Welcome to the 6th Annual

Amgen-Clorox Graduate Student Symposium

Friday, October 4, 2013

Department of Chemical Engineering

University of California, Santa Barbara

Program and Abstracts

UCSB ChE's 6th Amgen-Clorox Grad Student Symposium

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This symposium is generously supported by educations donations provided by Clorox and Amgen.

6th Annual Amgen-Clorox Graduate Student Symposium
Friday, October 4, 2013

8:00 AM	**Registration and Breakfast**		**ESB Courtyard**
8:30 AM	**Welcome**		**ESB 1001**
	Professor M. Scott Shell, Symposium Chair		
8:45 AM	**Session I**	**Catalysis**	**ESB 1001**
	Louis Jones	Correlating morphology and electronic properties of Pt and Pt-alloy nanoparticles with catalytic activity and selectivity	
	Alan Derk	Novel core-shell nanostructures for selective hydrogen combustion in hydrocarbon streams	
	Anthony Fong	Computational mechanistic study of the Phillips ethylene polymerization catalyst	
	Ming-Feng Hsieh	Measuring and controlling heteroatom distributions in zeolite catalysts	
10:15 AM	**Break**		**ESB Courtyard**
10:30 AM	**Session II**	**Materials**	**ESB 1001**
	Christopher Carach	Raman and low temperature photoluminescence analysis of polymer disorder in bulk heterojunction solar cell films	
	Scott Carmichael	A simple mechanism for emergent chirality in achiral hard particle assembly	
	Nathan George	Design rules for finding new phosphors for solid-state lighting	
	Preshit Dandekar	A mechanistic growth model for ionic crystals	
Noon	**Lunch**		**ESB Courtyard**
1:00 PM	**Poster Session**		**ESB Courtyard**
2:00 PM	**Session III**	**Polymers & Complex Fluids**	**ESB 1001**
	Ting Ann Siaw	Developing NMR methods to characterize polymer structures at nanometer scale	
	Kate Barteau	Ion transport in amorphous polymer electrolytes	
	Joel Paustian	Microfluidic dialysis: spatio-temporal control over solution micro-environments using microfabricated hydrogel membranes	
	Martin Keh	Fusion and deposition of vesicles and capsules in flow	
3:30 PM	**Break**		**ESB Courtyard**
3:45 PM	**Session IV**	**Bioengineering & Soft Matter**	**ESB 1001**
	Serra Elliott	Discovery of antibody biomarkers present in pre-eclampsia and reagents for their detection	
	Justin Lee	Enhanced insulin delivery and closed-loop control algorithm for development of an artificial pancreas	
	Joo-Hyun Jeon	Molecular insights into bio-nanostructure self-assembly	
	Saurabh Das	Interaction of adsorbed polymers with supported cationic bilayers	
5:15 PM	**Conclusion**		**ESB 1001**
	Peng Cheng, Symposium Co-Organizer		
5:30 PM	**Reception Dinner & Award Ceremony**		**Faculty Club**
	Industry guests, faculty and presenters are all welcome		

UCSB ChE's 6th Amgen-Clorox Grad Student Symposium

Oral Presentation Abstracts

Session I: Catalysis

Louis Jones: Distinguishing local molecular environments of Pt and their influence on the reactivity of heterogeneous nanoparticle catalysts

Alan Derk: Novel core-shell nanostructures for selective hydrogen combustion in hydrocarbon streams

Anthony Fong: Computational mechanistic study of the Phillips ethylene polymerization catalyst

Ming-Feng Hsieh: Measuring and controlling heteroatom distributions in zeolite catalysts

Session II: Materials

Christopher Carach: Raman and low temperature photoluminescence analysis of polymer disorder in bulk heterojunction solar cell films

Scott Carmichael: A simple mechanism for emergent chirality in achiral hard particle assembly

Nathan George: Design rules for finding new phosphors for solid-state lighting

Preshit Dandekar: Engineering growth shapes of inorganic crystals

Session III: Polymers and Complex Fluids

Ting Ann Siaw: Developing NMR methods to characterize polymer structures at nanometer scale

Kate Barteau: Ion transport in amorphous polymer electrolytes

Joel Paustian: Microfluidic dialysis: spatio-temporal control over solution micro-environmentsusing microfabricated hydrogel membranes

Martin Keh: Fusion and deposition of vesicles and capsules in flow

Session IV: Bioengineering and Soft Matter

Serra Elliott: Discovery of antibody biomarkers present in pre-eclampsia and reagents for their detection

Justin Lee: Enhanced insulin delivery and closed-loop control algorithm for development of an artificial pancreas

Joo-Hyun Jeon: Molecular insights into bio-nanostructure self-assembly

Saurabh Das: Interaction of adsorbed polymers with supported cationic bilayers

Session I: Catalysis

Distinguishing local molecular environments of Pt and their influence on the reactivity of heterogeneous nanoparticle catalysts

Louis C. Jones, Michael J. Gordon, and Bradley F. Chmelka

Department of Chemical Engineering, University of California – Santa Barbara

Heterogeneous Pt nanoparticle catalysts play vital roles in petroleum reforming and emissions control. As the demand for catalysts increases, so too must our understanding of how to utilize Pt-based materials more efficiently. However, due to the inherent heterogeneity of supported nanoparticle surfaces and their dynamic evolution during reaction, it remains a challenge to interrogate and intelligently modify local Pt environments to achieve specific and stable catalytic reactivities.

Using a combination of directed synthesis, molecular-to-macroscopic characterization, *in situ* spectroscopy, and catalytic testing,[1,2] we have investigated the influence of sub-monolayer levels of Ag on the reactivity of Pt nanoparticle surfaces. Ag-doped Pt nanoparticles were found to be highly active and selective for C_2H_2-to-C_2H_4 hydrogenation, even at high temperatures (100-300 ^oC) where the surfaces of traditional PdAg catalysts rearrange (Pd diffusion to surface) and lose selectivity. Ag was observed to segregate to Pt surfaces, which provided a thermodynamic driving force for stable surface compositions and reactivity. Furthermore, *in situ* spectroscopy of adsorption/desorption processes showed that the distribution of Ag at Pt step and terrace sites modified nanoparticle surface energies, which ultimately correlated with temperature dependent hydrogenation reactivity.

We have also developed advanced solid-state NMR techniques to resolve the local structural and chemical environments of ^{195}Pt species in supported catalysts. Using these advanced methods, an order of magnitude improvement in ^{195}Pt signal resolution and sensitivity has been achieved, enabling the influences of oxidation, sulfidation, and support interactions on Pt environments to be studied in detail.

[1] L. C. Jones, Z. Buras, and M. J. Gordon. *Journal of Physical Chemistry C* **2012**, 116, 12982-12988.

[2] L. C. Jones and M. J. Gordon. *Journal of Physical Chemistry C* **2012**, 116, 23472-23476.

Novel core-shell nanostructures for selective hydrogen combustion in hydrocarbon streams

Alan R. Derk [a], Erin Orazem-Stoimenova [b], Horia Metiu [b], and Eric McFarland [a]

(a) Department of Chemical Engineering, UCSB
(b) Department of Chemistry and Biochemistry, UCSB

Recent trends indicate a strong demand for propylene which traditional sources (e.g. cracking) are failing to meet. On-purpose propylene production has seen a boom in interest, although current processes are limited by the reaction equilibrium of propane dehydrogenation to propylene. To break these limitations, we propose using copper oxide in silica (CuO@SiO2), a novel solid reactant, to selectively combust hydrogen in situ in order to produce heat and draw the equilibrium forward by Le Chatelier's principle (while being inert towards propane and propylene). We have synthesized a range of CuO@SiO2 nanostructures (and controls) and characterized them with XRD, TEM, XPS, BET, and cyclic reaction studies using online mass-spec. Notably, certain CuO@SiO2 structures are stable for over 50 cycles and show excellent selectivity towards hydrogen combustion. These results are shown and discussed along with future work.

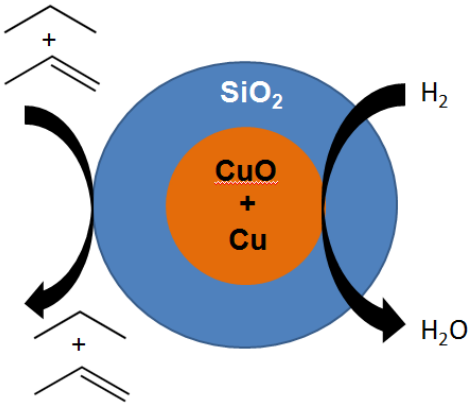

Figure 1: A schematic of selective hydrogen combustion using CuO@SiO_2 core-shells

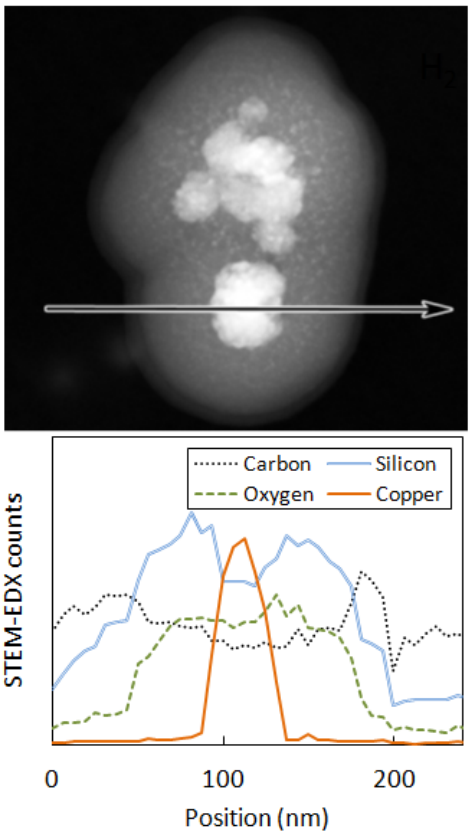

Figure 2: STEM-EDX linescan shows the silica shell and copper(II) oxide core

Computational Mechanistic Investigation of the Phillips Ethylene Polymerization Catalyst

Anthony Fong, Baron Peters, and Susannah Scott

Department of Chemical Engineering, University of California Santa Barbara

The Phillips catalyst, chromium oxide supported on amorphous silica, produces half of the world's annual supply of high-density polyethylene [1]. However, the mechanism by which the catalyst polymerizes ethylene is unknown, because only a small fraction of chromium sites are active and are therefore difficult to detect experimentally. Without a molecular model of the catalyst, it is difficult to understand how catalyst preparation (calcination temperature and addition of cocatalyst) affects the properties of the polymer product (average molecular weight and branching). A computational model could aid in catalyst design.

We used density functional theory to evaluate the feasibility of potential mechanisms. As in previous studies [2], our calculations rule out propagation by a metallacycle ring expansion or alternating carbene/chromacyclobutane intermediates: both mechanisms have activation barriers much greater than what is measured experimentally [1] and contradict isotopic labeling experiments [3]. We also discovered two new pathways with low propagation barriers: oxachromacycle ring expansion, and chain growth from a monoalkylchromium(II) site. However, the oxachromacycle sites initiate too slowly, while the monoalkylchromium(II) sites terminate too quickly (Figure 1). The only propagation mechanism whose computed kinetics are comparable to the experimental kinetics and which does not terminate to produce oligomers instead of polymer chains is Cossee-Arlman polymerization by a monoalkylchromium(III) site, although the precise nature of the initiation step remains unknown.

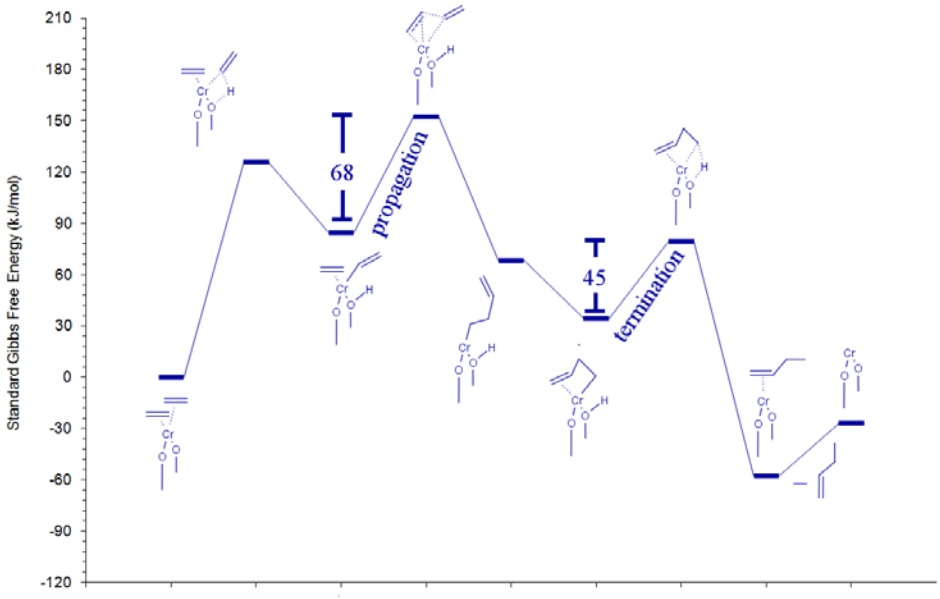

Figure 1: Free energy diagram for chain growth from a monoalkylchromium(II) site. Propagation barrier exceeds termination barrier, so no polymers are formed.

[1] McDaniel, M.P. *Adv. Catal.*, **2010**, *53*, 123-606.
[2] Espelid, Ø.; Børve, K. *J. Catal.*, **2000**, *195*, 125-139.
[3] McGuinness, D.S.; Davies, N.W.; Horne, J.; Ivanov, I. *Organometallics*, **2010**, *29*, 6111-6116.
[4] McDaniel, M.P.; Cantor, D.M. *J. Polym. Sci., Part A: Polym. Chem.*, **1983**, *21*, 1217-1221.

Measuring and controlling heteroatom distributions in zeolite catalysts

Ming-Feng Hsieh

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Many heterogeneous catalysts are based on layered silicates or zeolites, which exhibit high activities and selectivities in different processes, such as fine chemical production, commodity chemical syntheses, and petroleum refining. In such processes, chemical reactions are often catalyzed at surface acid sites in layered silicates or zeolites that are introduced by heteroatom incorporation (e.g., aluminum or boron). Such catalytic performance is influenced by several factors, including pore sizes, heteroatom contents, and heteroatom distributions. While new methods of preparing zeolite catalysts with different topologies are being reported, the molecular-level (<nm) understanding of heteroatom structures, especially the types of sites and their distributions, is still very limited. This is in part because diffraction and other conventional techniques cannot probe the complicated local order and disorder of heteroatom-containing silicate frameworks. By comparison, solid-state nuclear magnetic resonance (NMR) spectroscopy is sensitive to local atomic environments and spatial and/or bonding interactions between heteroatoms and silicates. In particular, two-dimensional (2D) NMR methods are capable of identifying and resolving molecular interactions of specific 11B-O-29Si or 27Al-O-29Si framework species by detecting their through-space (dipole-dipole) or through-bond (scalar, J) interactions, which allow boron and aluminum distributions in silicates to be determined. For the first time, we unambiguously establish the local structures and distributions of boron and aluminum atoms in layered boro- and alumino-silicates. The 2D NMR results reveal that boron heteroatoms can be preferentially incorporated into specific Si sites in layered and zeolitic boro-silicate frameworks. In contrast, aluminum heteroatoms appear to be broadly distributed in otherwise identical layered alumino-silicates. More importantly, selective boron incorportion provides opportunities of controlling acid site distributions to improve the perfermance of catalytic materials. These results provide insights on local heteroatom environments and their distributions in boro- and alumino-silicates, which are expected to enable optimization of synthesis protocols, compositions, and structures of zeolites and other heteroatom-containing siliceous catalysts to improve their catalytic reaction properties.

Session II: Materials

Raman and low-temperature photoluminescence analysis of polymer disorder in bulk heterojunction solar cell films

Chris Carach, Isaac Riisness, and Michael J. Gordon

Department of Chemical Engineering, University of California – Santa Barbara

Understanding and controlling carrier transport in conjugated polymer films and composites is critical to the development and application of plastic solar cells. Recent efforts have focused on "bulk heterojunction" structures where a conjugated polymer donor is mixed at the nanoscale with a fullerene acceptor to achieve large interfacial areas for exciton splitting. In these systems, fabrication protocols dramatically affect device efficiency and charge transport is intimately tied to film morphology through local order, domain formation, and compositional heterogeneity. We employ both far-field and confocal/near-field optical spectroscopy (absorbance, low-temperature photoluminescence, Raman) to study chain order (aggregation, π-stacking), photo-oxidation, and local morphology in conjugated polymer (PPV and polythiophene) – fullerene (PCBM) blends. Through quantitative analysis of exciton bandwidths, emission intensity, and vibronic lineshapes, we demonstrate that competition exists between the chemical "disordering" effect of photo-degradation and the physical "ordering" effect of aggregation, each of which dominate under different processing conditions [1]. Large changes in photoluminescence and Raman show that PCBM begins to significantly hinder intra-chain planarization and inter-chain π-overlap at a critical PCBM weight fraction [2]. Furthermore, the critical weight fraction is a function of the polymer regiochemistry, occurring at lower PCBM weight fractions for a more regio-random polymer. Mild thermal annealing of blended films was seen to restore order, which results from PCBM phase segregation (lower dispersion) and growth of polymer aggregates. Spatially resolved spectral analysis of photoluminescence was also used to map fullerene diffusion and agglomeration as well as detect local changes in interfacial contact between donor and acceptor domains due to thermal annealing [3].

[1] C. Carach and M. J. Gordon. *Journal of Physical Chemistry B* **2013,** 117, 1950-1957.
[2] C. Carach, I. Rissness, and M. J. Gordon. *Applied Physics Letters* ***2012,*** 101, 083302.
[3] I. Riisness, C. Carach, and M. J. Gordon. *Applied Physics Letters* ***2012,*** 100, 073308.

A simple mechanism for emergent chirality in achiral hard particle assembly

Scott P. Carmichael, M. Scott Shell

Department of Chemical Engineering, University of California – Santa Barbara

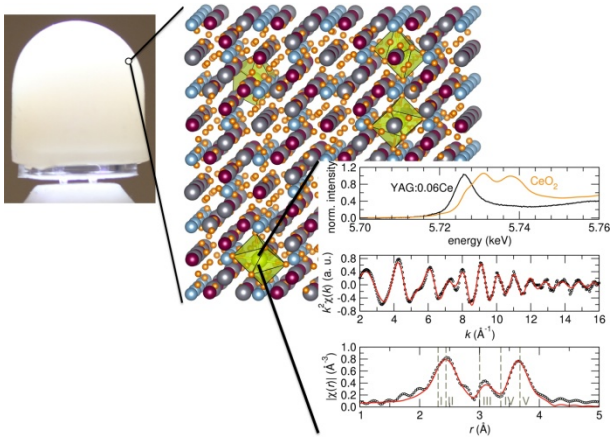
For centuries, chirality has been appreciated as a key component in understanding how matter orders. While intuitively chiral particles can self-assemble into chiral superstructures, it is often less obvious how achiral particles can do the same. Here we show that there is a potentially general, packing-based mechanism that explains why many simple achiral particles can assemble into chiral materials. Namely, we use simulations of hard, regular polygons to show that the surprisingly subtle shape modification of corner rounding can induce chiral symmetry breaking by deforming the underlying close-packed lattice. The mechanism quantitatively explains recent experimental results reporting local chiral symmetry breaking in the hard triangle system. Moreover it predicts similar chiral symmetry breaking in the rounded hard rectangle system, which we verify through simulations. Because effective corner rounding is easily realized by modulating repulsive interactions in real systems, this simple mechanism suggests tremendous potential for creating dynamically tunable chiral surfaces with a variety of applications.

Design rules for finding new phosphors for solid-state lighting

Nathan George[(a)], Bradley F. Chmelka[(a)], and Ram Seshadri[(b)]

(a) Department of Chemical Engineering, UCSB
(b) Materials Department and Materials Research Laboratory, UCSB

Compared to conventional incandescent sources of light, solid-state devices have the potential to conserve significant amounts of energy by efficiently generating white light from long-lasting and durable new semiconductor compounds. An example is a yellow down-converting phosphor powder on top of a blue InGaN light source; white light is created by combining the broad green/yellow/orange phosphor emission with blue light that passes through the phosphor powder. A high onset temperature for thermal quenching of the phosphor is desirable, because device temperatures up to 200 °C can occur in LED devices. The phosphor material often is comprised of a host oxide crystal lattice, such as $Y_3Al_5O_{12}$, that is only photo responsive when doped with small amounts (around 1%) of rare-earth ions, such as Ce^{3+}. An unpaired electron ($4f^1$ for Ce^{3+}) undergoes vibronic transitions, which are responsible for the down-conversion of high-energy light. The local structure around Ce^{3+} ions, their distribution within the host lattice, and their oxidation states critically influence the optical properties, such as temperature-dependent quantum efficiency and excitation/emission energies. For example, concentrations of rare-earth ions above a few percent tends to substantially decrease the quenching onset temperature, due to migration of excited electrons to non-radiative quenching sites. Small Ce^{3+} substitution levels make experimentally probing the local structures and compositions around Ce^{3+} dopants challenging, and new phosphor compositions have typically been identified by trial-and-error. Here, new understanding of phosphor materials is obtained by experimentally probing the structures of the canonical yellow phosphor, $Y_{3-x}Ce_xAl_5O_{12}$ (YAG:Ce, $x < 0.12$). Results from complementary techniques including solid-state NMR, ESR, total neutron scattering, EXAFS, and XANES establish the local environments, overall distributions, and oxidation states of the crucial dopant ions. The resulting insights, combined with analyses of synchrotron X-ray and neutron scattering data, establish the importance of the rigidity of host crystal lattices and use of the smallest amount of Ce or other rare-earth ion dopants while maintaining a sufficient phosphor emission optical density. Such understanding leads to general criteria that are expected to be useful for identifying and designing new phosphor compounds at a molecular level. This has been demonstrated for a new nitride phosphor, $La_{3-x}Ce_xSi_6N_{11}$ ($0.18 \leq x \leq 3$), and is being used to find phosphors with high-quenching-onset temperatures and desirable color properties to improve solid-state lighting devices.



Engineering growth shapes of inorganic crystals

Preshit Dandekar and Michael F. Doherty

Department of Chemical Engineering, University of California Santa Barbara, Santa Barbara CA.

The crystal growth process and the growth morphology determine the end-use functionality of inorganic crystalline solids in various fields of application such as catalysis, photovoltaics, etc. A mechanistic understanding of the crystal growth process is therefore required to engineer desired crystal shapes for any specific application.

A crystal grows via a kinetically controlled mechanism by the attachment of growth units from the solution onto steps of growth spirals emanating from screw dislocations on the surface. The concept of Periodic Bond Chains (PBCs) is used to identify the directions of these steps that form the edges of growth spirals on inorganic crystal surfaces such as the (104) surface of calcite ($CaCO_3$) crystal (Figure 1). PBC vectors correspond to the lattice directions inside the crystal along which strong intermolecular interactions between the growth units exist[1]. A general methodology has been developed that identifies the PBC vectors and helps predict the shapes of the growth spirals on any inorganic crystal surface. The growth rate of a crystal face depends on the kinetics of net attachment of growth units into kink sites along the edges of growth spirals. The rate of attachment is governed by the electrostatic interactions between a kink site ion and its solid and solvent neighbors. A systematic method is presented here that calculates these electrostatic interactions and helps predict the growth rates of calcite crystal faces.

This mechanistic crystal growth model gives a better understanding of the effect of growth medium parameters such as solvent species, supersaturation, pH, presence of impurities or additives, etc. on the growth morphology of inorganic solids. Molecular rules can now be developed to reduce the experimental design space and engineer the growth process to suit the specific application.

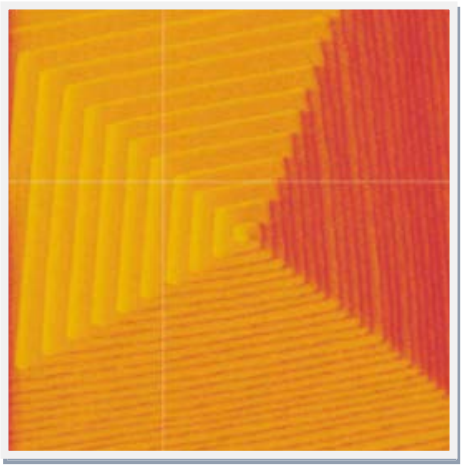


Figure 1: AFM image of growth spirals on the (104) surface of calcite ($CaCO_3$) crystal[2].

References:
[1] Hartman, P. and Perdok, W. G. *Acta Crystallogr.* **1955**, *8*, 49-52.
[2] Davis, K. J.; Dove, P. M.; Wasylenki, L. E.; De Yoreo, J. J. *Am. Mineral.* **2004**, *89*, 714-720.

Session III: Polymers and Complex Fluids

Developing NMR methods to characterize polymer structures at nanometer scale

Ting Ann Siaw[(a)], Kuo-Ying Huang[(b)], Jeffrey Gopez[(a)], Alicia Lund[(b)], Matthias Fehr[(c)], Ed Kramer[(a,d)], Craig Hawker[(b,d)] and Song-I Han[(a,b)]

(a) Department of Chemical Engineering, University of California Santa Barbara
(b) Department of Chemistry and Biochemistry, University of California Santa Barbara
(c) Department of Physics, University of California Santa Barbara
(d) Materials Department, University of California Santa Barbara

Solid state dynamic nuclear polarization (ssDNP) is an electron-nuclear magnetic resonance technique that can generate large amounts of nuclear spin polarization localized around a polarizing spin probe, usually a paramagnetic site that occurs naturally, or introduced strategically to a soft material. The generation of localized high nuclear spin polarization can create a magnetization gradient across nanometer scale heterogeneities native to the material of interest, which activates spin diffusion that is responsible for spatial equilibration of magnetization. In conventional NMR studies on polymers, spin diffusion is activated via pulse sequences that exploit unique chemical shifts specific to one domain to selectively build up magnetization within these spatial regimes, where the diffusion times of the local magnetization to a different domain can yield domain size and separation. However, spin diffusion assisted NMR methods suffer from sensitivity constraints, and thus have not been widely used. We aim to overcome these limitations with ssDNP by selectively polarizing domains that are strategically labeled with a paramagnetic spin probe, which provides both sensitivity enhancement and structural information at the same time. We have applied this technique to study a coacervate forming triblock copolymer hydrogel, and I will expound upon the instrumentation and methodology studies that were required to perform such spin diffusion measurement. The 3 key components required to perform ssDNP spin diffusion measurements are: (1) generation of large nuclear polarization in the coacervate domain through electron paramagnetic resonance (EPR) excitation of the paramagnetic species that are introduced via covalent spin-labeling, (2) stable measurement of the time evolution of the NMR signal in the two domains (coacervate and continuous domain) during ssDNP conditions; and, (3) separation of the spin diffusion timescale independent of NMR spin-lattice relaxation and buildup of DNP polarization.

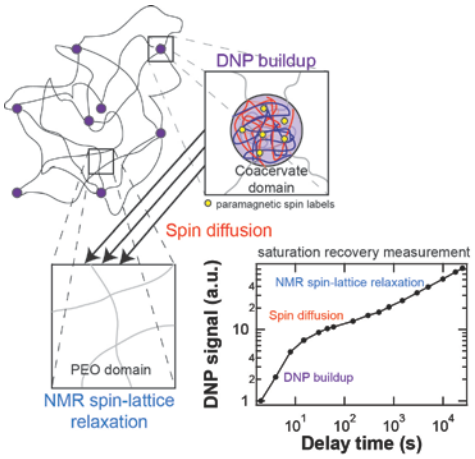


Figure 1: Spin diffusion from coacervate domain to PEO domain in hydrogel. This process can be characterized by 3 timescales (DNP buildup in the coacervate domain, spin diffusion to the PEO domain, NMR spin-lattice relaxation of the PEO domain)

Correlating polymer properties to ion transport in amorphous polymer electrolytes

Katherine P. Barteau[a,b], Nathaniel A. Lynd [b], Glenn H. Fredrickson[a,b], Craig J. Hawker [b,c,d], and Edward J. Kramer [a,b,c]

(a) Department of Chemical Engineering, University of California, Santa Barbara
(b) Materials Research Laboratory, University of California, Santa Barbara
(c) Department of Materials, University of California, Santa Barbara
(d) Department of Chemistry and Biochemistry, University of California, Santa Barbara

Lithium polymer batteries offer a number of advantages to standard lithium ion batteries, including an all-solid state structure, increased safety, and the potential to be combined with lithium metal anodes for increased energy density over lithium intercalation anodes. However, the low-temperature (< 80 °C) ionic conductivity of polymer electrolytes has remained a major limitation over the past 40 years of academic investigation into polymer electrolytes. Progress in understanding strategies for systematic improvement in ionic conductivity has been dominated a single polymer for elucidating structure-property relationships in ionic conducting polymeric solids, i.e., poly(ethylene oxide). By increasing the domain of polymer materials to include a family of structurally related polymers with systematic variation in physical properties, fundamental insight into the relationship between polymer properties and ionic conductivity can be gained. We have synthesized a library of poly(glycidyl ether)s that exhibit systematic differences in glass transition temperature (Tg), viscosity, oxygen-content, dielectric constant, and ionic conductivity. In this presentation, we will discuss the synthesis, characterization, and performance of poly(glycidyl ether) based electrolytes and the insights they provide into future polymer electrolyte design.

Microfluidic dialysis: spatio-temporal control over solution micro-environments using microfabricated hydrogel membranes

Joel S. Paustian, Rodrigo Nery Azevedo, Sean B. Thomas Lundin, Matthew J. Gilkey, Todd M. Squires

Department of Chemical Engineering, University of California, Santa Barbara CA 93106

We have developed a simple technique to synthesize hydrogel membranes locally within microfluidic channels, with high precision and resolution. Using a standard fluorescence microscope, we photopolymerize thin (W=10-25μm) hydrogel membrane 'microwindows' (HMMs) between microfluidic channels. The hydrogels have a pore size large enough to admit solute and solvent diffusion, yet small enough to prevent significant fluid flow. Constant-concentration 'reservoir' channels may thus be maintained or rapidly switched on one side of the HMM by flowing solutions, provoking changes in solution composition on the other (sample-containing) side without mechanical disturbances often associated with flow.

We demonstrate applications of HMMs for local dialysis in microfluidic channels, as well as for imposing local electric fields and chemical gradients. Dynamics of salt transport are investigated by quickly switching reservoir solutions and measuring the HMM and sample channel response. The thin width of the hydrogels allows rapid diffusion, enabling flow-free swapping of salt solutions (0 to 250 mM NaCl) in a microfluidic channel in under 6 seconds. Local electric currents and chemical gradients are also demonstrated by visualizing the phoretic motion of suspended colloids.

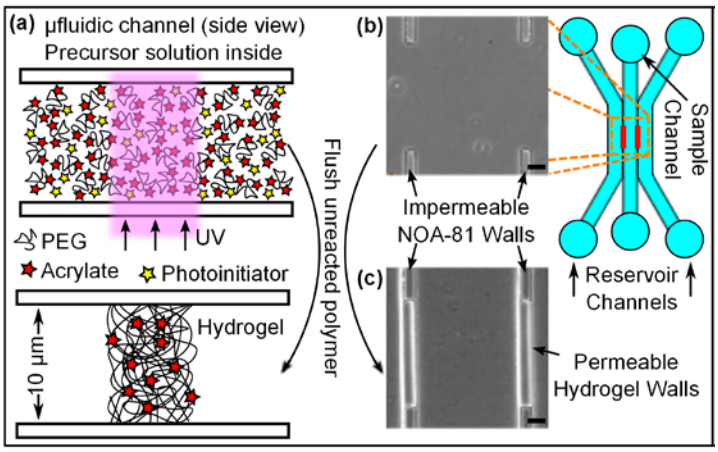


Figure 1: (a) A UV-polymerizable solution initially fills a 3-channel microfluidic device, (b) with gaps in the walls between channels. Patterned UV light is used to crosslink the hydrogel in two specified regions, filling the gaps with hydrogel. (c) After flushing out the unreacted solution, hydrogel membranes remain. Scale bar: 20 μm.

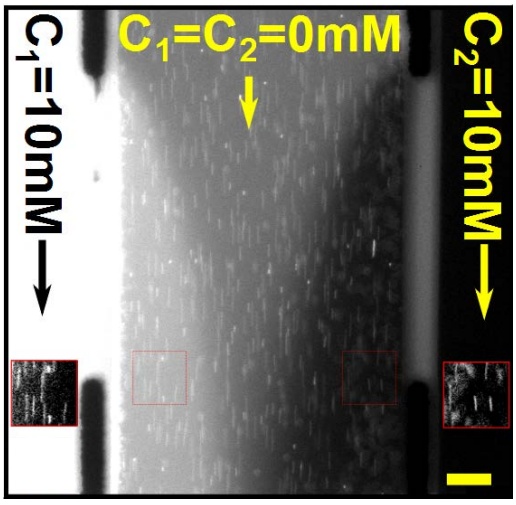


Figure 2: Hydrogel membrane micro-windows are permeable to small molecule solutes, yet admit no measurable hydrodynamic flow. Channels are buffered at pH 8.1 (left), 6.3 (center), and 4.7 (right).and contain a fluorescent pH indicator. Diffusion of pH buffer is clearly evident, while fluorescent tracer particles in the center channel (bright lines) flow straight past membranes, indicating no convective inflow. Scale bar: 20 μm.

Fusion and Deposition of Vesicles and Capsules in Flow

Martin Keh, Johann Walter, and Gary Leal

Department of Chemical Engineering, University of California, Santa Barbara

Capsules and vesicles are often used as vehicles to carry active ingredients or fragrance in drug delivery and consumer products and sometimes in these applications the particles may be pre-inflated due to the existence of a small osmotic pressure difference between the interior and exterior fluid. We study the dynamics of thin film drainage between capsules and vesicles in flow as it is crucial to fusion and deposition of the particles and, therefore, the stability and effectiveness of the products. Simulations are conducted using a numerical model coupling the boundary integral method for the motion of the fluids and a finite element method for the membrane mechanics. For low capillary numbers, the drainage behavior of pre-inflated vesicles and capsules are approximately the same, and also similar to that of drops as the flow-independent and uniform tension due to pre-inflation dominates. The tension due to deformation caused by flow will become more important as the strength of the external flow (i.e. the capillary number) increases. In this case, the shapes of the thin film region are fundamentally different for capsules and vesicles, and the drainage behavior in both cases differs from a drop.

Session IV: Bioengineering and Soft Matter

Discovery of antibody biomarkers present in pre-eclampsia and reagents for their detection

Serra E. Elliott[a], Alex R. Soffici[b], and Patrick S. Daugherty[a]

(a) Department of Chemical Engineering, University of California, Santa Barbara Affiliation
(b) Maternal-Fetal Medicine Unit, Cottage Health System, Santa Barbara

Discovery of biologic molecules specific to a diseased state, or biomarkers, can lead to diagnostic development, therapeutic target identification, and improved understanding of disease pathogenesis. Antibodies remain an attractive class of biomarkers given their amplification by the immune system, stability, and current clinical use. In this work, we demonstrate the utility of bacteria-displayed peptide libraries in conjunction with fluorescence activated cell sorting to identify the presence of novel antibody biomarkers by quantitatively screening for peptides with enhanced binding to antibodies in a diseased state over normally present antibodies. We applied these methods to advance molecular diagnostics for pre-eclampsia (PE), a condition with unknown etiology that affects 5-8% of pregnancies. Previous studies have implicated a pathologic role for autoantibodies against a specific epitope on the angiotensin II AT_1 receptor in PE (AT_1-AA) [1][2]. However, these antibodies remain difficult to detect, vary in prevalence amongst studies, and most importantly, lack specificity. We hypothesized that additional PE specific antibody biomarkers may exist, and this complex disease could serve as a model for developing methodologies to identify novel antibody biomarkers using the known AT_1 epitope as a control. Therefore, we expressed the seven amino acid epitope on the surface of *E. coli* to determine the cross-reactivity and specificity in a set of 45 PE and 48 healthy-outcome pregnancies (HOP), and we applied two distinct screening strategies to a fully randomized 15 amino acid peptide library with a subset of this cohort. At an optimized cutoff, the cell-surface expressed epitope detected AT_1-AAs in 78% of PE and 44% of HOP samples. For screening, we used either antibody enriched fractions or unprocessed, diluted plasma. Although both screens resulted in peptides with significantly ($p < 0.05$) higher PE reactivity than HOP and diagnostic potential in a validation set, sequence analysis yielded a stronger consensus family from the dilute plasma screen. Based upon this consensus, we created and screened a focused library further evolving the motif and enhancing diagnostic efficacy. Furthermore, we linked this motif to a viral antigen and evaluated PE and HOP activity using a cell-surface displayed antigen fragment and commercialized enzyme-linked immunosorbent assay. This work demonstrates the utility of bacteria-displayed libraries to identify novel diagnostic reagents for antibody biomarker detection in PE. The present methodology may thus improve understanding of disease pathogenesis and guide therapeutic development.

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The Impact of Insulin Pharmacokinetics and Pharmacodynamics on the Closed-loop Artificial Pancreas Design

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Type 1 diabetes mellitus (T1DM) is a metabolic disorder that is caused by the destruction of the insulin-producing pancreatic beta-cells. Due to a lack of insulin production and secretion, people with T1DM are dependent on insulin therapy to regulate blood glucose (BG). If untreated, they may experience chronic hyperglycemia (high BG, > 180 mg/dL), which may result with long term complications such as nephropathy, neuropathy, retinopathy, or cardiovascular disease. Also, severe hyperglycemia (BG > 300 mg/dL) may cause ketoacidosis, which can be fatal.

An artificial pancreas (AP) is a device that automatically measures BG and delivers insulin to regulate BG for people with T1DM. Since the first introduction of such a system in the 1970s, several insulin formulations (e.g., aspart, lispro, and glulisine) and delivery routes (e.g., inhaled, subcutaneous, and intraperitoneal) with different pharmacokinetic and pharmacodynamic characteristics have been developed for insulin therapy, and these insulin deliveries (i.e., combinations of insulin formulations and routes) have been utilized in the AP development. Due to the critical roles of the insulin pharmacokinetic/pharmacodynamic characteristics on the performance and robustness (e.g., after-meal BG peak and low BG condition risk) of the AP, one of the main design interests is the expected performance and robustness envelope from the different pharmacokinetic/pharmacodynamic characteristics.

To that end, a systematic approach that can be used to explore the envelope of an AP using different insulin deliveries is proposed. Pharmacokinetic models of different insulin deliveries were identified and incorporated into the UVA/Padova FDA-accepted metabolic simulator. In the model structure, the insulin model time constant (τPK) can be adjusted to represent different pharmacokinetics of insulin from long-acting insulin to ultra-rapid insulin. After the model development, Proportional-Integral-Derivative controllers were designed based on the pharmacokinetic/pharmacodynamic models of insulin delivery and the metabolic simulator, using the Internal-Model-Control methodology. Then, the controllers were evaluated on the ten in silico subjects from the metabolic simulator following a single meal (75 g-carbohydrates) protocol. Robust stability analysis, assuming 50% uncertainty on the model gain, was also performed on the controller.

The simulation results suggest that the controllers based on the proposed method can achieve satisfactory performance over a wide range of insulin pharmacokinetic/pharmacodynamic characteristics, demonstrating that a faster acting insulin delivery achieves superior meal disturbance rejection without inducing a dangerous overshoot (i.e., low BG condition). The average maximum BG concentration decreased by 11 mg/dL per 25 min decrease of τPK, and the average duration in the hyperglycemia decreased by 0.6 h per 25 min decrease of τPK. The robust stability analysis showed that the controllers can achieve safe BG regulation (i.e., no instability) within the evaluated pharmacokinetic/pharmacodynamic range even in the presence of a large gain uncertainty.

Molecular insights into bio-nanostructure self-assembly

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The simple diphenylalanine (FF) peptide self-assembles in aqueous solutions into nanotubes (FFNTs) [1] with remarkable strength, thermal stability and other promising physical properties [2-4]. FFNTs have found use in many applications, including as sacrificial templates and scaffolds for structuring inorganic materials, and as new hydrogels and biosensors [5]. FFNTs can also form on substrates using vapor-deposition in vacuum, to create dense FF-nanoforests that have already found use in super-hydrophobic surfaces and high-performance supercapacitors [6]. However, little is known about assembly mechanisms of FFNTs or the forces underlying their stability.

Here, we use detailed molecular simulations to study the early self-assembly stages of FF in water and in vacuum. First, we perform a variety of molecular dynamics (MD) simulations on small-oligomer formation in water and assess the balance of hydrogen bonds, electrostatic interactions, and side chain aromatic or hydrophobic forces, as well as the emergent structural motifs. We find that while electrostatic interactions steer FF peptides into more ordered dimers and trimers, the hydrophobic side chain interactions play a strong role in determining the structures of larger oligomers. However, capped (uncharged) versions of the peptide display dramatically different assembly behavior, and emphasize the importance of amphiphilicity to FF assembly. By comparing these results to simulations of the experimental FFNT X-ray crystal structure [7], we propose that the early structural templates to be formed are more amphiphili-like, rather than the salt-bridge-stabilized hexamer ring motif that has been proposed in the literature.

Second, we study the assembly of FF peptides in vacuum. During the vaporization process, the linear backbone of FF peptides is cyclized, and so its chemical structure is distinct from that in solution. We find that cyclo-FF molecules indeed have strong preferences to form vertically aligned ladder-like structures stitched together by hydrogen bonds. Such structures are reminiscent of the solution-phase oligomers, but appear much more stable. Importantly, the obtained ladder structures have some structural similarities with the crystal structure of cyclo-FF nanowires, although future work mush address how these ladders pack in a way to form nanotubes. In total, our results suggest novel pathways for assembly of FF in different environments and offer plausible explanations for the interactions that drive their unique properties.

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Interaction of adsorbed polymers with supported cationic bilayers

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The interaction forces between bilayers of the cationic surfactant di(tallow ethyl ester) dimethyl ammonium chloride (DEEDMAC) were measured using a Surface Forces Apparatus (SFA) with and without an adsorbing polymer, polyacrylamide (PAM). In the absence of PAM, the forces measured between the bilayer surfaces were purely repulsive on approach and separation and is charge regulated. Addition of PAM induced structural changes to the bilayer interfaces, and resulted in the formation of bilayer-like patches of DEEDMAC decorated PAM (hydrated) on the mica surface. The interaction potential between these surfaces showed a modified DLVO interaction with an additional monotonic steric hydration repulsion on approach with an exponential force decay length of $D_{\text{steric}} \sim 1$ nm consistent with the measurements of hydration forces. On separating the surfaces, interdigitated polymers bridge between the two surfaces, resulting in a weak adhesion (Adhesion energy, $W_0 \sim 0.1$ mJ/m^2). Our results provide a picture of the complex molecular structure and interactions between uncharged adsorbing water soluble polymers and supported charged bilayers, and highlight the effects of adsorbing polymers on the structure of bilayers. Implications for the stability of vesicles in dispersions have been also discussed.

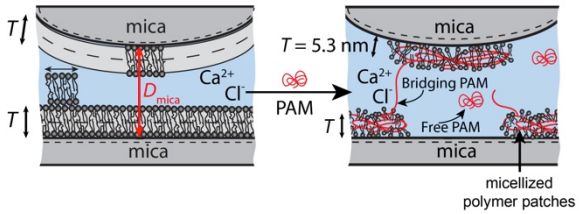

Figure 1: Destabilization of supported DEEDMAC bilayers by adsorbing polymer, Polyacrylamide (PAM).

UCSB ChE's 6th Amgen-Clorox Grad Student Symposium

Poster Presentation Abstracts

Materials, Energy and Catalysis

Matthew Aronson:	Understanding aluminum heteroatom local environments in bulk and mesostructured zeolite catalysts
Daniel Coller:	Extracting Quantitative Kinetic Information from Light-off Profiles
Brian Giera:	Local-density approximations and atomistic models of electric double layers with excluded volume effects
Matthew Idso:	Assessing fullerene proximities to donor and acceptor moieties in bulk heterojunction materials
Ryan Mullen:	Grote-Hynes theory, recrossing and dynamics of the committor in ion-pair dissociation
Geoffrey Poon:	A stochastic model for nucleation in the boundary layer during solvent freeze-concentration

Biophysics and Bioengineering

Natalie Forbes:	Thermosensitive Liposomes with Photo-Activated Small Molecule Release
Jennifer Guerrero:	Methodology for redesigning the specificity of secreted proteases
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Complex Fluids, Colloids and Interfaces

Rodrigo Nery Azevedo: Electrophoretic Mobility Measurement in Controllable Chemical Environments

Peng Cheng: Probing the Effect of Flow Type on Nonlinear Viscoelastic Instabilities of Polymeric Fluids

Chia Chun Fu: A Systematic Coarse-graining of Molecular Dynamics Simulations: Thermodynamic and Transport Properties

Mark Joswiak: The Surface Energy of Nanoscale TIP4P/2005 Water Droplets

Dong Woog Lee: Synergistic cartilage lubrication and effects of HA molecular weight

Craig Angulo: Microscale Salt Manipulation Using Charged Hydrogel Membranes in Microfluidic Devices

Michael Rapp: Hydrophobic, electrostatic, and time-dependent polymer bridging forces at surfactant-modified surfaces

Mansi Seth: Investigations of the Instantaneous Formation and Aging Behavior of Charged Vesicle Gels

Materials, Energy and Catalysis

Understanding aluminum heteroatom local environments in bulk and mesostructured zeolite catalysts

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The chemical reaction activities and/or selectivities of heterogeneous catalysts depend strongly on the local compositions and structures near active site moieties. In zeolite catalysts, the locations and properties of the Brønsted acid active sites are governed by the positions of heteroatoms (*i.e.,* Al, B) in the silicate framework. However, the incorporation behavior and molecular-level (*ca.* sub-nm) distributions of heteroatoms and their correlations with macroscopic acidity and catalytic properties are challenging to understand and control, in part because of inherent framework defects and subtle differences in nearest-neighbor environments and local bonding geometries near heteroatom sites. Despite this lack of long-range atomic ordering, the structural features of framework heteroatoms can be understood by combining spectroscopic, scattering, and macroscopic property analyses that provide complementary insights across multiple length scales. Specifically, solid-state nuclear magnetic resonance (NMR) spectroscopy, which is sensitive to local interactions and electronic environments of heteroatoms, provides detailed short-range information via through-bond scalar (*J*) couplings. Taking advantage of new two-dimensional NMR methodologies [1-2], we establish the site connectivities of ^{27}Al heteroatoms with nearby ^{29}Si framework moieties in conventional bulk and surfactant-directed mesostructured zeolites Beta [3]. Furthermore, these analyses reveal that the incorporation of Al heteratoms in specific zeolite framework sites manifests differences in measured Brønsted acidity. Such molecular-level insights about the local compositions and structures near the catalytically active sites are expected to provide criteria for the rational design of new zeolite catalysts with improved macroscopic reaction, adsorption, and transport properties for diverse engineering applications.

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Extracting Quantitative Kinetic Information from Light-off Profiles

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Kinetic parameters such as the activation energy, E_a, and the Arrhenius pre-exponential factor, A, are typically obtained from measurements made under isothermal reaction conditions. Their accuracy can be poor (although it is often unacknowledged to be so), due to the small number of data points and the limited temperature range used. Curve-fitting of rate equations to non-isothermal light-off profiles is rarely attempted, and can be problematic if the activation energy is not constant, or if the catalyst undergoes significant changes during the course of the experiment, or if reaction and diffusion occur on similar timescales. Nevertheless, we explore whether such analysis could be informative in certain cases, and whether it could be used to generate faster and more accurate information about both the rate law and the kinetic parameters.

The design equation for a plug-flow reactor (assuming negligible change in volumetric flow rate with conversion) was combined with rate laws for various reaction orders, using the Arrhenius equation to represent the temperature-dependence of the rate constant. The equations were integrated and rearranged to solve for conversion, X, as a function of temperature, T. Values of E_a were obtained by curve-fitting these equations to light-off profiles. Light-off profiles were simulated under the presence of mass-transfer limitations to qualitatively explore their effects.

In suitably designed systems, kinetic parameters obtained by quantitative analysis of non-isothermal kinetic data make use of much more data and are more accurate than parameters obtained by linearizing single activity measurements recorded over a narrow range of temperature and conversion.

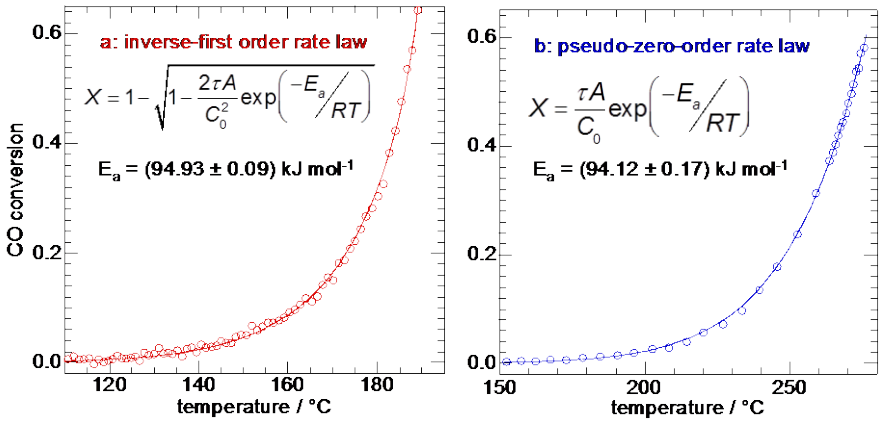

Figure 1. Light-off profiles for CO oxidation by (a) Nd_2BaPdO_5 under CO-lean conditions, and (b) Dy_2BaPdO_5 under CO-rich conditions, showing curve-fits to the integrated design equations. Both profiles were truncated at high conversion to eliminate mass transfer effects.

Local-density approximations and atomistic models of electric double layers with excluded volume effects

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Electric double layers (EDLs) form when a charged electrode is brought in contact with an electrolyte. The thin cloud of ions that screens the oppositely charged surface is called the EDL, which are important in a wide range of disciplines and technologies including soft matter, protein biophysics, semiconductors, ionic liquids, and supercapacitors. The mean-field local-density approximation (LDA) to modeling EDLs that is used most commonly assumes averaged ion interactions that disregard the shape of ions and neglect the chemistry of the solvent and electrode. LDAs thus inherently neglect ion ordering and are known to fail when describing experimentally relevant EDLs due to their assumptions. The more advanced "Primitive Model" of the EDL seeks to address the multi-body interactions that govern the structure and capacitance of the EDL. Despite these improved approaches, LDAs have served as the starting point for modeling EDLs for over a century because they are simple and provide physically insightful EDL predictions. Moreover, it is straightforward to quickly screen empirically or computationally derived EDL profiles to first verify whether the general LDA approach will fail. Here, we evaluate long-standing LDAs that seek to address only ion size effects by comparing against extensive atomistic simulations of the Primitive Model for the EDL profiles that treats the ions as charged Weeks-Chandler-Andersen (WCA) spheres in an implicit solvent.

Assessing fullerene proximities to donor and acceptor moieties in bulk heterojunction materials

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Organic photovoltaics are a promising technology because of the potential for low-cost and high-throughput device production, however a major limitation of these materials is low power conversion efficiency (PCE). Many high efficiency organic photovoltaic cells include conjugated polymers that consist of distinct donor and acceptor moieties whose off-set band gaps may be manipulated to extend the absorption band of the polymer and achieve low optical band gaps. For example, benzodithiophene-thiopyrroledione (BDT-TPD) conjugated polymers, featuring repeating units of BDT donor and TPD acceptor moieties, have achieved PCEs of up to 7.3% in polymer-fullerene bulk heterojunction morphologies. High charge transfer efficiency for these heterojunctions requires fullerene species to be in close proximity to polymer acceptor moieties and, based on macroscopic device measurements, it is hypothesized that moieties functionalized with straight-chain alkyl groups are more accessible to fullerene species than those with branched functional groups. 2D solid-state NMR was used to establish a molecular-level understanding of the mobilities, proximities, and intra- and intermolecular interactions amongst specific species in bulk heterojunctions. This molecular understanding of bulk heterojunction materials can be correlated with macroscopic device performance, and this information will aid in the design and optimization of highly efficient organic photovoltaic devices.

Grote-Hynes theory, recrossing, and dynamics of the committor in ion-pair dissociation

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For chemical reactions in a solvent, friction emerges as a consequence of projecting multidimensional dynamics onto the dynamics of a single reaction coordinate. Friction causes recrossing of the dividing surface which can either be accounted for with a transmission coefficient or variationally minimized by optimizing the dividing surface. From a perfect non-recrossing dividing surface, all trajectories would commit to opposite basins in forward and backward time, transition state theory would become exact, the transmission coefficient would become one, and the committor distribution would become perfectly focused at ½. For NaCl dissociation in TIP3P water, we show that recrossing persists even when the ½-committor surface itself is used as the dividing surface. We provide evidence that recrossing cannot be fully eliminated from the dynamics for any configurational coordinate. Consistent with this finding, inertial likelihood maximization finds a combination of ion-pair distance and two solvent coordinates that improves the committor distribution and increases the transmission coefficient relative to those for ion-pair distance alone, but recrossing is not entirely eliminated. Free energy surfaces for the coordinates identified by inertial likelihood maximization show that the solvent friction stems from anharmonicity and shallow intermediates that remain after dimensionality reduction to the dynamically important variables.

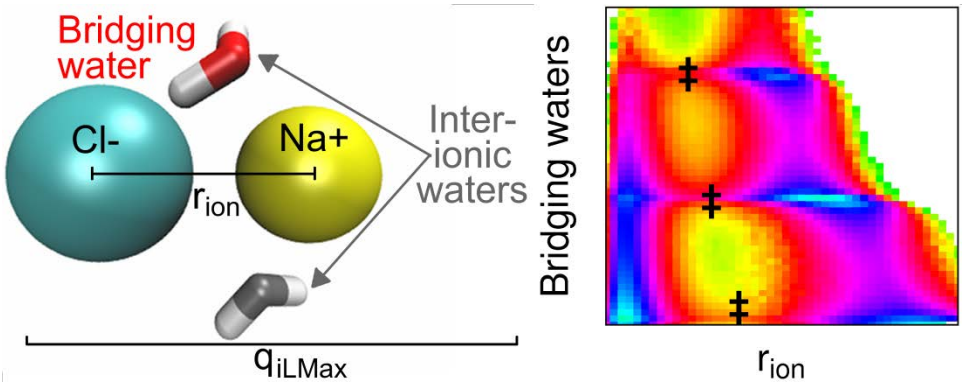

Figure 1. *Left*: Inertial likelihood maximization revealed that the location and orientation of waters proximal to both ions modifies the transition state. *Right*: Projection of the free energy onto dynamically important coordinates reveals shallow intermediates and multiple reactive pathways.

A stochastic model for nucleation in the boundary layer during solvent freeze-concentration

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Nucleation kinetics, induction times, and metastable zone widths are often modeled in quiescent, quasi-steady, and/or spatially uniform concentration fields. However, freezing an aqueous solution can concentrate the solute and effectively increase the supersaturation. During the freezing process, a boundary layer of giant supersaturation develops ahead of the moving ice front. We develop stochastic models of nucleation in the boundary layer when the growing ice perfectly excludes the solute. Whether heterogeneous on the ice surface, or homogeneous in the boundary layer, nucleation is dramatically accelerated by the growing ice. For methane hydrates, which form at conditions similar to that of ice, induction times for hydrate nucleation can be reduced by as much as 10^{105} times because of the moving supersaturation zone.

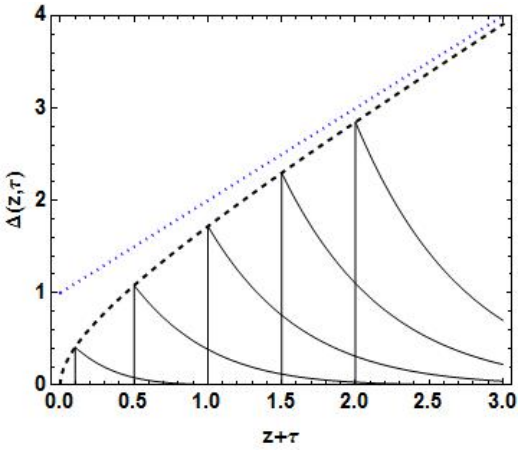

Figure 1: Concentration boundary layer

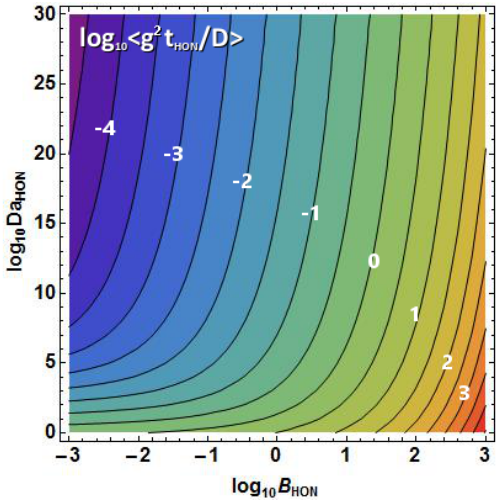

Figure 2: Contours of average nucleation induction times

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This work: submitted to Crystal Growth & Design

Biophysics and Bioengineering

Thermosensitive Liposomes with Photo-Activated Small Molecule Release

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A drug delivery system with rapid contents release under continuous-wave near-infrared (NIR) light will enable precise spatial and temporal control of drug release. The drug is encapsulated within a thermosensitive liposome, and rapid drug release is triggered under irradiation by the localized photothermal heating of metallic nanoparticles coupled to the liposome. These nanoparticles heat the liposome membrane through its phase transition at 39-42°C to induce an increase in membrane permeability. A fluorescent dye was encapsulated as a model agent to study dye release kinetics. A small fraction of lysolipid (single-chained phospholipid) enhances the rate of release at the transition. The lysolipid can partition into pre-formed liposomes to enhance membrane permeability, and this partitioning is impacted by bilayer hydrophilicity and phase. Two metallic nanoparticles which absorb NIR light, hollow gold nanoshells and copper sulfide nanoparticles, were compared in terms of their liposomal attachment and heating characteristics. Finally, the anticancer agent doxorubicin was encapsulated within the liposomes and the system was used to deliver doxorubicin to drug-resistant prostate cancer cells (PPC-1) in vitro. Near-complete cell killing was observed by the photothermally triggered thermosensitive liposomes at an order of magnitude lower doxorubicin concentration relative to non-irradiated liposomal doxorubicin. The enhanced cell killing at low total concentration may be due to the rapid release of the doxorubicin, which provides locally higher concentration combined with the thermal damage of the locally increased temperatures. This device provides externally targeted, tumor-specific delivery of small molecule anti-cancer agents from thermosensitive liposomes without requiring bulk tissue hyperthermia, along with expanded control of drug release rate.

Methodology for redesigning the specificity of secreted proteases

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Proteases constitute 2% of the human proteome and regulate many biological processes including cell growth and migration, blood coagulation, and programmed cell death. A generally applicable, high-throughput strategy to engineer proteases to cleave a target substrate with high specificity and high catalytic efficiency would greatly expand the use of proteases for analytical, biotechnological, and therapeutic applications. We have developed a cell-based assay for redesigning protease selectivity by screening protease mutant libraries for cleavage of a fluorogenic peptide substrate exhibiting Förster resonance energy transfer (FRET). Our screening method relies on using fluorescence activated cell sorting (FACS) for detecting cleavage of the FRET reporter substrate, which will allow screening of large protease mutant libraries ($\sim 10^7$ members) to identify the activity of interest. As a model system, these novel methods were applied to the protease human kallikrein 7 (hK7) to identify variants that selectively cleave the central hydrophobic core of the amyloid beta (Aβ) peptide, involved in Alzheimer's disease pathology.

Using *Saccharomyces cerevisiae,* an expression system was designed and constructed to produce active hK7 and a FRET substrate probe intracellularly. Expression of correctly folded, active hK7 was detected in the yeast cell lysate using an hK7 FRET reporter substrate and confirmed by Western blot. We optimized expression conditions to detect hK7 activity in yeast with a co-expressed Aβ8 (KLVF↓F↓AED) FRET substrate using flow cytometry. No activity was detected for yeast cells co-expressing an inactive hK7 mutant or the FRET substrate alone. hK7 displays modest activity towards the target Aβ8 substrate but prefers tyrosine (Y) at the P1 position. We hypothesize that amino acid substitutions around and in the active site may yield variants that prefer the phenylalanine (F) at P1 of Aβ8 and exclude tyrosine, thereby narrowing the specificity towards Aβ8. We randomly mutated the hK7 gene using error-prone PCR to generate two libraries. These libraries were then screened for enhanced activity and selectivity towards the therapeutically relevant target substrate Aβ8 using FACS. This methodology may be useful to engineer other human proteases for highly specific degradation of proteins or peptides implicated in disease.

Impact of Continuous Glucose Monitor Performance on Closed-Loop Control of Type 1 Diabetes

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A promising area of research in the treatment of type 1 diabetes is the application of closed-loop control to regulate blood glucose concentration (BGC) by delivering insulin based on continuous glucose monitor (CGM) measurements; however, there are concerns that current CGM technology is not ready to be used for this application. To investigate this problem, CGM measurements from closed-loop clinical trials using Dexcom® Seven® Plus (SP) or G4® Platinum CGMs were compared to reference measurements to determine the risk of erroneous controller action caused by sensor error, as well as to quantify improvements in accuracy between the SP and G4.

The mean sensor error decreased from 13mg/dL (SD 10mg/dL) to 11mg/dL (SD 14mg/dL) between the SP and G4, respectively. In a Clarke Error Grid Analysis, 98.4% of CGM-reference pairs fell into the accurate (A) or benign (B) zone (A=65.8%, B=32.6%) for the SP, whereas 97.1% were in the A or B zone for the G4 (A=75.5%, B=21.6%). In a Continuous Glucose-Error Grid Analysis, the number of clinically acceptable CGM-reference pairs increased from the SP to the G4 for BGC above 70mg/dL, but decreased below this threshold. While the sample size below 70mg/dL in both studies was low, the G4 demonstrated a weakness in this range that may be detrimental to controller performance.

The results of this analysis are encouraging, especially when coupled with the high quality control achieved in the studies. While the results indicate that CGM technology may be satisfactory for closed-loop control, further improvement could be made by including algorithms to detect persistent sensor error, particularly in the low BGC range.

A Novel Model-Based Approach to Safe Personalized PID Controller Design for Artificial Pancreas

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Prevention of hypoglycemia caused by excess insulin delivery is paramount in artificial pancreas (AP) design for blood glucose (BG) regulation. We present a personalization scheme based on readily available clinical parameters that is applied to a control-relevant model of insulin-glucose response. This model is incorporated through an internal model control based approach into a proportional-integral-derivative (PID) controller for an AP device.

Individual basal levels based on daily insulin profiles are used to optimize closed-loop performance. The controller calculates relative deviation of the subject's basal profile compared to recommended basal levels calculated from individual clinical parameters and adjusts insulin delivery accordingly. An insulin feedback mechanism ensures safety of the design by preventing excess insulin delivery when given previous deliveries.

The controller was evaluated using a 31 hour protocol and challenged with two announced and one unannounced meal disturbances of 65g, 50g, and 65g CHO. In-silico simulations of this design on 100 subjects through the FDA accepted Univ. of Virginia/Padova metabolic simulator provided excellent results. 90% of overall simulation time was spent within acceptable clinical range of 70-180mg/dl and 72% in tight glycemic range of 80-140mg/dl. Overall, 97% of all subjects were maintained within the A-B zone of the control variability grid analysis system.

This novel personalization scheme can maximize clinical benefits of closed-loop BG control by ensuring safe delivery of insulin through appropriate attenuation of control action based on readily available clinical parameters. Clinical trials of this algorithm are underway at the Sansum Diabetes Research Institute.

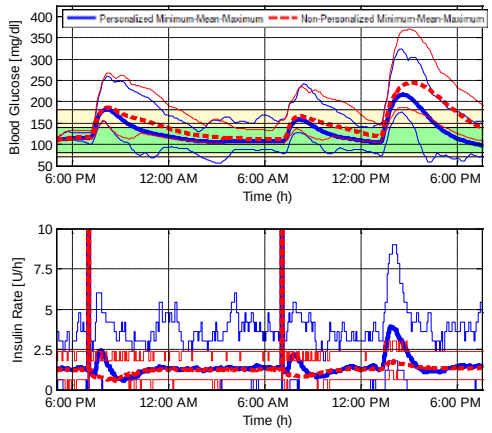

Figure 1: Blood glucose and insulin delivery traces for personalized and non-personalized controllers.

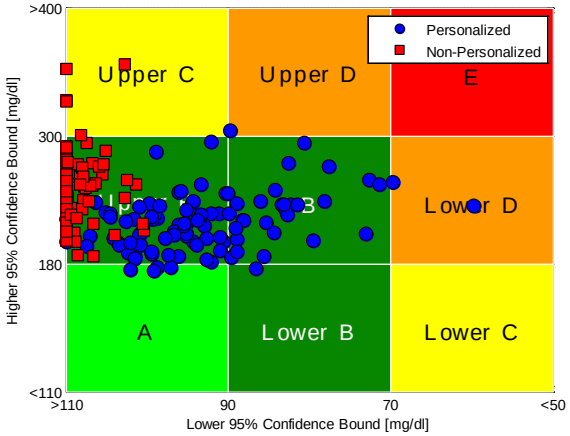

Figure 2: CVGA plot of the performance of personalized and non-personalized controllers.

Engineering GPCR Oligomers for Application in Drug Design

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Dopamine G-protein coupled receptors (GPCRs) mediate many neurological processes, and are often drug targets for psychological disease, such as schizophrenia. However, design of structurally inspired pharmaceuticals is limited due to a lack of structural data and the added complexity that these receptors homo- and hetero-oligomerize to form functionally distinct protein complexes. As such, therapeutics often engage in nonspecific interactions giving rise to side effects. This project takes a two-pronged approach to develop new expression and biophysical tools to decipher the functional consequences of GPCR oligomer formation and structurally characterize the oligomer complex at the molecular scale to aid in structure-based drug design.

In one effort, high-level expression in *Saccharomyces cerevisiae* will facilitate the employment of techniques such co-immunoprecipitation and ligand binding assays *in vivo* to detect and functionally characterize oligomers prior to purification into membrane mimetic environments. We will explore the effects of the membrane mimetic environment on oligomer formation *in vitro*, by varying protein detergent complex (PDC) composition and analyzing protein stability, ligand binding ability and oligomer presence. While these methods are established for the dopamine receptors, biophysical methods will be pioneered for *in vitro* characterization of homo-oligomers formed by Proteorhodopsin (PR), a GPCR-like protein responsible for energy generation in marine bacteria. Application of Electron Paramagnetic Resonance (EPR) and development of novel Overhauser Dynamic Nuclear Polarization (ODNP) to study membrane protein oligomers will site-specifically probe mobility and hydration dynamics within 5 Å to characterize the oligomer interface. As these efforts evolve, we will merge them to biophysically characterize dopamine GPCR oligomers, thus creating a methodical toolset for the study of the structure-function relationship of membrane protein complexes. Toward these goals, we have laid the groundwork for functional expression of dopamine receptors D_1, D_2, D_3 and the adenosine A_2a receptor known to hetero-dimerize with D_2 and D_3, and are beginning efforts to identify and purify oligomers for *in vitro* characterization.

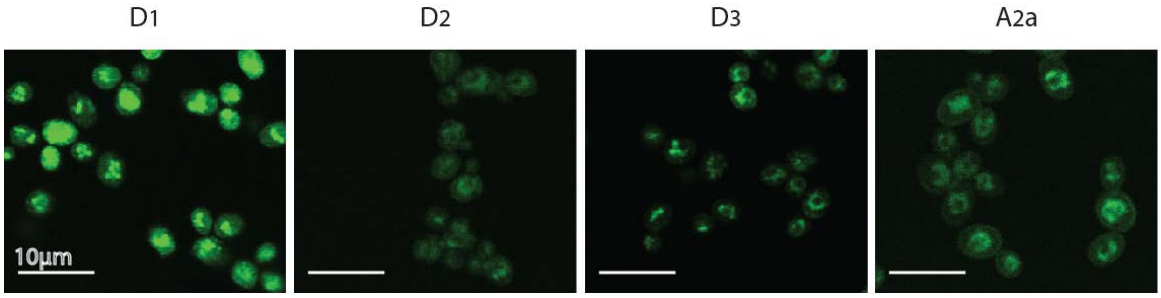

Figure 1: Expression of enhanced green fluorescent protein tagged GPCRs in *S. cerevisiae*

Topical Drug Delivery Using Novel Ionic Liquids

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The skin provides a large, compliant interface for needle-free drug delivery, while avoiding major degradative pathways associated with the GI tract. Therefore, topical drug delivery results in improved patient compliance and sustained and controlled release compared to other standard delivery methods. Concurrently, for the treatment of skin related diseases like superficial bacterial infections, topical application provides targeted delivery to the diseased site, allowing the use of more potent therapeutics with fewer systemic side effects. Unfortunately, the skin functions to resist transport of most foreign material. This is particularly true for large hydrophilic molecules (>500Da), which must partition through tortuous lipid channels in the stratum corneum to penetrate viable tissue layers where the majority of skin-related diseases reside.

Interestingly, over the last few decades ionic liquids (ILs) have emerged as a useful class of designer solvents. Indeed, ILs have been proven beneficial for use in industrial processing, catalysis, pharmaceuticals, and electrochemistry to name a few. The ability to modulate either the cation or anion individually presents an advantageous framework for tuning secondary characteristics without sacrificing the primary function of the IL. We report the use of novel ILs for topical drug delivery. The ILs employed were rationally designed by incorporating known chemical penetration enhancers (CPEs), and retained tunability of secondary properties through manipulation of ion pairing. The work presented shows the potential of ILs for topical drug delivery.

Complex Fluids, Colloids and Interfaces

Electrophoretic Mobility Measurement in Controllable Chemical Environments

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Electrophoresis is phenomenon in which a particle moves in a fluid due an externally applied electrical force acting on its double layer. It is a crucial transport phenomenon used in many applications within colloidal science and bioanalysis. The electrophoretic mobility of a colloidal particle is directly proportional to its surface charge and thus it is highly dependent the local chemistry characteristics such as pH, concentration, surface reactions and adsorption phenomena. In this sense, the electrophoretic mobility of a particle offers great insight as to how a particle chemically interacts with its surrounding medium. Here, we present a method for the directly manipulation of a particle's chemical environment while simultaneously measuring its electrophoretic mobility.

We have built microfluidic devices made of either polydimethylsiloxane (PDMS) or NOA81 photocurable resin consisting of a microchamber surrounded by two channels. Our technique involves crosslinking hydrogel membranes which separate the chamber from its side channels and loading it with a suspension of fluorescent colloids to be analyzed. The hydrogel membranes act as barrier for fluid flow while allowing for free diffusion of molecules in and out of the chamber, thus enabling us to rapidly deliver different ion concentrations as well as set up concentration gradients. Using electrodes connected to our device, we set up AC currents at low frequency (30 Hertz) and multiple potentials which forced the colloids into a rapid oscillatory motion forming streaks of length proportional to their mobility. We recorded the moving particles using a fluorescent camera and, using a custom MATLAB algorithm for image analysis, which measured streaks and calculated the mobility as well as the zeta potential of the particle. Using this approach, we are able to determine the electrophoretic mobility of polystyrene colloids at different pH environments as well as pH gradients. We've demonstrated the usefulness of this approach for easily determining particle zeta potential and its potential for extracting information about adsorption dynamics and reactions at the particle surface.

Probing the Effect of Flow Type on Nonlinear Viscoelastic Instabilities of Polymeric Fluids

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Viscoelastic instabilities pose a significant challenge to designing processes (e.g., injection molding, enhanced oil recovery) and products (e.g., consumer products, foods, pharmaceuticals) involving polymeric liquids. It remains largely unknown how nonlinear viscoelastic instabilities of polymeric fluids manifest under complex and mixed types of flows. Representative shear-thinning and shear-banding wormlike micelles were studied using four-roll mill, which is capable of generating various complex flows under steady state conditions. Under two-dimensional extensional flow, a monotonic increase of the observed deformation rates was found with shear-thinning fluid, but the observed deformation rates were lower than those observed with Newtonian fluid above a critical roller speed. The observed deformation rates around the stagnation point plateaued for shear-banding wormlike micelles within the non-Newtonian regime. When applying strong flows on shear-banding fluid, changes in the applied flow type does not necessarily lead to changes in the observed one.

A Systematic Coarse-graining of Molecular Dynamics Simulations: Thermodynamic and Transport Properties

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Coarse-graining techniques have recently attracted great interest for providing descriptions at a mesoscopic level of resolution that preserve fluid thermodynamic and transport behaviors with a reduced number of degrees of freedom (DOFs) and hence less computational effort. One fundamental question arises: how well and to what extent can a "bottom-up" developed mesoscale model recover the physical properties of a molecular scale system? To answer this question, we explore *both* the thermodynamic and transport properties of a systematically-developed coarse-grained (CG) model that represents an intermediate mesoscale fluid between the atomistic and continuum scales [1,2]. The model is developed using the iterative Boltzmann inversion (IBI) technique to determine a CG potential for a $(1-\phi)N$ mesoscale particle system, where ϕ is the fraction of removed particles from an atomic system. The uniqueness theorem guarantees a one to one relationship between the radial distribution function (RDF) and such effective pairwise potentials, but we find that RDFs are insensitive to the long-range part of the IBI-determined potentials, which provides significant flexibility in further matching other properties.

We subsequently propose a reformulation of IBI that enables simultaneous matching of the RDF and the fluid pressure. This new method mainly changes the attractive tail region of the CG potentials, and it improves the isothermal compressibility relative to pure IBI. We also find that there are optimal interaction cutoff lengths for the CG system, as a function of ϕ, that are required to attain an adequate potential while maintaining computational speedup. Dynamical properties such as the self diffusion coefficient and viscosity cannot be matched directly during coarse-graining by modifying the pair interaction. Instead, one can introduce a dissipative and random forces characterized by a friction coefficient γ, which becomes an additional parameter in the CG model that can be tuned. Using the Galilean-invariant dissipative particle dynamics thermostat, we show that a value of γ for each degree of coarse-graining ϕ can be found for which both viscosity and diffusion match the reference LJ liquid. Importantly, we show that Stokes-Einstein behavior persists for these coarse models and offers a useful perspective for interpreting the dynamics of mesoscale CG models.

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The Surface Energy of Nanoscale TIP4P/2005 Water Droplets

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Nucleation is critical in numerous processes as it is the first step in the growth of crystals, vapor bubbles, and liquid droplets. Classical Nucleation Theory (CNT) models the nucleation process by describing the reversible work required to form a nucleus from a parent phase. CNT predictions are very sensitive to the surface energy of the nucleus, which is difficult to calculate as no widely accepted method exists. Thus, the bulk surface energy is frequently used for all nucleus sizes. Consequently, predicted and experimental nucleation rates often differ by many orders of magnitude. In an attempt to improve CNT, we have implemented a mitosis method [1] to calculate the surface energy of nanoscale TIP4P/2005 [2] water droplets. The mitosis process involves reversibly separating two sub-clusters of molecules (see insets of Figure 1). We perform biased sampling in an order parameter, q, which is a measure of the amount of contact between the two sub-clusters, and unbiased sampling in the center of mass separation of the sub-clusters, r. Our sampling yields the free energy landscape (Figure 1), from which we can calculate the surface energy. We find that the surface energy is 12 to 23 mJ/m^2 greater than the bulk surface energy for droplet radii ranging from 1.6 to 0.7 nm, respectively (Figure 2). Our results suggest that homogeneous water droplet nucleation is even less probable than previously believed, 10^{30} times less likely at a supersaturation of 2. Additionally, the surface energy exhibits a linear relationship with droplet curvature as predicted by Tolman [3]. We calculate the Tolman length to be -1.1 Å for water. Incorporating our results into CNT produces more accurate predictions of the critical cluster size and height of the free energy barrier.

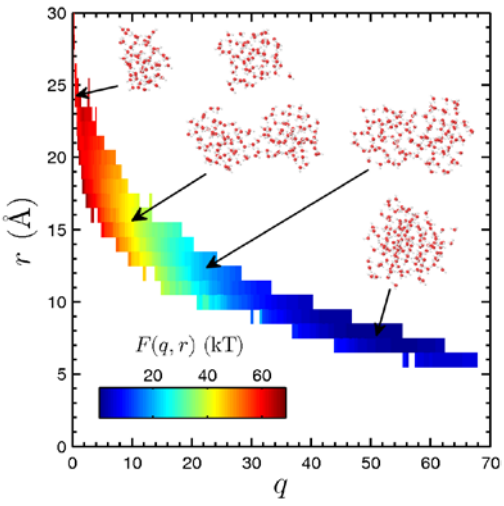

Figure 1: The free energy landscape, $F(q,r)$, for a system of 128 molecules. Insets are configurations at the indicated points.

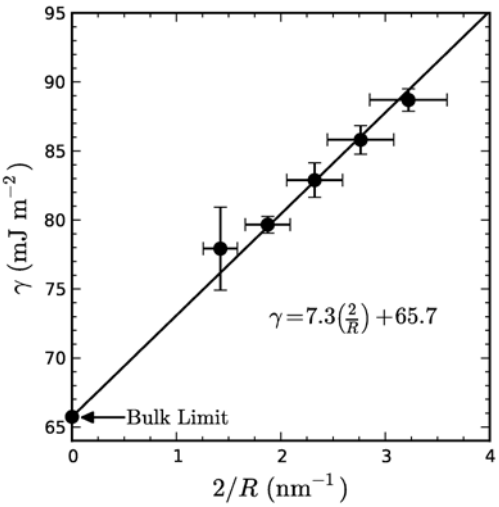

Figure 2: The surface energy of TIP4P/2005 as a function of curvature at 300K.

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Synergistic cartilage lubrication and effects of HA molecular weight

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Articular cartilage is a complex, multi-component, hierarchically structured tissue which is responsible for efficient lubrication. Despite the importance of cartilage lubrication, the molecular mechanisms leading to good lubrication and wear protection are still not well known.

Throughout the years, we have found that cartilage lubrication and wear protection are not the result of one single component or one key mechanism as previously thought, but rather the result of multiple mechanisms since the joints are exposed to an extremely large range of mechanical, dynamic, and environmental conditions. This presentation will show the role of synovial components (e.g., Hyaluronic acid (HA), Lubricin (LUB) and glucosaminoglycans (GAGs))[1-3] on the synergistic, adaptive lubrication mechanisms and wear protection [2, 4, 5, 6]. Also, the effects of HA molecular weight on wear protection will be discussed [6].

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Microscale Salt Manipulation Using Charged Hydrogel Membranes in Microfluidic Devices

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When an electric current is applied across a charged membrane with nanoscale pores in salt solution, an electrokinetic effect known as Concentration Polarization (CP) occurs. During CP, exclusion of co-ions from the charged membrane results in salt enrichment on one side of the membrane and depletion on the other. CP is a robust method for manipulating salt concentration, and is exploited on industrial scales for desalination via electrodialysis. Concentration of salt via CP could also be exploited in microfluidic Lab-on-a-chip devices for detecting ionic species (e.g. biomolecules) with increased signal, while reducing cost of experiments due to the small (nL) reagent volumes used at the microscale. In order to create portable and automated devices for detection or separation of charged species, a simple and robust method for creating charged membranes in microchannels is a necessity.

Here we describe a simple method to fabricate thin (10-20 μm) hydrogel membranes with controllable charge in microchannels. The technique relies on co-photopolymerization of reactive monomers with reactive ionic species. The concentration of ionic species in the precursor solution can be modified to manipulate the resulting membrane charge density. In order to understand and engineer the electrical properties of the hydrogels, we measure the hydrogel conductance as a function of precursor composition. After optimizing the hydrogel charge, we perform proof-of-concept experiments demonstrating CP and salt enrichment/depletion in microchannels. Finally, we report on efforts to optimize the salt enrichment/depletion to allow the eventual use of the charged hydrogel membranes in Lab-on-a-chip devices.

Hydrophobic, electrostatic, and time-dependent polymer bridging forces at surfactant-modified silicone surfaces

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We have synthesized covalently grafted polydimethylsiloxane (PDMS) thin films on extended gold surfaces that behave as collapsed polymer brush surfaces in solution, with uniform thickness, surface coverage, and surface chemistry. The Surface Forces Apparatus (SFA) was used to measure the surface forces due to surfactant adsorption and self-assembly at these hydrophobic interfaces. We show that polymeric surfactants—containing PDMS anchoring domains and quarternary ammonium cationic headgroups—assemble at the PDMS surface, leading to both an effective charge reversal at the hydrophobic interface and strong adhesion energies to mica surfaces. Molecular structure and charge are shown to govern the assembly of surfactants on these surfaces: PDMS bola-surfactants assemble to form fluctuating surface aggregates that extend into solution, leading to long-ranged and time-dependent attraction to mica surfaces, while other surfactants behave as an adsorbed layer of smeared-out charges and their interaction with mica can be described by the electric double layer theory of asymmetric surfaces. Additionally, specific Coulombic interactions between the surfactant headgroups and mica result in time-dependent polymer bridging forces as surfactants are pulled from the PDMS interface. Thus, surfactant self-assembly is presented as a method to tailor the complex and dynamic surface forces at hydrophobic interfaces, and can promote strong wet adhesion between hydrophobic and mineral surfaces.

Investigations of the Instantaneous Formation and Aging Behavior of Charged Vesicle Gels

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Colloidal dispersions of cationic bilayer vesicles serve as base materials for commercial household products. During the manufacturing process, these dispersions are subject to a number of expansion/contraction flows and thermal gradients. The long-term stability of such dispersions can depend, amongst other factors, on their processing history. Here, we study dispersions of charged multilamellar vesicles (MLVs) made from the cationic surfactant diethylesterdimethyl ammonium chloride (DEEDMAC), whose bilayers are in the crystalline (solid) state at room temperature. Typically under the application of shear, MLV dispersions display strong shear-thinning behavior. However when subject to a contraction flow through an extruder, above the main phase transition temperature of the bilayers, we find that such vesicle dispersions instantaneously transform into a 'jammed', glassy-state at the extruder outlet. The glassy dispersions behave as stiff gels, having visco-elastic moduli that are several orders of magnitude higher than their un-extruded counterparts. We use tools such as rheology and cryo TEM imaging to probe mechanisms that lead to the formation of such vesicle gels. Further, we closely examine the subsequent aging or breakdown of their microstructure; a process which occurs over time scales that depend on the dispersion composition as well as the thermotropic phase behavior of the surfactant.

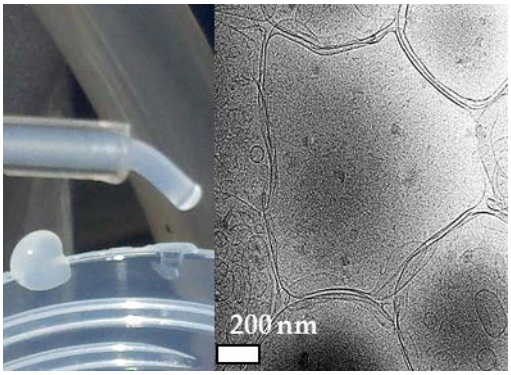

Figure 1: Images of extruded 'jammed' gels

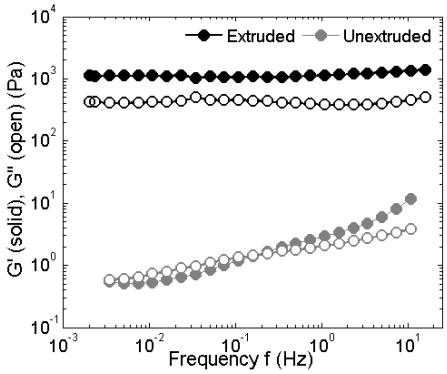

Figure 2: Visco-elastic moduli of unextruded and extuded dispersions

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