i>Web-based software for polymer property prediction (Freed/de Pablo)</i> |

COLLABORATIONS

Design of materials for graphoepitaxy and hole-shrinking processes

Collaborators: Scientists from TEL and Global Foundries

The **de Pablo** Research group is collaborating with scientists and engineers from TEL and Global Foundries on computational designs of materials for graphoepitaxy. The collaboration resulted in a publication.

Design of materials for commercial chemical epitaxy processes.

Collaborators: Scientists from IMEC (Belgium) and INTEL

The **de Pablo** and **Nealey** research groups are collaborating with scientists and engineers from IMEC in Belgium. The collaboration requires that two CHiMaD students (Grant Garner and Robert Seidel) be placed at IMEC facilities in

Belgium, under the supervision of Dr. Roel Gronheid, for assembly-line development and testing of new materials. **De Pablo** and **Nealey** are also collaborating with Dr. Younkin from Intel on development of X-ray based metrology tools and development of software for industrial design of DSA processes.

RSoXS of Block Copolymer Directed Self Assembly

Collaborators: Joseph Kline Materials Science and Engineering Division, NIST

RSoXS characterization of the in-film structure of block copolymer directed self assembly. Scattering experiments were performed at Advanced Light Source by Jiaxing Ren (**Nealey** group) and Joseph Kline.

Block Copolymer Directed Self Assembly

Collaborators: Jack Douglas

Materials Science and Engineering Division, NIST

Sibener and **de Pablo** research groups are collaborating with Jack Douglas at NIST for directed self assembly of block copolymers.

PUBLICATIONS

Brandon L. Peters, Ben Rathsack, Mark Somervell, Takeo Nakano, Gerard Schmid and Juan J. **de Pablo** (2015), "Graphoepitaxial assembly of cylinder forming block copolymers in cylindrical holes," *J. of Polymer Science B, Polymer Physics*, Article first published online: 16 DEC 2014 | DOI: 10.1002/polb.23652. CHiMAD primary support.

Khaira, Gurdaman S.; Qin, Jian; Garner, Grant P.; **Nealey**, Paul F., **Jaeger**, H., and **de Pablo**, Juan J., (2014) "Evolutionary Optimization of Directed Self-Assembly of Triblock Copolymers on Chemically Patterned Substrates," *ACS Macro Letters*, 3, 747-752. CHiMAD primary support.

Tong, Q.; Malachosky, E.W.; Raybin, J.; Guyot-Sionnest, P.; **Sibener**, S.J., (2014), "End-to-End Alignment of Gold Nanorods on Topographically Enhanced Cylinder-Forming Templates and their Surface Enhanced Raman Properties." *Journal of Physical Chemistry C*, 118 (33), 19259-19265. Partial CHiMaD support/primary CHiMaD support for DSA components of this project.

DATABASES

Polymer Design Data Base

System of interest: Characteristic properties for design of polymer blends and copolymers for engineering applications, including DSA. The database is now being populated by resorting to automated techniques that extract target content from the literature. Human intervention is then required to verify relevance and accuracy of computer-generated entries. The data base will be tested through a formal course, to be taught at the University of Chicago in Spring 2015, with collaborators from NIST (Debra Audus and Jack Douglas). The data base also includes a thermodynamic property prediction set of modules based on state-of-the-art molecular models.

Methodology: Theory and experiment

Distribution: Not released yet

Collaborators: Juan **de Pablo**, Ian **Foster**, Paul **Nealey**, and Heinrich **Jaeger**

Prediction of Phase behavior of polymers and polyelectrolytes

System of interest: Polymer blends, polyelectrolytes, copolymers

Methodology: Computational and experimental

Distribution: Under development

Collaborators: Juan **de Pablo**, Ian **Foster**, Paul **Nealey**, Matthew **Tirrell**, Heinrich **Jaeger**, Jack Douglas, Carl Freed

SOFTWARE

Simulation Software

Authors: Juan **de Pablo**, Gurdaman Khaira

Type: Licensed

Software for simulation of block copolymer directed self assembly was released to INTEL in November 2014. ■

BIOMATERIALS

Matthew Tirrell (lead)¹, Juan J. de Pablo¹, Monica Olvera de la Cruz², Erik Luijten^{2,3,4}

¹Institute for Molecular Engineering, University of Chicago

²Department of Materials Science and Engineering, Northwestern University

³Department of Engineering Sciences and Applied Mathematics, Northwestern University

⁴Department of Physics and Astronomy, Northwestern University (by courtesy)

The Biomaterials Use-Case Group is developing new materials based on multi-valent ionic interactions. This direction is significant because it can yield new types of self-assembled structures that: (a) do not depend on typical and well-studied hydrophobic interactions to create the assembly; (b) yield materials with useful gelation, surface coating and self-healing properties; (c) are biocompatible; (d) can be used to sequester solid particles and nucleate the formation of inorganic phases, as in biomineralization; and, (e) afford routes to numerous design innovations. Knowledge of the as-yet unexplored phase behavior of polyelectrolyte complexes, which we are creating, is scientifically significant and technologically relevant. We are learning when and, more importantly why, polyelectrolyte complexes may be solid or liquid. We are building a database of phase behavior to comprehend the stability of complexes with respect to salt, with a variety of salt valences.

DESIGN GOALS

The knowledge foundation we are creating, via experiment, theory and simulation, will enable the design of new materials based on multi-valent ionic interactions in several domains of materials development: coatings for biomaterials, encapsulants for particles, self-healing hydrogels as biomaterials, and biomineralization with applications to bone and dental repair.

SIGNIFICANT ACCOMPLISHMENTS

The principal accomplishments have been (a) the development of a new liquid state capable of both predicting and interpreting experimental phase behavior, leading to (b) a better understanding of the interfacial tension property at the interface between polyelectrolyte complexes and water; (c) simulations that shed light on how stereo-regularity and -sequences influence whether a complex is liquid or solid.

RESEARCH ACCOMPLISHMENTS

A mixture of oppositely charged polyelectrolyte chains in solution can associate and form various kinds of complexes, collectively known as polyelectrolyte complexes (PECs). Broadly, these complexes can be classified as solid phase

PEC precipitates, or fluid phase complexes known as coacervates. The basic physics of why complexes form is well-understood: compensation of charges on one polyelectrolyte chain in solution by charges of opposite sign that are intrinsically entropy-deprived by virtue of being on another polymer chain, while maintaining electro-neutrality, thereby liberating entropy-rich small ions into a co-existing aqueous solution favors formation of PECs. Thus, polymer concentration in the complex phase is presumably governed by a balance between attractive interactions from electrostatics and repulsive excluded volume interactions. However, more detailed, and especially quantitatively predictable physical understanding of polyelectrolyte complex formation remains elusive. We envisage these studies are essential for the expansion of PECs as platforms for next generation designer materials.

The phase behavior of polyelectrolyte blends is described by incorporating local ionic correlations via liquid state (LS) theory. This theory accurately describes strongly enhanced phase separation that is experimentally observed in polyelectrolyte mixtures. In addition to strongly enhanced macrophase separation between the two polymer types, liquid-liquid phase separation within the charged polymer is found at high electrostatic

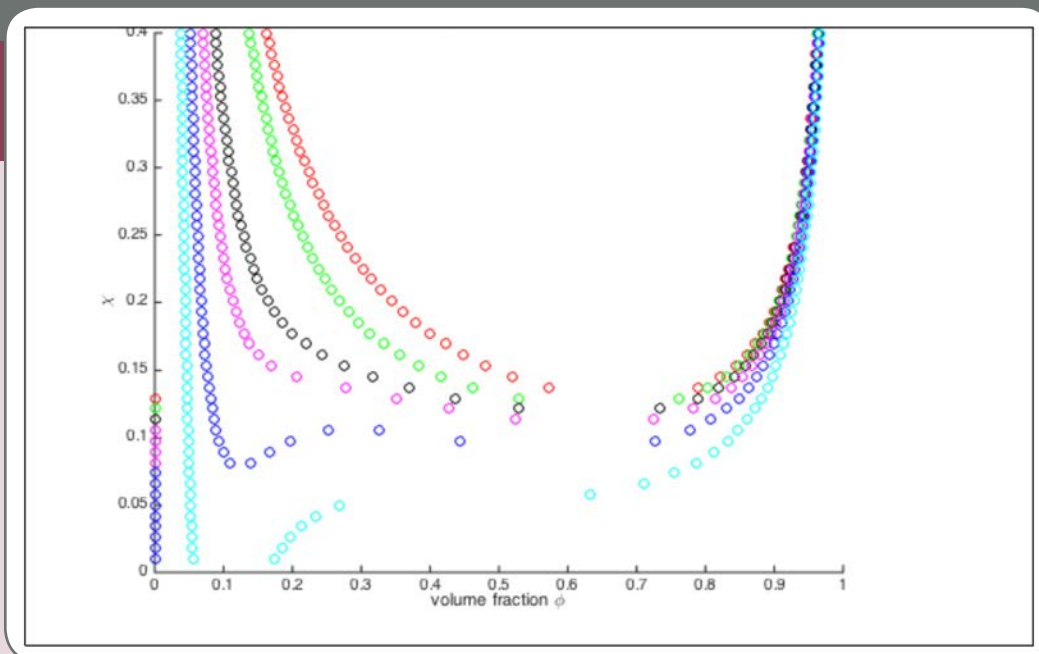


Figure 1. Spinodal lines for a symmetric polymer blend system with $N = 40$, charge fraction $f_q = 0.1$, and $\Gamma = 0.24, 4.02, 9.23, 12.07, 17.28, 23.43$ from top to bottom.

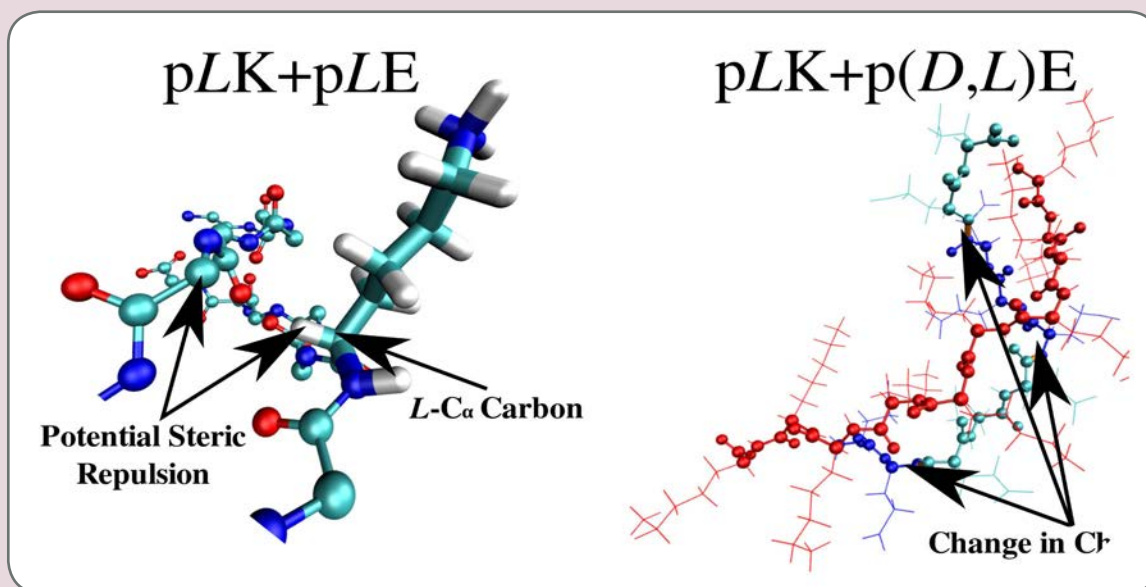


Figure 2. Chiral polymers (left) can conform to one another in a beta sheet arrangement leading to solid complexes; racemic polymers (right) cannot.

interaction strengths. Above a threshold value, which depends on the number of mers of polymer, the charge fraction of the charged polymer, and the Flory-Huggins interaction χ , the charged polymer separates into regions of ion-rich and ion-poor regions, forming ion clusters within the charged polymer phase. This is indicated by multiple spinodal regions shown for Γ of 17.28 kT and 23.43 kT in Figure 1.

We have illustrated the phase determining role of chirality of chain backbone in polyelectrolyte complexation in Figure 2. Systematic atomic-level simulations of short poly(glutamic acid) and poly(lysine) chains revealed that achiral chains formed unstructured complexes. In contrast, antiparallel stable β -sheets were formed between homochiral polypeptides.

We attribute the changes in chirality along the peptide backbone to cause “kinks” in the backbone, thus inhibiting extended β -sheet formation. We provide new insights that allow for facile morphology control in polyelectrolyte complexes, and will be useful in developing of simple yet strong bio-inspired polyelectrolyte based hybrid materials.

Biomaterialization is another area of research activity and accomplishment in our multi-valent ionic materials use-case. Calcium phosphate (CaP) is an important material in biology and biomedical applications. Moreover, calcium phosphate nanoparticles has been used as stable, biocompatible, non-toxic and cheap inorganic materials in cosmetics and pharmaceutical applications. A particularly interesting design

goal for CaP consists of development of injectable, self-setting cements for bone regeneration. Such cements would offer significant advantages over conventional, pre-shaped bone substitutes. During minimally invasive bone regenerative surgery, CaP based cement materials can be directly injected into irregular bone defects and act as an osteoconductive material. Importantly, the performance of the cement predominantly relies on the structural characteristics of the CaP nanoparticles that constitute the cement. In our biomaterials use-case, we have adopted a biomimetic approach to synthesize CaP nanoparticles with controlled size (Fig. 3a) and surface properties for formulation of a new class of injectable materials (Fig. 3b). The approach includes precipitation of CaP from aqueous solution in the presence of different well-characterized polyelectrolytes. Subsequently, we exploit interparticle interactions to induce self-assembly of the CaP nanoparticles into an integrated gel (Fig. 3c and 3d). Our approach requires precise control of multiple interactions between calcium and phosphate ions, polyelectrolyte additives and other precipitating phases that are being modeled, characterized, and optimized. Important parameters such as pH, temperature, polymer concentration and polymer molecular weight all play a significant role in the proposed process.

Finally, work by **Luijten** investigates how self-assembly involving biological and synthetic components is affected by nonuniform dielectric properties. As a prototypical model system, we consider dielectrically heterogeneous Janus particles—spherical colloids with a dielectric mismatch between their two hemispheres. When such particles are suspended in solution, this mismatch leads to different polarization charges induced on the two hemispheres. Employing a new and efficient computational approach that dynamically and spatially resolves the polarization charge distribution within molecular dynamics simulations, we found that dielectric effects can significantly alter the ion distribution around dielectric Janus colloids. More importantly, large-scale molecular dynamics simulations

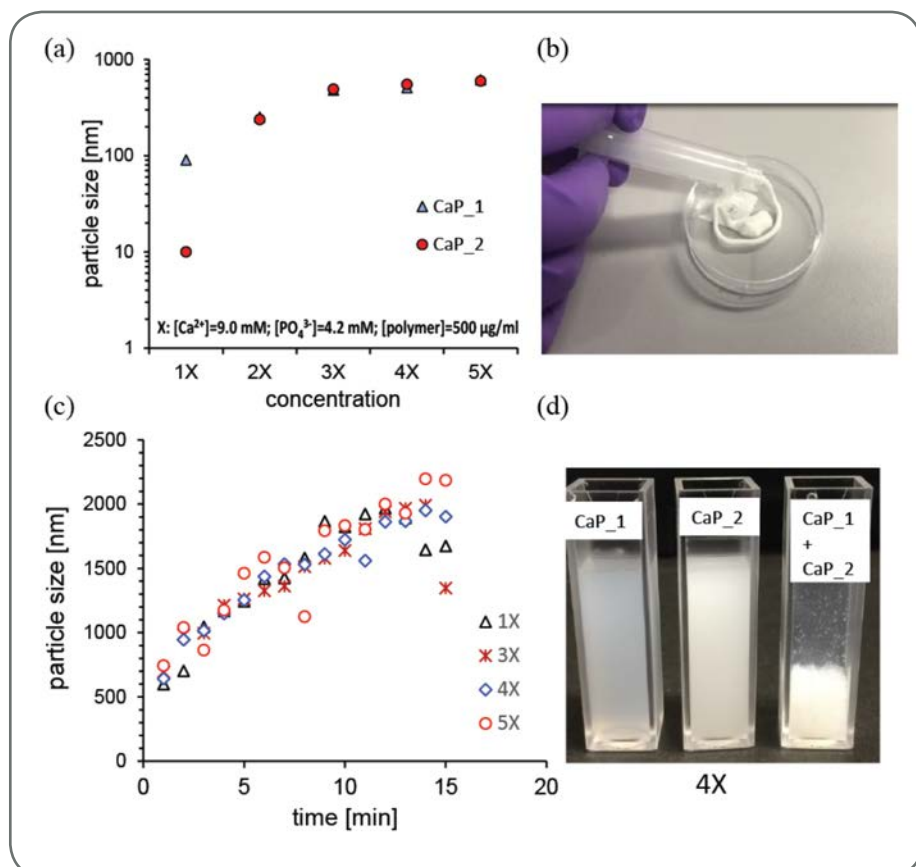


Figure 3. (a) Effect of concentration on the size of CaP nanoparticles stabilized by two different polyelectrolytes. (b) Gel extrusion of CaP_1 + CaP_2 by a conventional medical syringe. (c) Effect of initial concentration on the aggregation of the CaP_1 + CaP_2 systems. (d) Representative CaP_1 + CaP_2 aggregation.

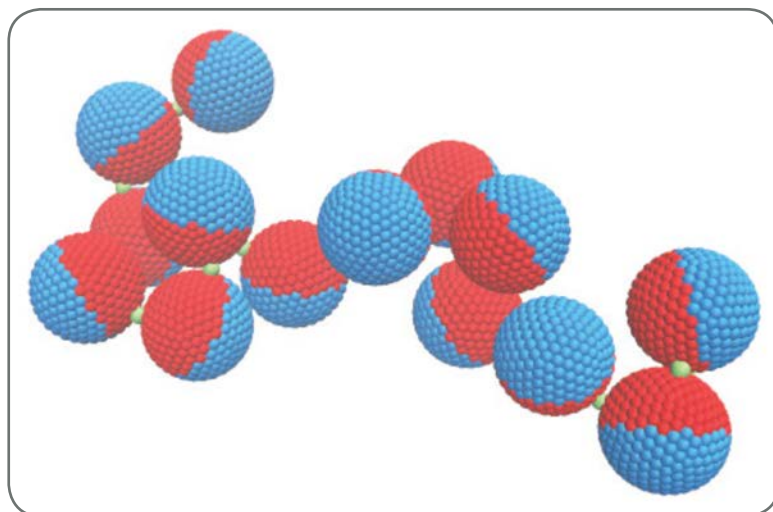


Figure 4. Self-assembly of colloids with anisotropic dielectric properties (red and blue surfaces), bound by charged nanoparticles. Depending on the solvent selected, the nanoparticles preferentially bind (electrostatically) to surfaces with either low or high dielectric constant, thus opening the possibility of solvent-dependent structures.

RESEARCH HIGHLIGHT

have shown that within self-assembled aggregates these Janus particles can have various orientational preferences, controlled by the surrounding medium. We envisage that this property can be exploited to create nanostructures that are responsive to their dielectric environment.

COLLABORATIONS

SANS investigations of copolyelectrolyte micelles and hydrogels

Collaborators: Vivek Prabhu

Chemical Engineer, Materials Science and Engineering Division, NIST

Srivastava, **Tirrell** and **de Pablo** are collaborating with Prabhu on synthesis of deuterated copolyelectrolytes and conducting subsequent SANS experiments on copolyelectrolyte based micelles and hydrogels. The aim of the work is to illustrate the structural hierarchy in the hybrid materials, thus enabling intelligent design of drug carrying and tissue scaffold materials.

This active collaboration initiated in October 2014. Two postdocs from the **Tirrell** group visited NIST in December 2014 to conduct SANS experiments. A joint proposal at CNMS, ORNL has also been accepted for synthesis of deuterated polymers.

Inorganic Hierarchical Materials

Collaborators: Sheng Lin-Gibson

Biosystems and Biomaterials Division, NIST

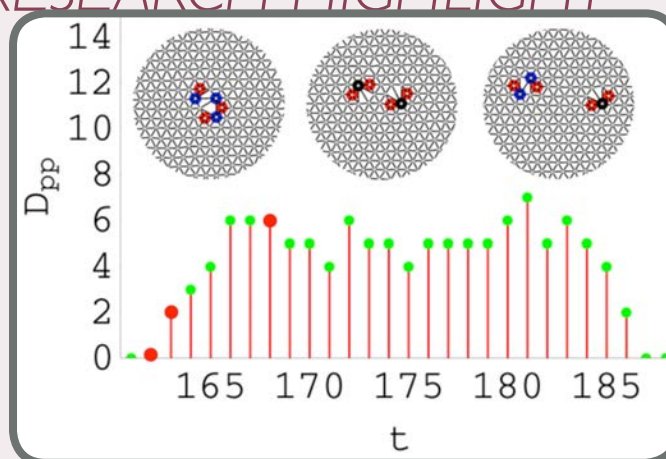
Qazvini, **de Pablo** and **Tirrell** are collaborating with Lin-Gibson on biomineralization and biomimetic approaches to generate hierarchical structures based on inorganic materials such as CaP and complex coacervates.

Modeling of polymeric materials

Collaborators: Jack F. Douglas

Materials Science and Engineering Division, NIST

The **De Pablo** research group is collaborating with Douglas in studying transport properties of polymer blends and solutions, polymer films and glasses. A postdoctoral researcher, jointly advised by **de Pablo** and Douglas, will start at NIST in March 2015 to further the collaborative work on polyelectrolyte biomaterials.



DYNAMICS OF VACANCIES IN TWO-DIMENSIONAL LENNARD-JONES CRYSTALS

Zhenwei Yao¹, Monica Olvera de la Cruz^{1,2,3,4}

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SCIENTIFIC ACHIEVEMENT

Vacancies represent an important class of crystallographic defects, and their behaviors can be strongly coupled with relevant material properties. In this work, we study the dynamics of generic n -point vacancies in two-dimensional Lennard-Jones crystals in several thermodynamic states. Simulations reveal the spectrum of distinct, size-dependent vacancy dynamics, including the nonmonotonously varying diffusive mobilities of one-, two- and three-point vacancies, and several healing routines of linear vacancies. Specifically, we numerically observe significantly faster diffusion of the two-point vacancy that can be attributed to its rotational degree of freedom.

The high mobility of the two-point vacancies opens the possibility of doping two-point vacancies into atomic materials to enhance atomic migration. The rich physics of vacancies revealed in this study may have implications in the engineering of defects in extensive crystalline materials for desired properties.

SIGNIFICANCE

The dynamics of crystallographic defects influences many aspects of crystalline materials. The two dimensional Lennard-Jones crystal has been extensively used to describe the physical properties of materials such as metals and nanoparticles. This study shows that it also serves to perform fundamental researches on the defect dynamics. Counterintuitive results emerge in the two dimensional Lennard-Jones crystal: two-point vacancies diffuse significantly faster than one-point and three-point vacancies. In addition, rich dynamics of vacancies with different sizes are found in simulations. These results may be useful as well with more complex and realistic three-dimensional structures.

CITATION INFORMATION

Zhenwei Yao and Monica Olvera de la Cruz, *Phys. Rev. E*, 90, 062318 (2014)

ACKNOWLEDGEMENTS

M.O. thanks the financial assistance of the U.S. Department of Commerce, National Institute of Standards and Technology as part of the Center for Hierarchical Materials Design (CHiMaD) award 70NANB14H012. Z.Y. thanks the Office of the Director of Defense Research and Engineering (DDR&E) and the Air Force Office of Scientific Research (AFOSR) under Award No. FA9550-10-1-0167 for financial support. We thank Alexander Patashinski, Chandler Becker, and Carrie Campbell for stimulating discussions..

| Biomaterials | | | |
|-----------------------------------|-------------------------|-----------------------------|---------------------------------------|
| Group Researchers and Their Roles | | | |
| Name | Position | Institution/ Affiliation | Project Title (PI) |
| Matthew Tirell | PI | UC/IME | Biomaterials |
| Juan de Pablo | PI | UC/IME | <i>Biomaterials</i> |
| Monica Olvera de la Cruz | PI | NU/MSE | <i>Biomaterials</i> |
| Erik Luijten | PI | NU/MSE | <i>Biomaterials</i> |
| Samanvaya Srivastava | Postdoctoral Researcher | UC/IME | <i>Biomaterials (Tirell)</i> |
| Nader Taheri Qazvini | Postdoctoral Researcher | UC/IME | <i>Biomaterials (Tirell/de Pablo)</i> |
| Sanaz Sadati | Postdoctoral Researcher | UC/IME | <i>Biomaterials (de Pablo)</i> |
| Andres Cordoba Uribe | Postdoctoral Researcher | UC/IME | <i>Biomaterials (de Pablo)</i> |
| Zhenwei Yao | Postdoctoral Researcher | NU/MSE | <i>Biomaterials (de la Cruz)</i> |
| Kyle Hoffman | Graduate Student | UC/IME | <i>Biomaterials (de Pablo)</i> |
| Joshua Lequieu | Graduate Student | UC/IME | <i>Biomaterials (de Pablo)</i> |
| Huanxin Wu | Graduate Student | NU/MSE | <i>Biomaterials (Luijten)</i> |

Development and application of strategies for incorporating nonuniform dielectric media in particle-based simulations

Collaborators: Zhenli Xu

Department of Mathematics, Institute of Natural Sciences, Shanghai Jiao Tong University

The **Luijten** research group works with an Applied Mathematics group at the Institute of Natural Sciences at Shanghai Jiao Tong University, aiming to develop efficient algorithms for solving the Poisson equation in inhomogeneous dielectric media. Prof. Xu's group has expertise in the image-charge method while the **Luijten** research group is specialized in fast boundary-element-based algorithms. By combining the advantages of both methods, we will have the capability to simulate dynamic systems with full dielectric effects.

This collaboration focuses on algorithms for the Poisson equation. **Luijten** and graduate student Huanxin Wu visited Shanghai Jiao Tong University in December 2014.

PUBLICATIONS

K.Q. Hoffmann, S.L. Perry, L. Leon, D. Priftis, M. **Tirrell**, J.J. **de Pablo** (2014), "A Molecular View of the Role of Chirality in Charge-driven Polypeptide Complexation" *Soft Matter*, DOI: 10.1039/C4SM02336F. Primary CHiMaD support.

J. P. Lequieu, D. M. Hinckley, J.J. **de Pablo** (2014), "High-Precision Characterization of DNA-Nanoparticle Association Energies" *Soft Matter*, DOI: 10.1039/C4SM02573C. Primary CHiMaD support.

Zhenwei Yao and Monica **Olvera de la Cruz**, "Dynamics of vacancies in two-dimensional Lennard-Jones crystals," *Phys. Rev. E*, 90, 062318 (2014). Partial CHIMAD Support.

DATABASES

Prediction of Phase behavior of polymers and polyelectrolytes

System of interest: Polymer blends, polyelectrolytes, copolymers

Methodology: Computational and experimental

Distribution: Under development

Collaborators: Juan **de Pablo**, Ian **Foster**, Paul **Nealey**, Matthew **Tirrell**, Heinrich **Jaeger**, Jack Douglas, Carl Freed

Polymer Design Database

System of interest: Characteristic properties for design of polymer blends and copolymers for engineering applications, including DSA. The database is now being populated by resorting to automated techniques that extract target content from the literature. Human intervention is then required to verify relevance and accuracy of computer-generated entries. The database will be tested through a formal course, to be taught at the University of Chicago in Spring 2015, with collaborators from NIST (Debra Audus and Jack Douglas). The database also includes a thermodynamic property prediction set of modules based on state-of-the-art molecular models.

Methodology: Theory and experiment

Distribution: Not released yet

Collaborators: Juan **de Pablo**, Ian **Foster**, Paul **Nealey**, and Heinrich **Jaeger** ■

ORGANIC BULK HETEROJUNCTION POLYMER SOLAR CELLS

Luping Yu (lead)¹, Juan de Pablo², Giulia Galli², Tobin Marks³

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²Institute for Molecular Engineering, University of Chicago

³Department of Materials Science and Engineering, Northwestern University

Bulk heterojunction organic solar cells (OSCs) represent an alternative solar energy harvesting system. This use-case group is addressing critical issues in material design and synthesis, morphological control and influence on OSC performances, device optimization, data collection on material and device characteristics and structure/property relationship. New polymers exhibiting low absorption band gaps are synthesized, which act as either electron donors or acceptors. New polymers exhibiting proper energy levels match are also developed for use as charge relay or energy harvesting antenna in ternary OSCs. New theoretical methods were developed to investigate the electronic processes (electronic excitation, charge separation and transport). Large scale modeling approach are being developed to investigate the morphological formation and control. These studies are also closely coupled with NIST scientists to fully utilize their expertise in structural and morphological investigation. These new materials and basic knowledge gained will deepen our understanding in structure/property relationship and push the performance of OSCs towards commercial application.

DESIGN GOALS

Organic Bulk Heterojunction Polymer Solar Cells use-case group explored the development of ternary OSCs system, which can further enhance the power conversion efficiency from the binary OSCs system. Efforts involving synthesis, characterization and device evaluation were pursued. New polymers with varied band gaps are synthesized and evaluated for OPV applications. The group aims to describe the morphology of the PTB7/PCBM light-absorbing layer in organic photovoltaic devices (see Figure 1 for structures). Of particular interest is the interface between crystalline PTB7 and amorphous PCBM regions and its relevance to the charge transfer through the film. To that end, molecular dynamics models to capture the behavior of these molecules are in development. The group aims to carry out large simulations of these systems on GPU-enabled computing clusters.

SIGNIFICANT ACCOMPLISHMENTS

Bulk heterojunction (BHJ) polymer solar cells (PSCs) are a popular research subject currently pursued by many groups around world.^{1,2} The state-of-the-art PSCs are composed of a polymer donor and a fullerene acceptor as the active layer and their overall photovoltaic performance is dependent on many factors, such as the electrical and optical properties of donor polymers, device architectures and interfacial layers used.³⁻¹³ Among them, the nature of donor polymer is without doubt the determining factor in power conversion efficiency (PCE) of PSCs. In this work, we report for the first time the study of the influence of polymer polydispersity (PDI, ratio between weight-averaged molecular weight and number-averaged molecular weight) on the performance of polymer solar cells (PSCs) composed of PTB7 and PC₇₁BM as the active layer materials. It was found that polymers exhibiting large polydispersity index contain structural defects

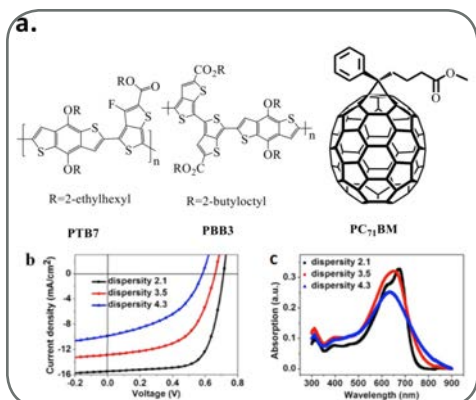


Figure 1. (a), Chemical structures of PTB7, PBB3 and PC71BM. (b), Current-voltage characteristics of PTB7 solar cells with different \mathcal{D} values. (c), UV-vis absorption spectra of PTB7 with different \mathcal{D} values.

that play the role of energy transfer and charge trapping/recombination centers. The results highlighted the importance of controlling PDI of donor polymers for polymeric solar cells.

RESEARCH ACCOMPLISHMENTS

The synthetic chemistry for these polymers exhibits side reactions and generally resulted in polymers exhibiting large PDI. We found that PDI of PTB7 could dramatically influence its photovoltaic performance. Detailed studies led us to conclude that side reactions introduces structural defects that could act as energy transfer and trapping centers in the solar cell devices that hinder the charge generation process and facilitate charge recombination in BHJ organic photovoltaic (OPV) cells (Figure 2). Model reaction confirmed this conclusion.

Chemical structures of PTB7 and PC71BM are shown in Figure 1. Three batches of PTB7 used in this work have PDI values at 2.1, 3.5 and 4.3 with similar molecular weight values at 100, 118 and 103 kg/mol, respectively. When these polymers were used as the donor materials in solar cells under AM 1.5 G illumination at 100 mW/cm², the corresponding current

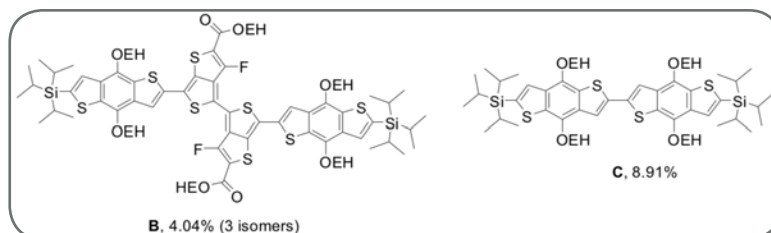


Figure 2. Reaction formula for normal polymerization and model reaction.

density versus voltage (J-V) characteristics of the solar cells are shown in Figure 1b, which indicate dramatic differences in the solar cell parameters for these devices. The external quantum efficiency (EQE) of the three solar cells showed the same trend and was found to extend to longer wavelength and external quantum efficiency (EQE) values decreased dramatically from 300 nm to 700 nm as PDI increases. Since Tunneling electronic microscopy (TEM) studies indicated that morphology is almost identical in these samples, the effect of structural defects is mainly electronic and manifested in deterioration of almost every aspect of associated physical properties in OSCs, ranging from exciton and charge dissociation to charge transport. The mobility decreased from $5.87 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (PDI 2.1) to $4.39 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (PDI 3.5) and $3.44 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (PDI 4.3) for PTB7 hole only devices. The bimolecular recombination of charge carriers increased. The structural defects was shown to act as trapping centers in the devices.

Recently, our group initiated synthesis of donor polymers and developed the bithiopheneimide (BTI) building block, which has been successfully used for the synthesis of a

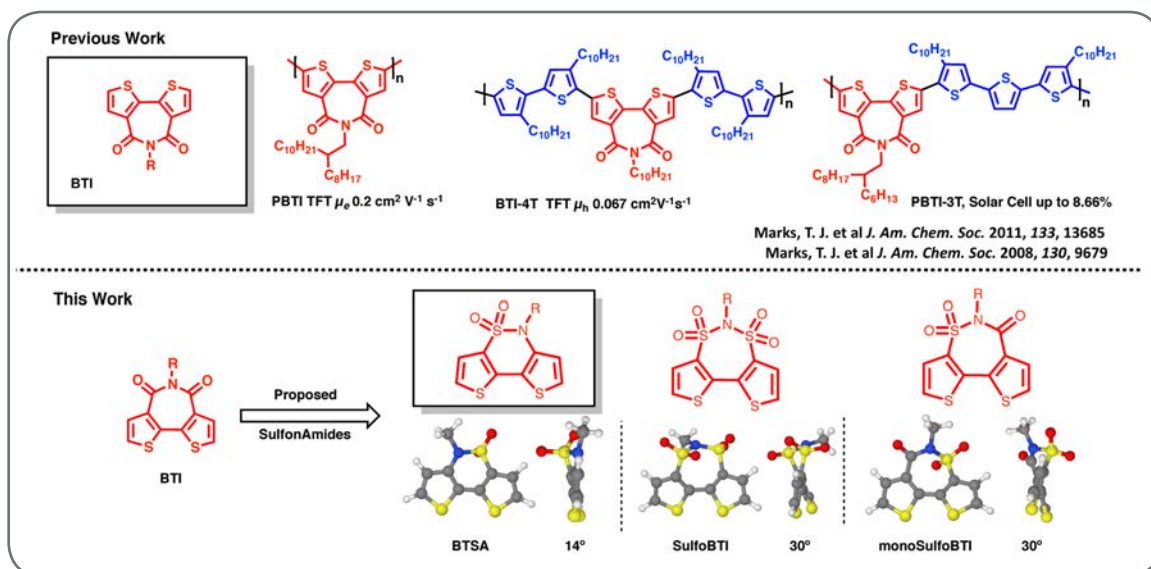


Figure 3. Structures of previously developed thiophene imide semiconductors and the new sulfonamide semiconductors developed in this study.

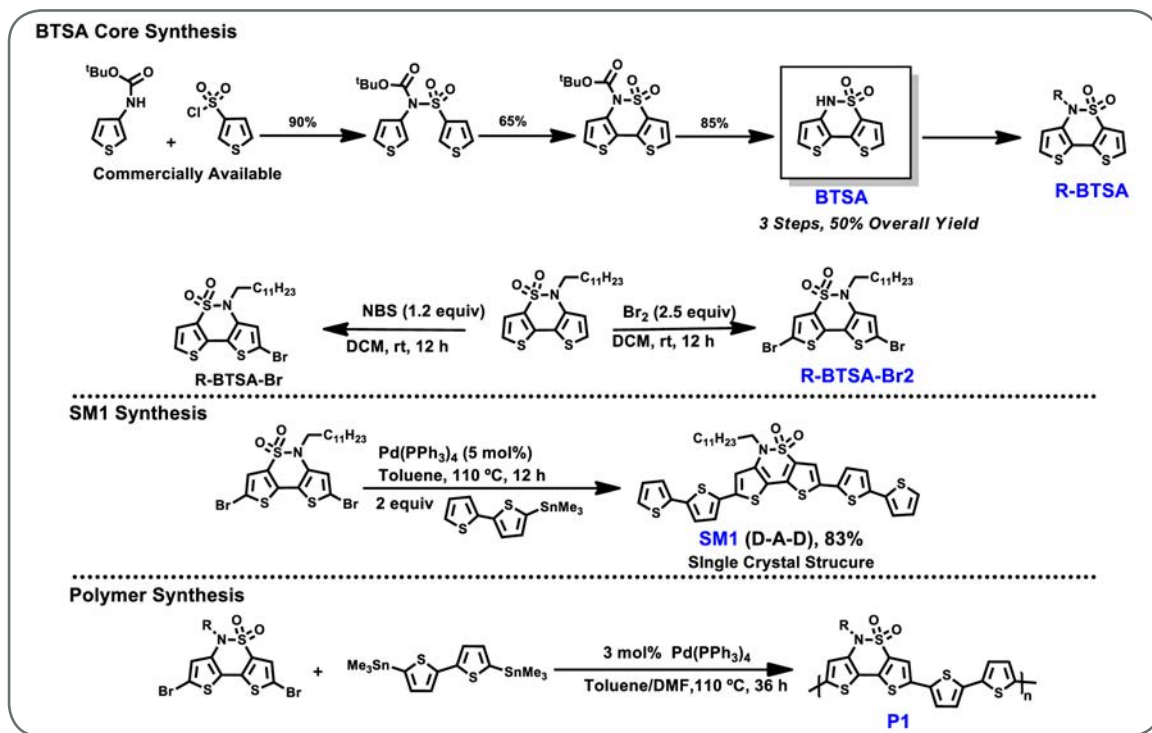


Figure 4. Synthesis of the bithiophenesulfonamide (BTSA) core, halogenated derivatives, and two representative molecular and polymeric semiconductors.

number of high performing organic semiconducting materials including n- and p-type semiconductors for OFET and donor materials for OPV (Figure 3, top). Under the CHiMaD program we have now developed, based on DFT molecular orbital calculations, a new acceptor unit for organic semiconductors based on a cyclic sulfonamide, bithiophenesulfonamide (BTSA) (Figure 3, bottom).

In an initial effort we developed an optimized method for the BTSA core synthesis allowing for the multi-gram scale synthesis of this building block (Figure 4). Next, we studied several alkyl-functionalized derivatives of the BTSA unit so that to tune the solubility, aggregation, and processing parameters of the corresponding polymers. Thus, several synthetic methodologies for the functionalization were explored, including simple alkylation and more sophisticated procedures based on catalytic alkylation. Furthermore, due to the asymmetric reactivity of this core, it was important to develop selective methods for the mono- and di-bromination of the BTSA unit, which is critically important for the ultimate synthesis of the specifically-designed polymeric and molecular semiconductor targets.

Several BTSA molecular and polymeric systems were synthesized. Figure 4 shows only two examples. The BTSA

based small molecule SM1 was prepared, and single crystal analysis of SM1 revealed interesting packing features due to close contacts between the SO_2 group and H atoms for adjacent molecules. Furthermore, we synthesized and fully characterized a series of 12 new BTSA polymers, with the BTSA-dithiophene copolymer P1 being an example (Figure 4, bottom). All the polymers were fully characterized in regard to structure,

purity, and molecular mass. Currently their implementation into OFETs and OPV is in progress. Preliminary results are promising with OFET mobilities approaching $0.1 \text{ cm}^2/\text{Vs}$ and OPV power conversion efficiencies $> 5\%$. Figure 5 shows representative FET characteristics for two polymers and OPV data for P1.

On the simulation front, current generic molecular dynamics force fields such as Optimized Potentials for Liquid Simulations (OPLS) and Assisted Model Building with Energy Refinement (AMBER) do not provide parameters to fully describe these aromatic molecules. Daniel Reid (de Pablo group), is using and developing methods to generate these missing parameters, specifically the bond, angle, dihedral, and partial charge parameters for atoms in and near aromatic regions.

Given the long timescales necessary to see polymer crystallization occur, we would like to hold bonds, angles, and dihedrals with high vibrational frequencies rigid, as this will allow for a larger simulation timestep. A frequency analysis was performed on PTB7 using Gaussian. It was found that vibrational modes of roughly 450 cm^{-1} or greater occurred within the rings while modes of 175 cm^{-1} or less occurred around bonds connecting rings. This large difference and

high frequency of the ring vibrations suggests that we can perform simulations with the aromatic rings held rigid without significant loss in realism, allowing us to use a much larger time step and sample longer timescales. The frequency analysis was done using b3lyp/6-311g on a single monomer.

Since the rings are fairly stiff, the parameters governing the bonds connecting the aromatic rings will be key in reproducing the polymer's properties. To calculate the relevant bond, angle and dihedral parameters, we use electronic structure calculations to find the energy at points in each parameter's stretch, bend or twist, then employ error minimization techniques to assign relevant values. Several methods and basis sets were used, including HF/6-311g, b3lyp/6-311g**, and mp2/cc-PVDZ. Unfortunately, each pairing of method and basis set gives an appreciably different result. Higher-theory methods such as b3lyp and mp2 agree on equilibrium configurations, though show different energy barriers to rotation. For the time being, these equilibrium configurations will be used with placeholders for more refined force constants.

The delocalized π structure of the aromatic rings persists over multiple monomers. We find that the dihedrals between groups of rings vary with polymer length until the chain consists of roughly 3 monomers. Since the electronic structure methods used scale with either n4 or n5, where n is the number of electrons, this limits the level of theory that can be accessed for these more relevant longer chains.

To fully specify these molecular dynamics force fields, partial charges for atoms in and near the aromatic regions must also be determined, as OPLS does not provide values for atoms in these situations. Purely electronic structure-driven

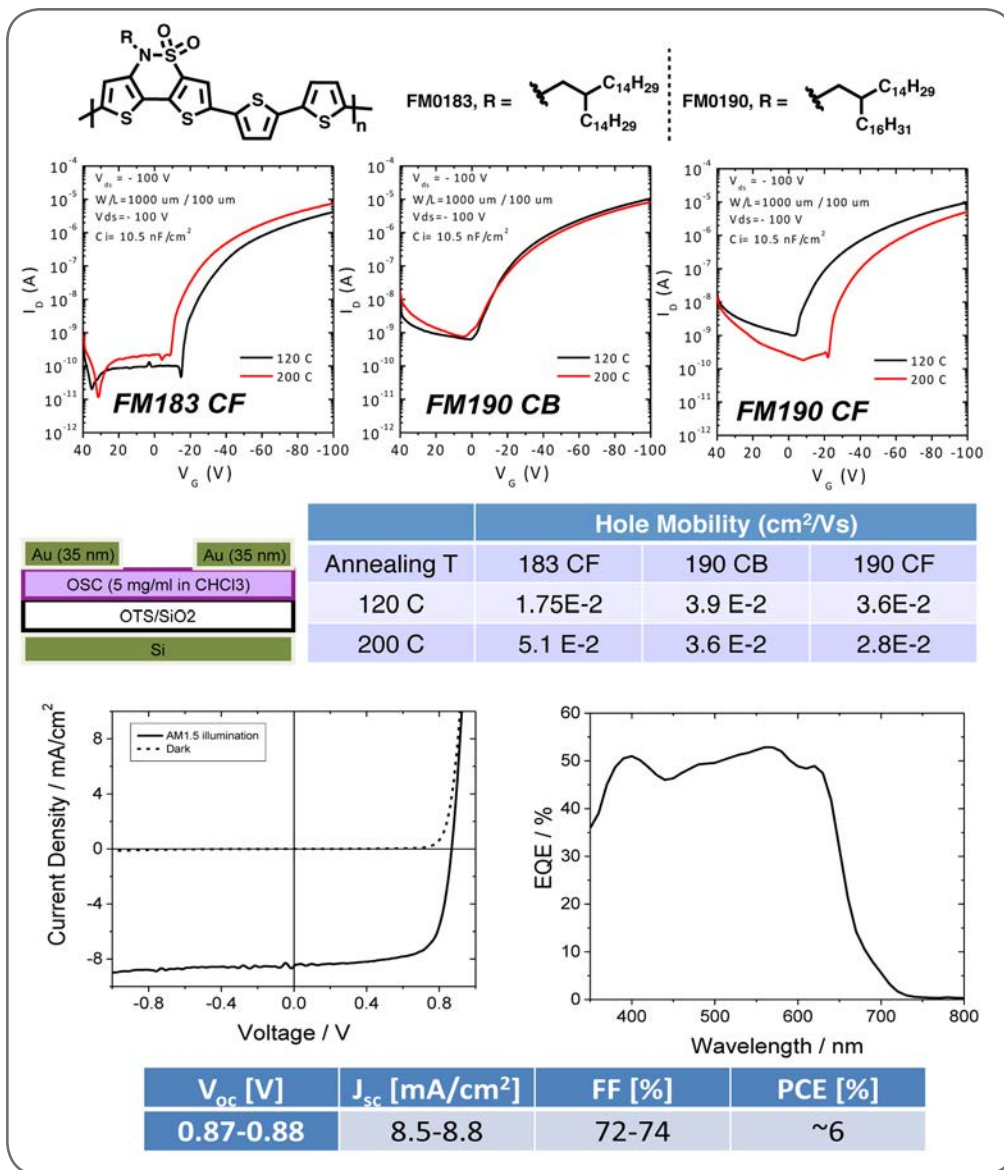


Figure 5. Top: Examples of OFET (bottom-gate, top-contact) performance for the indicated BTSA-bithiophene copolymers. CF means the polymers were processed from CHCl_3 ; CB means processed from chlorobenzene. Bottom: Example of OPV J-V and EQE characteristics for a PI-based inverted OPV cell.

approaches such as natural bonding orbitals give results inconsistent with OPLS in test cases. We achieve better results by modifying and using a method called RESP, restrained electrostatic potential fitting. This method attempts to minimize the error between the electric potentials generated from electronic structure calculations and those generated by a set of point charges (such as one for each atom). Error between these potentials is minimized at a series of coordinates formed in a shell around the molecule. The standard

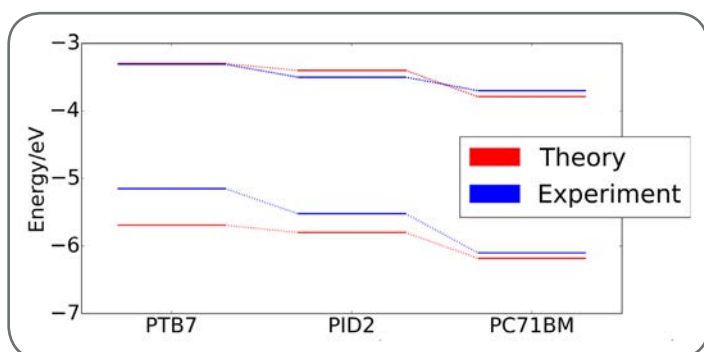


Figure 6. HOMO and LUMO energy levels of the ternary mixture described in ref. [1] (experiment), compared with DFT, periodic calculations (Theory).

| | PTB7 | PID2 | PC71BM |
|------------------------------------|------|------|--------|
| E_g^{Exp} | 1.84 | 2.02 | 2.40 |
| Opt. E_g^{Exp} | 1.68 | 2.03 | – |
| $[E_g@B3LYP]_{geom1}^{PBC}$ | 2.38 | 2.40 | 2.39 |
| $[E_g@B3LYP]_{geom2}^{PBC}$ | 2.28 | – | – |
| $[E_g@B3LYP]_{geom1}^{Isol.}$ | 2.56 | 2.83 | 2.53 |
| $[Opt. E_g@B3LYP]_{geom1}^{Isol.}$ | 3.32 | 3.48 | 2.52 |
| $[E_g@PBE]_{geom1}^{\Gamma}$ | 1.27 | 1.25 | – |
| $[E_g@PBE]_{geom1}^{10k-points}$ | 1.27 | 1.26 | – |

Table 1. Fundamental and optical band gaps for PTB7, PID2, and PC71BM from theory and experiment

method adds a quadratic restraint on partial charges to prevent the values of highly shielded charges from becoming too large or otherwise unphysical. This method closely reproduces values given by OPLS in test cases without significant shielding.

To make this method more robust in cases with shielded atoms, we have modified it to weight regions along the potential-fitting shell such that each atom is of nearly equal importance in the fitting. We have also allowed the shell to become thicker in regions near shielded atoms. These modifications give more physical partial charges for molecules such as TPD, where atoms such as nitrogen are buried.

The **Galli** group is performing electronic property modeling on polymer solar cells. He has focused research on the proper tools for identifying the band gap size and location of donors and acceptors in the ternary blend synthesized by Lu et al. For this work, a cascade of energy levels was measured, and it was suggested that such a cascade improves charge separation and prevent charge recombination. The proposed

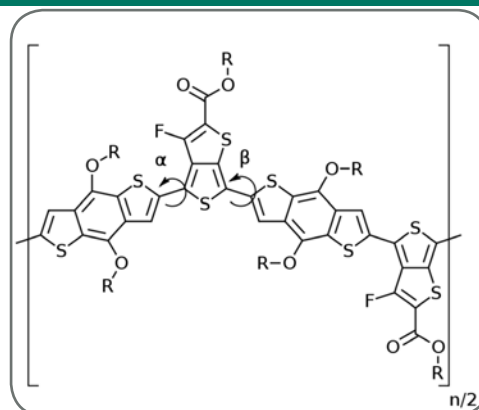


Figure 7: Relevant dihedrals of PTB7

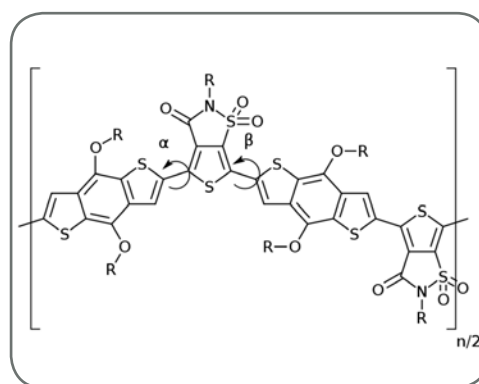


Figure 8: Relevant dihedrals of PID2

cell consists of poly-3-oxothieno[3,4-d]isothiazole-1,1-dioxide/benzodithiophene (PID2) and polythieno[3,4-b]-thiophene/benzodithiophene (PTB7), along with the common electron acceptor [6,6]-phenyl C71 butyric acid methyl ester (PC71BM). The experimental values, along with our best theoretical estimates, are presented in Figure 6. In our calculations PTB7 and PID2 are approximated as periodic systems using plane wave Density Functional Theory (DFT) (B3LYP for energy levels and PBE for geometries) with a single monomer in the periodic cell, neglecting the 2-ethyl hexyl side chains, so as to reduce computational cost. Our preliminary results support the ordering of the band edge positions presented.

A summary of our findings for the band gaps of all systems of Figure 6 is presented in Table 1. We use long-range corrected ω B97X/def2-TZVP for the TD-DFT estimates of the optical gap and B3LYP/def2-TZVP for estimates of the fundamental gap. All isolated system geometries are PBE-D3BJ-gCP/def2-TZVP, which differs minimally from B3L-

YP-D3BJ-gCP/def2-TZVP geometries. Our band gaps for periodic systems systematically overestimate experimental values, which is surprising as we were expecting the opposite error, with respect to experiments, and the reasons of this overestimate is under investigation. However we note that the trend of increasing band gap size reported is reflected in our calculations. The band gap of the isolated monomers of PTB7 and PID2 are overestimated as well, which is to be expected in the case of π -conjugated systems. Efforts to model these polymers in the past have varied, somewhat inconsistently, in their treatment of the flexible dihedrals contained within the polymer chains [2, 3, 4, 5], which are visualized in Figures 7(PTB7) and 8(PID2). We have performed our own potential energy scans along the dihedrals and chosen the optimal conformers for our own use in Figure 6 and Table 1. The potential energy surfaces along these dihedrals are presented in Figures 9 and 10, and the HOMO/LUMO separation is presented in Figures 11 and 12. Barriers of 3-6 kcal/mol are present in these dihedral rotations. The band gap has significant variation with the rotation along these dihedral angles, especially when π -conjugation is severely disrupted, overall suggesting that structural deformation must be accounted for in order to reproduce the band gap accurately. Work is in progress to fully understand these issues.

In short, we have modeled the band gap size and location for the ternary blend of Lu, et al., supporting the cascade alignment of the HOMO energy levels. Ongoing work is focused on refining our models, in particular, on the investigation of the connection between structure and energy level alignment.

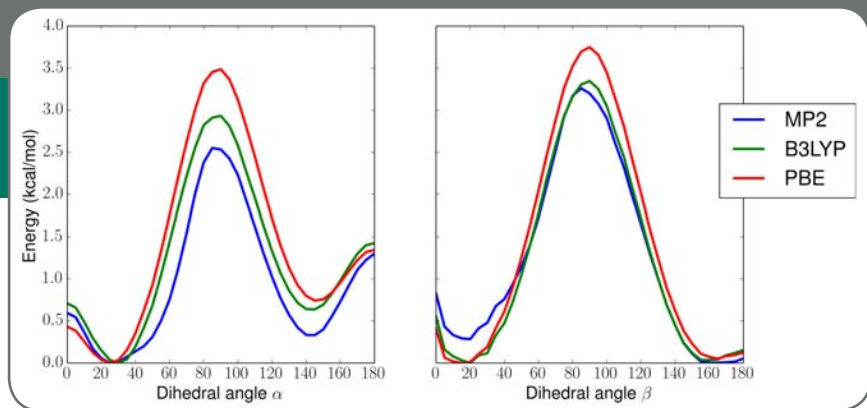


Figure 9: PES along dihedrals of PTB7

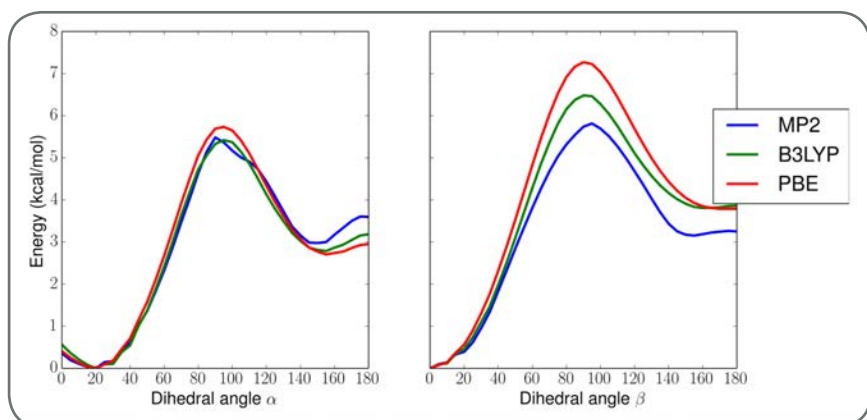


Figure 10: PES along dihedrals of PID2

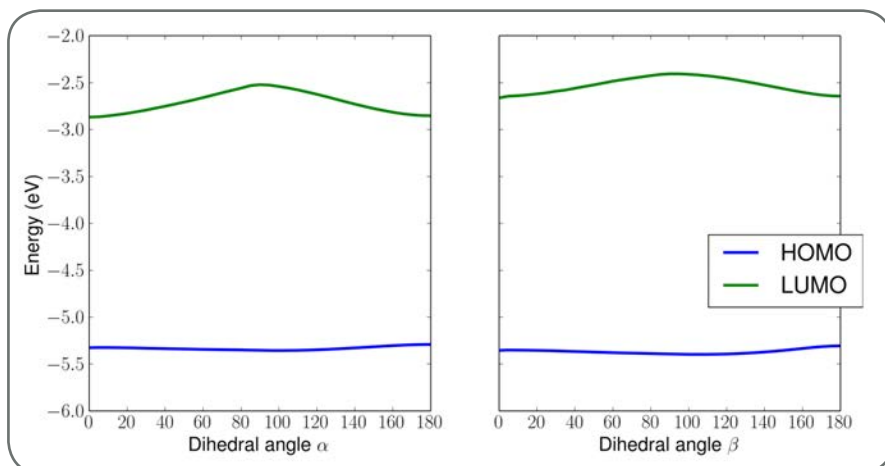


Figure 11: The HOMO/LUMO levels of PTB7 versus structural deformation along dihedral angles

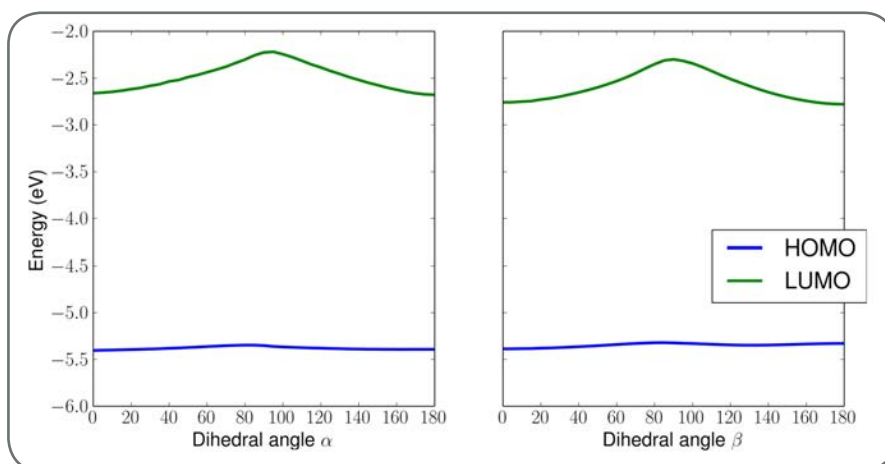


Figure 12: The HOMO/LUMO levels of PID2 versus structural deformation along dihedral angles

**Organic Bulk Heterojunction Polymer Solar Cells
Group Researchers and Their Roles**

| Name | Position | Institution/ Affiliation | Project Title (PI) |
|---------------------|-------------------------|-----------------------------|---|
| Luping Yu | PI | UC/Chem | <i>OPV solar cells</i> |
| Juan de Pablo | PI | UC/IME | <i>Simulation of OPV Materials</i> |
| Giulia Galli | PI | UC/IME | |
| Tobin Marks | PI | NU/MSE | |
| Ferdinand Melkonyan | Postdoctoral Researcher | UC/Chem | <i>Novel Materials for Optoelectronic Application</i> |
| Zhenxu Cai | Postdoctoral Researcher | UC/Chem | <i>Novel Materials for OPV Application (Yu)</i> |
| Mathew Goldey | Postdoctoral Researcher | UC/IME | <i>Simulation of OPV Materials (Galli)</i> |
| Luyao Lu | Graduate Student | UC/Chem | <i>Novel Materials for OPV Application (Yu)</i> |
| Daniel Reid | Graduate Student | UC/IME | <i>Simulation of OPV Materials (de Pablo)</i> |

COLLABORATIONS

Morphological studies of Ternary OPV systems

Collaborators: [Dean M. DeLongchamp](#)

Materials Science and Engineering Division, NIST

Materials Synthetic Design and Evaluation

Collaborators: [Antonio F. Facchetti^a](#), [Wei Zhao^b](#)

^aDepartment of Chemistry, Northwestern University

^bPolyera Corporation

Polymeric Materials Microstructural Characterization by Synchrotron Grazing Incidence Wide Angle X-ray Scattering

Collaborators: [Lin X. Chen](#)

Department of Chemistry, Northwestern University

Chemical Sciences and Engineering Division

Argonne National Laboratory

Molecular Materials Microstructural Characterization by Thin Film X-ray Diffraction

Collaborators: [Michael Bedzyk](#)

Department of Materials Science and Engineering

Northwestern University

Materials Electronic Structure Computation

Collaborators: [Rocío Ponce Ortiz](#)

Departamento Química Física

Universidad de Málaga, Spain ■

TOOL DEVELOPMENT

Consonant with NIST's unique role in the MGI, a major thrust of CHiMaD will be designing and prototyping tools that enable materials design. CHiMaD has identified two major thrust areas: database development and tools for computational design.

DATABASES

In collaboration with NIST scientists, CHiMaD aims to make significant advances in data-driven informatics to accelerate material discovery, assessment, research and innovation. We are moving on a number of fronts in this area:

- **CALPHAD protodata databases (Olson, Voorhees, Wolverton, Campbell, Kattner):** Assessment of phase diagrams and the resulting free energy functions provide essential information for materials design. Unfortunately, the data upon which these assessments rely are frequently lost following the assessment making it extremely difficult to easily modify existing ones. We are developing publicly accessible CALPHAD protodata databases that contain fundamental phase-level raw data consisting of, for example, measured phase relations (tie-lines), calorimetric measurements, DFT-predicted quantities such as elastic constants of existing and new compounds. Furthermore, with the goal of creating a community wide pre-Calphad protodata database, we will also be inviting researchers with other existing databases to contribute. As examples, we are creating these databases for the alloy systems under investigation in the CHiMaD use-case groups, specifically: Si-alloys for structural applications and Co-based alloys for high-temperature applications. *Please see Precipitation-Strengthened Alloy and Si Alloys use-case group for more information.*
- **NanoMine (Brinson, Chen):** This database contains processing, structure and property parameters for polymer nanocomposite systems. The system employs the new NIST Materials Data Creator system. Detailed templates and material data structures ("schemas") have been developed to account for processing, structure and property information of material systems. *Please see Polymer Matrix Materials use-case group for more information.*

- **Polymer Design (de Pablo, Foster, Nealey, Jaeger):** This database will contain characteristic properties for design of polymer blends and copolymers for engineering applications, including directed self-assembly. *Please see Directed Self Assembly of Block Copolymers Films for Lithographic Applications use-case group for more information.*
- **Prediction of Phase Behavior of Polymers and Polyelectrolytes (de Pablo, Foster, Nealey, Tirrell, Jaeger, Douglas, Freed):** This database will employ both data from both simulations and experiments on polymer blends, polyelectrolytes, copolymers, focusing on phase behavior to comprehend the stability of complexes with respect to salt, with a variety of salt valences. *Please see Biomaterials use-case group for more information.*
- **Materials Data Facility (Foster, Choudhary, de Pablo, Voorhees):** With the advent of techniques that can measure the three-dimensional micro- and nano-structure of a material as well as its temporal evolution, the materials community is facing the challenge of handling, storing, and sharing large datasets. We are developing a large-data storage and sharing system to address this challenge.

SOFTWARE TOOLS

CHiMaD is also developing computational tools that can be used to follow the evolution of the micro- and nano-structure of both soft and hard matter:

- **Community Standard Phase Field Methods (Voorhees, Warren):** In the hard matter area, one of the key computational materials approaches is the phase field method. While the method has been used with

great success in a research environment, its utility as a materials design tool is hampered by the lack of a community standard phase field code. The objective of this work will be to create such a community standard by convening workshops and facilitating interactions between the many groups working in this area.

■ **Fatigue Modeling using Phase Field Methods:**

Umantsev (FSU) is developing phase field methods specifically for fatigue modeling. This code, in collaboration with the nonlocal mechanics methods developed by **Liu** (NU), will be used in the Precipitation-Strengthened Alloys use-case group to follow the evolution of fatigue. Please see Precipitation-Strengthened Alloys use-case group for more information.

■ **Locally Adaptive Time Stepping for Parallel Architectures:**

Chopp (NU) developed a modified 2D parallel implementation of a recently introduced algorithm called LATS (Locally Adaptive Time Stepping). This method, while considering a domain subdivided into multiple subdomains, allows each subdomain to advance according to its own time step size. In context of solving a parallel architecture, such as a phase-field type model, allowing each subdomain to progress with a different time step leads to being able to concentrate the computational effort where it is needed, for example, at the interfaces.

■ **Theoretically Informed Coarse Grained Simulations**

(**de Pablo, Olvera de la Cruz, Luijten**): The primary computational tool for prediction of structural, thermodynamic, and dynamic properties of functional polymers and block polymers must rely on a coarse-grained modeling approach capable of describing the structure and dynamics of soft matter, including block polymers during solvent mediated assembly, both in the bulk and in films. Our proposed strategy will be based on the “Theoretically Informed Coarse Grained” (TICG) simulation formalism, developed by **de Pablo**. TICG

simulations rely on a particle-based representation, thereby providing a means to describe large, three-dimensional systems in the presence of fluctuations and their corresponding dynamics. A beta version of this software has been released to INTEL. *Please see Directed Self Assembly of Block Copolymers Films for Lithographic Applications use-case group for more information.*

EXPERIMENTAL TOOLS

Experimental data is required in a number of the databases that we are developing. These data are being created using both standard approaches and new tools that we are developing. These new tools are:

■ **Rapid Assessment of Phase Relations:**

Co-alloy team, part of the Precipitation-Strengthened Alloys use-case group, identified the highest priority alloying elements for thermodynamic and mobility database development. This then formed the basis for thin-film-based initial high-throughput experiment design by **Chung** and **Bedzyk** of Northwestern University that employs the Advanced Photon Source characterization facilities at the Argonne National Laboratory. *Please see Precipitation-Strengthened Alloys use-case group for more information.*

■ **Resonant Soft X-ray Scattering (Nealey):**

(**RSoXS**) The **Nealey** group is collaborating with the Argonne National Laboratory to commission a new Intermediate X-ray Energy beamline at Sector 29 of the Advanced Photon Source that will allow access to a larger area of reciprocal-space than standard two- and three-circle diffractometers typically found in RSoXS endstations. This new capability will be used to follow the evolution of polymer nanostructures for the directed self-assembly use-case group. *Please see Directed Self Assembly of Block Copolymers Films for Lithographic Applications use-case group for more information.*

In its first year CHiMaD has initiated several outreach programs including the dissemination of the ASM Materials Genome toolkit with the aim to encourage educational institutions to incorporate materials design into their curricular, and the MGI Seminar Series, which hosted ten international researchers in 2014. Our researchers also organized numerous workshops and short-courses around the world as well as symposia in prestigious conferences. Many of the events are organized in conjunction with NIST researchers, strengthening CHiMaD-NIST collaborations.

ASM Materials Genome ToolKit

One of the objectives of CHiMaD is to expand the knowledge of current and future generation of researchers and scientists by providing opportunities for them to explore and learn core computational materials engineering tools and methods. To facilitate this objective, CHiMaD has partnered with ASM International to provide a number of qualified undergraduate level Materials Science and Engineering programs in United States with **ASM Materials Genome Toolkit** at a substantially reduced license fee. The toolkit provides a bundle of the *ThermoCalc*, *DICTRA* and *PRISMA* software of general applicability across materials classes. Building on our unique successes in metals applications, the bundle includes a first set of thermodynamic and mobility databases for metallic alloy systems. As a part of this initiative, the selected programs are expected to actively participate in the ASM Undergraduate Design Competition.

Workshop, Symposium and Short Courses

Paul Nealey, Ricardo Ruiz and Juan de Pablo (UChicago) co-organized the *SPIE Short Course on Directed Self Assembly* at the SPIE 3-beam Conference, San Jose, California, USA. (02/14).

Gregory Olson (NU) hosted the *30th Annual Review Meeting for the Materials Technology Laboratory/Steel Research Group* at Northwestern University, Evanston, Illinois, USA. (03/14)

Carelyn Campbell (NIST) organized the *NIST/CHiMaD CALPHAD Data Workshop: Building a Data Infrastructure for Phase-Based Materials Data* at NIST. During the workshop, plans were made for the pre-CALPHAD protodata repository to be hosted at NIST, and the metal alloy project

was selected as the first to begin populating this database using a specified DSpace format. (04/14)

Juan de Pablo (UChicago), Jack F. Douglas (NIST), Frederick R. Phelan Jr. (NIST) were co-organizers of the Workshop on Coarse-Grained Modeling of Polymers and Soft Materials for the Materials Genome Initiative at the National Institute of Standards and Technology, Gaithersburgh, Maryland, USA. (09/14)

Wei Chen (NU) acted as the review coordinator and special session organizer of *Multiscale Materials and Product Design*, ASME International Design Technical Conference, Design Automation Conference 2014, Buffalo, New York, USA. (09/14)

Juan de Pablo (UChicago), Joseph Kline (NIST), Roel Gronheid (IMEC), Philip Hustad (Dow Electronic Materials) co-organized symposia on *Directed Self-Assembly for Nanomanufacturing*, at Materials Research Society Fall Meeting, Boston, Massachusetts, USA. (12/14)

Erik Luijten (NU) taught a 10-hour course on *Computational Modeling of Soft Matter* at the International Winter School on Soft Matter at Shanghai Jiao Tong University, Shanghai, China. This course was attended by ~40 undergraduates and beginning graduate students from Shanghai Jiao Tong University and other institutions in China and Singapore. (12/14)

Vacuum Science and Macroscopic AFM Workshop, University of Chicago, Chicago, Illinois, USA. This workshop featured science demos (macroscopic AFM for examining corrugated surfaces) for visiting elementary school parents and teachers, and was organized by the **Directed Self-Assembly of Block Copolymers Films for Lithographic Applications Use-case Group**.

Seminars

The following seminars were hosted as a part of the *MGI Seminar Series* in 2014.

Field Simulations of Phase Transformations in Materials Alexander Umantsev

Professor, Fayetteville State University, USA.
May 14 (Questek), May 20 (ANL), May 21 (NU), 2104

The Exascale Co-design center for Materials in Extreme Environments (ExMatEx)

James Belak
Co-Director, DOE/ASCR Exascale CoDesign Center for Materials in Extreme Environments Lawrence Livermore National Laboratory, USA.
May 27, 2014

A Computational Approach to Materials Design Shengyen Li

Postdoctoral Researcher, Materials Science and Engineering Division, National Institute of Standards and Technology
June 2, 2014

Computational Materials Design for High Plastic Formability of Mg Alloys

Motohiro Yuasa
Researcher, National Institute of Advanced Industrial Science and Technology, Japan
August 21, 2014

Introduction of Thermodynamic-Fluctuation-Based Nucleation to Phase-Field Model

Machiko Ode
Senior Researcher, Computational Materials Science Unit, National Institute for Materials Science, Tsukuba Ibaraki, Japan
August 28, 2014

Martensitic Transformations in Engineering Materials: A Mesoscale Study

Hemantha Yeddu
Postdoctoral Researcher, Los Alamos National Laboratory
October 6, 2014

An Insider View on Scientific Publishing Baptiste Gault

Journal Publisher, Materials Science, Elsevier Ltd.
October 9, 2014

The Materials Genome Initiative and the Data Revolution

Carelyn Campbell
Materials Science and Engineering Division, National Institute of Standards and Technology, USA
October 28, 2014

Integrated Computational Materials Engineering and the Materials Genome Initiative: Activities at the Hero-m Center

Annika Borgenstam
Materials Science and Engineering, KTH, Sweden
December 4, 2014

Architected Steel

Toshihiko Koseki
Professor, Department of Materials Engineering, University of Tokyo, Japan
December 11, 2014

Other Activities

CHiMaD organized the *CHiMaD Inaugural Meeting*, bringing together more than 100 researchers from its partner institutions. (05/14)

CHiMaD website went live at chimad.northwestern.edu. (05/14)

Illinois Science & Technology Council newsletter, *Catalyst*, highlighted CHiMaD in their October issue with an article authored by CHiMaD co-director **Peter Voorhees** and associate director **Begum Gulsoy** entitled *Illinois Demonstrates the Materials Genome Initiative: Center for Hierarchical Materials Design*. (10/14)

Wei Chen, serves as the Director of *Predictive Science & Engineering Design (PS&ED) Cluster* at Northwestern University. The current focus of the PS&ED cluster is on research topics that address predictive science, design, and manufacturing of emerging materials and structure systems. Several PS&ED supported cluster projects in 2014-2015 are focused on Materials Genome Initiative.

Science Club, Andrew Carnegie School, Chicago, Illinois, USA. A weekly club for middle school students was organized by the members of the **Directed Self-Assembly of Block Copolymers Films for Lithographic Applications Use-case Group** for interactive science demonstrations. ■

HONORS AND AWARDS

In 2014, CHiMaD researchers were recognized for contributions to their fields and were the recipients of numerous prestigious honors and awards. CHiMaD graduate and undergraduate students were also recognized among their peers for their work regarding CHiMaD related research projects.

L. Catherine Brinson

*Department of Materials Science and Engineering
Department of Mechanical Engineering
Northwestern University*

Nadai Medal, American Society of Mechanical Engineering

Mark C. Hersam

*Department of Materials Science and Engineering
Northwestern University*

MacArthur Fellowship, 2014

American Association for the Advancement of Science (AAAS) Fellow, 2014

Wing K. Liu

*W. P. Murphy Professor
Department of Mechanical Engineering
Northwestern University*

President of the International Association for Computational Mechanics

Chair of the US National Committee on Theoretical and Applied Mechanics within the National Academies

2014 highly cited researcher in the field of Computer Science and listed as a member of the World's Most Influential Scientific Minds by Thompson Reuters for the period 2002 through 2012.

Tobin J. Marks

*Department of Materials Science and Engineering
Department of Chemistry
Northwestern University*

2013 Alan G. MacDiarmid Medal, University of Pennsylvania

2014 Sir Geoffrey Wilkinson Medal, UK Royal Society of Chemistry

2013 Bayer Lecturer, Cornell University

2013 Bayer Lecturer, University of Pittsburgh

2014 M.D. Rausch Lecturer, University of Massachusetts, Amherst

2014 Xingda Lecturer, Peking University

2014 Frontiers in Molecular Sciences Lecturer/Professor, Chinese Academy of Sciences

2014 Distinguished Clean Energy Lecturer, University of Washington

2014 R.B. King Lecturer, University of Georgia

Gregory B. Olson

*W. P. Murphy Professor
Department of Materials Science and Engineering,
Northwestern University*

Honorary Doctorate, Royal Institute of Technology (KTH), Sweden

Evanston/Northwestern Catalyst Award for Entrepreneurship

David N. Seidman

*W. P. Murphy Professor
Department of Materials Science and Engineering,
Northwestern University*

ASM International Edward DeMille Campbell Memorial Lectureship, 2015

AIME Honorary Member Award—nominated by the TMS

Fellow, American Association for the Advancement of Science

Steven J. Sibener

*Professor
Department of Chemistry
University of Chicago*

Two-day "Science at the Interface" SibenerFest Symposium with 150 attendees, March 28–29 2014. This conference brought together a diverse collection of scientists from

around the world whose common focus is understanding the complex chemistry and physics that take place at interfaces while emphasizing the intuitive approach that has often characterized Steve's many contributions to the field. In addition to the Scientific Conference, there was also a Pedagogical Tutorial for students and postdoctoral researchers.

Wei Xiong

Research Associate (**Olson** Research Group)
Materials Science and Engineering
Northwestern University

TMS Young Leader Award

Gurdaman Khaira

Graduate Student (**De Pablo** Research Group)
University of Chicago

First Prize — Best Paper Award, 2014 International
TECHON Conference

Luayo Lu

Graduate Student (**Yu** Research Group)
Department of Chemistry
University of Chicago

Selected speaker for "Excellence in Graduate Polymer
Research," American Chemical Society symposium

Qianqian Tong

Graduate Student (**Sibener** Research Group)
Department of Chemistry
University of Chicago

Yang Cao-Lan-Xian "Best Thesis Award" in the
Department of Chemistry

Jonathan Raybin

Graduate Student (**Sibener** Research Group)
Department of Chemistry
University of Chicago

First Prize Graduate Student Poster Presentation Award
at the 2014 Prairie Chapter Meeting of the American
Vacuum Society

Joan Shiu Award for Student Service

Hongyi Xu¹, Ruoqian Liu², Alok Choudhary¹, and Wei Chen²

¹Department of Electrical Engineering and
Computer Science

²Department of Mechanical Engineering
Northwestern University

Best Paper Award, 40th ASME Design Automation
Conference, "A Machine Learning-Based Design
Representation Method for Designing Heterogeneous
Microstructures," IDETC2014-34570, August 17-20,
Buffalo, New York, 2014.

R. DeBlock, K. Jorgensen, C. Lynsky, E. Pang, S. Plain, P. J. Santos, R. Wang

Materials Design (MAT390) class undergraduate students
(**Olson**, PI)

3rd Prize, ASM 2014 undergraduate design competition

PUBLICATIONS

De Pablo, J. J., Jones, B., Kovacs, C. L., Ozolins, V., & Ramirez, A. P. (2014). The Materials Genome Initiative, the interplay of experiment, theory and computation. *Current Opinion in Solid State and Materials Science*, 18(2), 99-117.

Hoffmann, K. Q., Perry, S. L., Leon, L., Priftis, D., Tirrell, M., & de Pablo, J. J. (2015). A molecular view of the role of chirality in charge-driven polypeptide complexation. *Soft matter*, 11(8), 1525-38.

Jariwala, D., Sangwan, V. K., Seo, J. W. T., Xu, W., Smith, J. N., Kim, C. H., Lauhon, & L. J., Hersam, M. C. (2014). Large-area, low-voltage, anti-ambipolar heterojunctions from solution-processed semiconductors. *Nano letters*.

Khaira, G. S., Qin, J., Garner, G. P., Xiong, S., Wan, L., Ruiz, R., Jaeger, M. H., Nealey P. F., & de Pablo, J. J. (2014). Evolutionary Optimization of Directed Self-Assembly of Triblock Copolymers on Chemically Patterned Substrates. *ACS Macro Letters*, 3(8), 747-752.

Kim, I. S., Sangwan, V. K., Jariwala, D., Wood, J. D., Park, S., Chen, K. S., Shi, F., Ruiz-Zepeda, F., Ponce, A., Jose-Yacamán, M., Dravid, V. P., Marks, T. J., Hersam, M. C., & Lauhon, L. J. (2014). Influence of Stoichiometry on the Optical and Electrical Properties of Chemical Vapor Deposition Derived MoS₂. *ACS nano*, 8(10), 10551-10558.

Lequieu, J. P., Hinckley, D. M., & de Pablo, J. J. (2015). A Molecular View of DNA-conjugated Nanoparticle Association Energies. *Soft Matter*, Advance Article. DOI: 10.1039/C4SM02573C.

Peters, B. L., Rathsack, B., Somervell, M., Nakano, T., Schmid, G., & de Pablo, J. J. (2014). Graphoepitaxial assembly of cylinder forming block copolymers in cylindrical holes. *Journal of Polymer Science Part B: Polymer Physics*. DOI: 10.1002/polb.23652.

Tong, Q., Malachosky, E. W., Raybin, J., Guyot-Sionnest, P., & Sibener, S. J. (2014). End-to-End Alignment of Gold Nanorods on Topographically Enhanced, Cylinder Forming Diblock Copolymer Templates and Their Surface Enhanced Raman Scattering Properties. *The Journal of Physical Chemistry C*, 118(33), 19259-19265.

Xu, H., Liu, R., Choudhary, A., and Chen, W., "A Machine Learning-Based Design Representation Method for Designing Heterogeneous Microstructures", IDETC2014-34570, August 17-20, Buffalo, New York, 2014.

Yao, Z., & de la Cruz, M. O. (2014). Dynamics of vacancies in two-dimensional Lennard-Jones crystals. *Physical Review E*, 90(6), 062318.

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