



Penn State Chemical Engineering Research Symposium

*Friday, September 11, 2015
The Nittany Lion Inn*

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11:00 AM	Registration				
11:30 AM	Session 1	Ballroom AB		Ballroom DE	
		<i>Free surfaces overcome superheating in simulated melting of isotactic polypropylene</i>	Qin Chen	<i>Fast estimation in multi-scale chemical engineering models</i>	Negar Hashemian
		<i>Addition of ferrocene controls polymorphism and enhances charge mobilities in P3HT thin-film transistors</i>	Brandon Smith	<i>Predicting nematic phases for semiflexible polymers from simulations</i>	Wenlin Zhang
		<i>Pumping ions with light</i>	Hasin Feroz	<i>Use of preconditioning to control membrane fouling and enhance performance during ultrafiltration of plasmid DNA</i>	Ying Li
12:30 PM	Lunch - Ballroom C				
1:30 PM	Keynote Speaker – Jack McWhirter - Ballroom C				
2:15 PM	Session 2	Ballroom AB		Ballroom DE	
		<i>Effect of organic and alkali metal cations on the hydrogen oxidation reaction</i>	Ian McCrum	<i>Rapid microfluidic transport of droplets with ratcheted contact charge electrophoresis</i>	Charles Cartier
		<i>Use of ultrafiltration membranes for the purification of novel vaccines made from bacterial polysaccharides</i>	Mahsa Hadidi	<i>Combinatorial pathway engineering for improved NADPH production</i>	Chiam Yu Ng
		<i>Structure and dynamics of glass-forming hard spheres</i>	Yuxing Zhou	<i>High performance polymer-cellulose composite electrolyte for Li-ion battery</i>	Pengfei Zhan
3:15 PM	Poster Session – Ballrooms AB and DE				

4:00 PM	Session 3	Ballroom AB		Ballroom DE	
		<i>Reversing methanogenesis for production of biofuels and biofuel precursors from methane</i>	Michael McNulty	<i>Fouling mitigation in reverse osmosis/nanofiltration systems: electrokinetic, genetic and catalytic approach</i>	Rajarshi Guha
		<i>Zeta potential of polymeric particles at high ionic strength</i>	Astha Garg	<i>PEE-PEO block copolymer exchange rate between micelles is detergent and temperature activated</i>	Allen Schantz
		<i>Assessing nitrogen metabolism using genome-scale models in maize</i>	Margaret Simons	<i>Multi-scale modeling for electrocatalytic applications</i>	Sneha Akhade
5:00 PM	Happy Hour & Awards – Ballroom AB				

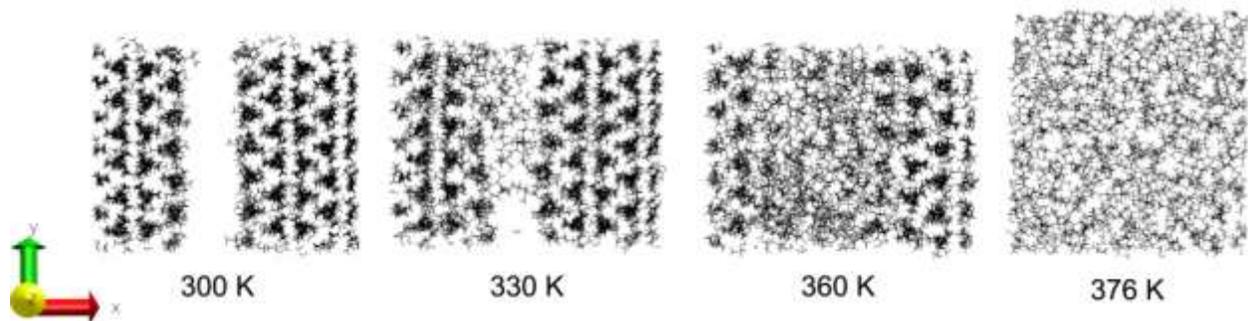
Session 1

Free surfaces overcome superheating in simulated melting of isotactic polypropylene

Presenter: Qin Chen

Advisor: Scott Milner

The equilibrium melting temperature T_m is a challenging experimental benchmark for molecular dynamics (MD) simulations of polymer melting and crystallization. T_m obtained from MD heating scans of α phase isotactic polypropylene (α iPP) can exhibit superheating of over 100°C. This superheating has been attributed to the combined effects of periodic boundary conditions and ultrafast heating rates, both of which inhibit nucleation of the melt. We have developed a simple method to minimize this superheating; we replace the periodic crystal structure with a periodic array of finite thickness slabs, separated by vacuum gaps. Thermal disorder at the slab surface promotes melting, by reducing the melt nucleation barrier. For experimental comparison, we synthesized and measured the melting temperatures of a series of low molecular weight iPP oligomers. In simulations of slab systems, melting initiates at the free surface; as the temperature rises above T_m , the interface advances into the crystal, with a velocity proportional to $T - T_m$. At a constant heating rate, this results in a quadratic rise in the system energy versus temperature. We obtained T_m as the onset of this quadratic rise in system energy, which corresponds well to the experimental melting points. The same simulations give reasonable values for the crystal-vacuum interfacial free energy, from the energy difference between crystalline slabs and periodic crystals.



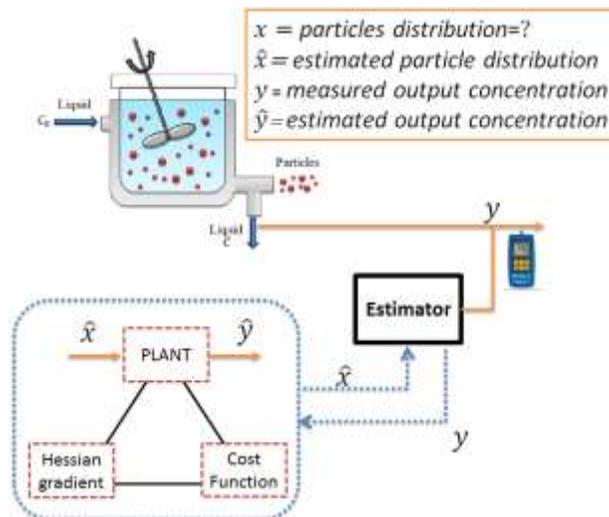
Fast estimation in multi-scale chemical engineering models

Presenter: Negar Hashemian

Advisor: Antonios Armaou

In control engineering, some state variables, which describe the mathematical status of a dynamic system, are not easily measurable. There are examples where these states even lack a physical interpretation. However, knowledge of these state variables is critical in order to effectively control the system and reach the desirable output performance. The state estimation becomes even harder when the measurements are corrupted with noise. Moving Horizon Estimation is a state estimation method which accounts for noise and/or disturbance on system output and system transition. Indeed, MHE employs an optimization method to find the most probable current state variable given the past and current output measurements. Although this method has many advantages over other alternative methods, it is computationally demanding. In this project, to deal with this issue, we propose a new approach to MHE design and investigate its stability requirements. In this modified design, first, Carleman linearization is used to represent nonlinear systems in a bilinear form. Not only we can reduce computations by analytically solving for the response of the bilinear system, but also the sensitivity of the optimization problem is found analytically which decreases the computations even further.

Next, we focus on applying this design framework on dispersed systems which are found in chemical engineering, material science and biology. These systems merit a particle population study rather than the traditional mass balance performed for continuous media. Crystallization, polymerization, viral infections, and colocalization of enzymes in cells are just a few instances of these processes that occur in our everyday life. The common characteristic of all these phenomena are the individual members of the population or the *particles*. These particles are distinguished by their type, size and/or composition. Mostly, a population balance governs the dynamic behavior of particulate systems. This results in complex mathematical models i.e. integro-differential equations. The method of moments is a powerful technique in this matter. It can be used to transform these multi-scale models into a set of ordinary differential equations. In the reduced order model obtained from application of the method of moments, the states are statistical moments of the particles' distribution. Knowledge of these states yields comprehensive information on different output properties. The new MHE design framework is employed for the coagulation process as an instance of disperse systems. Lastly, the designed estimator is shown to closely track the evolution of the statistical moments of the particles using only noisy measurements of the particle population in the exit flow.

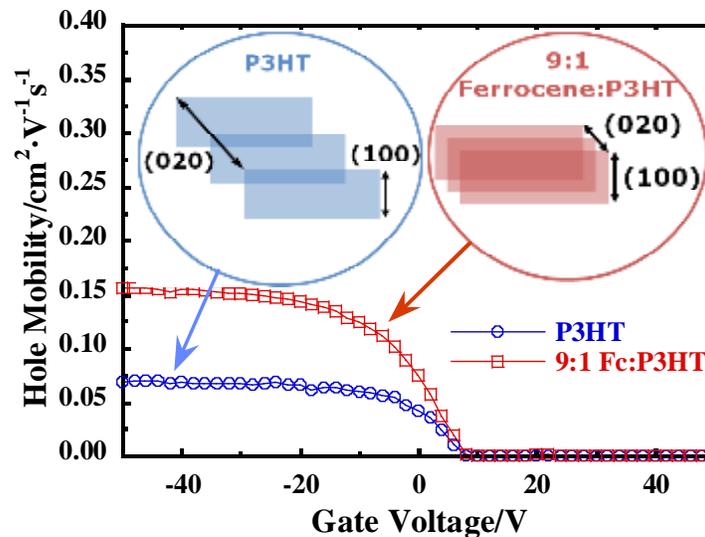


Addition of ferrocene controls polymorphism and enhances charge mobilities in P3HT thin-film transistors

Presenter: Brandon Smith

Advisor: Enrique Gomez

Crystalline organic molecules often exhibit the ability to form multiple crystal structures depending on the processing conditions. Exploiting this polymorphism to optimize molecular orbital overlap between adjacent molecules within the unit lattice of conjugated polymers is an approach to enhance charge transport within the material. We have demonstrated the formation of tighter π - π stacking poly(3-hexylthiophene-2,5-diyl) polymorphs in films spin coated from ferrocene-containing solutions using grazing incident X-ray diffraction. As a result, we found that the addition of ferrocene to casting solutions yields thin-film transistors which exhibit significantly higher source-drain current and charge mobilities than neat polymer devices. Insights gleaned from ferrocene/poly(3-hexylthiophene) mixtures can serve as a template for selection and optimization of next generation small molecule/polymer systems possessing greater baseline charge mobilities. Ultimately, the development of such techniques to enhance the characteristics of organic transistors without imparting high costs or loss of advantageous properties will be a critical factor determining the future of organic components within the electronics market.

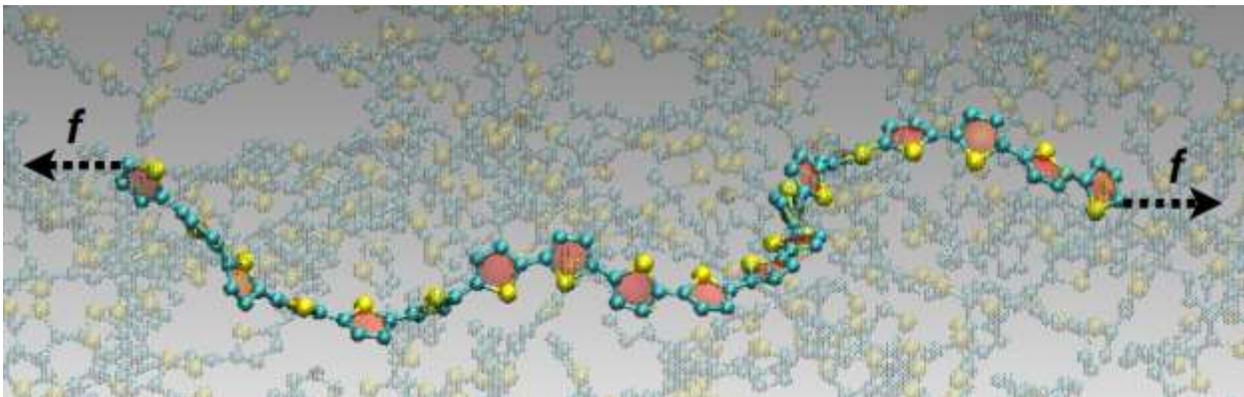


Predicting nematic phases for semiflexible polymers from simulations

Presenter: Wenlin Zhang

Advisor: Enrique Gomez and Scott Milner

The nematic phase affects the properties of semiflexible polymers used in many applications, including displays, high strength fibers, and biomedical devices. The existence of nematic phases can also improve the processing of functional semiflexible polymers such as semiconducting conjugated polymers. Crystallization from the nematic phase promotes the formation of ordered final structures, which can in turn enhance the electric properties and the resulting device performance for conjugated polymers. Directly observing the nematic phases, however, is challenging for many semiflexible polymers. The narrow temperature window of the nematic phase and the low isotropic-to-nematic (IN) transition enthalpy limit the observation of nematic phase using techniques such as differential scanning calorimetry (DSC). Equilibrating molecular dynamic simulations of molten semiflexible polymers near the phase transition is also difficult. We develop a method for predicting the nematic phases of semiflexible polymers by first estimating the nematic coupling constant α , a material parameter characterizes the orientational coupling between backbone segments. Together with the chain stiffness K , α governs the IN transition temperature T_{IN} and the chain alignment in mesophases and at interfaces. Because crystallization or thermal degradation can preclude the IN transition, T_{IN} is not always accessible for predicting α . By combining self-consistent field theory (SCFT) with atomistic molecular dynamics (MD) simulations of semiflexible chains under external tension in the isotropic phase, we can predict the nematic coupling constant α . In simulations, we apply external tension to the polymer backbones to induce uniaxial alignment, which is enhanced by the presence of nematic coupling. Using SCFT, we compute the order parameter q for the same semiflexible chains under the same tension for a given α . The value of α is determined by fitting the SCFT predicted order parameter $q(\alpha)$ to the simulation results. Using the predicted α , we obtain the variational free energy, from which the IN transition temperature T_{IN} is determined. We demonstrate our method by predicting α and T_{IN} of a commonly studied conjugated polymer, poly(3-hexylthiophene) (P3HT). The estimated T_{IN} suggests that oligomeric 3-hexylthiophene is nematic after melting from crystal. Using our mean field free energy, we also predict the IN transition transition enthalpy is much smaller than the enthalpy of fusion for P3HT. Our predictions are consistent with experiments, in which a nematic phase is reported based on polarized optical microscopy (POM) and only a single crystal melting peak is observed using DSC for P3HT.

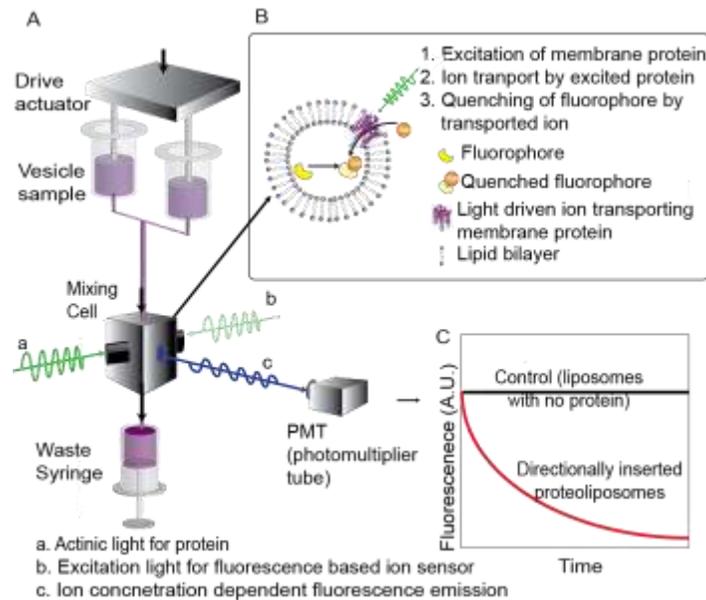


Pumping ions with light

Presenter: Hasin Feroz

Advisor: Manish Kumar

Understanding the neural circuitry has important applications in treatment and therapeutic/pharmaceutical processes. In an attempt to find the perfect neural probes, scientists have stumbled upon a unique class of membrane proteins called microbial opsins (MO) that pump ions in response to specific-wavelength light. Despite the discovery of MOs in salt-loving halophiles in the 1970's, their expression in mammalian neurons to excite/suppress neural pathways is a recent advancement. Now, as the array of native and engineered opsins continues to expand, no standard technique exists to determine the transport properties of these light-driven ion pumps or channels for quantitative comparison of one opsin with another. My research focuses on bridging this gap by developing a simple and robust technique for measuring the single-molecule transport properties of these light-driven membrane proteins. We have combined opsin-reconstituted liposome-based stopped flow fluorimetry with time correlated single photon counting (TCSPC) to quantify the ion transport rate of the inward-directed chloride ion pump, halorhodopsin. By complementing our assay with patch clamp measurements of ion-transport in cell-mimicking giant unilamellar liposomes (GUVs), we intend to develop a rapid screening tool to choose an anion or cation transporting opsin for optical control over targeted neurons.



Quantification and comparison of light-driven ion transport rates of different microbial opsins. A. Experimental set-up for stopped flow fluorimetry. B and C. Ion transport in proteoliposomes and expected trend in fluorescence. Combining the stopped flow results for $\# \text{ ions} \cdot (\text{liposome} \cdot \text{photon} \cdot \text{s})^{-1}$ with TCSPC data for $\# \text{ opsin molecules} \cdot (\text{liposome})^{-1}$, we obtain the light-driven single molecule transport property of microbial opsins, $\# \text{ ions} \cdot (\text{opsin molecule} \cdot \text{photon} \cdot \text{s})^{-1}$.

Use of preconditioning to control membrane fouling and enhance performance during ultrafiltration of plasmid DNA

Presenter: Ying Li

Advisor: Andrew Zydney

Several recent studies have demonstrated that small pore size ultrafiltration membranes can be used for purification of supercoiled plasmid DNA for therapeutic applications, but the performance of these membrane systems is severely limited by membrane fouling. The objective of this work was to examine the potential of pre-conditioning, in this case accomplished by pre-elongating the DNA by passage through a region with large pore size, to minimize fouling and enhance DNA separations.

Data were obtained using both asymmetric hollow fiber membranes, with flow in either the normal or reverse orientation, and with composite membrane structures made by placing a larger pore size flat sheet microfiltration membrane in series with an ultrafiltration membrane. In all cases, flow through the larger pore size region pre-stretched the plasmid, leading to an increase in plasmid transmission and a significant reduction in fouling. This pre-conditioning also provided a significant increase in selectivity for separation of the linear and supercoiled isoforms. Effectiveness of different pre-conditioning conditions on the transmission of plasmid isoforms was investigated by alternating the top layer pore size and morphology in the composite membrane structure. These results clearly demonstrate the potential for dramatically increasing the performance of membrane systems for plasmid DNA separations by controlling the pore morphology to pre-stretch the DNA before passing through the narrow pores of an ultrafiltration membrane.

Session 2

Effect of organic and alkali metal cations on the hydrogen oxidation reaction

Presenter: Ian McCrum

Advisor: Michael Janik

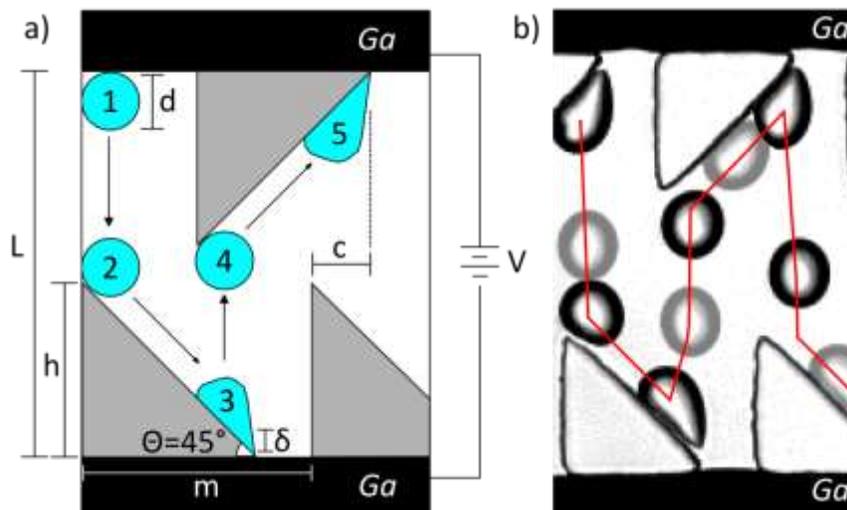
It is well known that many anions including hydroxide, (bi)sulfate, and organic sulfonate can specifically adsorb to electrode surfaces and affect the rate and mechanism of a variety of electrocatalytic reactions. Recent evidence has shown that alkali metal cations can affect a variety of electro-catalytic reactions on platinum as well, including methanol oxidation, hydrogen oxidation, and oxygen reduction, but direct experimental evidence for their specific adsorption is lacking. We have previously used density functional theory (DFT), an *ab initio* quantum mechanics based technique, to show that alkali metal cations can specifically adsorb to platinum and palladium electrodes at low potentials and compete with hydrogen adsorption in high pH electrolytes. We find experimentally that the rate of the hydrogen oxidation reaction is dependent on the cation present in an alkaline electrolyte solution and propose and evaluate a mechanism for this effect. Using DFT, we show that alkali metal cations can specifically adsorb to the low index facets of platinum and weaken the adsorption of hydroxide, an important reaction intermediate. We have extended both our computational and experimental work to find that quaternary ammonium cations can also specifically adsorb to low index platinum electrode surfaces. The development of the mechanism for the effect of alkali metal cations on the rate of the hydrogen oxidation reaction and the DFT methods for simulating alkali metal cation and organic cation specific adsorption will be discussed.

Rapid microfluidic transport of droplets with ratcheted contact charge electrophoresis

Presenter: Charles Cartier

Advisor: Kyle Bishop

Contact Charge Electrophoresis (CCEP) occurs when a charged conductive shuttle (e.g. droplet or solid particle) immersed in a dielectric medium oscillates continuously and rapidly ($\sim 100\text{Hz}$) between two electrodes due to a DC electric field. If dielectric ramps are placed on the electrodes, they act as barriers forcing the shuttle to slide or roll in a direction transverse to the electric field. These barriers act to ratchet the particle along a microfluidic channel independent of fluid flow. These electrostatic motors can be used for mixing, separations, or particle transport. Particle transport of colloids in microfluidic devices is particularly appealing because this mechanism scales well to smaller dimensions, has low power requirements ($\sim 100\text{nW}$) and operates via a DC field. We present simple heuristics for the design and implementation of droplet transport in microfluidic devices. We discuss how droplet properties such as electrical conductivity and surface tension change the mechanism behavior. Finally we demonstrate the use of these heuristics to design new applications such as an electrostatic droplet generator.



a) Schematic of droplet undergoing Contact Charge Electrophoresis. A droplet of diameter d , initially uncharged (1), contacts a gallium electrode of potential V . It then moves towards the oppositely charged electrode (2). As it rolls down the dielectric barrier and approaches the oppositely charged electrode the shape of the droplet distorts due to a field focusing effect (3). After a charge transfer event occurs, the droplet reverses directions (4) and repeats the oscillatory process rolling down a dielectric barrier and (5) proceeding along the length of the channel. b) Sequence of experimental images in microfluidic device depicting the mechanism describes in schematic a).

Use of ultrafiltration membranes for the purification of novel vaccines made from bacterial polysaccharides

Presenter: Masha Hadidi

Advisor: Andrew Zydney

Polysaccharide-based vaccines can protect against important infectious diseases such as pneumonia and meningitis. These vaccines are developed by conjugating the capsular polysaccharide from pathogenic bacteria to a highly immunogenic protein, e.g., a protein from the diphtheria toxin. Purification of the resulting conjugate can be a significant challenge in the commercialization of these vaccines. The objective of our work was to develop a fundamental understanding of the potential of using membrane ultrafiltration for the separation / purification of these polysaccharides and their corresponding conjugates. Experiments were performed using several pneumococcus polysaccharide serotypes (with different size and electrical charge) over a range of solution conditions. Ultrafiltration data were obtained in a stirred cell using composite regenerate cellulose and polyethersulfone membranes with different pore size. Polysaccharides were characterized using both dynamic light scattering and size exclusion chromatography. Polysaccharide transmission in dilute solutions was a strong function of filtrate flux due to concentration polarization effects, with the data in good agreement with available hydrodynamic models. Polysaccharide fouling became significant at high filtrate flux and when using more concentrated solutions, consistent with the presence of a critical wall concentration for fouling for each serotype. The flux and polysaccharide transmission were also strong functions of solution ionic strength due to a combination of inter- and intra-molecular electrostatic interactions between the charged polysaccharides and the charged membrane. These results provide important insights into the factors controlling the ultrafiltration behavior of bacterial polysaccharides and a framework for the design of membrane processes for the purification of polysaccharide-based vaccines.

Combinatorial pathway engineering for improved NADPH production

Presenter: Chiam Yu Ng

Advisor: Costas Maranas

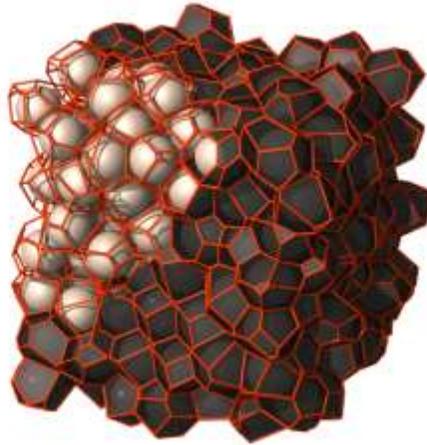
Microbial metabolism can be engineered to produce a wide range of chemicals. One of the major challenges in metabolic engineering is to ensure consistent supply of redox cofactors, which participate in over 100 reactions in a cell, to the desirable biosynthesis reactions. In particular, NADPH is an essential cofactor for the biosynthesis of high-value chemicals, including isoprenoids, chiral alcohols, and biopolymers. In this project, we optimized a synthetic Entner-Doudoroff (ED) pathway in *Escherichia coli* using combinatorial engineering approach to improve the availability of NADPH. We then demonstrated that improving NADPH regeneration rate and balancing of precursor availability enhanced the yield of an isoprenoid, neurosporene, by up to 1.97-fold.

Structure and dynamics of glass-forming hard spheres

Presenter: Yuxing Zhou

Advisor: Scott Milner

Glasses have been a part of our lives for thousands of years, but the nature of glass transition remains one of the deepest unsolved problems in condensed matter physics. Any liquid cooled sufficiently fast to avoid crystallization will eventually become glassy, i.e., the relaxation time of the liquid exceeds the observation time given to reach equilibrium. Surprisingly, the rigidity (or sluggish motion) developed in the glass transition does not derive from crystalline lattice -- the microscopic structure of a glass remains as random as a liquid. How to reveal the length scale associated with the growing relaxation time when there is no obvious structural change? Is there a structural motif of glass transition in real space? To address these questions, we numerically study the simplest glass former -- hard spheres. Previously, only polydisperse hard sphere fluid dynamics could be simulated, because of the rapid crystallization of monodisperse glassy fluids. We develop a "crystal-avoiding" hybrid Monte Carlo method to study the dynamics of glassy monodisperse hard sphere fluids. We then use dynamical scaling to obtain the structural length scale from the effect of pinning on dynamics without assuming the detailed nature of the transition. Pinning particles and dynamical scaling directly reveals the underlying cooperative length scale. Finally, to explore the structural origin of slow dynamics, we introduce a purely geometric criterion for potentially mobile particles in a dense hard-sphere fluid: namely, "T1-active" particles, which can gain or lose at least one Voronoi neighbor by moving within their free volume with other particles fixed. We find that the fraction of T1-active particles vanishes at random close packing, while the percolation threshold of T1-inactive particles is essentially identical to the commonly identified hard-sphere glass transition, $\phi_g \approx 0.585$.



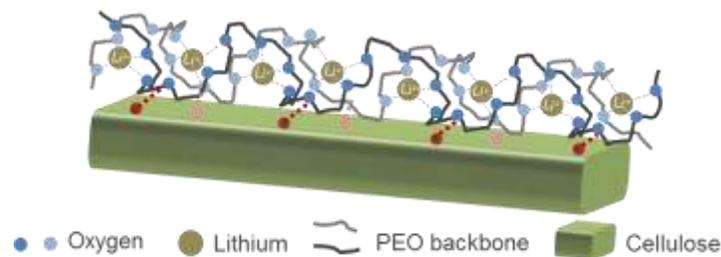
High performance polymer-cellulose composite electrolyte for Li-ion battery

Presenter: Pengfei Zhan

Advisor: Janna Maranas

Polymer electrolytes are safer, cleaner, and more flexible than liquid electrolyte that is currently being used in Li batteries. However, polyethylene oxide (PEO) based electrolytes are not stiff enough to prevent dendrite formation, which limits the use of Li metal anode. They also do not have high enough conductivity to be practical. In amorphous polymer electrolytes, stiffness and conductivity are inversely related because Li motion is coupled to polymer motion, and any attempt to improve conductivity through faster polymer motion results in decreased stiffness. Crystalline PEO₆LiX complex is a tunnel-like polymer/salt structure that promotes fast Li motion. The application is limited because high ion conductivity is only observed with short molecular weight PEO, as the molecular weight increase, tunnels are misaligned and the conductivity is decreased.

High aspect ratio nanofillers based on cellulose nanowhiskers are hypothesized to promote the formation of tunnel structures. These fillers offer controllable surface chemistry, degree of functionalization and aspect ratio, thus forming an ideal model system. In this work, we fabricate high molecular weight PEO/cellulose nanowhiskers nanocomposite. Compared with unfilled electrolyte, the room temperature ion conductivity increased as much as 1100% in filled electrolyte. With wide angle x-ray scattering (WAXS), we observe that the structure transitions from amorphous phase to crystalline phase as we add cellulose nanowhiskers and this is because the interaction between acidic cellulose surface and polymer chain enhances the crystallization. From the temperature dependence of conductivity, the calculated Li⁺ hopping activation energy is shown to be lower in acidic cellulose nanowhisker filled samples. Our quasi-elastic neutron scattering (QENS) indicates with acidic surface, the rotation of PEO₆ channels are more stabilized and this could be the origin of the low activation energy and high conductivity.



Conductive PEO₆ tunnel is formed on cellulose surface through surface interaction.

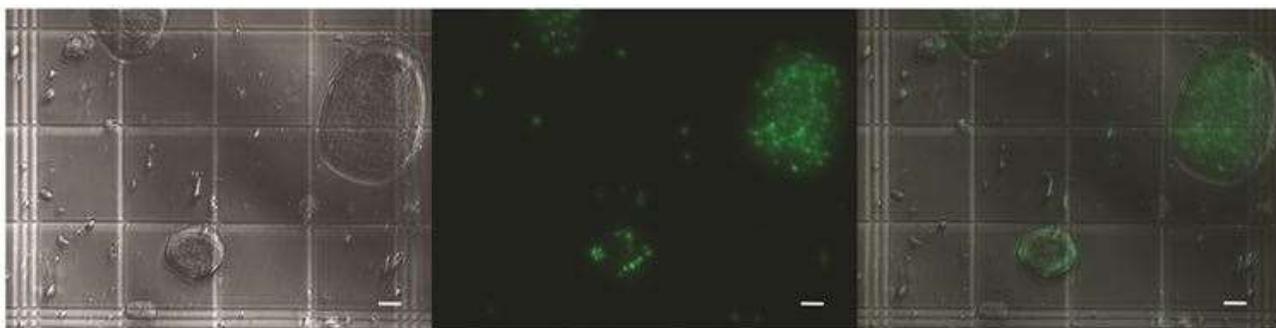
Session 3

Reversing methanogenesis for production of biofuels and biofuel precursors from methane

Presenter: Michael McNaulty

Advisor: Thomas Wood

In an effort to gain energy independence, natural gas deposits especially in the Marcellus shale region in Pennsylvania have seen great increases in extraction in the past several years. Increases in natural gas extraction inevitably lead to more methane gas emissions, with methane being a potent greenhouse gas. Therefore, methods for converting methane gas to more easily transported value-added products, such as liquid biofuels, are sought after. In nature, the biotic process of anaerobic oxidation of methane (AOM) plays a key role in curtailing methane concentrations in the atmosphere. Little is known about AOM, although a reversal of the methanogenic pathway has been implicated. Further complicating matters is the fact that no pure cultures of anaerobic methane consumers have been isolated. Only interdependent consortia have been characterized consisting of methane-degrading archaea and sulfate reducing bacteria. Previously characterized microbial growth of non-defined consortia on methane as carbon source is slow with some doubling times reported at over 1 month. Nevertheless, an enzyme homologous to methyl coenzyme-M reductase (MCR), responsible for the last enzymatic step in methanogenesis, from a non-culturable anaerobic methane degrading sample has been characterized. We report the production of this enzyme from the non-cultured AOM sample within a methanogen host to effectively run methanogenesis in reverse to allow for growth on methane as main carbon source. The characterization of liquid metabolic by-products from the resulting consumption of methane has led to the identification of biofuel precursors such as acetate. Current and future work involves further conversions of these precursors into value-added products, including methanol and butanol. Metabolic pathway engineering to complete the biofuel production pathways will be discussed. Furthermore, consortia will be developed to mimic AOM processes that are found in nature by splitting metabolic tasks between syntrophs, and to potentially remove intermediates and end-products that may be inhibitory to growth of either syntroph. This would be the first time that synthetic, defined consortia would be developed for the purpose of anaerobic methane consumption, and will shed more light on the natural process of AOM that plays a major role in the methane cycle in the environment.



Engineered *Methanosarcina acetivorans* grown with methane as main carbon source. Cells were incubated under a methane headspace for 42 days before staining with Syto9 and visualizing on a hemocytometer (400× magnification) with epifluorescence. Cells, stained green, are seen conglomerating as biofilm growth on the iron precipitates, which remain unstained.

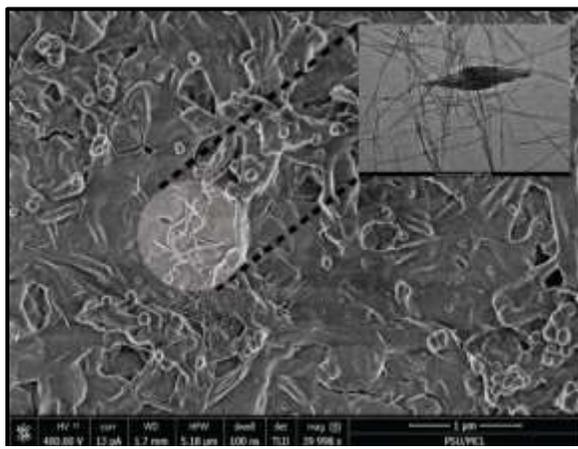
Fouling mitigation in reverse osmosis systems using a catalytic approach

Presenter: Rajarshi Guha

Advisor: Manish Kumar and Darrell Velegol

Reverse osmosis (RO) is the most energy efficient desalination process available and enables utilization of almost any marginal water resource to produce potable water. However, one of the unmet challenges in such processes is to minimize membrane fouling and the necessary pretreatment for its prevention. Both these result in significant energy consumption. RO systems are prone to fouling due to innate pressure driven filtration mechanism. Moreover, the cake formed by particle filtration enhances salt concentration at the membrane surface (cake enhanced concentration polarization). Formation of a cake also leads to diffusio-phoretic fouling. These cake layers are very difficult to remove and due to their process implications of higher effective osmotic pressure, lead to increased operating cost. Developments such as polymer chain grafted on to RO membrane surface, TiO₂ or carbon nanotube composite RO membrane have not addressed the core operational issue of fouling elimination in real time. We have taken a simple, scalable and versatile catalytic approach to combat the fouling challenge without hindering the actual process or building expensive new infrastructure or membrane materials. In our novel approach, bound metal oxide nanoparticles on thin polydopamine layers attached to any RO/ NF membrane surface acts as catalytic centers for H₂O₂ dissociation. Generation of oxygen bubbles disperse the foulants by bubble release/ bursting and van der Waals repulsion mechanism.

Such mechanism was further applied to mitigate concentration polarization and enhance flux by catalytic properties of one of the foulant moieties- humic acid. CuO nanoparticles functionalized RO membrane was also demonstrated to reduce biofilm formation compared to control cases. Therefore, this simple and efficient approach holds the promise to reduce energy consumption of RO systems; provides a platform of advanced catalytic reactions for environmental remediation and also can be used as real time flux improvement strategy in other filtration (eg. ultrafiltration) operations.



SEM image of 80 ppm CuO nanorods functionalized NF90 membrane. The inset shows TEM image of such nanorods with 200 nm scale bar.

Zeta potential of polymeric particles at high ionic strength

Presenter: Astha Garg

Advisor: Darrell Velegol

The electrokinetic behavior of surfaces at high ionic strength in water is largely unexplored though it is relevant to a number of situations of modern day significance such as physiological systems, sea water and geological reservoirs. A key parameter for electrokinetic effects is zeta potential, an indicator of charge. Zeta potential is believed to be insignificant for most of these systems and techniques to measure it are limited to dense particles at high volume fractions. We have developed an electrophoresis based technique to measure zeta potential on model polymeric microparticles at high ionic strength, approaching saturation. The technique utilizes AC electric fields of $f \sim 100$ Hz and high speed microscopy. Our research has shown that the surfaces are charged, subject to movement in the presence of electric fields and the charge is depends on the surface functionalization. This opens up the way for systematic studies of electrokinetic effects such as diffusiophoresis in these systems as well as gives clues to understanding that structure of the double layer at high ionic strength, approaching saturation.

PEE-PEO block copolymer exchange rate between micelles is detergent and temperature activated

Presenter: Allen Schantz

Advisor: Janna Maranas and Manish Kumar

We examine the kinetics of polymer chain exchange between polymer/detergent micelles, a system relevant to the synthesis of protein-containing biomimetic membranes. Although chain exchange between polymer aggregates in water occurs too slowly to observe, the presence of detergent allowed us to determine chain exchange rate constants using time-resolved small-angle neutron scattering (TR-SANS). We chose to examine a membrane-protein-relevant, vesicle-forming, ultra-short polymer, Poly(ethyl ethylene)₂₀-Poly(ethylene oxide)₁₈ (PEE₂₀-PEO₁₈). PEE₂₀-PEO₁₈ was solubilized in mixed micelles with the non-ionic detergent octyl- β -D-glucoside (OG), which is compatible with many membrane proteins. Cryo-TEM and SANS are used to determine complete solubilization of the polymer into micelles. We show for the first time that detergents activate block copolymer chain exchange, and determine kinetic parameters at two detergent concentrations above the CMC (critical micellar concentration) of OG. We find that chain exchange increases two orders of magnitude when temperature increases from 35 to 55 °C, and that even a 1 mg/mL increase in OG concentration leads to a noticeable increase in exchange rate. Using the Arrhenius equation, we determine that at detergent concentrations above the CMC, the activation energy for chain exchange is 2-3 times higher for PEE₂₀PEO₁₈ than for lipids. However, the large uncertainty in the activation energy prevents us from proving definitively that the faster kinetics at higher OG concentration result from a lower activation barrier. These findings explain the need for high detergent concentration and/or temperature to synthesize polymer/protein membranes, and kinetic measurements at a wider range of OG concentrations will allow us to determine the exact relationship between activation energy and detergent concentration.

Assessing nitrogen metabolism using genome-scale models in maize

Presenter: Margaret Simons

Advisor: Costas Maranas

A second-generation metabolic genome-scale model of *Zea Mays* L. has been constructed to investigate nitrogen assimilation and to capture C₄ carbon fixation. The maize model simulates the interactions between the bundle sheath and mesophyll cells in the leaf tissue. Incorporation of the previously published *iRS1563* model, the MetaCrop database, and the MaizeCyc database using Metrxn yielded a model spanning 5,824 genes and 8,525 reactions. Biomass proportions were experimentally measured under excess nitrogen, limited nitrogen, and two glutamine synthetase mutants (i.e. *gln1-3* and *gln1-4*) yielding condition-specific biomass equations. By applying the condition-specific biomass equations and condition-specific regulatory constraints based on transcriptomic and proteomic data, four nitrogen conditions were simulated. The flux through chlorophyll biosynthesis decreases in the limited nitrogen, *gln1-3* mutant, and *gln1-4* mutant conditions compared to the nitrogen complete wild-type condition confirming the important association between nitrogen metabolism and chlorophyll synthesis. Regulatory constraints based on the enzyme activity levels for 19 maize lines were applied to the model to determine the metabolic differences in a pair-wise manner. Of the 2738 reactions that are active in at least one line at the maximum leaf biomass production, a total of 312 reactions make up the set of reactions that vary between at least two of the maize lines. The metabolic differences observed mimic both the genetic origin of the species and the experimental hypotheses based on the enzyme activity levels and metabolomics data. Ultimately, the goal is to reconstruct a multi-tissue model of all major tissue-types in maize (i.e. the root, stalk, leaf, tassel, and seed) using the phloem as a metabolite transporter. This model will be applied to analyze the flow of nitrogen from the plant root to the other tissues, suggest genetic interventions to improve nitrogen use, and study the effect of nitrogen on sugar storage in the seed.

Multi-scale modeling for electrocatalytic applications

Presenter: Sneha Akhade

Advisor: Michael Janik

Present day advances in computer simulation have greatly accelerated material discovery and investigation of bulk and surface properties that are relevant to the reactivity and performance of the material. However, all processes involving heterogeneous catalysis within the electrochemical device occur at the interface. Our main objective is to develop robust methods that can provide a reasonable description of the electrode/electrolyte interface and can correctly mimic the complex underlying interfacial chemistry. We employ a combined Density Functional Theory (DFT) with a force field (FF) based classical approach to construct an atomistic modeling tool to consider this interface. Using DFT, we present a simple and transferable method to estimate the reaction energetics and activation barriers for inner sphere elementary electrochemical reactions, specifically in the context of carbon dioxide electroreduction (CO₂ ER). Mechanistic conclusions drawn on the CO₂ ER pathway will be discussed. Efforts in modeling a rigorous representation of the electrode/electrolyte interface at length and time scales beyond the framework of DFT will also be briefly presented. Two key features of the complex interface – electrode polarization and the interfacial chemistry in the presence of a potential-controlled field are addressed using classical FF with a dynamic charge equilibration scheme (Charge Optimized Many Body potentials (E-COMB3)).

Poster Session

How do we grow nanocrystals with selective sizes and shapes?

Presenter: Tonnam Balankura

Advisor: Kristen Fichthorn

Achieving shape and size controlled synthesis of nanostructures can enable us to exploit their unique catalytic, optical, and magnetic properties. In the past decade, a number of promising solution-phase synthesis techniques have been developed to fabricate various nanostructures. A deep, fundamental understanding of the structure-directing mechanism in these syntheses would contribute towards improving the selectivity of next-generation techniques. In our study, molecular dynamics simulation is used to probe the structure-directing mechanism of colloidal Ag nanostructure synthesis. We study the structure-directing agent polyvinylpyrrolidone (PVP), which is well-known for producing {100}-faceted Ag nanostructures such as nanowires. The proposed structure-directing mechanism of PVP is they preferentially bind to Ag(100) over Ag(111) surfaces. To confirm this hypothesis, we calculate the potential of mean force (PMF) to quantify the solution-phase binding energies of PVP-derived molecules on Ag(100) and Ag(111) surfaces. We also study the effect of PVP on the relative atom deposition rate on Ag(111) over Ag(100) surface. By calculating the PMF profiles, we show how PVP influence the formation of {100}-faceted Ag nanostructures.

Tight-binding model of conformational disorder effects on optical absorption spectra of polythiophenes in solution

Presenter: Joel Bombile

Advisor: Michael Janik and Scott Milner

Polythiophenes have potential applications as semiconducting materials for organic electronic devices. However, the widespread usage of these polymers is limited by their low performance relative to inorganic semi-conductors. Polymers are soft materials with many conformational degrees of freedom. Limited understanding of how conformational disorder affects optical and electronic properties is a key source of difficulties in developing high performing materials. In this work, we develop a coarse-grained approach based on the tight binding approximation to model the electronic degrees of freedom of a single chain, taking into account conformational degrees of freedom. Particularly important is dihedral disorder, which disrupts extended electronic states. Our model is parameterized using density functional theory (DFT) calculations of the one-dimensional band structures for chains with imposed periodic variations in dihedral angles. The tight binding model predicts valence and conduction bands for these chain conformations that compare well to DFT results. As a first application of our model, we compute the optical absorption spectrum of polythiophene chains in solution. We find good overall agreement with the broadening of the absorption edge, which is a consequence of dihedral disorder of chains in solution as compared to all-trans chains.

Bio-inspired colloidal machine: bringing colloids to life

Presenter: Syeda Sabrina

Advisor: Kyle Bishop

Active matter comprised of many self-driven units can exhibit emergent collective behaviors such as pattern formation and phase separation in both biological (e.g., mussel beds) and synthetic (e.g., colloidal swimmers) systems. While these behaviors are increasingly well understood for ensembles of linearly self-propelled "particles", less is known about the collective behaviors of active rotating particles where energy input at the particle level gives rise to rotational particle motion. A recent simulation study revealed that active rotation can induce phase separation in mixtures of counter-rotating particles in 2D. In contrast to that of linearly self-propelled particles, the phase separation of counter-rotating fluids is accompanied by steady convective flows that originate at the fluid-fluid interface. We investigate the influence of these flows on the coarsening dynamics of actively rotating binary liquids using a phenomenological, hydrodynamic model that combines a Cahn-Hilliard equation for the fluid composition with a Navier-Stokes equation for the fluid velocity. The effect of active rotation is introduced through an additional force within the Navier-Stokes equations that arises due to gradients in the concentrations of clockwise and counter-clockwise rotating particles. Depending on the strength of active rotation and that of frictional interactions with the stationary surroundings, we observe and explain new dynamical behaviors such as "active coarsening" via self-generated flows as well as the emergence of self-propelled "vortex doublets". We confirm that many of the qualitative behaviors identified by the continuum model can also be found in discrete, particle-based simulations of actively rotating liquids. Our results highlight further opportunities for achieving complex dissipative structures in active materials subject to distributed actuation. We are currently developing spinning micro-scale particles driven by induced-charge electrophoresis with the goal of studying their collective behaviors.

Nonlinear model predictive control via Carleman linearization-based formulations

Presenter: Yizhou Fang

Advisor: Antonios Armaou

The need of tight operating conditions in chemical, pharmaceutical, and petroleum industries has given rise to the development of Advanced Process Control (APC). Model Predictive Control (MPC), as a branch of APC, converts constrained control problems into optimization problems. It started gaining attention three decades ago for its capability of handling various state, input and performance constraints. Nonlinear MPC solves optimal control problems of nonlinear systems. This basic architecture enables Nonlinear MPC to handle large state-space multi-variable systems, and to deal with model-mismatches and disturbances readily.

One significant barrier in the application of Nonlinear MPC is the feedback delay. Since the optimal control problem is formulated as a receding horizon one, it solves a dynamic optimization problem at each sampling time, thus the computational time of the control policy is required to be less than one sampling time for online operation. However, this requirement is most of the times impossible to meet when the system has high nonlinearity. It becomes one of the most significant reasons holding back the application of Nonlinear MPC. As a result, there is strong motivation to develop an advanced formulation of Nonlinear MPC that demands less computational effort and thus decides the control actions faster.

The primary focus of this project is to develop an advanced formulation of Nonlinear MPC that decreases the amount of computational effort in order to circumvent feedback delay, to improve controller performance and to maintain the stability of the system. Multiple mathematics tools combined with optimization techniques are implemented for the purpose of accelerated searching algorithm. Based on Carleman linearization, the states of the system are extended to higher orders following the Kronecker product rule. The nonlinear dynamic constraints can thus be modeled with an extended bilinear representation while keeping the nonlinear information. The work of re-extending the states is repeated during the prediction to minimize simulation errors. It enables analytical prediction of system states and provides analytically computed sensitivity of the cost function to the control signals as the searching gradient in order to accelerate the optimization. The proposed method resembles both collocation and shooting methods.

Electrokinetics at high ionic strength

Presenter: Astha Garg

Advisor: Darrell Velegol

The Velegol group at Penn State works on understanding the electrokinetic behavior of surfaces at high ionic strength, where it was classically believed to be insignificant. We have developed a technique to measure the charge on model polymeric microparticles at high ionic strength, approaching saturation. Our research has shown that surfaces at high ionic strength in water are generally charged and are subject to movement in the presence of electric fields. We study 3 different systems namely: membranes, minerals and coffee rings where salt gradients cause spontaneous generation of electric fields, leading to motion of charged surfaces, called diffusiophoresis and diffusioosmosis. We work on using these electrokinetic effects for applications such as prevention of membrane fouling as well as extraction of oil trapped in minerals.

The Pathway Map Calculator: A learning algorithm to predict optimal expression levels from characterized pathway variants

Presenter: Sean Halper

Advisor: Howard Salis

Current metabolic engineering approaches seek to optimize the expression levels of multi-enzyme pathways by employing promoter and ribosome binding site libraries and altering plasmid copy numbers. These pathway optimization efforts are limited by the inability to fully characterize the expression space for a pathway. Optimizing expression levels for a many-enzyme pathway is infeasible when it requires characterizing millions of combinatorically mutated pathway variants. The Pathway Map Calculator efficiently and accurately maps the expression space of a pathway using a small number of well characterized pathway variants with known/estimated enzyme expression levels. The resulting Pathway Maps predict future pathway optimal enzyme expression levels to maximize a pathway's productivity. Preliminary testing of the Pathway Map Calculator shows that it can create accurate Pathway Maps when given 100 to 200 characterized pathway variants with up to nine enzymes in spite of experimental error and limited dataset sizes relative to pathway scale. Our approach converts sparse, combinatorial expression-flux measurements into continuous smooth Pathway Maps with well-predicted optimal expression levels, enabling systematic optimization of multi-enzyme pathways using a small number of measurements.

Oxidative coupling of methane: descriptors for activity and selectivity

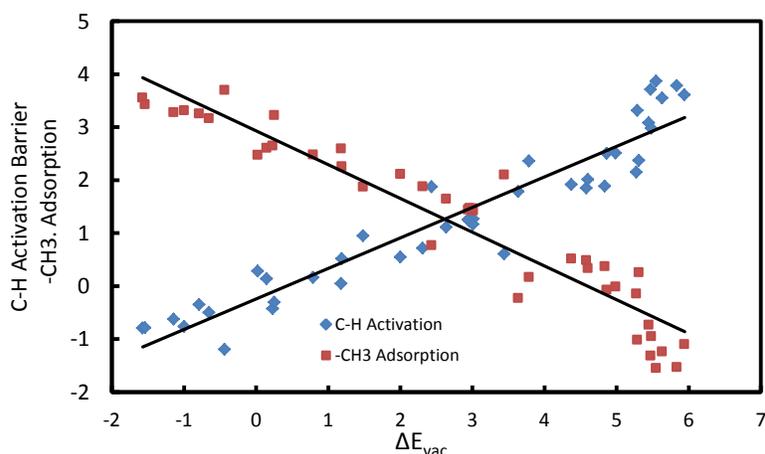
Presenter: Gaurav Kumar

Advisor: Michael Janik

Increasing natural gas reserves in the recent years motivate further development of processes to convert methane into value-added products. Since the initial description of catalytic oxidative coupling of methane (OCM) to form C_2 hydrocarbons, various pure/doped metal-oxide catalysts have been examined for their methane conversion and C_2 selectivity. This ongoing search to find high performing catalysts has been pre-dominantly empirical, and the relationship between active site properties and catalyst activity and selectivity remains unclear. A known dependence of the OCM activity and selectivity on material property(s) enables us to tune active site properties to optimize catalyst performance.

This study uses density functional theory (DFT) methods and the established OCM reaction mechanism to relate activity and selectivity to the surface electronic and structural properties of the catalyst. C-H activation and $\cdot CH_3$ radical adsorption determine the activity and selectivity of a catalyst, respectively. Since both of these elementary processes reduce the catalyst surface, *we hypothesize that the activity (measured by C-H activation) and selectivity (measured by $\cdot CH_3$ adsorption) of the catalyst correlate with surface reducibility*. C-H activation energy and $\cdot CH_3$ adsorption energy have been plotted against the oxygen vacancy formation energy ΔE_{vac} of various metal-doped CeO_2 , doped MgO, doped TiO_2 , ZnO and TbO_x . Computational results (Figure 1) show a linear relation of the vacancy formation energy (surface reducibility), with the C-H activation energy and $\cdot CH_3$ adsorption energy.

Ceria has a lower C-H activation energy which suggests that it is highly active and would offer better methane conversion. However, it also binds $\cdot CH_3$ strongly leading to over-oxidation of methane and thus gives low C_2 selectivity. Conversely, high C-H activation energy and weak $\cdot CH_3$ adsorption imply that pure/doped MgO catalysts will have better C_2 selectivity but low activity. Therefore, a trade-off between activity and selectivity is inherent in the active site. Sub-correlations to that shown in Figure 1 demonstrate that this correlation holds across a single material with increasing state of reduction as well as with change in U parameter used in the DFT+U method. Methods on finding an optimal trade-off in activity and selectivity, as well as potential approaches to breaking this correlation, will be discussed.



Correlation between surface reducibility and activity/selectivity.

Real-time numerical simulation of ozone transport and uptake in the respiratory tract

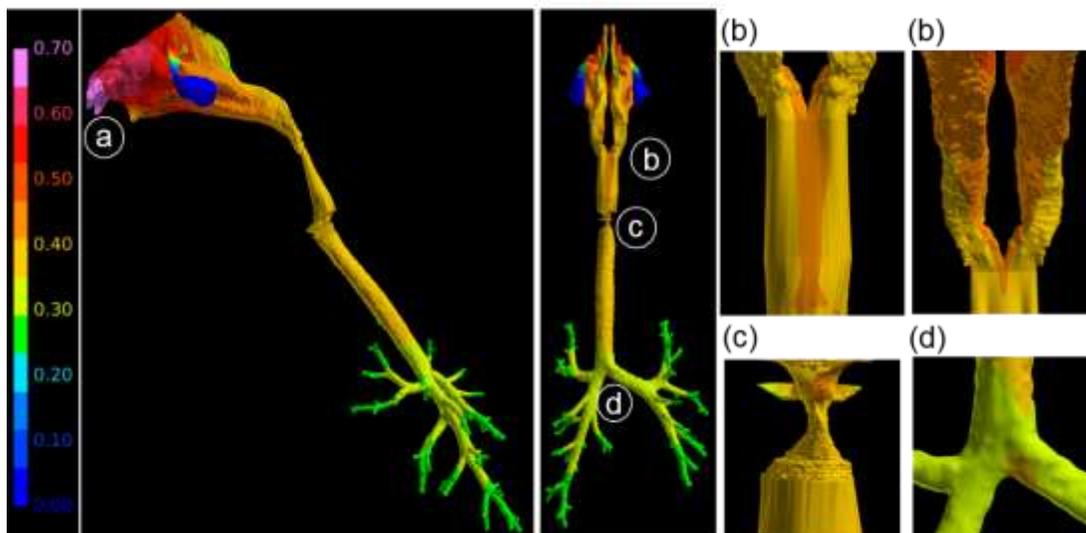
Presenter: Seyed Pouria Motevalian

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, an unstructured 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.

Numerical simulations carried out to date have explored the effects of ozone inhalation rate, breathing frequency, and chemical reaction rate on ozone uptake pattern inside the respiratory system. We have found that during a cycle of normal breathing, about 70% of inhaled ozone reacts with antioxidant and biological substrates at the airway wall with the nasal cavity, oral cavity, larynx, and conductive airways contributing to 76%, 3%, 1%, and 20% of the total uptake. Also, the time-averaged ozone flux distribution at the wall shows the presence of hotspots of flux at the entrance of the nasal cavity, medial part of the nasopharynx and oropharynx, inlet of the larynx, carina of bifurcations, and entrance of the respiratory bronchioles. Our predicted locations of the hotspots of ozone uptake are in an excellent agreement with experimental observations of ozone-induced damage sites in rhesus monkeys.



Time-averaged ozone flux distribution at the airway walls showing hotspots at the (a) entrance of the nasal cavity, (b) medial part of the nasopharynx and oropharynx, (c) inlet of the larynx, and (d) carina of bifurcations

Formation of silicon wires within optical fibers via high-pressure confined chemical vapor deposition

Presenter: Seyed Pouria Motevalian

Advisor: Ali Borhan

Microstructured optical fibers (MOFs) have attracted great interest among researchers in the areas of fiber and nonlinear optics, optical data transmission, and biomedical applications. Optical fibers are thin wires of glass or plastic which transmit light pulses. They are typically composed of a cylindrical core surrounded by a cladding of lower refractive index to allow light transmission along the fiber.

High-Pressure Confined Chemical Vapor Deposition (HPcCVD) can be used to produce semiconductor micro and nanowires in the capillary spaces of ordered MOFs. In the film deposition process, a mixture of a precursor (e.g., SiH_4) and a carrier gas (e.g., He or H_2) flows into capillary tubes at high pressure (~ 30 MPa). The microcapillary wall is heated to facilitate silane decomposition resulting in silicon film deposition. Although void-free filling of the microcapillary template is desirable to obtain high quality waveguides, complete filling of the plugged central channel over lengths of centimeters is challenging in view of its extreme aspect ratio.

To examine the non-uniformity in the film thickness, real-time numerical simulations of film growth are performed. Spatiotemporal variations of silane concentration profile, carrier gas flux, and film thickness are obtained within a closed-end microcapillary. Model predictions indicate that the permeabilities of the microcapillary wall (silica) and the deposited film (silicon) to the carrier gas (helium or hydrogen) and the reaction byproduct (hydrogen) can play a significant role in the deposited film profile.

Segmental and lattice dynamics in amorphous and crystalline 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.

In contrast, we have also examined various BTBT derivatives as model crystalline materials and we measured lattice fluctuations with inelastic neutron scattering using the cold neutron chopper spectrometer (CNCS) at the Spallation Neutron Source. The inelastic signals observed in BTBT crystals indicate the existence of collective motion and this motion is strongly suppressed once side-chains are added to the BTBT core. Thus, we demonstrate that side chains can either suppress or enhance the motion of the conjugated core in organic semiconductors. We can utilize simple theoretical concepts to describe the role of molecular motion on charge mobilities by considering the implications of our measurements on the fluctuations of the structure.