



# Penn State Chemical Engineering Research Symposium

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***Tuesday, September 16, 2014  
Celebration Hall Conference Center***

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11:00 am	Registration				
11:15 am	Keynote Speaker				
12:00 pm	Lunch				
1:00 pm	Session 1	Room 1		Room 2	
		Arrested Protein Synthesis Increases Persister Cell Formation	Brian Kwan	Miscibility and Acid Strength are Critical Parameters for Contact Doping of Organic Photovoltaics with Strong Electrolytes	Thinh Le
		Output Feedback Control of Nonlinear Distributed Parameter Systems via Adaptive Model Order Reduction	Davood Babaei Pourkargar	Development of a Core Escherichia coli Kinetic Metabolic Model using the EM Formalism	Ali Khodayari
		The Effect of Lubricant Molecular Structure on the Friction of Nano-textured Diamond-like Carbon	Ala' Al-Azizi	Towards Metabolism-Based Feed Forward pH Control of High-Density Microalgae Cultivation	Jun Wang
		Two-dimensional Protein Crystals for Solar Energy Conversion	Patrick Saboe		
2:20 pm	Break/Poster Session				
2:30 pm	Session 2	Room 1		Room 2	
		Controlling Superionic Conduction in PEO-based Single-ion Conductors	David Caldwell	High Performance Organic Thin Film Transistors for Flexible Electronics	Jwala Adhikari
		Orphan Toxin OrtT (YdcX) of Escherichia coli Reduces Growth During the Stringent Response	Sabina Islam	Developing Computational Tools to Redirect Metabolism	Anupam Chowdhury
		Flow Induced Crystallization of Isotactic Polypropylene	Fawzi Hamad	A Molecular View of the Electrical Double Layer on Latex Surfaces	Zifeng Li

3:30 pm	Break/Poster Session				
4:00 pm	Session 3	Room 1		Room 2	
		<i>Artificial Water Channels – Can They Reach the Performance of Biological Channels?</i>	Yuexiao Shen	<i>Synthesis of {111}-faceted Au Nanocrystals Mediated by Polyvinylpyrrolidone: Insights from Density-Functional Theory and Molecular Dynamics</i>	Shih-Hsien Liu
		<i>Real-Time Numerical Simulation of Ozone Transport and Uptake in an Anatomically-Accurate Model of the Respiratory Tract</i>	Seyed Pouria Motevalian	<i>Dynamic Ion Aggregates in Single Ion Conductors</i>	Keran Lu
		<i>Methods and Applications of Computational Enzyme Redesign</i>	Matthew Grisewood	<i>Locomotion of Microorganisms near a No-slip Boundary in a Viscoelastic Fluid</i>	Shahrazad Yazdi
5:00 pm	Happy Hour & Awards				

## Session 1

### ***Arrested Protein Synthesis Increases Persister Cell Formation***

**Presenter:** Brian Kwan

**Advisor:** Thomas Wood

Persister cells comprise a small sub-population within every bacterial population (less than 1%) that exhibit a nonhereditary, multidrug tolerance to lethal antibiotic treatments (attributed to a state of metabolic dormancy). Persisters often form within bacterial biofilms, and biofilms have been associated with numerous recalcitrant, clinical infections such as cystic fibrosis and gingivitis. Therefore, understanding bacterial persistence is imperative for developing treatments for biofilm-related diseases. Toxin-antitoxin systems are prevalent throughout the bacterial genome and serve as a highly redundant, genetic basis for persister cell formation. Previous work showed that overexpression of the toxins MqsR and YafQ, RNA endonucleases, as well as TisB, a membrane protein that reduces ATP, significantly increased persistence. Here, we demonstrate that chemical pretreatments, with rifampin, tetracycline, and carbonyl cyanide *m*-chlorophenyl hydrazone (CCCP), can effectively mimic toxin activity, thereby inducing a high level of antibiotic persistence (nearly 100%). This is a novel technique for increasing bacterial persistence through chemical pretreatment, which is applicable to studies requiring a largely uniform population (e.g., transcriptomics and proteomics). Furthermore, this study demonstrates conclusively that persisters are cells with little or no protein synthesis and that persistence may be triggered by environmental cues. These results also suggest that some antibiotic combination therapies may affect persister cell formation.

***Miscibility and Acid Strength are Critical Parameters  
for Contact Doping of Organic Photovoltaics with Strong Electrolytes***

**Presenter:** Think Le

**Advisor:** Enrique Gomez

One of the challenges with the development of high performance organic photovoltaic devices is extracting charges out of the active layer. An interface barrier of roughly a few tens of mV can lead to significant charge accumulation at electrode-organic semiconductor interface and result in significant recombination losses and sub-optimal photovoltaic performance. To minimize contact resistance, it is necessary to establish ohmic or nearly ohmic contacts to promote efficient charge collection. Such requirements have led to many efforts in interfacial engineering. One novel approach utilizes polyelectrolytes as dopants near the organic semiconductor-electrode interface to promote charge tunneling through contact barriers with reduced widths. Polyelectrolytes offer major advantages over small molecule dopants in interfacial doping of organic semiconductors, especially conjugated polymer systems. Doping of conjugated polymers can be achieved through redox chemistry, where the electrochemical potential of the dopant molecule can lead to oxidation or reduction of the organic semiconductors. Nevertheless, little is known regarding the factors which are critical for effective doping with polyelectrolytes.

Here we demonstrate that the miscibility between polyelectrolytes and active layer and acid strength of polymeric dopants govern the efficacy of contact doping in organic photovoltaics. We have varied the backbone and pendant acid group to create a series of polyelectrolytes. Utilizing mixtures of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PCBM) as a test bed, we show that stronger acid moieties are capable of donating more free carriers to the doped system. But, the miscibility between the polymeric dopant and the active layer also plays a role, that is higher miscibilities lead to a larger degree of contact between the active layer and the dopant molecules, thus improve doping effectiveness. The overall doping efficacy is therefore a complex interplay between the strength of pendant acid groups and phase separation between polymeric dopants and conjugated polymers.

***Output Feedback Control of Nonlinear Distributed Parameter Systems  
via Adaptive Model Order Reduction***

**Presenter:** Davood Babaei Pourkargar

**Advisor:** Antonios Armaou

We focus on output feedback control of nonlinear distributed processes whose infinite dimensional representation in appropriate functional subspaces can be decomposed to finite dimensional slow and infinite dimensional fast and stable subsystems. The controller synthesis issue is addressed using a refined adaptive proper orthogonal decomposition (APOD) approach to recursively construct accurate low dimensional reduced order models (ROMs) based on which we subsequently synthesize and couple dynamic observers with robust controllers. The novelty lies in reducing the measurement sensors requirements and modifying the data ensemble revision approach within APOD to enlarge the validity of ROMs. The proposed output feedback control structure is successfully applied to regulate a physico-chemical system that can be described in the form of the Kuramoto-Sivashinsky equation at a desired steady state profile when the process exhibits significant nonlinear behavior.

## ***Methods and Applications of Computational Enzyme Redesign***

**Presenter:** Matthew Grisewood

**Advisor:** Costas Maranas

Despite a handful of recent successes, computational design of active enzymes remains a difficult yet important task. Enzymes are ubiquitous commercially and achieve reaction rates that are typically unattainable with inorganic catalysts. Catalysts function by effectively lowering the reaction energy barrier, namely through transition state stabilization, ground state destabilization, or both. Because the transition state structure for a reaction is challenging to resolve, our design approach focuses on the use of transition state analogue compounds as proxies for the true transition state structure. This approach forms the foundation of OptZyme, which improves enzymes' catalytic properties by optimizing the corresponding computationally-accessible interaction energy.

The validity of the correlating expressions is supported by the benchmark system of *E. coli*  $\beta$ -glucuronidase. Furthermore, OptZyme is employed upon methyl-coenzyme M reductase from a consortia of methanotrophic archaea. Improving the activity of this enzyme may improve the conversion of methane to liquid fuels. Additionally, improving the selectivity of *E. coli* thioesterase could have a significant impact on biodiesel production. Here, a brief overview of OptZyme is provided, including the key assumptions underlying the method and a description of the results from the benchmark system. The preliminary results for improving methyl-coenzyme M specificity by improving selectivity for a modified cofactor are described. Finally, progress towards altering thioesterase fatty acid chain length specificity is provided.

***The Effect of Lubricant Molecular Structure on the Friction of Nano-textured Diamond-like Carbon***

**Presenter:** Ala' Al-Azizi

**Advisor:** Seong Kim

Effects of liquid lubricant molecular structure on the friction of elastically deforming nano-scale surface texture was studied in the boundary lubrication regime on flat and nano-textured diamond-like carbon. Friction tests in liquid lubricants with linear and branched molecular structure revealed that nano-texture reduces friction in the presence of linear lubricant molecules. Nano-confinement can significantly affect the friction behavior of textured solid interfaces by forming a long-range ordered structure between flat surfaces. When the deformation of solid surfaces under contact pressure is larger than the surface roughness, even rough surfaces can exhibit nano-confinement effects. However, liquid entrapped in the depressed region of nano-textured surfaces would not solidify which effectively reduces the solidified lubricant area and reduces friction. Surface texture has insignificant effect on the boundary lubrication of branched molecules as they hinder long-range ordering.

***Towards Metabolism-Based Feed Forward  
pH Control of High-Density Microalgae Cultivation***

**Presenter:** Jun Wang

**Advisor:** Wayne Curtis

Progress on metabolism-based feed forward pH control of high density microalgae mass production system will be presented. One of the most important issues toward the high density large scale algal biofuel production is the intrinsic instability of culture pH due to utilization of the two major types of nitrogen fertilizers, ammonium and nitrate, which lead to acidification and alkalization, respectively. Preferential assimilation of ammonium also precludes combining of the two types of fertilizer as having both present does not provide pH balancing without the use of a precise dynamic feeding strategy. With pH stat based cultivations, we thoroughly studied various feeding strategies and accurately measured the critical stoichiometric coefficients in the absence of buffering. A final demonstration of these principles achieved balanced algae growth on slowly fed nitric acid. This work on metabolism –based feed forward pH control sets the stage for implementation in the variable environment of agriculture scale algae culture.

## ***Two-dimensional Protein Crystals for Solar Energy Conversion***

**Presenter:** Patrick Saboe

**Advisor:** Manish Kumar

Photosynthetic proteins present in plant and cyanobacterial cell membranes use sunlight to provide the energy necessary to reduce CO<sub>2</sub> to carbohydrates. The high density of these proteins within native photosynthetic membranes, up to 76 % surface area, is optimal for light harvesting and energy transfer between independent proteins. Photosynthetic proteins have already been utilized in electrochemical systems to split water, generate photocurrent, and produce hydrogen. However, in these systems isolated proteins are either in solution or deposited on electrodes as single particles solubilized in detergents or small peptides. Here, we reconstituted the robust light harvesting protein Photosystem I (PSI) into lipid membranes at high densities to create ordered 2D crystalline arrays that have a flat morphology appropriate for efficient solar energy capture and that provide easy integration into photo-electrochemical cells. To stabilize the two-dimensional (2D) crystals on an electrode for photocurrent generation, we designed a hydrated biomimetic interface with integrated molecular species that have been used in the fields of organic electronics. This hybrid interface design stabilizes PSI at a high surface concentration within a lipid environment and uses a conjugated oligoelectrolyte (COE) to assist in the electron transfer from the electrode to PSI. The crystalline PSI within its membrane is aligned either up or down, facilitating electron transfer to and from the electron acceptor/donor sites of PSI. Our crystal and COE based device produces a photocurrent of  $17.3 \pm 1.2 \text{ mA cm}^{-2}$  (~600 mA per mg PSI deposited). A 4-fold enhancement of photocurrent was measured after incorporation of COEs into our device compared to devices without COEs. These photocurrents also represent an order of magnitude increase on a per mg basis over published PSI devices on SAMs, and may be the most efficient utilization of each PSI so far in a photo-electrochemical cell.

## Session 2

### ***Controlling Superionic Conduction in PEO-based Single-ion Conductors***

**Presenter:** David Caldwell

**Advisor:** Janna Maranas

The demand for portable, high energy-density storage has prompted industrial and academic research into novel battery technology. By replacing the traditional organic electrolyte with a Solid Polymer Electrolyte (SPE), a new class of flexible and light weight batteries can be developed. PEO-based single-ion conductors, dubbed ionomers, are a promising class of SPE due to its ability to reduce concentration polarization found in typical PEO/salt SPEs. This is achieved by binding the anion to the polymer backbone, reducing the anion's mobility and resulting in a near unity cation transference number. Additionally, ionomers can form string like ion aggregates that act as conduction pathways. These conduction pathways allow for partial decoupling of ionic conduction from polymer dynamics and enable long-range charge transfer through local cation motion. We perform Molecular Dynamics simulations where we vary ion content and temperature in order to quantifying ion aggregation and its influence on ionic conduction. We validate our conductivity and segmental dynamic results with dielectric relaxation spectroscopy and quasi-elastic neutron scattering.

## ***High Performance Organic Thin Film Transistors for Flexible Electronics***

**Presenter:** Jwala Adhikari

**Advisor:** Enrique Gomez

Polymer dielectrics are promising materials where the chemical flexibility enables gate insulators with desired properties. For example, polar groups can be introduced to enhance the dielectric constant, although fluctuations in chain conformations at the semiconductor-dielectric interface can introduce energetic disorder and limit charge mobilities in thin-film transistors. Here, we demonstrate a photopatternable high-K fluoropolymer, poly(vinylidene fluoride-bromotrifluoroethylene) P(VDF-BTFE), with a dielectric constant between 8 and 11. The bromotrifluoroethylene moiety enables photo-crosslinking and stabilization of gate insulator films while also significantly enhancing the population of trans torsional conformations of the chains. Using rubrene single crystals as the active layer, charge mobilities exceeding  $10 \text{ cm}^2/\text{Vs}$  are achieved in thin film transistors with cross-linked P(VDF-BTFE) gate dielectrics. We hypothesize that crosslinking reduces energetic disorder at the dielectric-semiconductor interface by suppressing segmental motion and controlling chain conformations of P(VDF-BTFE), thereby leading to approximately a three-fold enhancement in the charge mobility of rubrene thin-film transistors over devices incorporating uncross-linked dielectrics or silicon oxide.

***Orphan Toxin OrtT (YdcX) of Escherichia coli  
Reduces Growth During the Stringent Response***

Presenter: Sabina Islam

Advisor: Thomas Wood

Toxins are found in most bacteria and are paired with antitoxins which inactivate them until the toxins are utilized by the cells to reduce metabolism. Several roles for toxin-antitoxin (TA) systems have been proposed, such as gene regulation, phage inhibition (*J. Bacteriol.* **178**:2044, 1996), biofilm formation (*J. Bacteriol.* **191**:1258, 2009), and persister cell formation (*Biochem. Biophys. Res. Commun.* **391**:209, 2010). However, the significance of most of these roles is nebulous due to the subtle influence from individual TA systems due to redundancy. For example, a single TA system has only a small contribution to persister cell formation (*Biochem. Biophys. Res. Commun.* **391**:209, 2010). Here, we determine how a toxin plays a key role in the stringent response and explore a new paradigm in which the toxin functions alone without being guarded by an antitoxin (termed an orphan toxin). By focusing on a homologous protein of the membrane-damaging toxin GhoT of the *Escherichia coli* GhoT/GhoS type V toxin/antitoxin (TA) system (*Nat. Chem. Biol.* **8**:855, 2012), we found that YdcX, renamed OrtT, for orphan toxin related to tetrahydrofolate, is a bona fide toxin but is not a part of TA pair. OrtT is not inactivated by neighboring YdcY (which is demonstrated to be a protein) nor is it neutralized by the homologous antitoxin GhoS. Also, OrtT is not deactivated by small RNA upstream or downstream of *ortT*. OrtT is a small (57 aa) hydrophobic protein, and its toxicity stems from membrane damage as evidenced by transmission electron microscopy and cell lysis. Moreover, the membrane damage is associated with loss in intracellular ATP level, and this reduction in metabolism is important for weathering antifolate (i.e, trimethoprim and sulfamethoxazole) stress. These antimicrobials inhibit tetrahydrofolate (THF) synthesis which plays a vital role in biogenesis of amino acid glycine and methionine as well as the purine thymidine. Therefore, depletion in THF triggers the “stringent response” and activates OrtT. Collectively, our results demonstrate that OrtT acts as an independent toxin to reduce metabolism during stress related to amino acid and DNA synthesis.

## ***Developing Computational Tools to Redirect Metabolism***

**Presenter:** Anupam Chowdhury

**Advisor:** Costas Maranas

Bio-production is emerging as a competitive strategy for the production of a wide range of chemicals ranging from biofuels, precursor chemicals and bioactive molecules. The use of metabolic modeling and computations is increasingly becoming instrumental in deciding how to engineer the production strain. Existing computational strain-design approaches relying solely on knowledge of model stoichiometry ignore the effects of enzyme activity and substrate-level enzyme regulation while identifying metabolic interventions for targeted purposes. In this work, we developed the k-OptForce procedure which integrates the available kinetic descriptions of metabolic reactions with stoichiometric models to sharpen the prediction of intervention strategies for improving the bio-production of a chemical of interest. The suggested interventions are comprised of both direct enzymatic activity changes (for reactions with available kinetics) and indirect reaction flux manipulations (for reactions with only stoichiometric information). We applied the k-OptForce procedure on a kinetic model of *E. coli* core metabolism constructed using the Ensemble Modeling (EM) method and parameterized using multiple mutant strains data under aerobic respiration with glucose as the carbon source. Minimal interventions are identified that improve succinate yield under both aerobic and anaerobic conditions to test the fidelity of model predictions under both genetic and environmental perturbations. Under aerobic condition, k-OptForce identifies interventions that match existing experimental strategies pointing at a number of unexplored flux redirections such as routing glyoxylate flux through the glycerate metabolism to improve succinate yield. Many of the identified interventions rely on the kinetic descriptions and would not be discoverable by a purely stoichiometric description. In contrast, under fermentative (anaerobic) conditions, k-OptForce fails to identify key interventions including up-regulation of anaplerotic reactions and elimination of competitive fermentative products. This is due to the fact that the pathways activated under anaerobic conditions were not properly parameterized as only aerobic flux data were used in the model construction. This study shed light on the importance of condition-specific model parameterization while providing a framework for an integrated analysis of kinetic and stoichiometric models to elucidate system-wide metabolic interventions while capturing regulatory and kinetic effects.

## ***Flow Induced Crystallization of Isotactic Polypropylene***

**Presenter:** Fawzi Hamad

**Advisor:** Ralph Colby and Scott Milner

Brief intervals of strong flow followed by a temperature quench accelerates crystallization kinetics and transforms the morphology with respect to quiescent crystallization, phenomena widely found in industrial processing. One main requirement for flow induced crystallization (FIC) is applying a shear rate larger than the inverse Rouse time of some chains. The objectives of this study are 1) to explore the relation between amount of work, morphology and crystallization kinetics; and 2) to compare quiescent and flow induced nuclei. We study crystallization kinetics of polypropylene in a rheometer, by shearing then sample and then quenching; crystallization is monitored via linear viscoelastic response near the crossover frequency of  $G'$  and  $G''$ . Samples were also studied ex situ with DSC and microscopy. FI-nuclei increase the crystallization temperature, and also show a change in crystalline morphology. Morphology transitions from spherulitic to anisotropic structures at the critical work ( $W_C$ ). Crystallization rate, on the other hand, is faster as applied work increases and is not influenced by  $W_C$ . Morphology and crystallization kinetics both reach saturation at  $W_{SAT}$ , to thereafter become independent of work. This suggests that a maximum number density of nuclei is reached. To erase this persistent “memory” of FI-nuclei, samples must either be held for considerable time above 197°C, or for much shorter time above 210°C. These temperatures appear to correspond to the extrapolated extended-chain melting temperatures using the Gibbs-Thomson and Hoffman-Weeks approaches, respectively.

***A Molecular View of the Electrical Double Layer on Latex Surfaces***

**Presenter:** Zifeng Li

**Advisor:** Kristen Fichthorn and Scott Milner

An electrical double layer (EDL) forms near the surface of the latex polymer particle, which plays a key role in the stability of latex colloids. To visualize the EDL near such a rough polymer surface, we used atomistic molecular dynamics simulations, which naturally incorporate finite size effect of ions. Our model consists of a methyl methacrylate (MMA) /n-butyl acrylate (BA) random copolymer slab in aqueous solution, with either sodium dodecyl sulfate (SDS) surfactant, or dissociated methyl methacrylic acidic (MAA) comonomers at the interfaces. We found the electrostatic potential from simulation agreed with the predictions of the Poisson-Boltzmann equation, outside the Outer Helmholtz Plane (OHP). The potential at the OHP, which serves as an effective surface due to the ion condensation, is close to the zeta potential measured experimentally.

## Session 3

### ***Artificial Water Channels – Can They Reach the Performance of Biological Channels?***

**Presenter:** Yuexiao Shen

**Advisor:** Manish Kumar

Biological cells can conduct efficient water transport through water channel proteins known as aquaporins. The determination of the atomic structures of various aquaporins and their molecular transport mechanisms provides unique strategies to engineer high permeability while maintain selectivity and opens the door to a world of novel separation materials—artificial water channels.<sup>1</sup> The principles of the design of artificial water channels can be based on biological channels' structures and supramolecular assembly. The designed channels ideally should have a tubular transmembrane structure with the thickness on the order of nanometers and an outer surface which can favorably interact with hydrophobic lipid or block copolymer membrane environment. They should also be able to mimic the transport properties of aquaporins while maintaining chemical stability. Research in the area of artificial water channels is still in its infancy but might herald the coming of novel energy-efficient, stable water purification materials in the near future. Currently there are five published artificial water channels. These channels are still far from perfect compared to aquaporins either in terms of water permeability or selectivity. This is because of the lack of the available architectures that accurately mimic the structure of natural water channel proteins. The low permeability of these “first-generation” water channels also brings to fore the challenge of accurate characterization of these low-permeability channels. A critical concern is perhaps the determination of single channel permeabilities to allow for accurate comparison to natural channels and thus their screening for performance. An obstacle to determining single molecule transport rates is the unknown insertion properties of these channels into membranes formed by lipids or block copolymers.

This study focused on a new kind of artificial water channel—peptide-appended pillar[5]arene. This channel is composed of peptide-bond connected amino acids—phenylalanine,<sup>2</sup> which provides more hydrophobic regions compared to the first generation hydrazide-appended pillar[n]arenes<sup>3</sup> and is expected to improve both the membrane insertion efficiency and water permeability. The water transport, ion transport and solute rejection properties of this channel were systematically characterized in stopped-flow time resolved measurements. We further labeled this channel with a specific fluorescent dye and estimated the single channel's water permeability based on a newly developed fluorescence correlation spectroscopy (FCS) technique. The peptide-appended pillar[5]arene channel permeability was found to be  $(9.5 \pm 4.0) \times 10^{-15}$  cm<sup>3</sup>/s per channel or  $(3.3 \pm 1.4) \times 10^8$  H<sub>2</sub>O

molecules/s per channel. This permeability value is very close to that of natural water channel—aquaporins, when the low cross-sectional area ( $0.65 \text{ nm}^2$ ) is compared to larger cross sectional area biological water channels ( $\sim 10 \text{ nm}^2$ ). This is an orders of magnitude improvement over the first-generation of the artificial water channels reported before and is the fastest one reported so far. This channel was found to have a pore size of approximately 420 Da and showed ion selectivity in the order of  $\text{NH}_4^+ > \text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Cl}^-$  as determined by patch clamp studies. The ability to further chemically modify the versatile chemical architecture of the pillar[5]arene channels shows promise for further improving water permeability and selectivity.

***Synthesis of {111}-faceted Au Nanocrystals Mediated by Polyvinylpyrrolidone:  
Insights from Density-Functional Theory and Molecular Dynamics***

**Presenter:** Shih-Hsien Liu

**Advisor:** Kristen Fichthorn

We use density-functional theory (DFT) and molecular dynamics (MD) to resolve the role of polyvinylpyrrolidone (PVP) in the shape-selective synthesis of Au nanostructures. We first use DFT to probe the spatially-resolved binding of PVP monomer analogs, PVP-induced surface energies, and the mismatch between PVP dimers and Au(111), Au(100), and the reconstructed (5 X 1) Au(100)-hex surface. Further, we investigate the oxygen density profile of atactic PVP 20-mer molecules on Au(111) and (5 X 1) Au(100)-hex by MD. We conclude {111}-faceted Au nanocrystals are preferred in PVP-mediated synthesis of Au nanostructures. The reconstruction of Au(100) is important in achieving {111} facet selectivity.

***Real-Time Numerical Simulation of Ozone Transport and Uptake in an Anatomically-Accurate Model of the Respiratory Tract***

**Presenter:** Seyed Pouria Motevalian

**Advisor:** Ali Borhan

Ground-level ozone is a major air pollutant formed by the action of sunlight on hydrocarbon vapors and nitrogen oxides emitted by combustion of fossil fuels. Exposure to moderate levels of environmental ozone can cause people to experience difficulty in breathing, often requiring emergency medical assistance. Adverse health effects are particularly severe among children who can suffer impaired lung development, and asthmatics whose lung disease can be exacerbated by environmental exposure to ozone. Experimental observations have shown that chronic exposure to ozone can produce intense remodeling in the developing lungs of infant primates, resulting in dramatic loss of conducting airways. A reproducible pattern of tissue injury induced by inhalation of ozone is believed to depend on the local dose delivered to tissue sites in the respiratory tract. To predict the dose distribution, we perform real-time numerical simulations of ozone transport and uptake in an anatomically-accurate model of the lung of an infant rhesus monkey. Three-dimensional reconstruction of the airway geometry using *MRI* data of the tracheobronchial tree is performed, a structured mesh for the resulting geometry is generated, and time-dependent velocity and concentration distributions are obtained through numerical solution of the continuity, Navier-Stokes, and species convection-diffusion equations over a normal (quiet) breathing cycle. The wall flux distribution changes significantly with time during a cycle of normal breathing. The time-averaged ozone flux distribution at the wall shows the presence of hotspots of flux at the carina of the bifurcations, with the most pronounced hotspot occurring at the carina of the first bifurcation after the trachea.

## ***Dynamic Ion Aggregates in Single Ion Conductors***

**Presenter:** Keran Lu

**Advisor:** Janna Maranas

Polymeric electrolytes are desirable for the enhancements in safety and capacity they can bring to rechargeable metal-ion batteries. Ionomer-based electrolytes are further advantageous because counter-ion mobility is limited, reducing charge-polarization in the electrolytes. These materials are currently limited by low room-temperature conductivities several orders of magnitude too low for practical application. Conductivity can be enhanced through either increasing ion mobility or the collectiveness of ion motion. While it is known that ions aggregate in these systems, the exact structure of ion aggregates and their impact on ion mobility and collective motion are unclear. Using a well-equilibrated coarse-grained ionomer simulation of sodium-neutralized poly(PEO-co-sulfoisophthalate) ionomer, we show that an electrostatic screening length governs aggregate size distribution, radius of gyration scaling, ion transport and ion collective motion. We show localized defects on generally string-like ion aggregates are ions participating in an ion relay mechanism analogous to the Grotthuss mechanism in water.

## ***Development of a Core Escherichia coli Kinetic Metabolic Model using the EM Formalism***

**Presenter:** Ali Khodayari

**Advisor:** Costas Maranas

Recent availability of fluxomic and metabolomics data has paved the way for large-scale kinetic modeling of metabolism. Challenges still remain on deriving meaningful kinetic descriptions and parameterizations that faithfully replicate metabolic responses to genetic and/or environmental perturbations. In this study we introduce a kinetic model of *E. coli* core metabolism that satisfies the fluxomic data for wild-type and seven mutant strains by making use of the recently introduced Ensemble Modeling (EM) concepts. This model encompasses 138 reactions, 93 metabolites and 60 substrate-level regulatory interactions and accounts for glycolysis/gluconeogenesis, pentose phosphate pathway, TCA cycle, major pyruvate metabolism, anaplerotic reactions and a number of reactions in other parts of the metabolism. Parameterization is performed using a formal optimization approach that minimizes the uncertainty-scaled discrepancies between model predictions and flux measurements. The predicted fluxes by the model are within the uncertainty range of experimental flux data for 78% of the reactions (with measured fluxes) for both the reference (wild-type) and seven mutant strains. The remaining flux predictions fall within three standard deviations of the measured values. Converting the EM-based parameters into a Michaelis-Menten equivalent formalism revealed that 32% and 50% of  $K_m$  and  $k_{cat}$  parameters are within one order of magnitude of the literature available values, respectively. The predicted metabolite concentrations by the model are also within uncertainty ranges of metabolomic data for 68% of the metabolites. A leave-one-out cross-validation test to evaluate the flux prediction performance of the model showed that metabolic fluxes for the mutants located in the proximity of mutations used for training the model are predicted more accurately. The constructed model and parameterization procedure provides the means for the construction of even larger-scale models as well as models with more narrowly distributed parameter values as new metabolomics/fluxomic data sets are becoming available for *E. coli* and other well studied organisms.

***Locomotion of Microorganisms near a No-slip Boundary in a Viscoelastic Fluid***

**Presenter:** Shahrzad Yazdi

**Advisor:** Ali Borhan

Given the versatility of their natural habitats, microorganisms often encounter the presence of confining boundaries while moving in polymeric solutions. Some examples include swimming of spermatozoa in the mammalian reproductive tract or bacteria in extracellular polymeric matrices during biofilm formation. It has been shown that both confinement and viscoelasticity have significant impacts on the locomotion of microswimmers. However, the combined effect of these environmental conditions has not been fully understood yet. In this work, we investigate the low-Reynolds-number kinematics of locomotion for a self-propelled swimmer near a no-slip surface. Using a perturbation analysis, time-averaged and instantaneous locomotion kinematics for a squirmer in a viscoelastic fluid are compared to their Newtonian counterparts. Results of the time-averaged analysis show that a microswimmer moves towards the boundary, if it is initially located in close proximity of the boundary. We also present swimming trajectories for different types of swimmers as a function of Deborah number and the swimmer's initial location and orientation.

## Poster Session

### ***Ultrafiltration Behavior of Bacterial Polysaccharides***

**Presenter:** Mahsa Hadidi

**Advisor:** Andrew Zydney

Bacterial polysaccharides are an important component of newly developed vaccines against pneumococci, meningitis, and influenza. These vaccines induce a strong immune response against the capsular polysaccharides that are unique to specific microorganisms. Ultrafiltration can be used for concentration and purification of polysaccharides; however, there is relatively little information on the behavior of different polysaccharides during ultrafiltration.

Experiments were performed using purified bacterial polysaccharides provided by Pfizer Inc. Data were obtained in a stirred ultrafiltration cell using Ultracel composite regenerated cellulose and Biomax polyethersulfone membranes with nominal molecular weight cutoffs of 300, 500, and 1000 kDa. Polysaccharide concentrations were determined using high performance liquid chromatography (HPLC) with refractive index detection.

The filtrate flux and polysaccharide transmission were both strong functions of the solution ionic strength due to inter- and intra-molecular electrostatic interactions. The filtrate flux attained a pressure-independent value at relatively low pressures (around 1 psi = 6.9 kPa) even in dilute polysaccharide solutions (< 1 g/L). There was clear evidence of polysaccharide fouling, particularly in the high ionic strength solutions. Polysaccharide transmission was also a function of the stirring rate, providing clear evidence for the effects of concentration polarization. Much higher transmission could be obtained by using the membranes in the skin-side down orientation due to the strong degree of internal polarization under these conditions. These results provided important insights into the factors controlling the ultrafiltration behavior of bacterial polysaccharides of interest in bioprocessing applications.

***Illuminating Surface Atoms in Nanoclusters  
by Differential X-ray Absorption Spectroscopy***

**Presenter:** Charles Spanjers

**Advisor:** Robert Rioux

We use differential extended x-ray absorption fine structure ( $\Delta$ -EXAFS) to monitor the Ar-induced surface restructuring of Pd nanoclusters (1 nm diameter, silica-supported) at 77 K.  $\Delta$ -EXAFS analysis shows  $9 \pm 2$  nearest-neighbor Pd-Pd bonds expand by  $0.104 \pm 0.005$  Å as a result of Ar adsorption. Atomistic molecular dynamics simulations provide evidence for a model in which Ar drives restructuring of under-coordinated Pd atoms, leading to an increased Pd-Pd bond length of surface Pd atoms with no change in overall nearest-neighbor Pd-Pd coordination number. Based on observations of the atomistic simulations, it is likely that under-coordinated atoms are trapped in metastable states at 77 K and Ar provides the kinetic energy needed to overcome the barrier for surface restructuring. Together, experiment and theory highlight the ability of  $\Delta$ -EXAFS to probe surface atoms of Pd nanoclusters.

## ***Ion-Electrode Interactions at the Electrochemical Interface***

**Presenter:** Ian McCrum

**Advisor:** Michael Janik

The electrode/electrolyte interfacial structure impacts electrocatalytic kinetics. The position of solvent and distribution of ions near to and adsorbed on the electrode surface depend on the electrode composition/structure, solvent, ion identity and concentration, and electrode charge. Recent experimental evidence suggests that alkali metal cations in an alkaline electrolyte influence electrocatalytic reactions, though the mechanism by which this occurs is unknown. The interaction of these cations with the electrode surface can be modeled with *ab initio* methods, such as Density Functional Theory (DFT). This is not trivial in an electrochemical system, given the charged electrode surface and the long length and time scales over which solvent molecules interact. We have investigated the specific adsorption of alkali metal cations onto fcc (111) transition metal surfaces using DFT. Solvation of ions at the Pt(111) surface was considered using explicit water molecules. The adsorption of alkali cations is favorable onto Pt(111) and Pd (111) at low potentials and is competitive with hydrogen adsorption in alkaline electrolyte solutions. Specific alkali adsorption has the potential to impact hydrogen oxidation and hydrogen evolution reactions in fuel cells and electrolysis cells. We make comparisons with experimental results to demonstrate the importance of this specific adsorption to electrocatalytic kinetics.

***Structure and segmental dynamics in  
amorphous poly(3-alkylthiophene) organic semiconductors***

**Presenter:** Pengfei Zhan

**Advisor:** Janna Maranas and Enrique Gomez

Organic semiconductors such as poly(3-alkylthiophene)s (P3ATs) and [1]benzothino[3,2-*b*][1]benzothiophene (BTBT) derivatives are attractive materials for next generation flexible electronics. Although it is well established that the microstructure strongly affects charge transport, the role of fluctuations of the structure on charge mobilities is still not well understood. We have examined the dynamics and structure in both fully amorphous and crystalline systems with neutron and x-ray scattering. We measured the segmental dynamics in amorphous P3ATs with quasi-elastic neutron scattering (QENS) using the high-flux backscattering spectrometer (HFBS) at National Institute of Standard and Technology. The structure of amorphous P3ATs is measured with small-angle neutron scattering (SANS) and grazing incidence X-ray diffraction (GIXRD). We observe phase separation between the backbone and side-chains in all polymer samples for regiorandom P3ATs. Additionally, the analysis of the QENS data shows that the amplitude of proton motion on the thiophene rings increases by a factor of 3 as the side-chain length increases from 6 to 12, demonstrating that longer side chains lead to enhanced motion of conjugated rings.