

UCSB ChE's 4th Amgen-Clorox Grad Student Symposium  
**Oral Presentation Abstracts**

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Session I:  
Nucleation and Crystallization

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## Computational and Experimental Investigations of Laser-induced Nucleation

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Recent experiments have shown that nanosecond pulses of intense laser light can induce nucleation of crystals in supersaturated solutions. This phenomenon was termed nonphotochemical laser-induced nucleation by the discoverers because the solutions have no absorption bands at the applied wavelengths [1,2,3]. Previous work proposed that this effect is due to the alignment of solute molecules in solution by the electric field of the applied laser light, promoting crystalline order (consistent with the “optical Kerr effect”). We used Monte Carlo simulations of a Potts lattice gas model to test this hypothesis [4]. First, we tested a one-step, “classical” nucleation mechanism in which nucleation progresses solely along a size coordinate. We also investigated a two-step nucleation mechanism in which amorphous nuclei first grow, and then crystallize. We showed that the optical Kerr mechanism can lower the free energy barrier to nucleation and promote the crystallization of amorphous nuclei, but only at field strengths that are several orders of magnitude stronger than those used in experiments [4].

Motivated by this computational work which indicated that the predominant literature hypothesis is insufficient to explain the experimental results, we showed that laser pulses at similar conditions to those used previously with crystalline systems also induce CO<sub>2</sub> bubble nucleation in carbonated water [5]. Previous mechanisms for laser-induced nucleation cannot explain laser-induced nucleation of bubbles. We also showed in “co-supersaturated” solutions that argon gas bubbles escaping from the water induce the nucleation of glycine crystals [5]. Our findings suggest a link between laser-induced nucleation of bubbles and crystals, and may give promising direction for finding a unified mechanism for all laser-induced nucleation experiments.

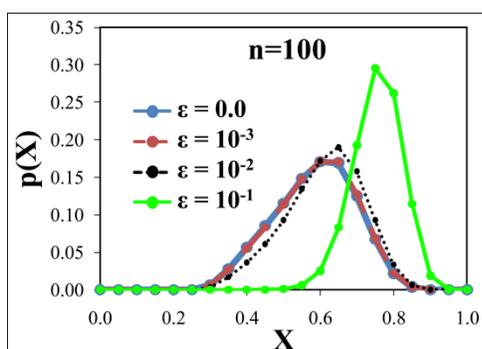


Figure 1: Computational test of the optical Kerr effect hypothesis for laser-induced nucleation

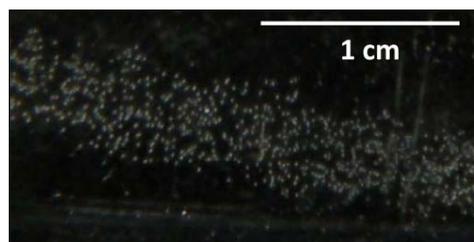


Figure 2: Laser-induced bubble nucleation

### References:

- [1] Garetz, B.A.; Aber, J.E.; Goddard, N.L.; Young, R.G.; Myerson A.S. *Phys. Rev. Lett.* **1996**, *77*, 3475.
- [2] Garetz, B.A.; Matic, J.; Myerson, A.S. *Phys. Rev. Lett.* **2002**, *89*, 175501.
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- [5] Knott, B.C.; LaRue, J.L.; Wodtke, A.M.; Doherty, M.F.; Peters, B. *J. Chem. Phys.* **2011**, *134*, 171102.

# Polymorph Specific Order Parameters: An Analysis of Surface Melted Layer Thickness for Glycine Nuclei

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Crystal nucleation is important in many processes including pharmaceutical crystallization, biomineralization and material synthesis. The progression of structural change that occurs during crystal nucleation is often described by order parameters. Polymorph specific order parameters have been developed for spherically symmetric systems; however the development of polymorph specific order parameters for molecular crystals remains a challenge. We developed a template based order parameter methodology for molecular crystals. For each molecule in the simulation, a polymorph specific order parameter is computed from the root mean squared deviation (RMSD) between the local environment of the molecule and a template based on the polymorphs experimental crystal structure. The RMSD order parameters can distinguish the  $\alpha$ ,  $\beta$ , and  $\gamma$ -glycine polymorph crystal structures in the bulk and in solvated nuclei. The structures of solvated glycine nuclei are examined using the newly developed order parameters. We show that the solvated  $\alpha$ -glycine nucleus has a thinner surface melted layer than the  $\gamma$ -glycine nucleus.  $\alpha$ -glycine forms first out of aqueous solution so the results may provide insight into interfacial energy and polymorph selection.

# A New Model to Predict Crystal Morphology of Non-Centrosymmetric Organic Molecules

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Crystal morphology influences the end-use efficacy of solid products as well as the downstream performance of the entire manufacturing and formulation process. The desired crystal size and shape distributions are governed mainly by the final application, hence a general methodology for the prediction and improvement of crystal morphology is one of the major goals in the field of crystallization. The classical Burton-Cabrera-Frank (BCF) spiral growth model [1] fails to work satisfactorily for many non-centrosymmetric organic molecules such as APIs, nonlinear optical compounds, etc., due to the assumption of Kossel crystal structure in the solid-state. These complex molecules call for a more thorough treatment for successful prediction of crystal shapes. We develop a general mechanistic spiral growth model that can be used to predict crystal morphology of any organic molecule, centrosymmetric as well as non-centrosymmetric.

This work describes the challenges that need to be overcome to predict crystal morphology for these complex molecules and steps to meet those challenges. A detailed demonstration on how to specifically account for non-isotropic behavior in terms of kink rates is also provided [2]. This work also discusses in detail the unstable edges that give rise to asymmetric spirals, a characteristic of crystal surfaces of non-centrosymmetric molecules. Modified step velocity expressions are derived that account for unstable edges. The entire model is successfully applied to industrially relevant systems such as paracetamol and lovastatin and the results are discussed in relation to experimental data from the literature and high-resolution AFM images of spirals measured in our laboratory. Finally, discussion is provided on how one can address the presence of imposters in the prediction of crystal morphology.

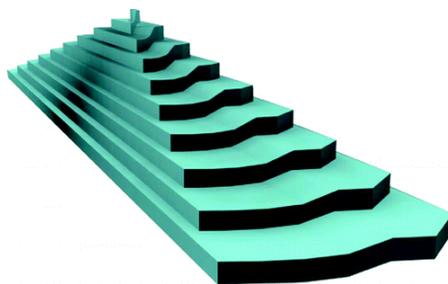


Figure 1: Spiral growth on a crystal face starting from a screw dislocation

## References:

- [1] Burton W.K., Cabrera, N. & Frank, F.C. 1951. The growth of crystals and the equilibrium structure of their surfaces. *Phil. Trans. R. Soc. A* **243**, 299-358
- [2] Kuvadia, Z. B & Doherty, M.F. 2011. *Cryst Growth Des* , **11** (7), 2780-2802

Session II:  
Polymers/Self-Assembly

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## Templating Non-hexagonal Monolayers of Block Copolymer Spheres in Confined Geometries

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We investigate the ordering of poly(styrene-*b*-2vinylpyridine) [PS-PVP  $M_n = 56$  kg/mol] sphere monolayers in wells of various shapes and sizes. Recent self-consistent field theory results [1] on ordering of block copolymer (BCP) cylinders in square surroundings suggest that adding homopolymers of higher  $M_n$  can allow square arrays of BCP to form in small (4 to 5 cylinders across) square wells by relieving packing frustration. Experimentally, we adopt a similar strategy for ordering BCP spheres on silicon nitride membranes patterned by electron beam lithography to produce SiO<sub>x</sub> mesas, adding various volume fractions of PS homopolymer of different  $M_n$ . Scanning force microscopy, transmission electron microscopy and X-ray scattering has been used in a complementary manner to quantify the structures obtained after thermal annealing of the blends at varying temperatures, revealing that the order-disorder temperature (ODT) and general mixing behavior is strongly dependent on PS concentration. These behaviors have a direct influence on the templating of nanopatterns that are typically unachievable in unconfined monolayers. For instance, in the absence of PS in the films, only defective hexagonal structures are observed even in wells containing 16 spheres. Adding 10% PS of  $M_n = 112$  kg/mol to the BCP results in a square packing of spheres in square wells containing as many as 81 spheres.

References:

[1] Hur et al. *Macromolecules* **2009**, 42, 5861

## Field-Theoretic Studies of Complex Coacervation

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Complex coacervation is a particular type of polyelectrolyte complexation that lends itself to a variety of applications including synthetic underwater adhesives, biosensors, and water purification systems. In these systems, oppositely charged polyelectrolytes in an aqueous solution undergo phase separation to form a dense, liquid, polymer-rich phase, known as the coacervate, and a supernatant with typically very low polymer concentrations. Working closely with experimental groups at UCSB, we have studied coacervate systems using field-theoretic techniques. First, we examined a system of oppositely charged homopolymers using a field-based analytical model and reproduced several experimentally observed trends. In particular, the effect of molecular weight on the concentration of the coacervate is directly compared with experimental results. We also studied triblock polyelectrolytes with charged endblocks and neutral, hydrophilic midblocks. Unlike the homopolymer polyelectrolytes, these triblock polyelectrolytes can microphase separate to form coacervate domains and midblock/solution domains where the midblocks act as bridges between the coacervate domains yielding a nanostructured gel. Due to the electrostatic driving force for the microphase separation, the morphology and properties of the gel can be tuned by adjusting salt concentration, pH, temperature, and polymer concentration, thus, making the gel reversible. Using field-theoretic simulations, we have examined the effect of various parameters on structure of the coacervate and have identified experimentally observed BCC structure, as well as, predicted the existence of a lamellar structure.

Session III:  
Catalytic Materials/  
Inorganic-Organic Materials

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## Origins of Saccharide-Dependent Hydration at Aluminate, Silicate, and Aluminosilicate Surfaces

Benjamin Smith,<sup>(a)</sup> Aditya Rawal,<sup>(a)</sup> Gary Funkhouser,<sup>(b)</sup> Lawrence Roberts,<sup>(c)</sup> Vijay Gupta,<sup>(d)</sup>  
Jacob Israelachvili,<sup>(a)</sup> and Bradley F. Chmelka<sup>(a)</sup>

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Sugar molecules adsorbed at hydrated inorganic oxide surfaces occur ubiquitously in Nature and in technologically important materials and processes, including marine biomineralization, abiotic biomolecule synthesis, bone resorption, heterogeneous catalysis, corrosion inhibition, and cement hydration. Among these examples, surprisingly diverse hydration behaviors are observed for oxides in the presence of saccharides with closely related compositions and structures. Importantly, the hydration kinetics of aluminosilicate-based cements are critical to a number of modern technologies, notably as synthetic structural materials for large-scale construction projects and oilwell cementing, where saccharide additives are used to slow hydration processes and alter rheological properties. Glucose, sucrose, and maltodextrin, for example, exhibit significant differences in their alkaline reaction properties, adsorption selectivities, binding strengths and coverages on hydrating aluminate, silicate, and aluminosilicate surfaces that are shown to be due to the molecular architectures of the saccharides.

Solution and solid-state nuclear magnetic resonance (NMR) spectroscopy measurements, including at very high magnetic fields (19 T), distinguish and quantify the different molecular species, their chemical transformations, and their adsorption behaviors on different aluminate and silicate moieties. Two-dimensional NMR results establish non-selective adsorption of glucose degradation products containing linear saccharinic and carboxylic acids on both hydrated silicates and aluminates. In contrast, sucrose, which is stable under alkaline conditions, adsorbs intact at hydrated silicate sites and selectively at anhydrous, but not hydrated, aluminate moieties. Quantitative surface forces measurements establish relatively weak binding of glucose degradation species on hydrated aluminosilicate surfaces; whereas, sucrose adsorbs strongly and forms multiple layers that result from sucrose–cation complexation. Maltodextrin exhibits intermediate alkaline reaction and sorption properties, due to its oligomeric architecture that yields linear carboxylic acids and stable ring-containing degradation products that are similar to those present for glucose and sucrose, respectively. The molecular structures and physicochemical properties of the saccharides and their degradation species correlate well with their adsorption behaviors and lead to different binding strengths and surface coverages in aluminosilicate-based cements. The results explain the dramatically different effects that small amounts of different types of sugar molecules have on the rates at which aluminate, silicate, and aluminosilicate species hydrate, with important implications for diverse materials and applications wherein organic species adsorb at heterogeneous oxide surfaces from aqueous solutions.

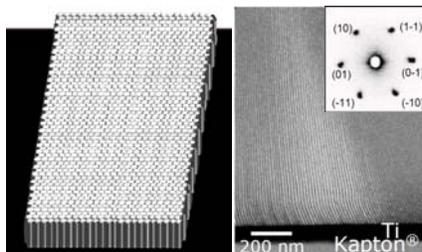
# Self-Assembled Inorganic-Organic Nanocomposites with Controllable Photovoltaic Properties

Justin Jahnke

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Nanostructured inorganic-organic materials exhibit novel macroscopic properties that reflect the combination of their dissimilar molecular components, but which are often extensively influenced by interactions among the different species across their large surface areas of contact. Understanding the compositions, structures, and surface interactions of such materials are crucial to controlling and improving their macroscopic properties for diverse applications, such as for catalysis, separations, electrochemical and optoelectronic devices, etc. In particular, surfactants can be used to direct the structures of network-forming inorganic oxide frameworks into continuous transparent films that open opportunities for optical applications, especially if photo-responsive molecular guest species are incorporated into the materials. By controlling synthesis and processing conditions, a wide range of liquid-crystal-like mesophases can be obtained (e.g., hexagonal, lamellar, or cubic), into which photo-responsive guest species can be distributed, although often with little control.

We have recently shown that surface interactions between dissimilar oxide, surfactant and functional guest species can be measured and used to control how conjugated polymer guest species are distributed in nanocomposites oxides. Furthermore, by understanding and controlling solvent mass transport, surfactant-solvent phase equilibria, surface nucleation phenomena, and sol-gel reaction kinetics, we have demonstrated for the first time that similar surface interactions can be controlled to generate high degrees of macroscopic orientational order in inorganic-organic nanocomposites materials. Using insights gained from X-ray scattering, electron microscopy, and two-dimensional NMR, films and monoliths with high degrees of controllable orientational order can be prepared over a range of material compositions, including different oxides, surfactants, solvents, and functional guest species. For example, the cylinders of hexagonal-phase materials can be controllably aligned either perpendicular or parallel to a substrate, depending on synthesis and processing conditions, which influence especially solvent flux and surfactant-substrate interactions. This general method allows inorganic-organic hybrid films and monoliths to be prepared with novel anisotropic properties that enable promising new applications. These include the incorporation of conjugated polymer or dye guest species into orientationally ordered nanostructured titania films with novel anisotropic photovoltaic properties. This general methodology should provide similar benefits in other applications where the aligned pore-structures can be harnessed to improve optical or transport properties.



## Determination of the Activation Mechanism of Supported Methyltrioxorhenium for Olefin Metathesis

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Metathesis has already found wide application in the chemical industry, including the production of propene, specialty polymers, and other chemical feedstocks,[1] as well as for converting dwindling petroleum supplies into more useful hydrocarbon stocks.[2] Although olefin metathesis with homogeneous transition metal complexes as catalysts is considered well-understood, the structures and activation mechanisms of the potentially more useful heterogeneous catalysts remain poorly defined.[3] Methyltrioxorhenium ( $\text{CH}_3\text{ReO}_3$ , MTO) is a well-known olefin metathesis catalyst whose spontaneous activation under mild conditions makes it potentially useful for the synthesis of specialty chemicals such as pheromones and fine chemicals. There are several potential activation pathways for MTO such as the formation of a carbene from the methyl group, or conversion of an oxo-group for to a methylidene group (pseudo-Wittig pathway), but there remains no clear evidence for which pathway is correct.

Our work has focused on the use of a recently reported, highly Lewis acidic support,[4] which has twice the catalytic activity of traditional  $\gamma$ -alumina without the onset of complicating side reactions such as isobutene and higher olefin formation, which are seen for both  $\gamma$ -alumina and amorphous silica-alumina, complicating analysis. Isotopic labeling experiments run with an equimolar amount of MTO and olefins were used to determine the source of the metal carbene. GC-MS results from propylene metathesis with  $^{13}\text{C}$ -enriched MTO show no isotopic enrichment in metathesis products, discounting the methyl group on MTO as the source of the carbene. Using deuterium enriched propylene, no change in the isotopic labeling of the metathesis products was seen, but when subsequent metathesis using unlabeled propylene was performed, deuterium exchange was seen suggesting that the pseudo-Wittig pathway was indeed the method of activation. Density functional theory calculations were run to determine the thermodynamics of MTO activation mechanism by both the pseudo-Wittig pathway as well as carbene formation from the methyl group. While the energy for forming a carbene by both pathways was shown to be comparable, only the pseudo-Wittig pathway had an achievable transition state, bolstering the likelihood of the pseudo-Wittig pathway. From these results, we have sought to definitively identify the mechanism of MTO activation supported on alumina.

### References:

- [1] Mol, J. C. J. *Mol. Catal. A: Chem.* 2004, 213, 39.
- [2] Goldman, A. S.; Roy, A. H.; Huang, Z. et al. *Science* 2006, 312, 257.
- [3] Rouhi, A. M. In *Chemical and Engineering News* 2002; Vol. 80, p 34.
- [4] Kozlov, A. I.; Kung, M. C.; Xue, W. M. et al. *Angew. Chem. Int. Ed.* 2003, 42, 2415.

# Session IV: Biomolecular Mechanisms

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## Controlling Self-assembly Properties of Peptide Amphiphiles

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*(b) Bioengineering Department, University of California, Berkeley*

*(c) Institute for Molecular Engineering, University of Chicago*

Peptide amphiphiles (PAs) are capable of self-assembly into micelles which can be used in the targeted delivery of peptide therapeutics and diagnostics. PA micelles exhibit a structural resemblance to proteins by having folded peptides displayed on the exterior of a hydrophobic core. However, PA self-assembly is often unpredictable and design insight is needed to control the properties of PA micelles from the bottom up. In this regard, we have studied design factors such as methods to control PA secondary structure, the relationship between PA structure and micelle activity, and how to tailor micelle stability.

This talk will focus on controlling the size and geometry of PA aggregates. PA self-assembly often results in high aspect ratio cylindrical micelles, precluding their use in applications where small, spherical particles are necessary. We demonstrate a modular approach for controlling the self-assembly of biorelevant PAs into spherical, sub-100 nm structures by using dendrimers as supramolecular templates. Our templating approach is a versatile platform method that results in biocompatible, stable protein-like assemblies displaying peptides with native secondary structure and biofunctionality.

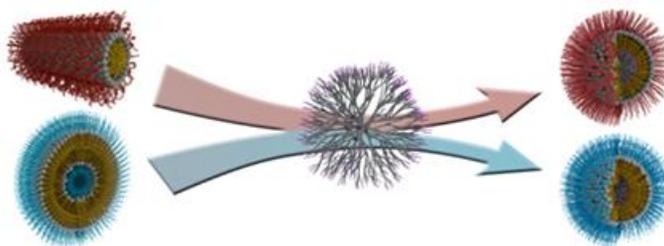


Figure 1: Schematic of the dendrimer templating approach

## The Importance of Interfacial Redox on the Mussel Protein Adhesion

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The underwater adhesion of marine mussels relies on mussel foot proteins (mfps) rich in the catecholic amino acid 3, 4-dihydroxyphenylalanine (dopa). As a side-chain, dopa is capable of strong bidentate interactions with a variety of surfaces, but its susceptibility to oxidation often renders it unreliable for adhesion. Mussels limit dopa oxidation by imposing an acidic, reducing regime in the confined space of mfp deposition. Using the Surface Forces Apparatus (SFA) technique, we demonstrate that the adhesion of mfp-3 to mica is closely coupled with dopa redox and pH. Raising the pH from 3 to 7.5 decreases the adhesion energy of mfp-3 on mica 20-fold and appears to be driven by the pH-dependent oxidation of dopa. Addition of thiol-rich mfp-6 restores mfp-3 adhesion by coupling the oxidation of thiols to the reduction of dopaquinones. How mussels preserve adhesive dopa-containing proteins from oxidation has considerable biological and technological value. [1], [2]

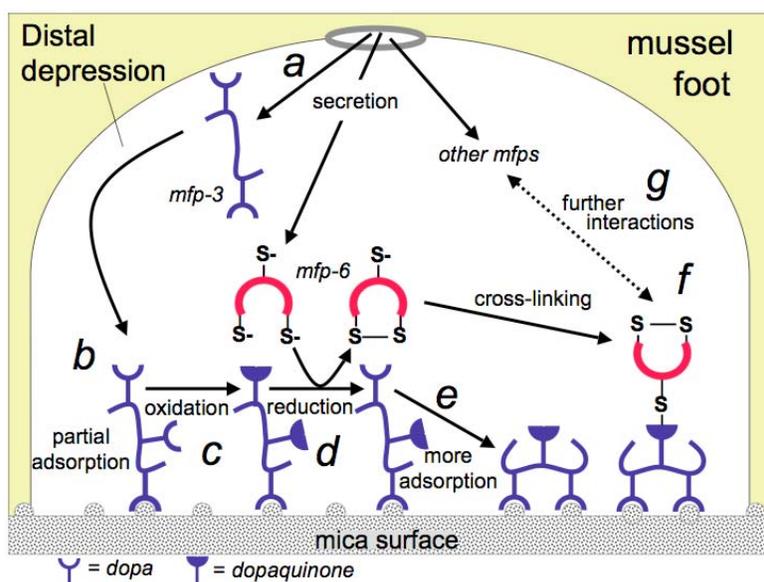


Figure 1: Redox control and the stepwise adsorption and cross-linking of mfp-3.

### References:

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- [2] Yu, J; Wei, W; Danner, E.; Israelachvili, J.N.; Waite J.H.; *Adv. Mater*, 2011, 23, 2362-2366.