

# 95th ACS Colloid and Surface Science Symposium

Virtual, 14-16 June 2021

## Co-Chairs

Matthew Helgeson, University of California, Santa Barbara

Sibani Lisa Biswal, Rice University

Ramanathan Nagarajan, DEVCOM Soldier Center

## Book of Abstracts

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Mon, 14 09:00 - 11:00

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Mon-LGS1-01

Ionomer/Catalyst Particle Interactions in Fuel-Cell Inks

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Fuel-cell catalyst layers (CLs) are complex, heterogeneous porous electrodes comprised of agglomerates of catalyst particles (platinum-on-carbon nanoparticles) bound with ion-conducting polymer (perfluorosulfonic-acid ionomer, PFSA). The electrochemical performance of the fuel cell is directly controlled by the ionomer/catalyst particle interface and the structure of these agglomerates. As such, there has been tremendous effort to characterize CL microstructure and understand structure-property-performance relationships. However, how and why these microstructures form remains unclear. The CL fabrication process has been primarily empirical, lending little insight into the fundamental interactions controlling agglomerate formation. To direct and control CL structures for improved device performance, we must understand these interactions. CLs are fabricated from precursor inks which are cast and dried to form the electrodes. These inks are colloidal dispersions of the catalyst particles and ionomer, suspended in a solvent (typically a water-alcohol mixture). The interactions between all three components control how the ionomer adsorbs to the catalyst particles, and how these complexes aggregate in solution, ultimately determining the final, dried CL microstructure. PFSA has a hydrophobic poly(tetrafluoroethylene) backbone, with pendant sidechains that terminate in charged sulfonic-acid groups. In mixed water-alcohol solvents, PFSA forms partially-solubilized rod-like aggregates; the water:alcohol ratio alters the ionomer conformation, and the relative number of sidechain versus backbone moieties exposed on the aggregate surface. This will affect the electrostatic and hydrophobic interactions of PFSA with itself and catalyst particles in the ink. In this talk, we investigate the ionomer/catalyst particle interaction, and how PFSA adsorption to catalyst particles is modulated by solvent identity and ionomer sidechain (charge) density. We use quartz crystal microbalance (QCM) to screen PFSA adsorption from solution to model surfaces, to understand how the ionomer/surface interaction is impacted by metal identity and surface hydrophobicity. We also quantify the thermodynamics of binding to carbon and platinum nanoparticles with isothermal titration calorimetry (ITC). Results reveal the adsorption is strongly affected by the ionomer charge density and solvent environment. Furthermore, this adsorption process is entropically-driven, suggesting hydrophobic association between the ionomer backbone and the nanoparticles. Finally, PFSA has a slight preference to adsorb to carbon versus platinum surfaces. Given the larger surface area of carbon in platinum-on-carbon nanoparticles, this suggests that ink structures are likely governed by PFSA/carbon interactions. These results provide guidelines on how we may influence adsorption to nanoparticle surfaces and control the ionomer/catalyst particle interface.

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Mon-LGS1-02

### Elastic turbulence generates anomalous flow resistance in porous media

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Princeton University

Polymer solutions are often injected in porous media for applications such as oil recovery and groundwater remediation. In many cases, the macroscopic flow resistance abruptly increases above a threshold flow rate in a porous medium, but not in bulk solution. The reason why has been a puzzle for over half a century. Here, by directly visualizing the flow in a transparent 3D porous medium, we demonstrate that this anomalous increase is due to the onset of an elastic instability in which the flow exhibits strong spatio-temporal fluctuations reminiscent of inertial turbulence, despite the vanishingly small Reynolds number. We find that the transition to unstable flow in each pore is continuous, arising due to the increased persistence of discrete bursts of instability above an onset flow rate; however, this onset value varies from pore to pore. Thus, unstable flow is spatially heterogeneous across the different pores of the medium, with unstable and laminar regions coexisting. Guided by these findings, we quantitatively establish that the energy dissipated by unstable pore-scale fluctuations generates the anomalous increase in flow resistance through the entire medium. Thus, by linking the onset of unstable flow at the pore scale to transport at the macroscale, our work provides generally-applicable guidelines for predicting and controlling polymer solution flows.

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Mon-LGS1-03

### Synthesis and Assembly of Polymer-Patched Nanoparticles

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I will present our most recent experiment-computation collaboration on a new strategy to site-specifically coat gold nanoparticles (NPs) with polymer patches. We experimentally demonstrate this strategy is generally applicable in patterning polymer patches of precise size and shapes on various anisotropic gold NPs. We realize highly uniform patchy NPs, from tip to facet-patches, as well as from symmetric to broken-symmetry patch arrangements. The patch grafting simulation based on polymer scaling theory reveals the crucial roles of polymer-polymer attraction and NPs local surface curvature for site-specific polymer grafting. Finally, we show that the as-prepared library of patchy NPs can assemble into unique structures, including small clusters (dimers, trimers) by self-limited attraction, and even large-scale open lattices, which are challenging to achieve from NPs of homogeneous surface chemistry. We expect the method can generate hybrid NPs with regioselectively programmable chemistries and interactions for the applications in catalysis, delivery, and directed assembly into exotic functional structures.

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Mon-LGS1-04

### Shear-Induced Grain Boundary Formation in Magnetically Actuated Colloidal Sheets

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Polycrystalline materials, such as metals and ceramics, contain interfacial defects between their crystalline grains, known as grain boundaries. Grain boundaries (GBs) play a pivotal role in determining bulk material properties, in part, because they are dynamic and can move to accommodate stresses in the material, such

as shear stress. Despite many efforts however, much of the shear-coupled GB dynamics are not well understood due to the short timescales at the atomic level. Here, we show a tunable system of superparamagnetic particles under a time-varying magnetic field creates two-dimensional crystalline sheets that contain inherent shear at particle-free voids. We describe the mechanism of shear in this system and showcase its effect on the polycrystalline bulk. Using the local bond orientational order parameter ( $\psi_6$ ), GBs in the system are identified and monitored with time. We observe reorganization of ordered grains and disordered grain boundaries under a constant magnetic field strength. We find new low angle grain boundaries form in the system. Furthermore, we apply classical material science theory to these shear-induced low angle grain boundaries and find good agreement, thereby directly connecting our soft colloidal system to hard-condensed matter.

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Mon-LGS1-05

## Quantifying In-Solution Biomolecular Exchange Dynamics on Carbon Nanotubes toward Improved Nanosensor Design

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Adsorption of polymers on single-walled carbon nanotubes (SWCNTs) has enabled developments in molecular sensing, *in vivo* imaging, and gene delivery applications.<sup>1–3</sup> Noncovalent functionalization of SWCNTs with polymers preserves the intrinsic near-infrared SWCNT fluorescence for sensing or imaging functions and offers a reversible binding mode for cargo delivery. However, noncovalent biomolecule adsorption is an inherently dynamic process, where exchange occurs between molecules in the bulk solution and molecules on the nanoparticle surface, into what is known as the corona phase. The nature, strength, and kinetics of polymer binding and unbinding processes on SWCNTs are important contributors to the success of such nanotechnologies. Understanding these binding processes is especially important for intended uses of functionalized SWCNTs in biological environments, where native biomolecules compete with the original polymer to occupy the SWCNT surface. Binding of proteins and other biomolecules to the SWCNT disrupts the intended functionality of the nanoparticle and can lead to adverse biocompatibility outcomes.<sup>4</sup> We present an assay to study the corona exchange dynamics between solution-phase and corona-phase polymers on SWCNTs.<sup>5</sup> This assay exploits the quenching property of fluorophores proximal to the SWCNT surface to monitor ligand binding and unbinding events. Experiments tracking real-time polymer adsorption and desorption on the SWCNT surface are conducted with varying polymer entities, specifically with a focus on DNA (as the sensing moiety) and protein (as the biofouling agent). Choice of model high- and low-binding proteins (fibrinogen and albumin, respectively) is informed by complementary whole biofluid protein corona studies with characterization by quantitative mass spectrometry-based proteomics.<sup>6</sup> Binding profiles are extracted from the exchange assay and used to inform a simple kinetic model. To further complement these kinetic exchange experiments, we apply a modified DLVO framework to deconvolute the interfacial interactions driving adsorption between DNA-SWCNTs and proteins in aqueous solution. The work presented herein develops an understanding of the fundamental corona exchange mechanism and provides insight into performance of these designed SWCNT-based systems in biologically relevant, protein-rich conditions. **References** 1. Pinals, R. L. et al. *Nano Lett.* 21, 2272–2280 (2021). 2. Beyene, A. G. et al. *Science Advances* 5, eaaw3108 (2019). 3. Demirer, G. S. et al. *Science Advances* 6, eaaz0495 (2020). 4. Pinals, R. L. et al. *Analyst* 145, 5090–5112 (2020). 5. Pinals, R. L.,\* Yang, D.,\* et al. *J. Am. Chem. Soc.* 142, 1254–1264 (2020). 6. Pinals, R. L. et al. *Angewandte Chemie International Edition* 59, 23668–23677 (2020).

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Mon-LGS1-06

## Investigating complex fluid interfaces with decoupled shear and dilational interfacial rheology

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Interfacial structure and rheological properties are important in biological (e.g. lung surfactants) as well as many synthetic systems (e.g. emulsions) and understanding the structure-property correlation can help guide the formulation of these systems with targeted interfacial properties. Mixed flow fields, typical of classical Langmuir trough experiments, convolute the interpretation of interfacial dilatational rheology for interfacial systems with both finite surface shear and dilatational moduli. Attempts have been made to resolve the anisotropic state of stress into their pure forms, either by multiple measurements in the Langmuir trough [1] or through the use of a radial trough [2]. In this presentation, we describe the design and implementation of a new “Quadrotrough” to better approximate pure dilation or shear interface kinematics. The rheological capabilities of this interfacial trough are demonstrated through proof-of-concept experiments on stearic acid, a simple model system. This new instrument allows us to systematically step through pure shear and pure dilatational flow to investigate the path dependence of interfacial isotherms more clearly. We demonstrate the critical importance of decoupling flow fields for complex interfaces with finite shear and dilatational elasticity for ease of data interpretation. Combining the new Quadrotrough with both Brewster angle microscopy and neutron reflectivity provides detailed structural measurements of the interface at the mesoscale and nanoscale that elucidates the source of this path dependence. The potential for coupling this trough with microstructural characterization via neutron reflectivity will be discussed and future investigations are reflected on for instrument development. References [1] Petkov, Jordan T., et al. Langmuir 16.8 (2000): 3703-3711. [2] Pepicelli, Martina, et al. Soft matter 13.35 (2017): 5977-5990.

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Mon, 14 09:00 - 11:00-

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Mon-AM1-01

Computer Simulation of Self-Assembly by Multipolar Colloidal Particles and Their Mixtures  
**(Keynote Lecture)**

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Colloids with anisotropic charge distributions hold promise for creating a number of useful new materials including optic materials with novel symmetries, materials for information storage, and dampers for controlling vibrations in structures. Experimentally manipulating properties of anisotropic particles in a controlled fashion can sometimes be difficult and is time consuming. The search for novel anisotropic colloidal materials can be enhanced and even guided by simulations of colloidal system assembly. We report the results of several studies of colloidal mixtures containing at least one dipolar component. The aim is to understand how particle shape and activity, and the presence or absence of an external magnetic field, affect the types of structures that form. The insights gained from these studies help our experimental colleagues to screen the many types of structures formed by anisotropic particles so as to identify those that would be of interest for advanced applications.

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Mon-AM1-02

Self-assembly of Symmetric Polystyrene-block-Poly(methacrylic acid) diblock copolymer in Salt-Free Aqueous Solution by Explicit Atomistic MD Simulations

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The structure, solvation, and thermodynamic behavior of symmetric PS<sub>15</sub>-b-PMA<sub>15</sub> polyelectrolyte-neutral block copolymer chains in salt-free aqueous solution were investigated as a function of charge density ( $f$ ) of PMA block by molecular dynamics simulations in explicit solvent. The shape of the micelle transforms from ellipsoid to spherical with increase in charge density in agreement with experimental data. The radius of the core and of the entire micelle shows a linear variation with  $f$  in good agreement with experimental results in literature [1]. Solvation of the micelle is influenced by number of hydrogen bonds formed between PMA units and surrounding water molecules, which increases with the charge density of PMA chains. The interaction of PMA with water becomes more favorable with increase in  $f$  due to the presence of COO<sup>-</sup> groups. The surface area of micelle decreases with an increase in  $f$ , commensurate with its shape transformation. The structure of water molecules near the core hydrophobic PS surface is independent of charge on PMA blocks. Most of the PS atoms were located near the COM of the micelle, which suggests the densely packed core of the micelle. However, the location of PMA chains varies from being on the surface of the PS core at  $f = 0$  (unionized state) to being extended as the classic corona at higher values of charge. The sodium (Na<sup>+</sup>) are condensed onto the PMA chains at higher charge density values as seen from the radial density profile and pair correlation functions. The total hydration enthalpy of micelle decreases with an increase in  $f$ , which indicates thermodynamically favorable interactions between micelle with surrounding water molecules. Sodium ions (Na<sup>+</sup>) have thermodynamically favorable interactions with PMA units as compared to their interactions with water molecules. The results of atom density profiles, solvation enthalpy values and correlation function of copolymer-Na<sup>+</sup> ion pairs confirm the existence of micelle in "Osmotic Regime", in agreement with results of mean-field theory [2]. [1] Groenewegen, W.; Egelhaaf, S. U.; Lapp, A.; Van Der Maarel, J. R. C. Neutron Scattering Estimates of the Effect of Charge on the Micelle Structure in Aqueous Polyelectrolyte Diblock Copolymer Solutions. *Macromolecules* 2000, 33 (9), 3283–3293. [2] Shusharina, N. P.; Linse, P.; Khokhlov, A. R. Micelles of Diblock Copolymers with Charged and Neutral Blocks: Scaling and Mean-Field Lattice Approaches. *Macromolecules* 2000, 33 (10), 3892–3901.

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Mon-AM1-03

Self-Assembly of an Amphiphilic Donor-Acceptor Isoindigo-based Fluorophore into Spherical Aggregates for use in NIR Bioimaging Applications

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Fluorescence imaging (FI) of biological systems in the near-infrared (NIR) region has drawn significant research interest due to an increase in spatial and temporal resolution when compared to traditional imaging techniques such as MRI, CT, and PET without the use of harmful radiation.<sup>1,2</sup> Various classes of materials can be employed for FI applications such as inorganic quantum dots, conjugated polymers, and fluorescent proteins. However, organic small molecular fluorophores have shown the most promise due to decreased cytotoxicity and the relatively simplistic ability to tune the optical properties of such molecules through structural design.<sup>3</sup> The hydrophobic nature of these organic fluorophores requires the use of a delivery system such as surfactants or amphiphilic nanoparticles to be used in biological systems. Previously we synthesized an alkylated donor-acceptor-donor (D-A-D) isoindigo (II) fluorophore functionalized with 3,4-ethylenedioxythiophene (EDOT) and triphenylamine (TPA). We replaced the alkyl groups with polyethylene glycol (PEG, Mw=900) to create an amphiphilic fluorophore (PEG-II-EDOT-TPA) capable of self-assembling into spherical aggregates in an aqueous environment.<sup>4</sup> PEG-II-EDOT-TPA was studied in a variety of organic solvents, exhibiting a  $\lambda_{\text{em,max}}^{\text{em}} = 770$  nm in DMSO. Nanoprecipitation formed aggregates which exhibited a noted bathochromic shift to  $\lambda_{\text{em,max}}^{\text{em}} = 815$  nm. DLS and TEM were used to characterize the aggregates with DLS providing an average size and PDI of 65.7 nm and 0.250, respectively, while TEM shows slightly larger aggregates with sizes ranging from 100-200 nm. Cytotoxicity and cellular imaging studies utilizing HEK 93 cells were performed with PEG-II-EDOT-TPA aggregates

showing low cytotoxicity values and successful lysosomal imaging of the HEK 93 cells. This work has provided insight into furthering the strategic design of self-assembling amphiphilic organic fluorophores for use as NIR FI agents. (1) Reineck, P.; Gibson, B. C. Near-Infrared Fluorescent Nanomaterials for Bioimaging and Sensing. *Advanced Optical Materials* 2017, 5 (2). <https://doi.org/10.1002/adom.201600446>. (2) Li, B.; Zhao, M.; Zhang, F. Rational Design of Near-Infrared-II Organic Molecular Dyes for Bioimaging and Biosensing. *ACS Materials Letters* 2020, 2 (8). <https://doi.org/10.1021/acsmaterialslett.0c00157>. (3) Shen, Q.; Wang, S.; Yang, N.-D.; Zhang, C.; Wu, Q.; Yu, C. Recent Development of Small-Molecule Organic Fluorophores for Multifunctional Bioimaging in the Second near-Infrared Window. *Journal of Luminescence* 2020, 225. <https://doi.org/10.1016/j.jlumin.2020.117338>. (4) Vijayan, S. M.; Sparks, N.; Roy, J. K.; Smith, C.; Tate, C.; Hammer, N. I.; Leszczynski, J.; Watkins, D. L. Evaluating Donor Effects in Isoindigo-Based Small Molecular Fluorophores. *The Journal of Physical Chemistry A* 2020, 124 (51). <https://doi.org/10.1021/acs.jpca.0c07796>.

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Mon-AM1-04

Charge transport of ionic liquids in self-assembly of triblock copolymer/ionic liquid/monomer mixtures

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Ionic liquids (ILs) have attracted significant interest due to their unique properties including high thermal stability, negligible vapor pressure, and high ionic conductivity and specific capacitance. To enhance the practicality of employing ILs in different applications, it is important to blend them with structuring polymers to form physically or chemically crosslinked networks, known as ion gels. Using block copolymers as polymer matrix provides the opportunities to control the gel nanostructure (lamellar, hexagonal, cubic, and gyroid) and physical properties through variation of the copolymer block lengths, architecture, or chemistry. In this study, nanostructured ion gels are prepared through polymerization of lyotropic liquid crystals (LLCs) made of monomers (styrene and divinylbenzene), ionic liquid ([EMIM][BF<sub>4</sub>]), and amphiphilic block copolymers. We investigate the molecular dynamics of nano-confined ionic liquids in these ion gels by broadband dielectric spectroscopy.

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Mon-AM1-05

Towards Supramolecular Self Assembly by Programmable Site-Specific Functionalization of DNA Origami with Polynucleotide Brushes

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We show that the synergistic combination of surface-initiated enzymatic polynucleotide brush synthesis with precisely engineered DNA origami nanostructures presents an innovative pathway for the generation of stable, polynucleotide brush functionalized origami nanostructures. Brush functionalization can be precisely controlled by the site-specific location of initiation sites on the origami core and by controlling brush height and composition. This synergistic combination of site-specific, surface-initiated enzymatic polynucleotide brush synthesis with precisely engineered DNA origami is new and presents an innovative pathway for the generation of stable and adaptive polynucleotide brush functionalized origami nano- and meso-structures that allow for further supramolecular assembly. We show that amphiphilic, brush-functionalized DNA origami can self-assemble into large micellar structures, thus opening up an entirely new architectural realm for DNA origami nanostructures. Next, we demonstrate that coarse-grained oxDNA simulations can predict the morphology of brush-functionalized origami and their assemblies and thus serve

as an expedient design tool. Finally, we show that polynucleotide brush-functionalized DNA origami have significantly higher nuclease resistance compared to unprotected DNA origami, and that this stability can be spatially programmed by designing the positions of the decorating sites on the surface of the origami. Together, these attributes will likely enable new applications of DNA nanotechnology in biomedicine, such as in vivo molecular sensors and smart nanoscale delivery systems.

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Mon, 14 09:00 - 11:00

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Mon-BM1-01

Continuous Production of Rugged Nanoemulsions/Nanoparticles Generated by the Ouzo Effect

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Nanoemulsions have attracted interest across numerous disciplines owing to their relatively small size, increased surface area to volume ratio, and enhanced colloidal stability. One emerging method for the production of nanoemulsions is the Ouzo effect, also known as nanoprecipitation or solvent shifting. Nanometric oil droplets are generated in a ternary mixture comprising an oil, solvent, and nonsolvent of the oil; the generated droplets are subsequently kinetically trapped by a stabilizer. These nanoemulsions have a low size polydispersity and the external energy required in this process is simply the energy of mixing two miscible fluids; the energy of creating oil droplets of high curvature is gleaned from the internal energy of the system undergoing phase separation. This technique has had much success in batch experiments, however, to avoid batch-to-batch variations and to allow for the possibility of production scale up, it is advantageous to translate this technique to a continuous process. This can be achieved using microfluidics which affords precise control of flow patterns which can allow for high degrees of homogeneous oil supersaturation in a small volume. Additionally, while nanoemulsions do have greater colloidal stability in comparison to micron sized emulsions, even greater colloidal stability can be achieved by utilizing robust interfacially active materials such as solid particles or polymers in comparison to small molecule stabilizers. We present here the capability of stabilizing core-shell nanoemulsions and nanoparticles generated by the Ouzo effect using either crosslinked polymers or solid nanoparticles, under continuous flow in glass capillary microfluidics. The low energy requirements of the process makes it economically feasible and continuous production using microfluidics allows for greater scales of emulsion/particle production. The use of a polymerizable oil allows for the creation of solid nanoparticles using the same technique. Using this technique, dextran nanocapsules have been formulated with an average size of 120 nm – about an 80 nm reduction in size from the batch case – with high uniformity, while silica Pickering nanoemulsions have been formulated with an average size of 300 nm. We will discuss the conditions that facilitate the stabilization and formation of nanocapsules with polymer and nanoparticle shells.

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Mon-BM1-02

Surface tension of micro- and milli-meter size bubbles in surfactant-laden aqueous solutions

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Surface tension is a key property that governs the formation processes of multiphase systems, ranging from sea spray aerosol generation to firefighting foam production. The size of sea surface bubbles and that of firefighting foams are usually from tens of micrometers to a few millimeters in diameter. Here, we use a microfluidic tensiometer (micrometer scale) and pendant drop (millimeter scale) methods to directly measure the surface tension of the air bubble in surfactant-laden aqueous solutions. The established

microfluidic platform is based on bubble deformation under an extensional flow with the deforming force mainly contributed by viscous effect instead of inertia force. Pendant drop measurements are carried out using a drop shape analyzer (Kruss DSA-30). Surfactant-free aqueous solutions are first studied to determine appropriate conditions for accurate measurement using microfluidics, including viscous effect quantification and the ratio of bubble size to the channel height. Then, dynamic surface tension is measured by adding Dow 502W additives to the system with a neat interface. The measurements indicate high curvature found with the micrometer sizes facilitates surfactant transport to the liquid-vapor interface.

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Mon-BM1-03

Artificial intelligence enhances control parameter space investigation in flow-focusing droplet generation

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Microfluidic-generated monodisperse, micron-scale droplets are widely used in research and industry, largely for applications in biomedicine, biosciences and engineering, and pharmaceutical sciences. Desired features of the process include controllable droplet size, uniform shape, and a high yield of drops. It may also be important to avoid the jetting regime in favor of dripping or pinch-off regimes. The phenomenon of droplet generation is controlled by dimensionless parameters including the Weber number, Capillary number and viscosity ratio between the fluids. We have some understanding of the dependence of droplet size and the dripping-to-jetting transition on these parameters. However, the governing equations are non-linear, and only few analytical approximations can be used to describe portions of the control space. In practice, the control parameters adjusted in lab include flow rates or driving pressures for the inner (droplet) and outer (suspending) fluid phases. This manuscript demonstrates the ability to efficiently investigate the lab-parameter space by using Bayesian optimization, a machine learning sequential design strategy. We use a flow-focusing geometry in a microfluidic chip and collect optical microscopy images of droplet formation. The AI/ML method starts with a training data set of droplet images and then directs users to test particular values of the oil and water pressure drops to optimize for desired drop features. In addition to exploring the parameter space efficiently and optimizing the target outcome, the results map the device configuration space. This configuration space mapping technique has tremendous potential to efficiently optimize the design and use of droplet-generating devices.

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Mon-BM1-04

Bijel derived hydrogel ropes via microfluidic twisting

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Bicontinuous interfacially jammed emulsion gels (bijels) are soft materials that retain a liquid bicontinuous network stabilized by an interfacially jammed layer of nanoparticles. [1],[2] Bijels have potential applications in tissue engineering, catalysis, electrochemical devices, filtration membranes, and food products. Solvent Transfer Induced Phase Separation (STRIPS) allows for the continuous production of bijel fibers.[3] Recently, we have introduced microfluidic twisting to fabricate high-tensile strength bijel fiber ropes. [4] However, the continuous production and collection of bijel fiber ropes still poses challenges. Here, we show that the centrifugal force is the central control parameter to enable continuous bijel fiber rope collection. To this end, we vary the densities of the bijel and the surrounding fluid during microfluidic twisting. High-speed



video microscopy shows that the continuous collection of infinitely long bijel fiber ropes can be realized when the density of the bijel fibers remain below the density of the surrounding fluid. This advance allows us to twist fibers with different mechanical properties, chemical compositions and building blocks into ropes. We investigate this by converting bijel fiber ropes into hydrogels with different swelling behaviors and analyze their chiral deformation response. Our work introduces stimuli-responsive composite hydrogel helices with potential applications in soft robotics and as active matter.

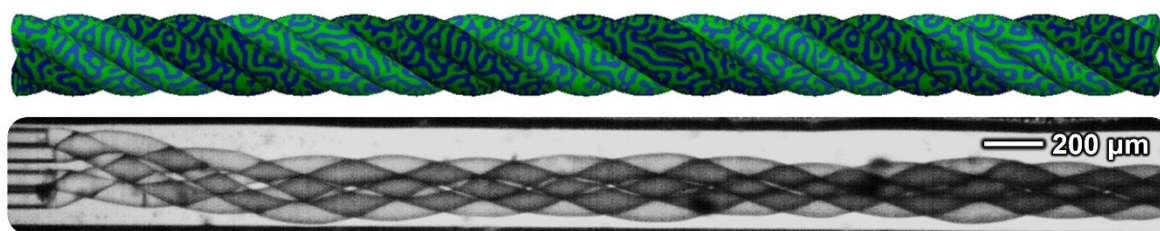


Figure: An animation representing structure of a bijel bundle (top) and a micrograph of a bijel bundle (bottom)

References: [1] K. Stratford, R. Adhikari, I. Pagonabarraga, J. C. Desplat, M. E. Cates, *Science*. 2005. [2] E. M. Herzig, K. A. White, A. B. Schofield, W. C. K. Poon, P. S. Clegg, *Nat. Mater.* 2007. [3] M. F. Haase, K. J. Stebe, D. Lee, *Adv. Mater.* 2015. [4] S. P. Kharal, R. P. Hesketh, M. F. Haase, *Adv. Funct. Mater.* 2020.

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Mon-BM1-05

Synthesis and concentration of size-selected acoustically vaporizable nanodrops

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Over the last few decades, ultrasound with microbubbles (MBs) has been developed as an efficient and economically viable method for biomedical diagnostics and therapeutics. Recently, this method has been employed for super-resolution ultrasound imaging of microvascular architecture and blood flow in deep tissue structures that are inaccessible with optical techniques. While MBs provide a strong acoustic signal, their concentration has to be carefully titrated to achieve sufficient numbers to map the micro-vessels while avoiding too many MBs that may cause overlap of their point spread functions, as well as attenuation and multiple scattering effects. One way to overcome this challenge is to use acoustically vaporizable nanodrops (NDs), which are non-echogenic but can be converted by phase transformation into echogenic MBs by application of an acoustic pulse. Conversion of NDs to MBs provides an on-demand way to generate acoustic signals within the target tissue. NDs may also have additional advantages, such as prolonged circulation lifetime and the ability to extravasate from leaky vessels in tumors and ischemic tissue. One method to produce vaporizable NDs is to condense fluorocarbon-filled MBs with pressure and cooling. Once condensed, the NDs are metastable against spontaneous conversion to MBs owing to the energy barrier for homogeneous nucleation, but they can be vaporized acoustically with pulses exceeding the threshold mechanical index. Here, we describe a method to formulate MBs prior to condensation to NDs, in order to tailor the size and concentration of the resulting ND suspension. Our formulation method yields a concentrated ( $\sim 10^9$ /mL) ND suspension with >90% of the population having a diameter less than 1  $\mu\text{m}$ . These NDs can be acoustically vaporized by a clinical ultrasound imaging scanner to MBs of 5  $\mu\text{m}$  diameter or less, providing safe and effective contrast for super-resolution and other imaging modes.

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Mon-BM1-06

Shape Memory Poly( $\beta$ -hydroxythioether) Foams for Oil Remediation in Aquatic Environments or Biomedical Tissue Scaffolding Implants

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Shape memory poly( $\beta$ -hydroxythioether) foams were produced using organobase catalyzed reactions between epoxide and thiol monomers, allowing for the rapid formation of porous media within approximately 5 minutes, confirmed using both rheology and physical foam blowing. The porous materials possess ultra-low densities ( $0.022 \text{ g} \times \text{cm}^{-3}$ ) and gel fractions of approximately 93%. Thermomechanical characterizations of the materials revealed glass transition temperatures tunable from approximately 50 to 100 °C, elastic moduli of approximately 2 kPa, yield stresses of up to nearly 65%, and complete strain recovery upon heating of the sample without a load. For environmental utility, the foams were characterized for their ability to take up oil from an aqueous multilayered ideal environment, revealing more than 2000% mass of oil (relative to the foam mass) could be collected. Importantly, while post-fabrication functionalization was possible with isocyanate chemistry followed by addition of hexadecanethiol or 3,3-bis(hexadecylthio)propan-1-ol, the oil collection efficiency of the system was not significantly enhanced, indicating that these materials, as porous media, possess unique attributes that make them appealing for environmental remediation without the need for costly modifications or manipulations. Subsequent studies have expanded the monomer library for additional thermomechanical property tuning, focusing on both commercially available monomers as well as bioderived materials including terpenes and terpenoid species. In this manner, SMP functionality and utility may be enhanced to include both environmental remediation as well as biomedical applications such as use as a tissue scaffold.

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Mon, 14 09:00 - 11:00

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Mon-CM1-01

Superdiffusive paste from active particles driven by collective phenomena of ionic salt dissolution

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One challenge in the field of active particles that has not been completely resolved to date is identifying applications where active propulsion will provide unique functionality without increased complexity and cost. Current types of active particles are subject to rather complex fabrication techniques, or the means of their propulsion (such as AC fields, magnetic fields or  $\text{H}_2\text{O}_2$  media) are difficult to transcribe in real world active systems. We are introducing here a new ultrasimple system of interacting active particles, which we name superdiffusive paste. This paste demonstrates the collective dispersal of rapidly dissolving particles. The radial dispersion is driven by osmotic propulsion, created by the solute concentration gradients formed by the dissolution of salt particles. The resulting paste has extraordinary properties in being able to immediately spread rapidly and infuse crevices and cavities due to the directional propulsion of the particles. Thus far, we have observed dissolving particles of  $\text{NH}_5\text{CO}_3$ ,  $\text{NaCl}$ , and  $\text{NaHCO}_3$  actively propelling radially to the respective dispensed paste bolus when released in acidic solution. The rate of particle dispersion is tunable by moderating the pH of the surrounding medium. These active ionic salt particles are able to move up to speeds of 2.2 mm/sec. With the ability to rapidly disperse across a relatively large area, this superdiffusive paste may have potential in biomedical applications for rapid disinfection and pharmaceutical delivery.

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Mon-CM1-02

Spontaneous helix formation in thermoresponsive colloidal chains

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We prepare thermoresponsive colloidal chains by lining up PNIPAM microgel-coated PS colloids in an AC electric field and crosslinking them. We control the flexibility of the colloidal chain by varying crosslinking time. Above the LCST of PNIPAM, these chains behave like they are in a bad solvent and exhibit strong monomer-monomer attractive interactions. Here, we demonstrate that these chains exhibit thermally-induced reversible transitions. All the chains show a decrease in size on heating. For rigid chains, the decrease is modest and is not accompanied by a change in shape. Flexible chains form relatively compact structures, resulting in a large increase in the local monomer number density. For chains with intermediate flexibility, the balance between chain rigidity and inter-particle attraction results in the formation of helix-like structures. The fraction of monomers that form helix-like structure increases with temperature and plateaus above the collapse transition temperature of the microgel particles. Thus, in chains where there is no directional specificity to the interactions between monomeric beads, we obtain helical structures when chains with intermediate flexibility collapse. Our work suggests that a purely mechanical instability for semiflexible filaments can drive helix formation, without the need to invoke any directional interactions. We also simulate a minimal model which suffices to explain the spontaneous emergence of the helical conformations of the polymeric chain.

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Mon-CM1-03

## NIPA-Shelled Liquid-Core Capsules Exhibiting Reversible Temperature-Induced Pearlescence

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Pearlescence, or pearl-like appearance, is a property exhibited by solid structures like nacre (also called 'mother-of-pearl'). Flowable formulations such as coatings and cosmetics (e.g., creams and shampoos) are also designed to be pearlescent because it creates a pleasing visual effect (with sheen and lustre). In the latter cases, pearlescence is induced by adding inorganic plate-like particles to a polymeric binder. Here, we demonstrate that a class of aqueous hydrogel capsules transition from a clear, transparent state to a pearlescent state upon heating (even though no plate-like particles are present in the capsule). The transition is reversible and the original state is recovered upon cooling. The structures exhibiting the above transition are capsules with a liquid core and concentric layers of a biopolymer gel and a covalent gel of N-isopropylacrylamide (NIPA). Such a multilayer capsule is prepared by an 'inside-out polymerization' technique recently developed by our labs. At room temperature, the above capsules are colorless and transparent. When heated above the lower critical solution temperature (LCST) of NIPA (~ 32°C), the capsule becomes turbid and pearlescent. The latter can be quantified by specular reflectance measurements. The mechanism for the onset of pearlescence will be discussed in this talk and correlated to the multilayer architecture of the capsule. Our work provides new insights into the origin of structural color and visual effects in nature as well as in biomimetic materials. The phenomenon could also find application in the cosmetics and coating industries.

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Mon-CM1-04

## Multi-stimuli responsive vesicles

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Catanionic vesicles are nanocontainers (size ~ 100 nm) that are formed by the self-assembly of two oppositely charged single-tail surfactants. They have an aqueous interior surrounded by a bilayer membrane formed by these surfactants. Solutes encapsulated in these vesicles slowly get released through the bilayer via diffusion. However, high solute concentrations usually cannot be achieved using passive diffusion from vesicle membranes. Hence, researchers have been working towards creating stimuli-responsive vesicles for enabling burst release of payloads by disrupting these vesicle membranes. In this regard, external stimuli such as pH, temperature and light are often used. One additional stimulus that is of interest to several researchers involves reactive oxygen species (ROS). These ROS are routinely generated in living organisms and are essential for maintaining a balance in several physiological processes. It is also well known in the literature that ROS levels are usually much higher in tumor microenvironments than in normal tissues. Thus, if vesicle membranes responsive to ROS can be developed, the system could potentially be useful in cancer treatment. By utilizing this idea, we developed low-cost, simple, ROS responsive catanionic vesicle containers made from commercially available surfactants. Especially, we use a light and ROS responsive cationic molecule that is a commonly used photoinitiator and a photo-acid generator. When exposed to ROS or when irradiated with ultraviolet light (UV) or when heated to a higher temperature, it converts to a more hydrophilic structure or loses its charge. In turn, the vesicles are converted into micelles due to an increase in the critical packing parameter or loss of ionic interactions, thereby ensuring burst release of contents. Such stable, multi-responsive vesicles are desirable in many applications.

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Mon-CM1-05

Enzyme-powered protocells from double emulsion-templated microcapsules

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Protocells are synthetic cells that mimic the size and organization of biological cells but can be built from novel components, including polymers. Unlike lipid-based protocells, which are fragile and have limited chemical functionality, polymer-based protocells are stable and can be imparted with advanced functionalities that enable greater control over their properties. A goal of our research is to make motile polymer-based protocells whose motion is driven by enzymatic reaction. Uniform protocells are templated from water-in-oil-in-water (W/O/W) double emulsions droplets, allowing for precise control over the size of the particles as well as their composition. We explore two possible polymer-based protocells: 1) polymersomes based on poly(ethylene glycol)-poly(butadiene) (OB) diblock copolymer and 2) microcapsules based on poly(lactic-co-glycolic acid) (PLGA). We show that highly uniform polymersomes can be rapidly generated by modulating the interfacial tensions of microfluidic double emulsion droplets using Pluronic triblock copolymers. PLGA microcapsules templated from double emulsion droplets provide a complementary core-shell structure. One significant advantage of using microcapsules over vesicles is that the core-shell structure is maintained during the dewetting transition, leading to the formation of relatively uniform shells with high stability. We demonstrate the use of these capsules by attaching enzymes, including catalase, to the shell through a combination of NHS-amine and biotin-avidin chemistry. We then examine their motion in solution in response to enzymatic turnover. Our work offers unique polymersome and microcapsule approaches for preparing highly uniform protocells that can be used to screen differences between the thermodynamic and kinetics properties of enzymes and the effects such properties have on observed particle motion.

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Mon-CM1-06

Methods for encapsulating mobile microparticles

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Particle containing composite microcapsules have become increasingly prevalent and are widely employed in a wide range of applications including pharmaceutical, personal care, nanocomposite self-healing barrier films and coatings industries. Most commonly, small particles are held at the interface (as seen in colloidosomes), or physically arrested in a solid core. Microencapsulation through polymerization or precipitation on the interface of emulsion droplets, has been widely successful in creating capsules of fluids that can be then incorporated in other media. However, due to surface energy, Pickering stabilization, or adsorption of particles at interfaces, it is difficult to synthesize microcapsules of suspensions of freely diffusive or movable particles. Various examples exist, however they typically lack robustness in their material and physical properties. We present various approaches to encapsulating spatially manipulatable microparticles, over a broad particle size range (1-50 microns in diameter), within the core of a microcapsule, avoiding substantial Pickering stabilization and adsorption. One approach uses an emulsified yield stress suspensions encapsulated through a standard polyurea interfacial polymerization. This yield stress material is tuned to match the physical properties of the encapsulated microparticles to hinder particle diffusivity to the capsule walls during polymerization and to balance gravity induced settling, whilst also not permanently fixing particle locations. Particles are actively released through either a temperature change or by manipulation of particles through external forces. This was demonstrated with a magnetic field for Janus particles functionalized with a ferromagnetic coating of iron oxide to directly visualize particle translation and rotation. A second approach looks at the use of density matching between binary solvents and microparticles in polyurea based microencapsulations to achieve a similar effect without the need for an external activating force. Both methods prove viable over a range of particle sizes and could be applicable to a number of composite microcapsule applications. This work was supported by the Applied Physics Laboratory at Johns Hopkins University.

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Mon, 14 09:00 - 11:00

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Mon-DM1-01

Colloidal vitrification is a spontaneous non-equilibrium transition driven by osmotic pressure  
**(Keynote Lecture)**

**Roseanna Zia (rzia@stanford.edu)**, **Jialun Wang (JGalenWang@lbl.gov)**

Stanford University

Persistent dynamics in colloidal glasses suggest the existence of a non-equilibrium driving force for structural relaxation during glassy aging. But the implicit assumption in the literature that colloidal glasses form within the metastable state bypasses the search for a driving force for vitrification and glassy aging and its connection with a metastable state. The natural relation of osmotic pressure to number-density gradients motivates us to investigate the osmotic pressure as this driving force. We use dynamic simulation to quench a polydispersed hard-sphere colloidal liquid into the putative glass region while monitoring structural relaxation and osmotic pressure. Following quenches to various depths in volume fraction  $\phi$  (where  $\phi_{RCP} \approx 0.678$  for 7% polydispersity), the osmotic pressure overshoots its metastable value, then decreases with age toward the metastable pressure, driving redistribution of coordination number and interparticle voids that smooths structural heterogeneity with age. Overall, the osmotic pressure drives structural rearrangements responsible for both vitrification and glassy age-relaxation. We leverage the connection of osmotic pressure to energy density to put forth the mechanistic view that relaxation of structural heterogeneity in colloidal glasses occurs via individual particle motion driven by osmotic pressure, and is a spontaneous energy minimization process that drives the glass off and back to the

metastable state. This connection of energy, pressure, and structure identify the glass transition,  $0.63 < \phi_g \leq 0.64$ .

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Mon-DM1-02

### Investigation of the Yielding Transition in Concentrated Colloidal Systems Via Rheo-XPCS

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We probe the microstructural yielding dynamics of a concentrated colloidal system by performing creep/recovery tests with simultaneous collection of scattering data via X-ray Photon Correlation Spectroscopy (XPCS). This combination of rheology and scattering allows for time-resolved observations of the microstructural dynamics as yielding occurs, which can be linked back to the applied rheological deformation to form structure-property relations. To more accurately track the non-equilibrium processes that occur under yielding, we utilize two-time correlation functions, which provide additional time-resolved information that is inaccessible via more typical one-time correlations. Under sufficiently small applied creep stresses, examination of the correlation in the flow direction reveals that the scattering response recorreates with its pre-deformed state, indicating nearly-complete microstructural recovery. Conversely, larger creep stresses lead to decorrelated structures, and increase the speed of the dynamics under both applied creep and recovery. The data show a strong connection between the microstructural dynamics and the acquisition of unrecoverable strain. By comparing this relationship to that predicted from homogeneous, affine shearing, we find that yielding transition concentrated colloidal systems is highly heterogenous on the microstructural level. We also show the presence of fractal 2-time correlations in less concentrated systems, as well as stochastic behavior in the vorticity direction.

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Mon-DM1-03

### Effect of Interdroplet Interactions on the Rheology of High Internal Phase Emulsions (HIPEs)

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High internal phase emulsions (HIPEs) are formed when the volume fraction of dispersed internal phase exceeds 74%. The HIPEs can be used in different applications such as cosmetics, food, and templates for producing the porous polymeric materials. The adhesive and non-adhesive droplets of HIPEs behave differently under shearing owing to the difference in the interdroplet interactions. However, the effect of droplet size on the rheological properties of HIPEs with different interdroplet interactions has not comprehensively been studied yet. Therefore, in the present work, we investigate the rheological properties, i.e. dynamic moduli and yield stress, of the adhesive and non-adhesive HIPEs with different droplet sizes. In addition, the scaling behaviors of the rheological properties with different droplet size are investigated.

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Mon-DM1-04

Glass and gel formations in macro- and nano-emulsions in the presence of micellar depletion attraction

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In this work, we study the rheological behaviors of o/w ionic emulsions from micro- to nano-size droplets with different volume fractions above the CMC of the surfactant. We determine the total interdroplet interaction from electrostatic, van der Waals, and depletion attraction contributions. We then discuss the rheological properties and physical state (liquid, gel, or glass) of these emulsions by considering the calculated interdroplet interactions. We suggest a phase diagram for studied emulsions in yield stress versus droplet size diagram. A model is proposed to describe the yield stress in attractive glass and gel regimes by considering contributions from Brownian motion and interaction between droplets. The yield strain results suggest that the dissipative rearrangement takes place sooner than macroscopic translational motion of droplets in gels.

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Mon-DM1-05

Shear thickening behavior of silica-based nanofluids

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Polyethylene Glycol (PEG)/silica nanoparticles (NPs) suspensions have been widely used as shear-thickening fluids for advanced applications such as bullet-proof vests. In this study, the effects of different fumed silica nanoparticles (NPs) varying in surface chemistry and particle size on linear and nonlinear rheological behavior of fumed silica NPs- PEG suspensions were investigated. The silica-PEG samples with different amounts of silica NPs were prepared by a mechanical mixer. The shear thickening behavior of silica-PEG samples was studied using a rotational rheometer in a steady state flow mode. Silica 200 (hydrophilic with average particle size (APS) of 12 nm)-PEG and silica 816 (slightly hydrophobic with APS of 12 nm)-PEG samples showed a strong shear thickening behavior at concentrations above 20 wt. %. Whereas silica 300 (hydrophilic with APS of 7 nm)-PEG suspensions follow a different scenario and their flow behavior features a shear thinning behavior at all concentrations. Critical shear rate (onset of shear thickening behavior) for 20 wt. % silica 200-PEG and 20 wt. % silica 816-PEG was determined to be 79.6 and 231 s<sup>-1</sup>, respectively indicating the effect of surface chemistry on shear thickening behavior. The extent of shear thickening behavior of silica 200 incorporated samples was also extremely higher than silica 816 incorporated samples. In the last step of this work, we scrutinized the effect of temperature on shear thickening behavior of silica 200-PEG. Results showed dramatic sensitivity of shear thickening response to the temperature.

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Mon, 14 09:00 - 11:00

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Mon-EM1-01

In Situ Methods to Probe Colloidal Assembly and Interactions in Nonclassical Crystallization  
**(Keynote Lecture)**

**Jeffrey Rimer** ([jrimer@central.uh.edu](mailto:jrimer@central.uh.edu))

University of Houston

Nonclassical pathways of crystallization involve diverse colloidal precursors that range in structure from liquid droplets and amorphous particles to small crystallites. Characterizing both nucleation and growth in systems where crystallization by particle attachment (CPA) is the dominant mechanism is often challenging owing to a series of complex, dynamic events. In this presentation, we will discuss how in situ atomic force microscopy (AFM) can be used to extract fundamental information of CPA processes during the formation of zeolites (i.e. nanoporous aluminosilicates utilized in diverse applications spanning from catalysis and ion

exchange to adsorption and separations). Examples of several zeolite structures will be presented to show their varied pathways of formation. A combination of in situ and ex situ studies using AFM and complementary techniques have been used to extract detailed information about growth by precursors that include amorphous particles, gel-like agglomerates, and nanocrystallites that incorporate into crystals via oriented attachment and/or colloidal assembly processes. Our group has developed a high temperature AFM liquid cell that can be used to track the growth of zeolites in real time, thus allowing for the evaluation of interfacial phenomena at near-molecular resolution. Examples from our studies of zeolites will be compared to other minerals that grow by CPA. We will also show how these unique mechanisms of growth can be used to engineer two-dimensional and hierarchical crystals (e.g. finned and self-pillared zeolites) with markedly improved physicochemical properties and performance in catalytic applications compared to materials prepared by conventional synthesis methods. To this end, we will demonstrate how fundamental knowledge of the colloidal interactions and processes involved in zeolite crystal nucleation and growth can be used to design new generation materials for widespread commercial applications.

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Mon-EM1-02

### Scattering Morphology Resolved Total Internal Reflection Microscopy of Anisotropic Particles

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Total internal reflection microscopy (TIRM) is used to measure the Brownian fluctuations in distance between a colloidal particle and a surface illuminated by an evanescent wave. For spherical particles, the fluctuations in total scattered light intensity are directly related to the fluctuations in separation distance between the particle and surface, typically at a resolution of a few nanometers as the evanescent wave decays exponentially with distance. However, for non-spherical particles, these intensity fluctuations not only result from changes in separation distance, but also from variations in the orientation of the particle with respect to the evanescent wave propagation vector. Hence, in order to retrieve the particle-surface separation distance, it is necessary to decouple the contribution of orientation changes from the total scattered light intensity. Here we present experiments of ellipsoidal particles deposited on a surface at random orientations under camera-based TIRM. We recorded the scattering images of these colloidal particles and then used a two-dimensional Gaussian function to characterize the scattering morphology (called Scattering Morphology Resolved Total Internal Reflection Microscopy (SMR-TIRM)). We measured how these distortions relate to the particle orientation, and local geometry. In addition, we compared our experimental results with simulated scattering images obtained by the T-Matrix method, which can be used to decouple the contribution of the polar and azimuthal angles in the total intensity, and systemically explore how the local geometry affects the scattering morphology. The scattering morphology and the scattering intensity relations could be used to probe the three-dimensional orientation of the particle and the particle-surface distance. We aim to use these data to extend the capabilities of TIRM to measure the interaction energy between an anisotropic colloid and flat plate.

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Mon-EM1-03



Can microfluidic SANS be used to probe the interfacial coating on a drop?

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Polymers and surfactants are commonly used to control the phase behaviour, stability, rheology and most importantly function of formulated products such as shampoos, pharmaceuticals and paints. Understanding how they interact and complex at the interface is critical to enhancing and refining the function of these multi-component emulsions. Measuring the structural properties of polymer-surfactant complexes at liquid-liquid interfaces is non-trivial, typically requiring well-defined and stable emulsions to perform scattering techniques such as small angle neutron scattering (SANS). However recent exploration into combined drop-based microfluidics and scattering techniques have emerged, introducing with it a new generation of microfluidic systems capable of measuring the structure, interactions and kinetic processes of the materials within emulsions. This presentation will explore the use of a novel microfluidic device for performing droplet microfluidic SANS with the purpose of analysing adsorbed layers at the drops interface and their structural confirmation while under flow. SDS and PVP in single and two-phase flow is analysed to understand the molecular structuring of the molecules with increasing degrees of complexity.

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Mon-EM1-04

Surface Tension of Binary Mixtures of Pentane and 2-Methylpentane for Use in Wickless Heat Pipes

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<sup>3</sup> Cleveland Diagnostics Inc.

<sup>4</sup> Scattering Solutions Inc.

Binary mixtures have been shown to improve the function of wickless heat pipes, which offer greater longevity over conventional heat pipes [1]. Fabrication of such wickless heat pipes relies on surface tension effects, such as Marangoni forces, making it essential to understand the interface properties of the liquid and its vapor. Recent improvements in Surface Light Scattering Spectroscopy instrumentation and its software, have not only improved its ease of use but have made possible a substantial improvement in the accuracy of surface tension measurements. With these improvements, we present surface tension and viscosity measurements of a binary mixture system of pentane and 2-methylpentane. The data are fit to an extended Langmuir isotherm model, giving insight into the relative concentration of the various components near the interface, quantified by the surface excess. [1] Nguyen TTT, Kundan A, Wayner PC, et al. The effect of an ideal fluid mixture on the evaporator performance of a heat pipe in microgravity. Int J Heat Mass Transf 2016; 95: 765–772.

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Mon-EM1-05

Interfacial flows and instabilities of Boger Fluids

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Constant viscosity, but finite elasticity make Boger fluids an ideal choice for investigation of the role and influence of elasticity on interfacial flows and instabilities. In this contribution, we examine the pinching dynamics and extensional rheology response of model Boger fluids using dripping-onto-substrate (DoS) rheometry protocols, showing measurable viscoelastic effects even though elastic properties like modulus and first normal stress difference are either below the resolution limit of torsional rheometers or source of elastic instabilities. We thereafter show how elasticity influences fingering instability by visualizing flows within Hele-Shaw cell, and discuss the connections with other free surface flows and instabilities where viscoelasticity can influence pattern formation and evolution.

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Mon, 14 09:00 - 11:00

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Mon-GM1-01

Cell-Material Interactions: Engineering Materials to Manipulate Cellular Processes (**Keynote Lecture**)

**Maryam Daviran (mad315@lehigh.edu), John McGlynn (jam217@lehigh.edu), Kelly Schultz (kes513@lehigh.edu)**

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During the wound healing process, human mesenchymal stem cells (hMSCs) are recruited to an injury where they regulate inflammation and initiate healing and tissue regeneration. To aid in healing, synthetic cell-laden hydrogel scaffolds are being designed to deliver additional hMSCs to wounds to enhance or restart the healing process. These scaffolds are designed to mimic native tissue environments, which includes physical cues, such as scaffold stiffness, and chemical cues, including incorporation of adhesion ligands. In this work, we focus on the feedback loop between presentation of cues to cells designed into the microenvironment and the new microenvironments cells engineer in response to these cues. We encapsulate hMSCs in a well-defined synthetic hydrogel scaffold that recapitulates aspects of the native extracellular matrix (ECM). We then characterize cell-mediated degradation in the pericellular region as a function of microenvironmental cues and cell-secreted molecules. Our hydrogel consists of a 4-arm poly(ethylene glycol) (PEG) backbone end-functionalized with norbornene which is chemically cross-linked with an matrix metalloproteinases (MMPs) degradable peptide sequence. This peptide sequence is cleaved by hMSC-secreted MMPs. We use multiple particle tracking microrheology (MPT) and bi-disperse MPT to characterize spatio-temporal cell-mediated degradation in the pericellular region. In MPT, fluorescently labeled particles are embedded in the material and their Brownian motion is measured and related to rheological properties using the Generalized Stokes-Einstein relation. Bi-disperse MPT embeds two different particle sizes into the material to simultaneously measure rheology on two lengthscales. Using MPT, we characterize the change in rheological properties in the pericellular region during cell-mediated degradation and remodeling. We determine that hMSCs create a microenvironment where the cross-link density decreases as distance from the cell increases. Cells create this microenvironment to keep the scaffold stiff directly around it to spread and attach prior to motility. This is done by simultaneous secretion of scaffold degrading MMPs and tissue inhibitors of metalloproteinases (TIMPs), which inhibit MMP activity and scaffold degradation. We reverse this degradation profile by inhibiting TIMPs after hMSC secretion. Using bi-disperse MPT, we simultaneously measure cell-mediated scaffold degradation and reversible cellular remodeling using cytoskeletal tension on two different length scales. This work highlights the ability for a cell to selectively remodel their microenvironment to enable motility. These measurements increase our understanding of cellular remodeling and the resulting rheological changes in the pericellular region which can then be used to design new implantable biomaterials that can instruct cellular processes for cell delivery to wounded areas.

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Mon-GM1-02

Drop oscillation dynamics on thin immiscible liquid films

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Mechanical Engineering at Baylor University

Drop oscillation dynamics are important to a variety of applications such as drop shedding on condensation surface and water harvesting. While the topic has been widely studied for many decades, the influence of a moving contact line on the oscillation modes of drops remains underexplored. Herein, we report the oscillation of drops on thin liquid films with different viscosities (5cSt, 1000cSt, and 10000cSt), drop sizes (radius: 300 - 1000  $\mu\text{m}$ ) and film thicknesses (1-100  $\mu\text{m}$ ). A gently deposited drop onto an oil film results in surface oscillations via capillarity where the frequency, amplitude, and contact angle are tracked via a high-speed camera. The experimental results between the first mode oscillation frequencies and the equilibrium contact angles for pinned and slipping contact lines were compared with numerical simulations with good agreement. We observed that with higher viscosities the decaying times of the oscillation increased due to slow contact line movement. Because the drop tended to push the oil film and wetted the surface, the equilibrium height of oscillation changed until the contact line was pinned. We hypothesize that the change of the oscillation on different film thicknesses is influenced by the dissipation energy from the contact line breaking the oil film.

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Mon-GM1-03

Relation between a Microphase-separated Structure and Adhesion Properties of Polyurethane-adhered Single Lap Joints

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Kyushu University

Adhesion properties of polyurethane -adhered single-lap joint was investigated. To investigate microphase-separated structure of adhesive of SLJ, small-angle X-ray scattering (SAXS) measurement and birefringence analysis were carried out. PU adhesive was synthesized with poly(oxypropylene) glycol (PPG,  $M_n = 1000$ ), 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD). PU-adhered SLJ exhibited 8 MPa of tensile strength by tensile testing. SAXS and birefringence analysis revealed that stress distribution of SLJ sample is quite complicated in comparison with bulk sample during mechanical deformation.

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Mon-GM1-04

How various surfactant transport pathways affect Marangoni spreading

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Marangoni spreading arises when surface tension gradients are present on a liquid surface. This spreading is common in natural settings and plays an important role in many technological processes, such as pulmonary drug dispersion, oil recovery, and coating processes. Nonuniform deposition of surfactant on a liquid surface drives Marangoni flow. Our goal is to characterize the impact of the various transport pathways surfactant molecules can take during spreading, such as desorption from the subphase surface to the subphase bulk or from the depositing drop surface to the subphase surface. To achieve this goal,

we study the deposition of a surfactant drop on a thick aqueous subphase. We vary the solubility of the surfactant in the subphase, insoluble or soluble, and the delivery environment of the surfactant, neat or in solution. Four surfactant systems provide these variations: insoluble neat surfactant (oleic acid), solution of a surfactant insoluble in the subphase (oleic acid in cyclohexane), soluble neat surfactant (C12E4), and solution of a surfactant soluble in the subphase (C12E4 in water, SDS in water, tyloxapol in water). We probe five characteristics when analyzing the spreading event: the depression of the interface near the surfactant deposition point, the height and speed of propagation of the Marangoni ridge, which is the characteristic surface deformation that forms in Marangoni spreading, the volume of fluid flowing away from the deposition position of the surfactant, and, the relative position of the surfactant front compared to the Marangoni ridge. We have found that the interface depression is affected by the deposition method for the insoluble surfactant case. The speed of the Marangoni ridge is the same for neat insoluble surfactant and two of the three solution soluble surfactant cases (SDS and tyloxapol) and at different concentrations above and below the critical micelle concentration. The differences in spreading between solutions of SDS, tyloxapol and C12E4 may be due to the final surface tension after spreading. SDS does not lower the subphase surface's surface tension after spreading, while C12E4 does. For neat insoluble surfactant and solution soluble surfactant, the Marangoni ridge is ahead of the surfactant front. There also is a linear correlation between the height of the Marangoni ridge and the outflow volume of Marangoni spreading. This signifies that all the characteristics of the ridge cannot be seen as independent.

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Mon-GM1-05

## Marangoni Transport Simulation for Two Interacting Surfactant Sources

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Recently, surfactant laden aerosols have become of particular interest for the possible use in the treatment of obstructive lung diseases. For cystic fibrosis, one of these diseases, mucus forms viscous plaques in the lung which limit airflow and harbor deadly infections. Typically, aerosolized drugs are poorly distributed in the lung because aerosols follow the path of least resistance, away from obstructed regions, and on branch points preferentially. Adding a surfactant to the formulation allows the drug to spread out after deposition due to the generation of surface tension gradients and induction of Marangoni flows driving the drug deeper into the lung. The current research on Marangoni stress driven transport can be split into two groups: in vitro or computational studies of single surfactant sources or in vitro or clinical studies of aerosol spreading. Both give valuable insight into understanding surfactant spreading to treat obstructive lung disease. This work bridges the gap between single-source and multi-source spreading. We model how two simultaneously deposited surfactant sources interact during spreading. Simultaneous spreading of two circular disks of surfactant deposited on the liquid vapor interface was simulated using COMSOL Multiphysics. As the spreading disks interacted, the behavior exhibited three distinct phases. First, the two pucks are isolated and spread without the influence of the other. Next, the disks start to interact which alters the subphase fluid flow, the interfacial height, and the spreading extent of the surfactant. Lastly, the profiles from all three of these indicators merge and produce extrema at the midpoint between the two disks. The onset of these phases is delayed as the initial separation distance between the disks increases. With sufficient separation, spreading slows before one or more of the phases ends. These simulations also give insight into two phenomena observed during in vitro surfactant aerosol experiments. First, individual surfactant laden droplets move along the interface away from other droplets. In the simulations, this occurs when the Marangoni front from one disk moves past the location of the other, dragging it along. Secondly, disks that are very close to one another begin to deform. Deformation in the simulation occurs when the surfactant fronts meet at the symmetry line between the two disks. This work starts the task of combining

the data from two disparate areas in the study of Marangoni driven transport and will lead to the formulation of better treatments for obstructive lung disease.

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Mon, 14 09:00 - 11:00

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Mon-IM1-01

Foam Trapping and Mobility in Porous Media in Surfactant-Alternating-Gas Injection for Enhanced Oil Recovery (**Keynote Lecture**)

**William Rossen (w.r.rossen@tudelft.nl)**<sup>1</sup>, **Jiakun Gong (gongjiakun@gmail.com)**<sup>1,2</sup>

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<sup>2</sup> Hohai University, Nanjing, China

Foam rheology in geological porous media is complex, reflecting capillary forces, non-Newtonian rheology, changing bubble size, and gas trapping. Foam is injected into geological formations for enhanced oil recovery, well stimulation, aquifer remediation, and CO<sub>2</sub> sequestration. Foam is usually placed in the formation through alternate injection of slugs of gas and surfactant solution ("surfactant-alternating-gas" or SAG). Pressure rise at the injection well, especially during liquid injection, is a major problem for foam application. We investigate gas trapping and phase mobilities in SAG processes using CT imaging, multiple gases and sandstone cores of different permeability. Processes that advance very slowly from the injection face have major impact on fluid mobility and pressure rise at the well. During gas injection a region of collapsed foam, related in part to water evaporation, slowly advances. CT images quantify the reduction in liquid saturation and allow an estimate of the limiting water saturation for foam stability. Foam is probably not completely collapsed here, but pathways for gas flow without bubbles enormously increase gas mobility. During liquid injection liquid first invades the collapsed-foam region with relatively high mobility. Ahead of this zone liquid mobility is at first very low. Then liquid fingers form, with some gas displaced within the fingers and a modest rise in mobility. Much more slowly, trapped gas within these fingers slowly dissolves into liquid, with an enormous increase in mobility. Gas trapped around the fingers remains in place, while gas near the edge of the fingers slowly dissolves into injected liquid. CT images confirm the fingering and dissolution processes, and experiments with different gases confirm the role of gas dissolution in the rise of liquid mobility. Thus there are various banks advancing at different velocities from the well: collapsed-foam during gas injection, liquid-fingering and gas-dissolution during liquid injection. Some of these banks show non-Newtonian mobility and variable advance rates as a function of superficial velocity. Upon reinjection of gas, foam immediately forms, even within even the "collapsed" foam region. Subsequent slugs thereafter follow the same behavior as earlier slugs. A model based on radial propagation of the banks incorporates these findings, including nonlinear bank mobilities and advance rates as functions of velocity in radial flow. Conventional reservoir simulators greatly overestimate pressure rise at the well. Partly the issue is grid resolution, but fingering, dissolution and evaporation are not accounted for in current foam models.

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Mon-IM1-02

Effects of interfacial properties on the nucleation of gas hydrates in sediments

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The formation of gas hydrates, a stochastic process, consists of three stages: saturation, induction, and growth. During the induction stage, small hydrate nuclei form or randomly dissociate until a critical cluster radius is achieved leading to hydrate growth. This stage, known as nucleation stage, is critical for hydrate formation. Naturally occurring gas hydrates are largely found in marine sediments. Heterogeneous nucleation takes place during the formation of gas-hydrates in sediments. Unfortunately, there is no clear

understanding on the effects of the various interfacial properties of sediments (i.e., surface wettability, interface curvature and interfacial energies) on the nucleation process of gas hydrates in porous media. Furthermore, it is very difficult to study this problem with experimental methods. In this work, a macroscopic mathematical model incorporating relevant interfacial properties that determine hydrate nucleation in sediments will be discussed. Effects of properties like wettability, interfacial curvature and interfacial energies on induction time and probability of hydrate nucleation will be presented. Model predictions suggest that longer induction time is required to form the same volume of hydrate crystal on gas/liquid/solid triple boundary lines than that on gas/liquid interfaces. That is, nucleation of methane hydrates preferentially occurs in large sediment pores rather than in small sediment pores. Furthermore, the preference in terms of formation of methane hydrates on different interfaces changes with the volume of the formed hydrate crystal and the curvature of the solid surfaces for any given driving force. Modeling predictions show that gas hydrates form first on the gas/liquid interface, then on the gas/liquid/solid triple boundary lines and last on liquid/solid interfaces.

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Mon-IM1-03

Electrolyte-dependent structural heterogeneity and its atomic origin within primary cathode nanoparticles

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<sup>4</sup> Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

We study the electrochemical and structural responses of primary cathode nanoparticles for magnesium ion insertion. By systematically varying the electrolyte, we observe a successful Mg<sup>2+</sup> insertion and the consistent solid-solution phase transition in the nanoparticles. Further examination by scanning electron nanodiffraction (SEND) in scanning transmission electron microscope (STEM) revealed two distinctive strain and phase distribution patterns in the cathode nanoparticles at nanometer resolution regulated by the electrolyte. One is consisted of a uniform, major phase domain distribution due to an elastic strain relaxation mechanism at the atomic level, whereas the other one is consisted of a non-uniform, scattered phase domain distribution or “core-shell” structure with a plastic strain relaxation mechanism. The varied chemo-mechanical behaviors are associated with the coherency strain and charge screening effect occurred in the Mg<sup>2+</sup> insertion revealed at the atomic level by STEM imaging and DFT calculations. Our work shows that electrochemical parameters such as the electrolyte have a direct influence on the cathode structural heterogeneity during Mg ion insertion, which rationally guide the design of battery materials with high stability and capacity.

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Mon-IM1-04

Characterizing solvency effects on asphaltenes in bulk dispersions and their connection to interfacial properties.

**Olivia Haider (ohaider@andrew.cmu.edu), Junchi Ma (junchim@andrew.cmu.edu), Lynn Walker (lwalker@andrew.cmu.edu)**

Carnegie Mellon University

The degree of aggregation and overall stability of asphaltene dispersions is highly dependent on the molecular makeup of asphaltenes, asphaltene concentration in the bulk, and solvent composition. These conditions vary widely between individual asphaltene studies. It has been determined that complex interfacial behavior of asphaltenes, which contributes to the development of highly stable water-in-oil emulsions, are defined by these bulk system conditions. The connection between solvent composition and asphaltene behavior is discussed in the context of asphaltene gradients in crude oil systems; however, further systematic, detailed characterizations of bulk solvency effects are needed in order to fully understand mechanical behavior. The goal of this work is to study the effects of solvent quality on the stability of bulk asphaltene dispersions, and demonstrate a powerful technique to efficiently analyze bulk stability in opaque colloidal systems. A millifluidic device was used to observe long-term stability of asphaltenes with varying ratios of aromatic and aliphatic solvents. These results identified the solvent compositions where the system transitions from globally stable to globally unstable dispersions at steady state. Mechanical measurements in good and poor solvent conditions demonstrate fluid-like behavior under small-amplitude compression and expansion despite showing solid-like behavior at larger compressions in the poor solvent, highlighting the importance of solvency on interfacial properties. This millifluidic technique is shown to be a powerful approach for stability studies in a wide range of opaque systems, and this work furthers the understanding of key system conditions that contribute to the development of highly stable emulsions of water in crude oil.

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Mon, 14 09:00 - 11:00

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Mon-KM1-01

Modelling of virus survival time in respiratory droplets on surfaces

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The microscopic droplets of saliva released when talking, coughing and sneezing remain partly suspended in the air and partly settle on the surfaces depending on their size. Various viruses, including coronaviruses, can survive several hours or days in deposited drops. Virological experiments have shown that temperature, relative humidity and surface properties of the materials influence the persistence of the viruses contained in the drops. In particular, the survival of some viruses has a so-called "U-shaped" dependence on relative humidity (RH), with a peak of mortality at intermediate humidity, while it increases with increasing temperature. Current hypotheses are that climatic conditions determine the physico-chemical history of a drop of saliva as they condition its evaporative process. Since saliva is a complex liquid made up of water and non-volatile compounds such as salts, biomolecules and proteins, the evaporation of water has an effect on the concentration of salts, on the pH, on the agglomeration of biological compounds and on the crystallization of salts, all of which non-physiological and potentially harmful conditions for a virus. However, there is still no mechanistic treatment that links the survival of a virus to the thermodynamic parameters involved. By combining a thermodynamic model of the evaporation of a saline sessile droplet and the relation between a virus viability and the so called cumulative dose of salts (time integral of the salt concentration) we show for the first time a description of the mechanism leading to higher mortality at intermediate RH, a prediction of the survival time of some coronavirus surrogate viruses (Fig. 1) and the foundations are laid to understand the link between viability and contact angle [1].

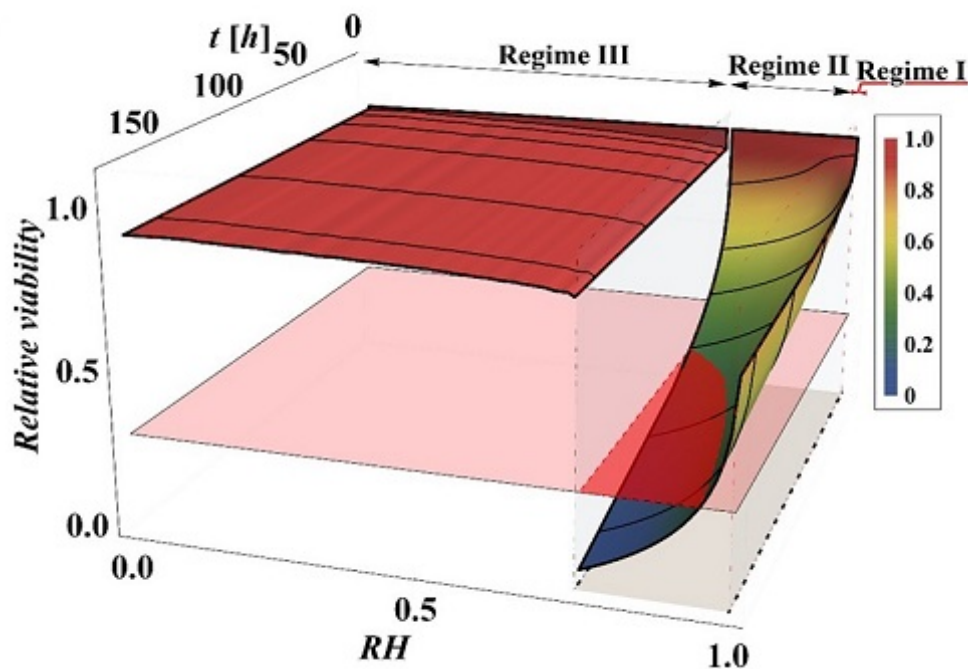


Figure 1. Model calculations of relative viability of a virus as a function of time and RH, for a starting volume of the drop equal to 1 ml, initial NaCl concentration 10 kg/m<sup>3</sup> and initial contact angle. [1] Di Novo NG et al. (2021) Modeling of Virus Survival Time in Respiratory Droplets on Surfaces: A New Rational Approach for Antivirus Strategies. *Front. Mater.* 8:631723. doi: 10.3389/fmats.2021.631723

Mon-KM1-02

Reversible capturing of living bacteria on a non-adhesive surfaces via depletion force

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The adhesion of bacteria to surfaces is associated with infections, biofouling, and biofilm formation. To avoid cell adhesion, researchers have been focusing primarily on surface chemistry and topography to develop resistant coatings. However, there have been very limited discussions of the role of non-adsorbing polymers in the cell suspension, and the role of polymer-induced depletion forces that drive cell adhesion on surfaces, even though bacteria are often found in polymer rich environments. Here, we demonstrate that with the presence of polyethylene glycol (PEG) in solution, *E. coli* can be captured on a carefully engineered non-bioadhesive surface that is fundamentally completely resistant to cell adhesion. The captured *E. coli* are alive, actively growing and can be released from the surface with the removal of the depletant. The PEG also causes cells to aggregate in bulk solution. The depletion driven aggregation and depletion driven surface capture are two competing mechanism in this system.

Mon-KM1-03

Continuous, Real-Time Detection of Protein-Protein Interactions at the Solid/Liquid Interface

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During disease spread, an infected individual can potentially infect more than 100 others during short time spans. Situations like these are known as super-spreader events and are common in pathogenic disease transmission. Real-time monitoring of airborne bioaerosols expelled from infected individuals could provide live updates on disease spread, and disease density if placed strategically throughout the civilian population. Due to the utility that real time bioaerosol sensing would provide to public health and safety, much research has been done to develop such platforms. Significant progress has been made on systems that collect and concentrate bioaerosols, but there is a need for development of low-cost detection systems capable of continuous sensing with the required sensitivity. Microfluidic-based fluorescence sensing technology is ideally suited for development of such a low cost, continuous sensor. The detection system is based on a fluorescent assay that detects the interaction between S1, the binding subunit of the SARS-CoV-2 SPIKE receptor recognition protein, and surface immobilized angiotensin-converting-enzyme 2 (ACE2), the SARS-CoV-2 receptor. ACE2 is immobilized in a microfluidic channel via biotin/streptavidin chemistry and sample is continuously flowed over it. A fluorescent label that is sensitive to the local electrostatic potential (local hydronium concentration, pH) can be attached to ACE2 via random labeling of free amine moieties and exhibits a change in fluorescence intensity when the positively charged S1 subunit binds and changes the local electrostatic potential (decreases local hydronium concentration). In the current design, ACE2 is randomly labeled with carboxy-fluorescein (CF), a pH sensitive label which shows a “turn-on” of fluorescence as the positively charged S1 subunit recruits hydroxide ions and induces reversible deprotonation and gain of fluorescence. This fluorescence detection system is applicable to any pathogen with a specific ligand receptor interaction. In its current state, the developed assay has application in single use, point of care settings, where a swab can be obtained directly from a patient. It is particularly suited for applications requiring mobile testing, or testing in resource limited environments, as microfluidic and mobile fluorescence detection technologies are portable and cheap to produce. The limitations of this device and other ligand-receptor sensing technologies for the purpose of real time, continuous bioaerosol sensing will be discussed.

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Mon-KM1-04

### Copper Oxide Coatings that Reduce Infection by SARS-CoV-2

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<sup>2</sup> School of Public Health, LKS Faculty of Medicine, The University of Hong Kong, Hong Kong Special Administrative Region, China.

COVID-19 is caused by the virus, SARS-CoV-2, that is known to remain viable for up to one week on certain solids. The aim of this research is to create coatings that lead to more rapid inactivation of the virus, thereby shortening the period during which people can be infected from solids. We have focused on copper-based coatings and here discuss the ability of a porous CuO coating to reduce infection from solids. We have fabricated a coating of CuO by oxidizing and sintering Cu<sub>2</sub>O particles into a 30-50 μm layer on glass and then tested infection of Vero E6 by SARS-CoV-2 extracted from the solid. Infection from the solid is much lower (99.9% lower) than from uncoated glass after half an hour on the 30 μm-thick coating. Unlike Cu<sub>2</sub>O, leaching of copper species is not important and contact killing is more likely. The imbibition of liquid droplets into the coating is very important for a fast reduction in infection because it reduces the transport distance, increases the area for adsorption, and speeds evaporation. We describe the imbibition as a function of humidity and the effect of the porous layer on drying of droplets.

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Mon-KM1-05

### kT-scale Colloidal Interactions Mediated by Protein Coronas on PEG and Zwitterionic Copolymers

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Proteins are a critical element of the immune system response to foreign particles via adsorption, or formation of a “corona”. Polymer coatings on particles with repulsive interactions towards proteins provide a potential mechanism for particles to evade detection by the immune system. Current methods to interrogate protein coronas are often expected to perturb weakly bound proteins, which perhaps provides some explanation for conflicting results from different assays. This talk will present findings on  $kT$ -scale measurements of how the most abundant serum proteins interact with PEG and zwitterionic copolymers adsorbed to hydrophobic colloids and surfaces. Specifically, we use total internal reflection microscopy (TIRM) to directly and sensitively resolve interactions mediated by adsorbed and unadsorbed proteins with nanometer- and  $kT$ - scale resolution. Given that different protein mediated interactions are mutually exclusive, our results provide unambiguous information on the presence of protein coronas. Our results include several qualitatively different interactions indicating either the presence or absence of protein coronas for combinations of different proteins (e.g., serum albumin, immunoglobulins) and PEG or zwitterionic copolymer coated colloids and surfaces. Measured interactions and corresponding corona states include: bridging interactions for incomplete coronas, increased steric interactions for saturated coronas, and depletion interactions for unadsorbed proteins (absence of corona). These findings demonstrate non-intrusive measurements of protein mediated colloidal interactions as a sensitive probe of corona formation with implications for immune responses to different polymer coatings adsorbed to colloidal particles.

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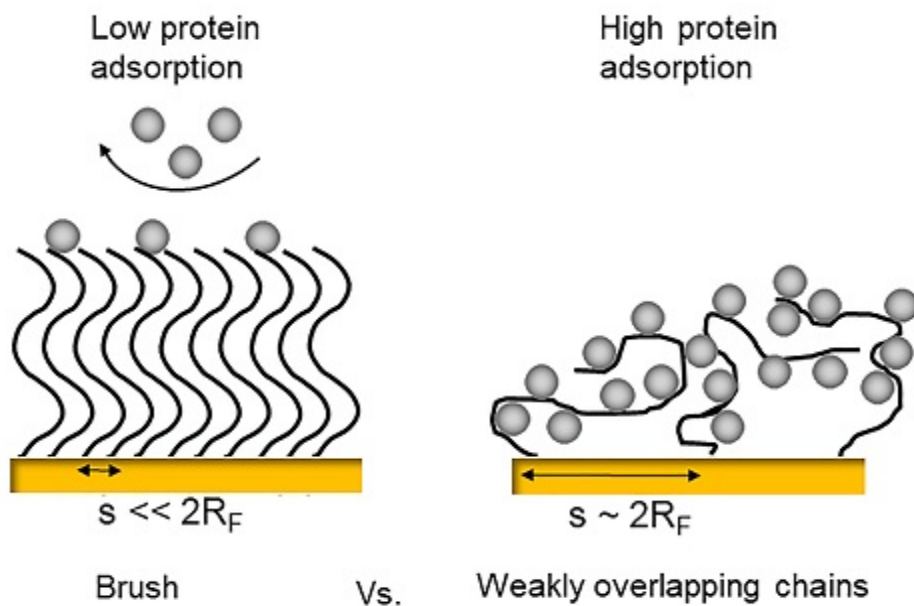
Mon-KM1-06

Design rules for tuning protein adsorption on grafted zwitterionic thin films

**Syeda Tajin Ahmed (tajinahmed0802@gmail.com), Deborah Leckband (leckband@illinois.edu)**

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This study demonstrates that protein adsorption on end-grafted poly(sulfobetaine) or pSB thin films depends on the chain grafting density, molecular weight, and ionic strength. Zwitterionic polymers contain cationic and anionic groups, and reportedly exhibit ultralow non-specific fouling (protein adsorption) and excellent biocompatibility. This picture contrasts with findings that that soluble pSB chains bind proteins and alter their folding stability. To address this apparent contradiction, we investigated the dependence of protein adsorption on end-grafted pSB thin films under a range of grafting conditions; namely, the grafting density, molecular weight and ionic strength. Guided by polymer theory, studies compared the adsorption of phosphoglycerate kinase (PGK) and positively charged Lysozyme as a function of the scaled grafting parameter  $s/2RF$ . Here,  $s$  is the distance between grafting sites, and  $RF$  is the Flory radius. With both proteins, plots of the adsorbed protein amount versus  $s/2RF$  exhibits a bell shaped curve, with a maximum near  $s/2RF \sim 1$  and an amplitude that decreases with ionic strength. This behavior is qualitatively consistent with theoretical models for colloid interactions with weakly attractive, grafted chains. In such models, adsorption is controlled by competition between protein-segment attraction and osmotic repulsion, which impedes protein insertion into the brush. The results from this study confirm that proteins do adsorb to pSB thin films. They also suggest an underlying mechanism. Comparison with polymer models further identify design rules for pSB films that effectively repel proteins.




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Mon, 14 09:00 - 11:00

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Mon-MM1-01

Aluminum Nanocrystal Growth Chemistry: Similarities to our Noble Neighbors (**Keynote Lecture**)

**Naomi Halas (halas@rice.edu)**

Rice University

The case for advancing the fundamental chemistry of Aluminum nanocrystals is a strong one: as the most abundant metal on earth with excellent optical/plasmonic properties, there is extraordinary potential for many applications initially envisioned for Au and Ag to be realized with Al NCs. For the past several years we have been studying the nucleation and growth chemistry of Al NCs to develop pathways towards highly regular size and shape control. Unique to Al nanocrystals is the dependence of Al NC growth on a catalyst, and both the molecular structure and the chemical composition of this catalyst have strong effects on the resulting nanocrystal morphology. The specific catalyst and solvent combination can control both Al NC morphology and size. Thermodynamic versus Kinetic controlled growth regimes can be obtained within this parameter space, resulting in pathways to reduced-symmetry nanocrystalline structures. While the nucleation and growth chemistry differs profoundly from that of the fcc noble metals, we are beginning to establish several routes to controlled Al NC growth of several of the canonical fcc morphologies, such as nanocubes, octahedral, nanorods, and nanoplatelets, as well as new morphologies that are rarely if ever seen in noble metal nanoparticle synthesis.

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Mon-MM1-02

Advances in Single-Particle Spectroscopy Using Fast Electrons

**David Masiello (masiello@uw.edu)**

Department of Chemistry, University of Washington

In this talk I will highlight our recent research in low-loss STEM-EELS. Emphasis will be placed on modeling the interaction of the fast electron probe with surface plasmon and photonic cavity modes in individual

nanoparticles and their few-particle assemblies. Several topics ranging from plasmonic energy transfer, weak-to-strong coupling, Fano antiresonances, and magnetic plasmon hybridization will be discussed.

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Mon-MM1-03

### Synthetic Size Control over Plasmonic Magnesium Nanoparticles

**Elizabeth Hopper (erh64@cam.ac.uk)**<sup>1,2,3</sup>, **Thomas Wayman (tmrw2@cam.ac.uk)**<sup>1,2</sup>, **Jeremie Asselin (ja680@cam.ac.uk)**<sup>1,2</sup>, **Christina Boukouvala (cb955@cam.ac.uk)**<sup>1,2</sup>, **Laura Torrente-Murciano (lt416@cam.ac.uk)**<sup>3</sup>, **Emilie Ringe (er407@cam.ac.uk)**<sup>1,2</sup>

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Plasmonic materials have broad applications in chemical and biological sensing, surface enhanced spectroscopy, photothermal cancer therapy and photocatalysis. Magnesium is a recent addition to the plasmonics toolbox and provides an earth-abundant alternative to gold and silver. Size and shape, in addition to composition and surrounding environment, dictate plasmonic behaviour; in principle the plasmon resonances in Mg nanoparticles can be maneuvered across the ultraviolet, visible, and near-infrared. However, limited size and shape control has been demonstrated so far, with most approaches relying on top-down fabrication such as electron-beam lithography and ion-beam milling, both slow and expensive. Our colloidal synthesis provides a facile, scalable and inexpensive route for the production of Mg nanoparticles via the reduction of an organometallic precursor, with the potential for considerable size and shape control. Mg's hexagonal close packed structure and variety of twinning patterns open the door to new morphologies unlike those of the common plasmonic materials crystallising in a face centred cubic structure. We produce single crystalline hexagonal platelets and a variety of twinned folded shapes such as tents, chairs, tacos and filled rods. Variation of the reaction temperature, dilution and electron carrier produces size-controlled particles from 80 nm to over a micron in size, with strong size- and shape-dependent plasmonic resonances across the ultraviolet, visible, and near-infrared. Further, our recent efforts on adapting the batch reaction to produce Mg NPs in scalable, continuous flow microreactors allows precise control over the reaction conditions and sequential addition of further reagents.

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Mon-MM1-04

### Nano-Plasmonic photo-catalysis - "Hot electrons" or just heating?

**Yonatan Dubi (jdubi@bgu.ac.il)**<sup>1</sup>, **Yonatan Sivan (sivanyon@bgu.ac.il)**<sup>2</sup>

<sup>1</sup> Department of chemistry, Ben Gurion University of the Negev

<sup>2</sup> School of Electrical Engineering, Ben Gurion University of the Negev

What happens to electrons in a metal when they are illuminated? This fundamental problem is a driving force in shaping modern physics since the discovery of the photo-electric effect. In recent years, this problem resurfaced from a new angle, owing to developments in the field of nano-plasmonics, where metallic nanostructures give rise to resonantly enhanced local electromagnetic fields (surface plasmons). Presumably, these plasmons can transfer their energy to the electrons in the metal very efficiently, creating "hot electrons", i.e. energetic electrons out of equilibrium. Such energetic electrons have been demonstrated to be useful in a variety of ways, most recently in catalysis of chemical reactions. Or have they? In this talk we argue that what appears to be hot-electron-mediated photo-catalysis is really a simple heating effect. We present a theory for plasmonic hot-electron generation, which takes into account non-equilibrium as well as thermal effects. Specifically, we consider the effect of both photons and phonons on the electron distribution function, and calculate self-consistently the full electron distribution and the increase in electron and lattice temperatures above ambient conditions (as observed experimentally), thus

going well beyond the limit of existing theories. Calculating the efficiency of hot-electron generation, we find that it is extremely small, and most power goes into heating. We use this theory to re-interpret data from central experiments claiming hot-electron generation, and find that the data fits remarkably a simple theory of heating. En route, we point to a series of experimental errors which may have led the experimentalists to make their false claims. Finally, we suggest control experiments to further test our conclusions, and discuss the prospect of using the hot electrons for photocatalysis. [1] Y. Sivan, J. Baraban, I. W. Un & Y. Dubi, *Science* 364, eaaw9367 (2019). [2] Y. Dubi & Y. Sivan, *Faraday Discussions* 2019, 10.1039/C8FD00147B. [3] Y. Dubi & Y. Sivan, *Nature Light: Science & Applications* 8, 89 (2019) [4] Y. Sivan, I. W. Un & Y. Dubi, *Chem. Sci.*, 11, 5017-5027 (2020) . [5] Y. Sivan, J. Baraban & Y. Dubi, *OSA Continuum* 3, 483-497 (2020). [6] Y. Sivan and Y. Dubi, *Appl. Phys. Lett.* 117, 130501 (2020).

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Mon-MM1-05

### Plasmon-Mediated Methyl Rearrangement with Nanoscale Spatial Control

**James Brooks (brooksjames10@gmail.com), Chris Warkentin\* (warke023@umn.edu), Dhabih Chulhai (chulhaid@uindy.edu), Jason Goodpaster (jgoodpas@umn.edu), Renee Frontiera (rrf@umn.edu)**

University of Minnesota, Department of Chemistry

Bulk chemical production is a major contributor to global energy consumption, typically requiring high temperatures and pressures to drive reactions. A promising pathway toward green chemical synthesis lies in utilizing the unique properties of plasmonic materials to drive photocatalytic reactions under standard conditions. Given the tunability of localized surface plasmon resonance, these materials have potential as versatile photocatalysts for a range of chemical reactions. Surface-enhanced Raman spectroscopy is an ideal tool to probe and understand plasmon-molecule interactions in these systems, combining the high specificity of Raman spectroscopy (SERS) with the high sensitivity afforded by surface enhancement effects. Importantly, SERS allows for simultaneous excitation of a plasmon resonance and observation of vibrations of nearby molecules, making this a bond-specific and highly sensitive method for studying chemical and physical changes to molecules on plasmonic materials.

Here, we report the observation of a plasmon-mediated methyl rearrangement of N-methylpyridinium to 4-methylpyridine, using a comparison of SER spectra and computational models to confirm the identity of the N-methylpyridinium photoproduct. This reaction, which is typically difficult to achieve under standard ambient conditions, involves the breaking of a C–N bond and formation of a new C–C bond, highlighting the ability of plasmonic materials to drive complex and selective reactions. Interestingly, we report that the reaction yield for this methyl rearrangement can be modified by a simple optical control, which we attribute to a combination of focus-dependent electric field redistribution and steric hindrance in specific regions on the nanostructured plasmonic substrate. This optical handle for control of plasmon-driven chemistry could have widely useful applications in nano-patterning for advanced electronic devices or new micro-diagnostic tools in the future.

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Mon, 14 09:00 - 11:00

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Mon-QM1-01

### Rotational and translational diffusion in a 2D colloidal glass-former (**Keynote Lecture**)

**Eric Weeks (erweeks@emory.edu), Skanda Vivek (skanda.vivek@gmail.com)**

Physics Dept., Emory University, Atlanta GA, USA

We conduct experiments and simulations studying diffusive motion of nonspherical tracers in 2D systems. Experimentally, we use video microscopy to observe the diffusive motion of dimer tracers in a quasi-2D sample of colloidal spheres. This sample is a good model for the glass transition, which occurs for a sufficiently high particle concentration. At lower concentrations, the dimer rotational and translational motions are coupled to each other: their ratio is a constant, independent of the concentration of the

spherical particles. At higher concentrations of the spherical particles (close to the colloidal glass transition), we observe decoupling between translational and rotational diffusion. In particular, small dimers rotate faster than might be expected. This is because small dimers can rotate within the cage formed by their spherical neighbors with little steric hindrance, in contrast with the larger dimers. We replicate these results with simulations, which see additional regimes where the translational and rotational diffusion are coupled (for intermediate length tracers) and where rotational diffusion is slower than translational (for sufficiently long tracers).

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Mon-QM1-02

### Simulation of Finite-sized Particle Transport through Porous Media

**Deepak Mangal (deepak.mangal.iit@gmail.com), Jacinta Conrad (jconrad@central.uh.edu), Jeremy Palmer (jcpalmer@uh.edu)**

Chemical & Biomolecular Engineering, University of Houston, Houston, TX, USA

Understanding the transport of finite-sized particles comparable to pore or throat diameter through a porous medium is important in many industrial and natural processes, including oil recovery, drug delivery, the dispersion of nutrients, minerals and contaminants through soil, and separations using techniques such as gel electrophoresis and chromatography. One of the key aspects influencing particle transport is the nature of their interactions with the porous medium, including steric repulsions and hydrodynamic interactions, that in turn are affected by the structure of the medium. Here, we perform Stokesian dynamics simulations to investigate the effect of steric and hydrodynamic interactions and system dimensionality on particle diffusion and dispersion over a broad range of flow rates in nanopost arrays. Whereas both types of interactions hinder particle diffusion under quiescent conditions, they are found to enhance longitudinal particle dispersion under flow. Longitudinal dispersion, however, is similar in two- and three-dimensional models of nanopost arrays. We also examine the effects of array structure and flow orientation on particle diffusion and dispersion in three-dimensional square and hexagonal nanopost arrays. We find that quiescent diffusion decreases as the volume fraction of nanoposts is increased, as expected, and is approximately independent of array geometry. Dispersion under flow depends on the direction of the incident flow relative to the array lattice vectors. For flow oriented along the lattice vectors, the longitudinal dispersion coefficient approximately recovers Taylor-Aris scaling behavior at high Péclet number ( $Pe$ ). For other flow orientations, however, the qualitative behavior of the longitudinal dispersion coefficient depends on the nanopost volume fraction and flow angle. Specifically, at large nanopost volume fractions, we observe non-monotonic dependence of the longitudinal dispersion coefficient on  $Pe$  when the flow orientation is slightly perturbed from certain lattice vectors.

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Mon-QM1-03

### Atmospheric Transport of Radioactive Debris

**Alexander Wiechert (awiechert3@gatech.edu)<sup>1</sup>, Austin Ladshaw (ladshawap@ornl.gov)<sup>2</sup>, Yong-ha Kim (yonghakim1@lsu.edu)<sup>3</sup>, Costas Tsouris (tsourisc@ornl.gov)<sup>2</sup>, Sotira Yiacoumi (sotira.yiacoumi@ce.gatech.edu)<sup>1</sup>**

<sup>1</sup> School of Civil and Environmental Engineering, Georgia Institute of Technology

<sup>2</sup> Oak Ridge National Laboratory

<sup>3</sup> Department of Environmental Sciences, Louisiana State University

In the event of a nuclear incident, intentional or otherwise, a large quantity of debris containing various radionuclides will be carried into the atmosphere and subsequently deposited in the surrounding regions. Given the grave danger that this debris would pose to the health of the individuals and communities living in the affected areas, it is paramount that we take the necessary steps to prepare for such incidents. To adequately prepare these countermeasures, however, the appropriate predictive tools needed to estimate transport and deposition of the radioactive debris must first be developed. Thus, in this work, a three-dimensional model capable of simulating the fate of radioactive debris particles in the atmosphere based

on particle aggregation and breakup, air ionization, and topographic effects is being developed. Furthermore, considering the acute hazards of radioactive fallout in an urban setting, experiments examining the adsorption rate of nuclides onto common urban construction materials, including brick and concrete, are being performed. Understanding how various isotopes are adsorbed will aid in determining how long the urban materials have been exposed and identifying the original isotopes to which they were exposed. This can then be used in forensic analysis of the nuclear incident after the fact to pinpoint an assortment of incident characteristics which, in turn, represents the other major objective of this research.

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Mon-QM1-04

Temperature dependence of diffusiophoresis using a novel microfluidic approach.

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<sup>2</sup> Department of Mechanical and Industrial Engineering, Northeastern University

<sup>3</sup> Department of Mechanics and Aerospace Engineering, Southern University of Science and Technology

<sup>4</sup> ETH Zurich

<sup>5</sup> Saudi Aramco, Dhahran

Diffusiophoresis (DP) is being explored for targeted delivery applications such as for drug delivery or transporting sensing and recovery agents to hidden oil in reservoirs. Although these applications involve temperatures higher than room temperature, most experimental studies of DP to date have been carried out at room temperature, and only one theoretical study has considered temperature dependence. Based on theory, DP mobility (DDP) depends on zeta potential of colloids, viscosity and permittivity of solvent and diffusivities of ions. Since, all these parameters depend on temperature, DDP does as well. In this work, we performed systematic DP measurements at a range of temperatures to test theoretical predictions. To do so, we developed a novel microfluidic approach that allows us to impose truly steady state gradients and make direct and repeatable DDP measurements at a range of temperatures. As a model system, we performed experiments with negatively charged polystyrene particles under NaCl gradients and validated the approach at room temperature. We carried out experiments at temperatures ranging from 200C to 700C and found DP velocities and DDP to monotonically increase with temperature in relatively good quantitative agreement with theoretical predictions. Our results give further confidence to DP theory to predict DP mobilities under high temperature conditions.

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Mon-QM1-05

Spatial Segregation of Spherical Microparticles by Rubbing-Induced Triboelectrification on Fluorocarbon-Patterned Surfaces

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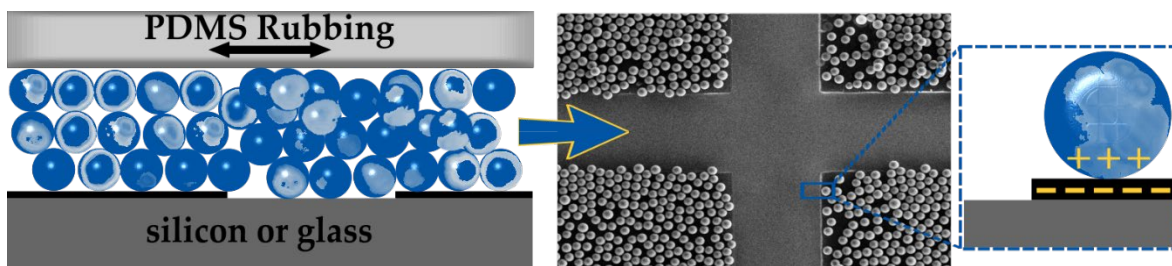
<sup>1</sup> Department of Chemical Engineering CHIS Vrije Universiteit Brussel

<sup>2</sup> Mesoscale Chemical Systems (MCS) University of Twente

<sup>3</sup> Physics of Interfaces and Nanomaterials (PIN) University of Twente

In a series of landmark papers, several wet and dry methods, including rubbing, have been reported to (self-) assemble particle monolayers. Here, we report on the serendipitous observation that spherical silica microparticles preferentially segregate to match the geometrical pattern of the fluorocarbon-coated parts of silicon and borosilicate glass wafers when manually rubbed with poly(dimethylsiloxane) slabs past these wafers, despite the circular motion of the rubbing movement. This result is unexpected, as our colloidal probe (CP) measurements consistently show a higher adhesion force between the hydrophilic silica probe and the uncoated hydrophilic silicon or glass parts compared to the hydrophobic fluorocarbon-coated

areas. To explore the extent of this counterintuitive segregation effect, we varied the geometry of the pattern, the substrate material (silicon and glass), the ambient humidity, and the material (polystyrene and silica) and diameter  $d$  ( $3 \mu\text{m} \leq d \leq 10 \mu\text{m}$ ) of the particles. Partitioning coefficients amounted up to a factor of 12 on silicon wafers and even ran in the 100s on borosilicate glass wafers at zero humidity. Using Kelvin probe force microscopy (KPFM), the observations can be explained by the triboelectrification mechanism, inducing a strong electrostatic attraction between the particles and the fluorocarbon zones. In contrast, the electrostatic interaction with the noncoated zones is insignificant or even weakly repulsive. Consequently, the rubbing motion creates a net transport of particles from the uncoated to the coated zones. In addition, we show that the humidity significantly affects the selective self-organization of the silica particles on the fluorocarbon-coated areas, whereas the segregation of the polystyrene particles is less pronounced and independent of the relative humidity. Moreover, the KPFM results show, albeit counterintuitively, that the fluorocarbon layer charges more negatively on the glass wafer than the silicon wafer. This observation corroborates with the CP measurements, in which a stronger long-range electrostatic force is measured between the silica colloidal probe and the fluorocarbon layer on the glass wafer than on the silicon wafer for all measured relative humidity levels (5 - 80 %). Altogether, these results highlight that the substrate material carrying the fluorocarbon layer and the relative humidity strongly affects the tribocharging process, i.e., the electrostatic attraction between the particles and the fluorocarbon layer.



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Mon, 14 11:20 - 12:10

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Mon-SM1-01

Colloidal assembly in 2D: From tunable pairwise potentials to elaborate contoured assemblies  
**(CSSS Plenary Lecture)**

**Maria Santore (santore@mail.pse.umass.edu)**

Department of Polymer Science and Engineering University of Massachusetts Amherst, MA 01003

Decades of research on colloids has revealed that, like small molecules, interactions between colloidal particles drive phase transitions of colloidal fluids and solids that can form the basis for novel materials. Targeted control over electrostatic and van der Waals interactions has led to the creation of colloidal crystals having structures that resemble those of minerals. Polymers added to colloidal dispersions adsorb or are depleted from particle surfaces to produce long-range interactions that enable further control. Colloidal assembly and crystallization on 2D templates opens the door to the creation of new ultrathin materials. In addition to the forces acting in 3D colloidal suspensions, at interfaces, assembling colloids additionally interact through surface tension and elasticity. This talk explores the interactions and assembly of flat rigid colloids at fluid interfaces. We demonstrate how the elasticity of the interfacial fluid gives rise to pair potentials with distinct minima, enabling control of colloidal positioning from less than a micron to tens of microns, spanning the size of the colloids themselves. We further demonstrate how interparticle potentials can be mechanically manipulated, giving rise to rapid responsive behaviors. Finally, we explore how interfacial curvature contributes to counterintuitive multibody interactions that produce extraordinary extended colloidal assemblies, with precise regularity and length scales that can be system-spanning.



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Mon, 14 12:40 - 13:30

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Mon-SM2-01

**Surfing the Surface of Colloidal Gold Nanocrystals (CSSS Plenary Lecture)**

**Catherine Murphy (murphycj@illinois.edu)**

Department of Chemistry, University of Illinois at Urbana-Champaign

Colloidal gold nanocrystals exhibit intense plasmon bands that controlled by nanocrystal size and shape. While gold is a noble metal and can be used passively as a nanoscale platform to bind and display molecules (e.g., for drug delivery), its plasmonic properties also enable chemical sensing, imaging, and photothermal applications. In this Plenary Lecture I will briefly describe the synthesis of these nanocrystals; the details of surface chemistry as measured by a battery of orthogonal techniques (NMR, STEM/EELS); and how these nanomaterials behave under a variety of conditions that span physics, biology and ecology.

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Mon, 14 13:40 - 15:00

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Mon-AM2-01

**Stable Positively Charged Polydimethylsiloxane Micelles with a Highly Hydrophobic Core**

**Sandrine Lteif (sl17d@my.fsu.edu)<sup>1</sup>, Neda Arabzadeh Nosratabad (na17c@my.fsu.edu)<sup>1</sup>, Khalil Akkaoui (ka18d@my.fsu.edu)<sup>1</sup>, Samir Abou Shaheen (saa16d@my.fsu.edu)<sup>1</sup>, Maya Chaaban (mc17r@my.fsu.edu)<sup>1</sup>, Sisi Wang (sw16f@my.fsu.edu)<sup>1</sup>, Yan Xin (xin@magnet.fsu.edu)<sup>2</sup>, Steven Weigand (weigansj@northwestern.edu)<sup>3</sup>, Biwu Ma (bma@fsu.edu)<sup>1</sup>, Joseph Schlenoff (jschlenoff@fsu.edu)<sup>1</sup>**

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Polydimethylsiloxane is a biocompatible polymer with rubbery characteristics. It is highly hydrophobic and can self-assemble in various solvents but shows poor stability as a colloid in aqueous solutions. We have made a stable polymer micelle using polydimethylsiloxane with positively charged ends. The stability of these micelles can be enhanced by incorporating a glassy polystyrene sulfonate shell. A polymer composite with unique properties can be formed when these two different types of polymers are incorporated. The micelle core is strongly hydrophobic and can be probed using the furanyl analog of 3-hydroxyflavone. This high hydrophobicity can be used to solubilize various nonpolar compounds including nanoparticles that are capped with hydrophobic ligands. This type of silicone-containing polymer particles has potential applications in drug delivery and sensing.

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Mon-AM2-02

**The effect of pi-interactions on the self-assembly of patterned polypeptides**

**Sara Tabandeh (sara.tabandeh@knights.ucf.edu)<sup>1</sup>, Lorraine Leon (lorraine.leon@ucf.edu)<sup>1,2</sup>**

<sup>1</sup> Department of Materials Science and Engineering, University of Central Florida, Orlando, FL, USA

<sup>2</sup> NanoScience & Technology Center, University of Central Florida, Orlando, FL, USA

Polyelectrolyte complexes form upon self-assembly of polyelectrolytes in aqueous solutions. The physical state of these complexes is either a solid precipitate or liquid coacervate. While liquid coacervates have weaker interactions and contain a high amount of water, polyelectrolyte chains in solid precipitates interact more strongly, resulting in a compact structure. The interplay between ionic and non-ionic interactions can affect phase behavior and the secondary structure of complexes. Here, by designing ionic peptide sequences that include aromatic residues, we investigate the effect of pi-interactions on complex formation. The patterned sequences contain phenylalanine, as an aromatic amino acid, with either lysine or glutamic acid as positive and negative amino acids, respectively. We then study the effect of charge density on the sequence and substitution of fluorine on the phenylalanine ring. Non-homochiral sequences of peptides promote liquid coacervation. However, despite having an alternating sequence of chirality in this study, complexes form solid precipitates identified using optical microscopy. Analysis of FTIR spectra of complexes shows higher hydrogen bonding for complexes with more phenylalanine content, stressing the role of pi-interactions. Fluorine substitution on the phenylalanine ring disfavors pi-interactions, resulting in a less compact structure. The high stability of these complexes against salt using turbidity measurements is another confirmation of the effect of pi-interactions on polyelectrolyte complexes. Finally, we evaluate the role of pi interactions in the encapsulation of a charged aromatic molecule using UV-vis spectroscopy. Higher charge density combined with pi-interactions resulted in a very high encapsulation efficiency, providing insight into the design and application of versatile peptide-based carriers for protein and therapeutic delivery.

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Mon-AM2-03

### Using Smart Hydrogel Interfaces to Lock DNA-Linked Nanoparticle Assemblies

**Mathew Maye (mmmaye@syr.edu)**

Department of Chemistry, Syracuse University

In this presentation we describe how the degree of crystallinity and the interspatial properties of DNA-linked nanoparticle superlattices can be tailored using smart hydrogel interfaces. Both low critical solution temperature (LCST) smart polymers as well as pH sensitive hydrogels were co-functionalized to the surface of DNA-modified gold nanoparticles and assembled into superlattices. The effects of polymer addition to the DNA-rich interface on the rate of assembly is described. Synchrotron based small angle x-ray scattering (SAXS) was used to probe the degree of ordering and temperature dependent interparticle properties of the superlattices. The potential to use these interfaces to lock-in ordering, as well as the use of pH triggers and enhanced coordination environments will be discussed.

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Mon-AM2-04

### Peptoid-directed assembly of CdSe nanoparticles

**Madison Monahan (gladdm@uw.edu)**<sup>1</sup>, **Bin Cai (bin.cai@pnnl.gov)**<sup>2</sup>, **Tengyue Jian (tengyuejian@gmail.com)**<sup>2</sup>, **Shuai Zhang (zhangs71@uw.edu)**<sup>2,3</sup>, **Guomin Zhu (gmzhu@uw.edu)**<sup>2,3</sup>, **Chun-Long Chen (Chunlong.Chen@pnnl.gov)**<sup>2,4</sup>, **James De Yoreo (James.DeYoreo@pnnl.gov)**<sup>1,2,3</sup>, **Brandi Cossairt (cossairt@uw.edu)**<sup>1</sup>

<sup>1</sup> Department of Chemistry, University of Washington

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<sup>3</sup> Department of Materials Science, University of Washington

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The high information content of proteins drives their hierarchical assembly and complex function, including the organization of inorganic nanomaterials. Peptoids offer an organic scaffold very similar to proteins, but with a wider solubility range and easily tunable side chains and functional groups to create a variety of self-assembling architectures with atomic precision. If we could harness this paradigm and understand the factors that govern how they direct nucleation and assembly of inorganic materials to design order within such materials, new dimensions of function and fundamental science would emerge. In this work, peptoid

tubes and sheets were explored as platforms to assemble colloidal quantum dots (QDs) and clusters. We have successfully synthesized CdSe QDs with difunctionalized capping ligands containing both carboxylic acid and thiol groups and mixed them with maleimide containing peptoids, to create an assembly of the QDs on the peptoid surface via a covalent linkage. This conjugation was seen to be successful with peptoid tubes, sheets and CdSe QDs and clusters. Particle identity was confirmed on the peptoid surface using EDX and high-resolution TEM. The particles were seen to have a high preference for the peptoid surface but non-specific interactions with carboxylic acid groups on the peptoids limited control over QD density via the maleimide conjugation. Replacing the carboxylic acid groups with methoxy ethers allowed for control over QD density as a function of maleimide concentration. <sup>1</sup>H NMR analysis demonstrated that binding of QDs to peptoids involved a subset of surface ligands bound via the carboxylate functional group, allowing sulfur to bind via covalent linkage to the maleimide. Overall, we have shown the compatibility and control of CdSe-peptoid interactions via a covalent linkage with varying peptoid structures and CdSe particles to create complex hybrid structures. Future work looks to expand the library of compatible nanoparticles to tune the properties of the hybrid materials and pattern complimentary nanoparticles onto a single peptoid surface and to investigate the assembly of peptoid nanostructures after conjugation with nanoparticles

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Mon, 14 13:40 - 15:00-

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Mon-BM2-01

Liquid Foams as Template for Macroporous Hydrogels Synthesis

**Ryan Zowada (rzowada@nmsu.edu), Reza Foudazi (rfoudazi@nmsu.edu)**

New Mexico State University

Foam templates are produced by a simple rapid gas dispersion into an aqueous monomer solution at various dispersion concentrations. The templates are crosslinked at room temperature to obtain interconnected polydisperse solid foams. The foams are analyzed for their stability by measuring coarsening rates and drainage times to quantify and compare the effect of the volume of gas dispersion. The pseudoplastic flow behavior of foams were fitted using Herschel-Bulkley model to calculate the required foaming energy. The benefits of using a foam templating method in comparison to emulsion templating method are the increased starting material efficiency and elimination of the removal step of the dispersed phase as in emulsion templating. Another challenge in emulsion-templating is to make porous polymers with pore size in the range of 50-200  $\mu\text{m}$  for applications such as tissue engineering, which can be resolved in foam-templating method. We investigate the morphological characteristics and mechanical properties of obtained porous polymers from foam- and emulsion-templating methods.

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Mon-BM2-02

Immobilizing hexadecane nanoemulsion drops in polyacrylamide hydrogels

**Reghan J. Hill (reghan.hill@mcgill.ca)**

Department of Chemical Engineering, McGill University

This study examines hydrogels as a physical barrier to nanodrop coalescence and as a thermodynamic barrier to Ostwald ripening. How these factors play a role in the encapsulation of oil drops for drug-delivery applications is largely unknown owing to the challenge of measuring in situ drop size and understanding the drop-hydrogel interface. In this study, the electrokinetic sonic amplitude of sodium dodecyl sulfate (SDS)-stabilized hexadecane-in-water nanoemulsion drops in polyacrylamide hydrogels was harnessed to ascertain dynamic mobility spectra, which we interpreted using a recently proposed model for highly charged nanodrops. These data were complemented with confocal microscopy, conductivity, rheology, and swelling studies. The nanodrop radius in hydrogels was close to their nanoemulsion counterparts ( $\sim 100$ - $600$  nm), with a frequency-independent shear viscosity ( $\sim 0.5$  mPa s at megahertz frequencies) and a frequency-independent shear modulus ( $\sim 1$  kPa). The findings point to an "ideal behaving" microstructure

that can be dried and rehydrated, preserving the oil-templated skeleton, which may be tailored for advanced drug-delivery systems. The electroacoustic testing platform developed in this work provides a beneficial tool for non-invasively characterizing nanoemulsion-doped hydrogels.

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Mon-BM2-03

Colloidal gelation of concentrated nanoemulsion at different depletant concentrations

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Nanoemulsions are metastable colloidal dispersions with a wide range of applications in the food, cosmetic, and pharmaceutical industries due to their unique structural properties. Gelation in nanoemulsions can effectively be used to expand the nanoemulsion applications as rheology modifiers and to design highly structured porous materials. In this research, we study the colloidal gelation of concentrated nanoemulsion with the oil volume fraction of 50% and 60% in the presence of depletant molecules. The resulting microstructures and rheological properties of the concentrated nanoemulsions are studied at different concentrations of polyethylene glycol diacrylate (PEGDA) as the depletant. The gelation behavior and the structure-flow relationship of nanoemulsions are examined through flow curve and oscillatory shear measurements. These results offer a foundation for controlling the properties of colloidal systems and nanoemulsion-templated porous materials.

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Mon-BM2-04

Co-surfactant based interfacial strategies for predicting multi-nanoemulsion formation

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There has been significant recent interest in the production of multi-phase emulsions, particularly at the *nanoscale*, as vehicles for controllably encapsulating and potentially delivering otherwise insoluble or chemically incompatible materials. However, due to the energetic cost of stabilizing multiple highly curved and confined interfaces, there has been limited success in designing and producing multi-nanoemulsions. Here, we propose and theoretically validate a general method for promoting and stabilizing multi-nanoemulsion structures by manipulating their interfacial mechanics *via* co-surfactant selection. Using equilibrium interfacial free energy models, we establish a theoretical basis for the preferred stabilization of multi-phase nanodroplet structures formed with co-surfactants of opposing spontaneous curvature and demonstrate these models may be used to predict and quantify conditions under which multi-nanoemulsions are produced. We experimentally verify the predictions made by these models using small-angle neutron scattering to characterize the morphologies of nanoemulsions made using asymmetric pairs of ethoxylated co-surfactants. We show that the interfacial strategy induces the preferential formation of multi-nanoemulsions with some degree of control over the internal droplet structure and provides a rational means of engineering desirable multi-phase nanodroplets.

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Mon, 14 13:40 - 15:00

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Mon-CM2-01

Light-powered motors and thermally reconfigurable low-symmetry fluids in nematic colloidal dispersions of discs (**Keynote Lecture**)

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Biological motors are marvels of nature that inspire creation of their synthetic counterparts with high efficiency, spontaneous self-assembly and diverse functions. We describe colloidal motors with a repetitive light-driven rotation of thin discs immersed in a liquid crystal and powered by a continuous exposure to unstructured ~1 nW light. Dispersing many charged colloidal discs in a nematic host provides a platform for observing many low-symmetry equilibrium liquid crystalline phases and out-of-equilibrium dynamic states. Depending on temperature, concentration and surface charge of the discs, we find nematic, smectic and columnar organizations with symmetries ranging from uniaxial to orthorhombic and to monoclinic. Most importantly, we demonstrate the possibility of thermal, optical and magnetic control of low-symmetry self-assembly and the monoclinic colloidal nematic order. We characterize this pseudo-polar monoclinic orientational order, along with the phase diagrams, orientational distribution functions and order parameters, as well as their dynamic evolution under out-of-equilibrium conditions. Our findings may lead to opto-mechanical devices and colloidal machines compatible with liquid crystal display technology, as well as low-symmetry active and driven soft matter.

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Mon-CM2-02

Self-propelled liquid crystal droplets that trigger local polymerization

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Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University

Recent studies of active soft matter systems have unmasked universal physical principles that can describe non-equilibrium states found in both synthetic and living systems. For example, as liquid crystalline oil droplets dissolve into aqueous micellar solutions, they propel themselves via creation of interfacial tension gradients (Marangoni stresses) and exhibit behaviors such as chemotaxis. In this presentation, we will report an experimental study in which we have found that circulating flows inside self-propelled LC droplets trigger the release of inclusions (small aqueous microdroplets) from within the LC. Whereas electrical double layer and elastic forces initially trap the inclusions within the LC droplets, coalescence and coarsening of the inclusions that accompanies the motion of the self-propelled LC droplets ultimately lead to ejection of the inclusions from the LC droplets. By dissolving an initiator for polymerization within the inclusions, we show that it is possible to program self-propelled LC droplets to exhibit chemotaxis and then trigger polymerization at a targeted spatial location. Overall, our results provide fresh ideas for the design of active colloidal systems that respond to non-equilibrium stimuli with spatially and temporally targeted synthesis of polymers.

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Mon-CM2-03

Self-Loomotive Antimicrobial Microparticles for Enhanced Biofilm Removal

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Biofilms are communities of bacterial cells that can cause a variety of healthcare problems. In particular, over 80% of microbial infections in human body are associated with bacterial biofilms, according to a survey from the US National Institutes of Health (NIH). However, traditional antibiotics treatments are not effective enough to remove the wound biofilm because the extracellular polymeric substances (EPS) can impede the diffusion of antibiotics into the biofilm. In this work, we developed a self-locomotive antimicrobial microparticle that can effectively remove biofilms through continuous bubble generation in an antiseptic H<sub>2</sub>O<sub>2</sub> solution. We hypothesized that the microparticles' continuous bubble generation would deform the EPS matrix and ultimately abrade biofilms due to the repeated bubble expansion and burst. To examine this hypothesis, we firstly improved our previously developed diatom microbubbler by increasing the loading mass of manganese oxide (MnO<sub>2</sub>) via polydopamine (PDA) coating. Then, we assessed and compared their self-locomotive capability by examining the propulsion speed and kinetic reaction in the H<sub>2</sub>O<sub>2</sub> solution. Using *Pseudomonas aeruginosa* (*P. aeruginosa*) biofilm formed in microgrooves of a silicon substrate, we examined the extent that MnO<sub>2</sub> nanocatalyst mass per diatom modulates the abrasion of biofilms. In the end, we evaluated the biofilm removal efficacy by treating *P. aeruginosa* biofilms with minimal biofilm eradication concentration (MBEC) assay.

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Mon, 14 13:40 - 15:00

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Mon-DM2-01

Three-Dimensional Technique for Measuring Sag in Drying Coatings

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Coatings are found in nearly every aspect of modern society including architectural, automotive, and consumer goods applications. Undesired coating defects often arise during the flash stage which constitutes the 10-minute interval immediately following the application stage for automotive coatings. Fundamental understanding of the transient rheology is essential for predicting and avoiding defects such as sag. Sag refers to the gravity-driven flow that commonly occurs following application, which leads to nonuniform flow and visually undesirable appearances. We used a new technique, called Variable Angle Inspection Microscopy (VAIM), to non-invasively measure sag through the volume of an arbitrarily oriented thin film. Initial benchmarking measurements in the absence of drying tracked the velocity of silica probe particles in ~140 μm thick films of known viscosity much greater than water at angles between 5° and 10°. Probe particles were tracked at speeds as high as ~100 μm/s deep into the film. The sag flow field was well-resolved in ~10 μm thick slabs and in general the VAIM measurements were highly reducible. Complementary profilometer measurements on film thinning were utilized to predict sag velocities with a known model. The model predictions and our measurements agree very well, which validates the effectiveness of this new method in relating material properties and flow regimes. Thereby, this work will assist in accelerating formulation efforts including the development of energy efficient coating systems for automotive applications.

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Mon-DM2-02

## In-situ Microrheology of Drying Paint

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Paint formulation and drying conditions have a strong influence on the final performances of the coating, yet there are few measurable variables between the formulation stage to the final film performance. The fast drying of thin films of paint, such as those used in automotive coatings, results in higher potential for fluid instabilities that often lead to defect formation in the final coating. The rheological properties of paint prior to and during drying is key in understanding the transition from a fluid coating to a solid film and is necessary for defining the connection between formulation and drying conditions, defect formation, and consequently the final paint performance. Passive microrheology, tracking the Brownian motion of passive tracers in the fluid, is used to characterize the properties of coating formulations in both quiescent liquids and during drying where the evaporative flux can cause partitioning and even strong Marangoni stresses that result in internal convection, leading to superimposition of the fluid kinematics on the random fluctuations of the probe particles. In this work, we implement a de-drifting algorithm to subtract the substantial influence of convection, allowing us to probe the time-evolved rheological properties of a drying film, by removal of the convective component of the initial measured particle Mean Square Displacements. We test thin films of model automotive paints in both the quiescent state and during drying in a range of different conditions, such as composition, molecular weight and polymer concentration. The local shear thinning resulting from drying-induced convection directly influences the local rheology and final behavior of the final coating.

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Mon-DM2-03

## Influence of Polymer Diffusivity in Nanoconfinement on the Onset of Viscous Fingering

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The onset of nanoscale viscous fingers within nanoporous media is a function of polymer concentration and molecular weight and the media permeability. Comparing the onset of these fingers to prior literature, it suggests the polymer effective viscosity and diffusivity must vary greatly in nanoconfinement as compared to in bulk solutions. Aiming to understand how confinement influences polymer dynamics, this work uses Fluorescent Recovery After Photobleaching (FRAP) via laser scanning confocal microscopy to measure the mobility of fluorescent poly(vinyl alcohol) (PVA) in both bulk solutions and in colloidal crystals. PVA used in this study has an average molecular weight of 67,000 Da and the colloidal crystal is fabricated from 1 micron silica microspheres. Diffusivity of PVA in both cases is extracted by fitting a model to the fluorescent intensity recovery in the bleached region. In the bulk, fluorescence recovery matches the model well. In the colloidal crystal, the model describes the initial fluorescence recovery, suggesting the effective diffusivity is two orders of magnitude lower than in the bulk solution, but overestimates the long-time polymer fluorescence. This deviation from the predicted longer recovery times within the colloidal crystal suggests either a partitioning of polymer by molecular weight or more complex interactions of polymer chains in confinement. Molecular dynamics simulations using coarse-grained models for polymer chains and explicit solvent in bulk (i.e., no confinement effects) and in nanoporous colloidal crystal describe the primary influence of nanoconfinement on the polymer chain conformations and diffusion. It is theorized that

a combination of pore size and molecular crowding, which is a function of polymer concentration and molecular weight, slows the polymer dynamics considerably. This effective decrease in polymer diffusivity and increase in effective viscosity results in the conditions that support continuous fingering in these films.

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## Mon, 14 13:40 - 15:00

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Mon-EM2-01

### Nanoparticle Tracking to Probe Transport in Porous Media (**Keynote Lecture**)

**Daniel Schwartz (Daniel.schwartz@colorado.edu)**

Department of Chemical and Biological Engineering University of Colorado Boulder

Highly interconnected interface-rich porous materials are ubiquitous in nature and industrial processes, with diverse length scales and topological structures. In general, hindered mass transport of (nano)particles and/or macromolecules is either essential to these process or a necessary, but undesirable limitation. Unfortunately, mass transport in porous material is poorly understood from a fundamental perspective in part because real porous materials are complex, and also because many coupled dynamic mechanisms (e.g. adsorption, steric effects, hydrodynamic effects, electrostatic interactions, etc.) give rise to macroscopic transport phenomena. Conventional ensemble-averaging characterization techniques provide practically useful information but generally fail to give insight into the microscopic mechanisms that give rise to complex phenomena such as anomalous diffusion, hindered pore-space accessibility, and unexpected retention. To address these issues, we have developed refractive index matching imaging systems, combined with single-particle tracking methods, allowing highly multiplexed direct visualization of single particle motion within a variety of porous materials. In this presentation, I will give an overview of single-particle tracking methods developed and employed in our lab to advance the understanding of nanoparticle transport in porous media in both fundamental and applied scenarios. This will include a description of the basic principles for two-dimensional and three-dimensional single-particle tracking in the bulk of porous materials. Several examples will be described, including research aimed at understanding fundamental elementary particle transport processes in model porous media (including pore accessibility and cavity escape, which limit transport in porous media) as well as research investigating applications to industrial processes, (e.g., understanding mechanisms of particle fouling and remobilization in polymeric filtration membranes).

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Mon-EM2-02

### Using Experimental 'Molecular Videography' to Resolve Nanostructure Dynamics in Soft and Biomolecular Materials

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In soft and biological materials, function—in forms as far-ranging as viscoelastic response and enzymatic catalysis—is tied to nanoscopic motion and morphological dynamics in the constituent building blocks, whether they be nano-colloids or macromolecules. These phenomena can be interrogated at the global level with spectroscopic or scattering-based techniques, in the form of snapshots using conventional high-resolution *ex situ* imaging methods, or at relatively small time scales (<μs) by means of molecular simulation. However, experimentally *filming* nanoscopic molecular morphology fluctuations is a methodological challenge. This presentation will demonstrate a form of experimental "molecular videography" which we have achieved through advancements in liquid-phase transmission electron



microscopy (TEM). In particular, we have combined graphene encapsulation and minimally invasive (low electron dose) liquid-phase TEM with molecular modeling and theoretical concepts from electron optics and biophysics to image and derive physical insight from the nanoscopic morphological dynamics of individual bio-macromolecular assemblies in liquid water. Specifically, through direct, real-time observations, we have found that nanodiscs—a colloidal form of membrane proteins—have fluctuations dominated by the molecular mechanics of their encircling scaffold proteins, in the form of an effective tension and bending rigidity. The same fluctuations are sensitive to noncovalent interactions between lipids and the membrane protein inside a nanodisc, because they delineate a structurally and dynamically modified oasis that can additionally protect nanodiscs from drastic “fingering” fluctuations. We will also showcase ways to combine these approaches with machine learning and other advanced data analysis methods to derive even more insight, in a wide range of polymeric and biomolecular materials.

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Mon-EM2-03

### Deep Learning-Assisted Analysis of Anomalous Nanoparticle Surface Diffusion in Liquid Phase Transmission Electron Microscopy

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University of California Berkeley

The motion of nanoparticles near surfaces is of fundamental importance in physics, biology, and chemistry. Liquid cell transmission electron microscopy (LCTEM) is a promising technique for studying motion of nanoparticles with high spatial resolution. Yet, the lack of understanding of how the electron beam of the microscope affects the particle motion has held back advancement in using LCTEM for in-situ single nanoparticle and macromolecule tracking at interfaces. Here, we experimentally studied the motion of a model system of gold nanoparticles dispersed in water and moving adjacent to the silicon nitride membrane of a commercial liquid cell in a broad range of electron beam dose rates. We find that the nanoparticles exhibit anomalous diffusive behavior modulated by the electron beam dose rate. We characterized the anomalous diffusion of nanoparticles in LCTEM using a convolutional deep neural-network model inspired by the canonical statistical tests. The results demonstrate that the nanoparticle motion is governed by fractional Brownian motion at low dose rates, resembling diffusion in a viscoelastic medium, and continuous-time random walk at high dose rates, resembling diffusion on an energy landscape with pinning sites.

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## Mon, 14 13:40 - 15:00

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Mon-GM2-01

### Stimuli Responsive Reversible Adhesion Between Physical and Chemical Networks

**Leah Borden (lkborden@umd.edu), Srinivasa Raghavan (sraghava@umd.edu), Ankit Gargava (ankitgargava26@gmail.com)**

University of Maryland College Park, MD

This work will present studies from our lab on the electrically induced adhesion of hydrogels and beads made from polyelectrolytes. The basic phenomenon involves crosslinked acrylate hydrogels made with either anionic co-monomers (such as sodium acrylate) or cationic co-monomers (such as aminated acrylates). When a rectangular strip of a cationic gel (connected to an anode) is contacted for just a few seconds with a strip of anionic gel (connected to a cathode) under a voltage of  $\sim 10$  V, the two gel strips form a strong adhesive bond. When the polarity of the electrodes is reversed, the phenomenon is reversed, i.e., the gels can be easily detached. While the above phenomenon of ‘electro-adhesion’ has been reported before for hydrogels, we show that it is much more general and widespread. Specifically, we can substitute

either of the above gels with a spherical bead made using charged biopolymers such as chitosan or alginate. The same electro-adhesion works to join beads to gels, or two beads to each other. In turn, electro-adhesion can be applied for the pick-up and drop-off of soft cargo, and for the sorting of beads.

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Mon-GM2-02

Selective flow through membrane pores with in situ change of wettability

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This report demonstrates in situ change of wettability of water on the gold surfaces adsorbed with various molecules responding to relatively low electric current and voltage. This tunable wettability is achieved by the conformational change of linear molecules adsorbed on gold surfaces when the functional groups with dipoles at the end of the molecules are attracted to the electric potential at the gold surface. While the water is in contact with the end groups before the conformation change without voltage, the water would be in contact with the backbone of the linear molecules after conformation change with voltage, resulting in the change in wettability. While there are many other ways of achieving the wettability of molecule-adsorbed surfaces, utilizing the conformation change with small voltage ( $< 2V$ ) is a more practical way of achieving in situ change because the liquid should neither have to be water as in manipulating pH, conductive as in electrowetting also requiring high voltage ( $> 100 V$ ), nor it requires high energy or long wait time as in achieving such change with temperature.

The realization of in situ wettability change can lead to the development of new kinds of membranes that can be used as selective control valves that can separate two-liquid mixture that permeate one liquid with no voltage while permeating the other liquid with voltage by adsorbing long linear molecules with dipoles on metal-coated membranes with a specific geometry. As the first step in preparing such membrane and to show the possibility of such application with the in situ change of wettability, each of four thiol molecules with long backbones was adsorbed onto flat gold and nickel surfaces. While changing the voltage across those metal surfaces were changed from 0 to 2 V, the advancing contact angles of water on those molecules were measured. The space between the long molecules were also varied by mixing those long thiol molecules with a short thiol molecule, i.e., ethanethiol, to provide more space for the long molecules to bend toward the metal surfaces, exposing the backbones to water. We found that the water contact angle increased up to  $30^\circ$  when the ratio of long molecules to the short molecule was at 1:1, providing enough difference to realize the fabrication of membrane control valve controlling the flow of water through membranes with 200- $\mu\text{m}$  openings.

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Mon-GM2-03

Contactless, Reversible Droplet Contact Angle Modulation by Dielectric Charge Injection

**Paradorn Rummaneethorn (pr9@seas.upenn.edu), Daeyeon Lee (daeyeon@seas.upenn.edu)**

Department of Chemical and Biomolecular Engineering, University of Pennsylvania

Electrowetting (EW) and electrowetting-on-dielectric (EWOD) are two traditional methods for contact angle modulation. However, EW and EWOD require direct droplet contact with an electrode, which may be challenging and undesirable when dealing with electrically sensitive cargo in the droplet or with microscale droplets. Although contactless methods that apply external physical stimuli to alter surface wetting properties have been reported, the range of contact angle modulation remains limited. Here we demonstrate a contactless method to induce reversible droplet contact angle modulation on chemically inert substrates via corona discharge-based dielectric charge injection (DCI). The method involves a sharp, conductive probe that can induce dielectric breakdown of the surrounding dielectric medium, such as air, under voltages exceeding the medium's dielectric strength. Breakdown leads to ionization of the dielectric, which then accelerates away from the sharp tip due to electrostatic repulsion, resulting in charge injection onto a target surface. With DCI, we induce wetting of a water droplet on non-wetting, non-contacting

surfaces in non-polar continuous phases. DCI can achieve up to 140° contact angle modulation – competitive or even exceeding the capabilities of traditional EW and EWOD . Furthermore, upon removal of the voltage and/or probe, droplet undergoes dewetting and returns to the initial non-wetting state. We show that DCI can be used to induce deposition of encapsulated materials from droplets to the non-wetting surface. DCI can also be applied for recovery of materials from such a surface. DCI presents a unique strategy for contactless, reversible contact angle modulation that is simple and powerful, with a wide application space that remains to be explored, especially in contexts where EW and EWOD become inapplicable.

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Mon-GM2-04

Using colloidal deposition to mobilize immiscible fluids from porous media

**Joanna Schneider (js105@princeton.edu), Rodney Priestley (rpriestl@princeton.edu), Sujit Datta (ssdatta@princeton.edu)**

Chemical and Biological Engineering, Princeton University

Colloidal particles hold promise for mobilizing trapped immiscible fluids from porous media, with implications for key water applications. Most studies focus on accomplishing this goal using particles that localize at immiscible fluid interfaces. Researchers typically seek to optimize the surface activity of particles while minimizing their deposition onto the surrounding solid matrix. Here, we demonstrate that deposition can, surprisingly, promote mobilization of a trapped fluid from a porous medium. Using confocal microscopy, we directly visualize colloidal particles and trapped immiscible fluid within a transparent, 3D porous medium. As particles deposit on the solid matrix, more trapped fluid become mobilized. We unravel the underlying physics by analyzing the extent of deposition and the geometry of trapped fluid droplets at the pore scale: deposition increases viscous stresses on droplets, overcoming the influence of capillarity that keeps them trapped. This analysis enables us to predict the extent of fluid mobilized through colloidal deposition and reveals a new way by which colloids can be harnessed to mobilize trapped fluid from a porous medium.

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Mon, 14 13:40 - 15:00

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Mon-IM2-01

Colloids & Interfacial Sciences in Energy Applications (**Keynote Lecture**)

**Krishnaraj Sambath (ksambath@chevron.com)**

Chevron

In meeting the world's growing energy demands, key components of the energy supply for the past 5 decades (and expected to remain for the next 3 decades) are crude oil and natural gas. Given the multiphase form of these energy sources, the phenomena of interfacial science is ubiquitous throughout the production, transport & refining journey. Colloids play a crucial role both as an aid and an obstacle in the production of these vital energy sources. As the world looks to transition into renewable energy, colloids and interfacial sciences are expected to continue playing a significant role in innovation of efficient & low-cost technologies for carbon capture and solar energy storage. In this talk, we plan to discuss a few existing applications and potential future opportunities of colloidal science in energy industry.

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Mon-IM2-02

Modified Interfacial Energy Stabilizes the Perovskite Phase of CsPbI<sub>3</sub> in Colloidally Assembled Oxide Scaffolds

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Department of Chemical and Biological Engineering, Drexel University

Though highly desirable for optoelectronic applications, perovskite-phase cesium lead iodide CsPbI<sub>3</sub> transforms into a high density, non-functional, non-perovskite yellow phase under ambient conditions. However, the perovskite-phase can be stabilized in the form of quantum dots and thin films. Proceeding with the hypothesis that this is a general effect of reduced dimensionality, we have sought a facile and robust approach for enforcing controlled nanostructure. To do so, we synthesized CsPbI<sub>3</sub> in the voids of TiO<sub>2</sub> nanoparticle scaffolds. Herein is described a study, comparing the phase transition sequence of CsPbI<sub>3</sub> synthesized in scaffolds with sizes ranging from few nanometers to mesoscopic dimensions. Due to the large surface energy contribution in the resulting composite, it is critical to understand the interfacial energy contribution to the phase stability. Thus, we systematically studied the effect of interfacial energy on the phase transition sequence of CsPbI<sub>3</sub> by employing different self-assembled monolayers (SAMs) added to the TiO<sub>2</sub> scaffold. We hypothesize that the greater affinity of the perovskite versus the non-perovskite phase towards an ionic surface lowers the Gibb's free energy of phase transition. We found a 270 °C drop in the phase transition temperature and enhanced thermal stability as a consequence of combined nano-templating and interface engineering; crystals synthesized in larger mesoscopic TiO<sub>2</sub> showed standard phase transition temperature of 330 °C, consistent with bulk CsPbI<sub>3</sub>, regardless of interface chemistry. This approach could potentially stabilize the functional perovskite phase of CsPbI<sub>3</sub> at ambient conditions.

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Mon, 14 13:40 - 15:00

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Mon-KM2-01

Cholesterol Induced Morphological Instabilities and Transitions in Phospholipid Monolayers

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Lung surfactant (LS) is a lipid-protein mixture that forms a monolayer that lines the alveolar air-liquid interface and acts to reduce the interfacial tension to a level necessary for breathing. The lack or inhibition of LS can be life-threatening and can result in acute respiratory distress syndrome (ARDS) which has a 40% mortality rate. Due to the complexity of native LS, 2 or 3 component mixtures are studied to elucidate the relationship between composition, monolayer microstructure, and phase behavior and how these factors affect physiological function. The primary lipid in LS is dipalmitoylphosphatidylcholine (DPPC) which accounts for 40-80 percent of native and replacement LS therapies. The addition of fatty acids, fatty alcohols, and cholesterol to replacement LS therapies is controversial. To address the role of these components on monolayer properties, we focus on mixtures of DPPC and hexadecanol (HD) or palmitic acid (PA) with small mole fractions of dihydrocholesterol (DChol). Of particular interest is the 2-dimensional microstructure of LS films as lipids self-assemble to form crystalline-like domains (liquid-condensed phase) within a liquid-like matrix (liquid-expanded phase). By spreading LS monolayers with trace amounts of fluorescent dye, the microstructure of these films can be observed via confocal microscopy. It is found that HD or PA and DPPC co-crystallize to form semi-circular domains that do not change shape with monolayer compression. With the addition of 1.5 mol% DChol to the DPPC/HD or DPPC/PA system, a fingering instability is observed during monolayer compression followed by a time-dependent circle-to-stripe transition at a fixed interfacial tension. The resultant stripes are of uniform width and variable length and provide the first quantitative experimental confirmation of McConnell's theory of shape transitions.

Measuring the stripe widths provides the first measurements of the Bond Number (ratio of the square of the dipole density difference to the domain line tension) as a function of composition, interfacial tension, and temperature for systems at liquid condensed – liquid expanded phase coexistence.

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Mon-KM2-02

Visualizing early-stage coacervate formation with a phase field model for mixed polyelectrolyte solutions

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Coacervation, driven by the complexation of aqueous proteins or polyelectrolytes, is a liquid-liquid phase separation (LLPS) process critical to the formation of many natural structural biomaterials and broadly relevant to industrial production of polyelectrolyte materials. To date, a majority of the research effort on coacervation has focused on equilibrium coacervate phase behavior and physical properties. Extending this understanding to the non-equilibrium kinetics and microstructure evolution associated with LLPS would better inform the design of processes to create coacervate-based materials. To this end, we present a phase field model of coacervation able to resolve the kinetics of coacervate formation from a system of oppositely-charged polyelectrolytes of same length and charge density. The model describes an incompressible, multicomponent system comprised of Gaussian chains with Coulombic interactions and short-range non-ionic (excluded volume) interactions, which is coupled to species and momentum convection-diffusion equations and solved using a pseudo-spectral method. The model correctly matches the equilibrium coacervate phase boundary, with phase separation occurring inside the spinodal. Using novel simulations upon quenching into the spinodal, we resolve distinct stages of spinodal phase separation and coarsening, including an initial space-spanning bicontinuous morphology and its evolution into coarsening polyelectrolyte-rich coacervate droplets. Composition-dependent studies inside the spinodal resolve the effects of quench depth on the phase separation kinetics, which we compare to conventional models of spinodal phase separation. We also present initial explorations of the influence of spatially-dependent mixing, flow, and coacervate rheology on non-equilibrium structure formation and evolution during coacervate formation. Finally, we discuss implications for current and future experiments, highlighting the broad utility of the model framework for understanding non-equilibrium behavior in polyelectrolyte complexation to inform materials design.

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Mon-KM2-03

A functional DNA liquid (**Keynote Lecture**)

**Omar Saleh (saleh@ucsb.edu)**

Materials Dept, UC Santa Barbara

We seek to create self-assembled biomolecular liquid droplets that act as rough mimics of biological condensates, and to engineer mesoscopic structure and function into the droplets through molecular design. We particularly form liquids from DNA nanostars, multi-armed DNA particles that condense through base-pairing interactions. These liquids show materials properties similar to condensates, while also displaying an extraordinary sensitivity to the number of arms of the constituent particles, indicating the system displays an isostatic transition. I will discuss various approaches to functionalizing these DNA liquids, including by infusing them with gene-length linear DNA strands; by interfacing the liquids with DNA enzymes; and by creating complex mesoscopic structures formed from 2 immiscible DNA liquid phases.

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Mon, 14 13:40 - 15:00

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Mon-MM2-01

Plasmon-induced hot carrier generation, relaxation, and applications (**Keynote Lecture**)

**Peter Nordlander (nordland@rice.edu)**

Rice University

Plasmons can serve as efficient generators of hot electrons and holes that can be exploited in light harvesting applications. The physical mechanism for plasmon-induced hot carrier generation is plasmon decay. Plasmons can decay either radiatively or non-radiatively with a branching ratio that can be controlled by tuning the radiance of the plasmon mode. Non-radiative plasmon decay is a quantum mechanical process in which one plasmon quantum is transferred to the conduction electrons of the nanostructure by creating an electron-hole pair, i.e., excitation of an electron below the Fermi level of the metal into a state above the Fermi level but below the vacuum level. These hot carriers interact with all charge carriers in the system and eventually transfer their energy into phonons (heat). In my talk, I will discuss the time-dependent relaxation of plasmon-induced hot carriers including electron-electron scattering, fluorescence, and electron-phonon coupling and show that the hot carrier lifetimes can exceed several picoseconds. I will also discuss recent applications of plasmon-induced hot carrier generation such as plasmon-enhanced photocatalysis, and how photocatalytic efficiencies can be enhanced and quantified by placing catalytic reactors in the nearfield of a plasmonic antenna in Antenna/Reactor geometries.

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Mon-MM2-02

Particle plasmons as omnipotent probe of surface photochemistry

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University of New Mexico

Understanding the interaction of molecules with metal nanoparticles is fundamental in mechanistic analysis of heterogeneous photocatalysis. In this presentation, it will be shown that localized surface plasmon resonances of metal nanoparticles can be used for obtaining in-depth understanding of surface photochemistry by probing different physicochemical processes. The plasmonic effect is used to initiate and probe model surface reactions (oxidation of non-resonant para-aminothiophenol and N-demethylation of resonant methylene blue) that reveal the roles of electron transfer and plasmon-pumped intramolecular electronic excitation. Our experimental results indicate that intermediary surface ligands can enhance or block electron transfer depending on the geometry of the analyte molecules. In addition, the presence of surface ligands can facilitate plasmon-pumped adsorbate intramolecular electronic excitation by orienting the analyte molecules along the surface field vector as well as by prolonging the excited state lifetime. In this presentation, it will be shown how particle plasmons enable us to provide key experimental evidences that are difficult, if not impossible, to obtain from any other techniques. Finally, the similarity of plasmon driven photochemistry to gas phase cluster anion photochemistry will be highlighted.

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Mon-MM2-03

The Connection Between Plasmon-Mediated Hot Carrier Dynamics and the Surface Enhanced Raman Spectroscopy Background

**Shengxiang (Joey) Wu (sxwu@csrc.ac.cn)**<sup>1</sup>, **Matthew Sheldon (sheldonm@tamu.edu)**<sup>2</sup>

<sup>1</sup> Beijing Computational Science Center

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Through the optical excitation of collective electron oscillations, known as localized surface plasmon resonances (LSPR), metallic nanostructures can concentrate electromagnetic fields directly above their surfaces. Therefore, metallic nanostructures are commonly used as plasmonic substrates in sensing applications, e.g., surface enhanced Raman spectroscopy (SERS). In addition to the sub-wavelength concentration ability, hot carriers generated by plasmon decay have shown remarkable performance in photodetection, solar energy harvesting, or initiation of chemical reactions. Through the generation of hot carriers, the inherently high losses of metallic nanostructures are turned into advantage. Recent studies have established that the anti-Stokes Raman signal from plasmonic metallic nanostructures can serve as a thermometer to determine two separate temperatures that characterize carriers inside the metal – photoexcited hot carriers and carriers that are thermalized with the lattice. However, the related signal in the Stokes spectral region has historically impeded SERS, as the vibrational peaks of adsorbed molecules are always accompanied by the broad background of the metal substrate. Here, we outline a unified theoretical model that describes both the temperature dependent behavior and the broad spectral background. We suggest that most of the Raman signal is from the inelastic scattering directly with carriers in a non-thermal energy distribution excited via surface plasmon damping. The temperature and optical power dependent Raman experiments demonstrate how a simple fitting procedure can reveal the plasmon dephasing information, as well as the temperatures of the hot carriers and the metal lattice. The model we provided here is able to correlate the plasmon dephasing information and the carrier energy distribution with the SERS signal, and therefore may be used to analyze the emerging plasmon-mediated photocatalysis in situ.

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Mon, 14 13:40 - 15:00

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Mon-QM2-01

Unexpected Chain Collapsing and Phase Separation in Polymer Solutions with Strong Polymer-Solvent Interactions

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Virginia Tech

Molecular dynamics simulations are used to investigate the conformations of a single polymer chain, represented by the Kremer-Grest model, in a solution as the interaction strength between the monomers and solvent atoms is varied. Results show that the chain conformation exhibits an unexpected collapsing behavior at very strong polymer-solvent interactions, similar to the case where the polymer-solvent interaction is unfavorable and the solvent is poor. This behavior makes the corresponding polymer solutions with strong polymer-solvent affinities to phase separate but the mechanism of phase separation seems to differ from that in systems with poor solvents. An approach, motivated by the concept of potential of force between particles in a colloidal suspension, is employed to compute the excluded volume of the monomers in a polymer solution, which is used to interpret the observed interaction-dependent variations of chain conformations and the corresponding phase behavior of polymer solutions. Supported by NSF (DMR-1944887).

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Mon-QM2-02

Synthesis of Nanoscale Polymer Particles: Key Roles of Interfacial Agents in Controlling Size, Shape, and In Situ Assemblies

**Nikunj Kumar Visaveliya (nvisaveliya@ccny.cuny.edu)**

The City College of New York

Nanoscale polymer particles are highly promising for a broad spectrum of various applications ranging from biomedical and energy to sensing and labeling. Controlled structural aspects of the polymer nanoparticles

such as size, shape, morphology, internal softness, interior cross-linking, etc. determine their impact on the cargo loading capacity and controlled/sustained release, the possibility of endocytosis, and degradability during their biomedical application. The designed interfacial features, however, such as stimuli-responsive surfaces, wrinkling, surface porosity, shell-layer swellability, layer-by-layer surface functionalization, surface charge, etc., regulate nanoparticles' interfacial interactions, controlled assembly, movement and collision, and compatibility with the surroundings like a solvent and biological environments. These characteristics define polymer nanoparticles' overall properties/functions based on homogeneity, stability, interfacial tension, and minimization of the surface energy barrier. If nanoparticles are not uniform in their size or shape, the resultant outcome may significantly lower directly related to the concept of structure-function relationship. Therefore, a key requirement is to produce well-defined and uniform polymer nanoparticles with controlled characteristics. In general, polymers are amorphous (or semi-crystalline), flexible, and soft, and hence controlling their structural/interfacial features through the single-step process is a challenge. In this regard, the microfluidic reaction strategy is very promising because of its wide range of advantages such as efficient reactant mixing and fast phase transfer. Here, in this presentation, the state-of-the-art fundamental characteristics of the polymer nanoparticles are presented through experimental results.

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Mon-QM2-03

### Effect of Extreme Nanoconfinement on the Thermodynamics of Polymer Blends in Dense Nanoparticle Packings

**Anastasia Neuman ([annaneu@seas.upenn.edu](mailto:annaneu@seas.upenn.edu)), Daeyeon Lee ([daeyeon@seas.upenn.edu](mailto:daeyeon@seas.upenn.edu)), Robert Riggelman ([rrig@seas.upenn.edu](mailto:rrig@seas.upenn.edu))**

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Infiltration of polymer into the interstices of dense nanoparticle packings leads to the formation of highly loaded nanocomposites with superb mechanical and transport properties. Capillary rise infiltration (CaRI) has emerged as a powerful method to prepare highly loaded composites with a wide range of polymers and nanoparticles. The CaRI system is unique in that regimes of confinement in which the polymer radius of gyration is up to an order of magnitude larger than the nanoparticle packing pore radius can be easily reached. Here, we present a computational study using self-consistent field theory (SCFT) to understand the thermodynamics of these highly confined composites containing two different polymers. We investigate the effects of confinement and polymer-nanoparticle interactions on the miscibility between the two polymers. Two polymers that would undergo macroscopic phase separation become miscible when they are subjected to extreme nanoconfinement. In addition, when a strong repulsive interaction exists between one of the polymers and the nanoparticles, the polymers become miscible over a much larger region. We will discuss the possible thermodynamic origin of such miscibility as a function of polymer-particle and polymer-polymer interactions, and the confinement ratio. The ability to create miscible polymer nanocomposites out of normally incompatible blends would unlock a myriad of novel properties and applications in the future.

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Mon-QM2-04

### Imaging nanoparticles with a trick of the light

**Christopher Bolton ([boltonc@unimelb.edu.au](mailto:boltonc@unimelb.edu.au)), Raymond Dagastine ([rrd@unimelb.edu.au](mailto:rrd@unimelb.edu.au))**

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Particulate imaging and metrology are central to a vast array of research areas and critical to many industrial processes for tuning product fabrication, formulation and quality control. In pushing to understand and control smaller and more complex systems, we have stretched the limits of conventional characterisation tools and are increasingly required to make compromises; for example, electron and super-resolution microscopies are generally harsh or require extensive sample preparation (extreme



temperatures or vacuum, sputter coating, chemical labelling, etc.), while nanometrology tools typically provide indirect measures of size and assume particulates are spherical (or some other convenient shape). Owing to these limitations, multiple tools sometimes need to be employed in concert to characterise even simple spherical particles, and for more complex systems we are forced to balance the time and expense of measurement(s) against the level of distortion considered acceptable for an application. Here we present a multi-source evanescent field scattering technique to enable high-speed, non-destructive, label and stain-free imaging of particulates with nearly any composition or shape, ranging in size from hundreds of microns to tens of nanometres. We outline a variety of different methods for implementing this technique, and describe both direct and statistical results validating the fidelity of geometric measurements for a selection of spherical calibration particles with radii spanning four orders of magnitude (10nm–100µm+). We also demonstrate *ad hoc* sub-wavelength imaging and measurement of a diverse range of particulates including nanospheres, nanotubes/rods and various biological materials. In addition to particle metrology applications, this technique will be especially useful in the life sciences for *in situ* imaging and measurement of delicate or transient biological systems under ambient conditions.

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Mon, 14 15:20 - 16:40

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Mon-AM3-01

Controllable Assemblies of Polymer Nanoparticles: A Hierarchical Approach

**Nikunj Kumar Visaveliya (nvisaveliya@ccny.cuny.edu)**

The City College of New York

In general, assemblies of various nanoscale components (nanoparticles) combine the properties and create the new one that is not possible to harvest by individual nanoparticles separately. The engineering of polymer nanoparticles with controlled properties is very promising for various applications. Furthermore, assembly architectures of functional polymer particles in hierarchical manners are useful because of their physicochemical and surface properties for multi-labeling and sensing to catalysis and biomedical applications. Usually, polymer nanoparticles' interior is mainly made up of the cross-linked network. On the other side, the surface of polymer nanoparticles can be tailored with soft, flexible, and responsive molecules and macromolecules as potential support for the controlled particulate assemblies. Molecular surfactants and polyelectrolytes as interfacial agents improve the stability of the nanoparticles whereas swellable and soft shell-like cross-linked polymeric layer at the interface can significantly enhance the uptake of guest nano-constituents during their interactions to form the assembly architectures. Moreover, layer-by-layer surface-functionalization holds the ability to provide a high variability in assembly architectures of different interfacial properties. Considering these aspects, various assembly architectures of polymer nanoparticles of tunable size, shapes, morphology, and tailored interfaces together with controllable interfacial interactions are presented here. The microfluidic-supported platform has been used for the synthesis of constituent polymer nanoparticles of various structural and interfacial properties, and their assemblies are conducted in batch or flow conditions. Overall, various classes of assemblies of polymer particles from lower nanometer to higher micrometer length scale have been synthesized and presented here.

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Mon-AM3-02

Structure and Phase Behavior of Polyelectrolyte–Nanoparticle Complexes

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Aqueous mixtures of oppositely charged polyelectrolytes (PE) and nanoparticles (NP) self-assemble into dense complexes. This self-assembly forms the basis of diverse phenomena ranging from flocculant action in water treatment, where the PE-NP flocs phase separate and sediment, to DNA compaction around histone proteins into chromatin. Factors such as the PE concentration, length, architecture and

concentrations; NP charge, morphology and concentrations; and solution conditions (pH and ionic strength) play key roles in directing these PE-NP assemblies. In this presentation, we will delineate fundamental investigations into the phase behavior and structure of polyelectrolyte-NP assemblies using small angle X-ray scattering, turbidimetry and rheology with systematic variation of PE sizes and flexibility, NP sizes, and a wide range of concentrations of both components. Trends in interparticle spacings correlations as well as fractal dimensions of assemblies with varying PE and NP concentrations will be discussed, presenting a comprehensive narrative of the hierarchical structure of PE-NP self-assemblies. A general collapse of these trends on a master curve will be highlighted, providing universal guidelines for tailoring the microstructure of these assemblies.

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Mon-AM3-03

### Polymer-Nanoparticle Complex Coacervates

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Complex coacervation is a process involving the complexation of oppositely charged polyelectrolytes, undergoing fluid-fluid phase separation to form a polymer-rich coacervate phase and polymer-poor supernatant phase. With promising applications in food and personal care, agriculture, adhesives, and the pharmaceutical industry, traditional polymer-based complex coacervation has been widely investigated. We were motivated to investigate the incorporation of electrostatically charged nanoparticles- into coacervates with an oppositely charged polyelectrolyte, which has rarely been reported. With intrinsic structural differences e.g., size, charge density, and rigidity, we expected nanoparticles would behave differently from conventional polyelectrolytes. Our previous work indicated strong interactions between bare silica nanoparticles with polyelectrolytes, resulting in solid precipitates instead of liquid coacervation. Herein, we synthesized nanoparticles containing covalently end-tethered polyelectrolyte oligomers, with tunable parameters including polymer chain length and density on the nanoparticle surface. We investigated their coacervation behavior, focusing on the salt resistance and the chemical composition in the coacervate/supernatant phases. Our work provides a rational strategy to introduce/deliver well-suspended nanoparticles in coacervate droplets. Beyond understanding nanoparticle-containing complex coacervates, our work also has the potential to enable the development of fully aqueous coacervate-based paints and composite coatings, as well as provide important insights in understanding bacteria/virus-polymer interactions.

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Mon-AM3-04

### Designing complex polymer colloids for films with enhanced properties and self-stratification

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<sup>5</sup> The Dow Chemical Company, Midland, MI

Latexes (polymer colloids) are frequently used in household paints and varnishes, pressure-sensitive adhesives, textile and carpet backings, paper coatings, inks and gloves etc. While the structure and morphology evolution of a homogenous latex film are well understood, polymer nanocomposite films made from, for example, mixture of latexes or multiphase latexes are still a topic of intensive research. Although a composite film reflects the properties of constituent polymers, the optimized design and composition for enhanced properties and self-stratification are not known, due to a competition between kinetic and thermodynamic effects, and various transport regimes. In this work, we study composite latexes to optimize them for self-stratified films, which provide strong adhesion with the substrate and water repellency (or any other desired property) at the air-film interface simultaneously. We tested various systems including, 1) a multiphase latex with a weakly entangled acrylic component and a strongly entangled acrylic-silicone copolymer, and 2) a blend of very low Mw silicone oil emulsion with a homogenous acrylic latex. A confident assessment of the morphology of composite films and the underlying mechanisms required complementary data from different techniques at various stages of drying: Cryo-TEM, rheology, microscopy, SIMS, SAXS and XPS etc. We observe that the morphology of multiphase latex film is kinetically controlled, and at room temperature ( $\sim T_g + 25^\circ\text{C}$ ) the large Mw acrylic-silicone cores are embedded in the lower Mw acrylic matrix. Drying at elevated temperatures ( $\sim T_g + 75^\circ\text{C}$ ) significantly changes the properties of film, resulting from the unraveling of cores to form interchain entanglements. However, the thermodynamic equilibrium state of two polymeric layers on top of each other is not achievable on the timescale of observations. The blend of oil emulsion with latex performs better in terms of self-stratification of silicone at air-film interface, but it requires very low concentrations of emulsion. Future directions for this work include studying blends of more than two latexes, and mixing anisotropic particles (nonspherical shape, Janus particles etc) with latex. Our work provides a robust toolbox and strategies for studying complex latexes, and fundamental insights into the development of new smart coating formulations.

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Mon, 14 15:20 - 16:40

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Mon-BM3-01

Evaluating the Surfactant Performance in Achieving the Optimal Oil-Water Separation in Emulsion Systems using HLD-NAC model

**Hassan Ghasemi (hassan.ghasemi@modares.ac.ir), Fatemeh Eslami (f\_eslami@modares.ac.ir)**

Tarbiat Modares University

One of the most applied industrial separation techniques to break oil-water emulsion systems is the chemical method. However, choosing the proper surfactant mixtures—as a demulsifier—for each emulsion system is a difficult task, demanding expensive and time-consuming experiments. Formulating the emulsion and microemulsion systems, which is possible through Hydrophilic-Lipophilic-Deviation (HLD) helps to fulfill this task. This semi-empirical model establishes a linear relationship between the influential variables of the phase behavior of surfactant, oil, water (SOW) systems such as salinity, temperature, and characteristic parameters of its constituents such as alcohol, oil, and surfactant. Here, HLD and its supplementary framework—net-average-curvature (NAC)—is applied to obtain an optimal condition for demulsification of oil-in-water emulsion system—real industrial wastewater—with different water in oil ratios (WOR). In this regard, performing the salinity phase scans, the proper parameter of the demulsifier is detected. Then, using the NAC approach, the solubilization properties, shape of droplets, and the optimal area of phase separation of the synthetic microemulsion systems are obtained. The modified curvatures of non-spherical droplets—as an indicator of how droplet sizes are changing with HLD—were consistent with the experimental separation results. This approach is shown to be a new promising method for the determination of the best surfactant mixtures to demulsify the industrial wastewater and reducing the experimental cost substantially.

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Mon-BM3-02

Effect of processing conditions on the stability and texture of cosmetic emulsions

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L'Oreal USA

The skin care products can be either Oil-in-Water (O/W), Water-in-Oil (W/O) or Silicone/W emulsion with skin active ingredients in either water phase or oil phase. The O/W emulsion product is more popular because it delivers the freshness feel upon applied on the skin. To stabilize such emulsions in the skin care formulas, many surfactant systems are used to achieve the long shelf life at various conditions such as temperature, shaking and transportation. In this presentation, we will discuss the use of steareth-2 and steareth-20 surfactants as the emulsification system for O/W emulsion in skin care formulation and the impact of process conditions on the stability and product texture.

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Mon-BM3-03

Getting out of a tight spot: Using complex fluids to remove trapped droplets from porous media  
**(Keynote Lecture)**

**Sujit Datta (ssdatta@princeton.edu)**

Chemical and Biological Engineering, Princeton University

Diverse energy and environmental processes, such as groundwater remediation and oil recovery, require the removal of trapped immiscible fluid droplets (e.g., non-aqueous contaminants or hydrocarbons) from porous media. Complex fluids like colloidal suspensions and polymer solutions have potential to enhance fluid removal *via* a range of different mechanisms. However, systematic studies of this behavior *in situ* are challenging due to the opacity of typical 3D media; as a result, general principles to guide the formulation and use of complex fluids are lacking. Here, I will describe our work addressing this challenge using confocal microscopy to directly visualize complex fluid transport, as well as droplet trapping and mobilization, in refractive index-matched 3D porous media. By shedding light on the multi-scale interactions between trapped fluid droplets, injected complex fluids, and porous media that have traditionally been represented in black-box models using “lumped” empirical parameters, we anticipate that our work will help guide the development of more accurate and generalizable models of fluid removal.

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Mon, 14 15:20 - 16:40

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Mon-CM3-01

Automating Bayesian inference and design for acoustic levitation and propulsion

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The propulsion of micro- and nanoparticles using ultrasound is an attractive strategy for the remote manipulation of colloidal matter using biocompatible energy inputs. By controlling the three-dimensional shape of the particle, it is possible to control its levitation and directed motion within simple acoustic fields. Nevertheless, there remain significant discrepancies between the experimental observations of particle motions in microchamber acoustic cells and the predictions of hydrodynamic models due to operation off-resonance. The reconciliation of these differences can benefit from the use of Bayesian inference and experimental design within a fully automated framework that iterates the processes of design, observation, and inference. Here, we demonstrate how this framework can be applied to accurately quantify the frequency dependent acoustic pressure within a resonant chamber using a minimal number of experiments. We compare the performance of such optimal experiments to an exhaustive grid search of the frequency domain. More generally, this normative framework represents a powerful strategy for automating the scientific method in the context of active colloids when strong guiding models are available.

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Mon-CM3-02

### Vapor pressure of superparamagnetic colloidal cluster

**Kedar Joshi (kedar.joshi@rice.edu), Sibani Lisa Biswal (biswal@rice.edu)**

Department of Chemical and Biomolecular Engineering, Rice University

Paramagnetic colloids undergo a phase transition in the presence of an external rotating magnetic field. This phase transition exhibits properties similar to vapor (bulk)- liquid (clusters) equilibrium of a single component system. We demonstrate the equilibrium between the cluster and bulk phases under the apparent temperature, which in this case, is related to the strength of an external magnetic field. We show that the system of paramagnetic colloids has an exponential trend between vapor pressure vs. apparent temperature, as found for any pure liquid. Additionally, this equilibrium between two phases follows Kelvin's equation, which relates the vapor pressure to the average size of droplets, in this case, the size of colloidal clusters. Even at a smaller number of particles, compared to millions of molecules in tiny droplets, these clusters exhibit bulk-like properties. This work demonstrates the potential of this system of paramagnetic colloids to learn the microscopic and macroscopic changes as a group of molecules manifest a collective behavior and common physical properties from individual molecules.

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Mon-CM3-03

### Biosensors Based on Complex Liquid Crystal Emulsions

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Liquid emulsions are of increasing importance for applications in pharmaceuticals, medical diagnostics, or chemical sensing. Our group is focused on developing sensing platforms based on multiphase liquid droplets consisting of organic and fluorocarbon oils, dispersed in an aqueous phase.[1] We have recently introduced liquid crystals (LCs) into these complex emulsions and demonstrated how the anisotropic nature of LCs provides new functionalities and unusual behaviors. For instance, we can prepare droplets with different internal configurations and create topological singularities with chemical functionality for the precise attachment of antibodies or nanoparticles at the interfaces. [2],[3] The ability to achieve precise organization of recognition sites can provide access to a variety of sensing applications, wherein the LC alignment acts as an amplifier for local perturbations. Nonetheless, in these sensors the observables require optical microscopies with crossed-polarizers, which can limit real-world utility. In order to improve the simplicity of the optical read-out, we targeted complex fluid emulsions that give color changes in response to pathogens by incorporating chiral nematic LCs (N\*). N\* are photonic materials that exhibit light reflection due to the presence of a helical organization. Herein, we exploit these rich photonic properties for constructing a new sensing paradigm. Specifically, we employed chiral polymer surfactants that have boronic acid receptors. Biomolecular recognition events are capable to vary the pitch length of the N\* organization due to the presence of binaphthyl units in the polymer structure, which are known to be powerful chiral dopants. We demonstrate that these interface triggered reflection changes can be used to create a rapid and sensitive method for the detection of the foodborne pathogen *Salmonella*. The simple to fabricate cholesteric emulsions and the facile optical read-out provides a new approach for biological and chemical sensing.

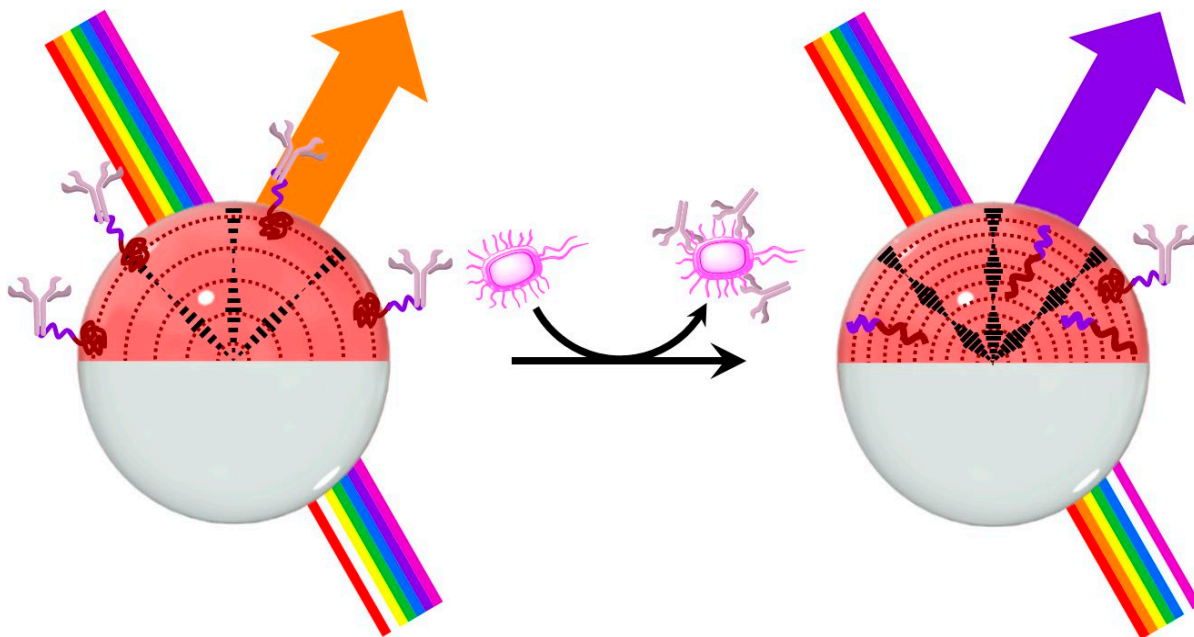


Figure 1. Conceptual scheme of the mechanism for the detection of *Salmonella enterica* using  $N^*$  complex emulsions. Changes in the reflected light are produced through changes in the interfacial activity of boronic acid polymeric surfactants, induced by reversible assembly of IgG antibodies at the LC/W interface and upon removal by competitive binding to *Salmonella* cells. [1] L. Zeininger et al. ACS Cent. Sci. 2019, 5, 789-795; J. Li et al. PNAS 2020, 117, 11923-11930. [2] A. Concellón, C. A. Zentner, T. M. Swager. J. Am. Chem. Soc. 2019, 141, 18246-18255. [3] C. A. Zentner, A. Concellón, T. M. Swager. ACS Cent. Sci. 2020, 6, 1460-1466.

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Mon, 14 15:20 - 16:40

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Mon-DM3-01

Temperature–structure–rheology response of portlandite suspensions

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The temperature dependence of the rheology of suspensions that feature attractive or weakly repulsive particles is complex because temperature induces changes in particle to particle and particle to suspending-medium interactions. However, the mechanisms by which temperature affects the structure of aggregating colloidal suspension and, in turn, how their structure governs rheology remain unclear. While processing concentrated cementitious suspensions and other particulate mineral suspensions in highly alkaline media, which are subjected to varying processing temperatures, the temperature-induced modification in the suspension rheology can be crucial and can impact processability. This study elaborates the mechanisms that control the temperature-dependent rheological behavior of portlandite (calcium hydroxide:  $\text{Ca}(\text{OH})_2$ ) suspensions, which present high ionic strength and strong charge screening behaviors. A special focus is placed on identifying the impact of temperature on the interparticle interactions, fractal structuring, and aggregation kinetics of the suspensions. Unlike the saturated  $\text{Ca}(\text{OH})_2$  solution suspending medium, the viscosity of dense portlandite suspensions increases with increasing temperature, featuring an anomalous “negative” effective activation energy for viscous flow. This behavior is shown to arise from the temperature-induced aggregation of portlandite particulates caused by the diminution of electrostatic repulsive forces with increasing temperature. The impact of temperature on the fractal structure of aggregates is evident in low volume fractions in the strong-link regime wherein branched flocs (i.e., more open structure) are formed, but weakened at higher volume fractions in the weak-link regime featuring densely packed flocs. Thus, the temperature dependence of the suspension viscosity is found to diminish with increasing particle volume fraction ( $\phi$ ) as a result of volumetric crowding and the formation of denser fractal structures in the suspension. Furthermore, it is shown that the suspending medium attributes (i.e., ionic strength and ion valance of the electrolyte) and the resulting interparticle interactions can modify the temperature–viscosity responses of a suspension. Further, in comb polyelectrolyte dispersant-based electro-sterically stabilized portlandite suspensions, the dispersant concentration is found to strongly influence the temperature-induced aggregation kinetics. The optimum dispersant dosage to mitigate the temperature-induced aggregation varies with the temperature. These outcomes provide new insights into aggregation processes that affect the temperature-dependent rheology of portlandite-based and similar suspensions that feature strong charge screening behavior.

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Mon-DM3-02

Understanding the true nature of Na-montmorillonite aqueous suspensions

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Na-montmorillonite (Na-Mt) is a naturally occurring clay which has remained the subject of numerous studies dated back to the work of Irving Langmuir and Herbert Freundlich. Na-Mt consists of an octahedral sheet (di-octahedral aluminium hydroxide) sandwiched between two tetrahedral sheets (silica). The sheets have isomorphic substitutions by less charged cations which provides a net negative layer charge compensated by interlayer exchangeable cations whose valency and hydration properties control both swelling and colloidal behaviour. Na-Mt suspensions display a sol-gel transition at very low volume fractions. The structure of the gel formed has remained a point of contention in literature. Two main models are proposed based on either the formation of a tridimensional network governed by electrostatic attraction between platelets, or the formation of an oriented network stabilized by repulsive forces caused by interacting double layers. Previous SAXS based experiments proposed a repulsive microstructure for Na-Mt gels. However, these experiments were limited by the minimum scattering angle which could only cover a length scale up to 1 micron. In this talk, we will provide a brief overview of our recent USAXS and USANS experiments which show the presence of entities much larger than the individual particles at concentrations above the gel point. Characteristics such as birefringence below and above the gel point, physical ageing, thixotropy and effect of particle size on the microstructure will be presented.

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Mon-DM3-03

Microrheological characterization of covalent adaptable hydrogel degradation in response to environmental pH changes that mimics in the gastrointestinal tract

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Covalent adaptable hydrogels (CAHs) are synthetic 3D polymeric scaffolds which are designed using dynamic covalent chemistry. These materials dynamically change their structure in response to environmental stimuli, such as the addition of shear or change in pH, such as in the gastrointestinal (GI) tract. This stimuli-responsive structural evolution makes CAHs ideal for biological applications, including as a delivery vehicle for controlled and targeted oral delivery. To use CAHs for this application, we must first understand material property evolution and dynamic structural changes during degradation that are induced by pH changes that mimic the pH in the GI tract. The material we are characterizing is a CAH, composed of 8-arm poly(ethylene glycol) (PEG)-hydrazine that self-assembles with 8-arm star PEG-aldehyde to form a hydrazone bond. To mimic pH changes in each part of the digestive tract and simultaneously characterize scaffold degradation, we use  $\mu$ 2rheology.  $\mu$ 2rheology is multiple particle tracking microrheology (MPT) in a microfluidic device. In MPT, we measure Brownian motion of fluorescent probe particles embedded in the sample and material rheological properties are calculated from this particle motion. To mimic each pH in the GI tract, we use a two-layer microfluidic device that enables consecutive fluid exchange around a single sample with minimal sample loss. Using  $\mu$ 2rheology, we characterize CAH degradation at a single pH (pH 4.3, 5.5 and 7.4), with a single pH exchange (pH 4.3 to 7.4 and pH 7.4 to 4.3) and during temporal pH changes that mimic the pH of the whole GI tract. We calculate the critical relaxation exponent for degradation at a single pH and with a single pH exchange to quantitatively characterize the gel-sol transition, which is independent of incubation pH. From measurements of a single pH exchange and temporal pH changes through the whole GI tract, we determine that CAH degradation kinetics and material property evolution are not influenced by degradation history. However, the initial cross-link density of the scaffold at each pH exchange can be reduced by previous degradation, which decreases the degradation time for the scaffold to transition from a gel to a sol. This change in degradation time will inevitably change molecular release. These results indicate degradation can be tuned by changing scaffold cross-link density, which can be done by changing the ratio of backbone to cross-linker functionality, to design this CAH as a controlled and targeted oral delivery vehicle.

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Mon-DM3-04

Rheological properties of phase transitions in polydisperse and monodisperse colloidal rod system

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Rheological modifiers are used to tune the rheology or drive phase changes, and it is crucial to understanding material structure and properties. Hydrogenated castor oil (HCO) is a colloidal rod that is currently used as a rheological modifier in homecare products, but these rods are polydisperse leading to complex heterogeneous structures and can be hard to control. To determine the effect of this polydispersity on rheological modification, this work characterizes two colloidal rod systems of similar size, HCO and polyamide (PA, a monodisperse colloidal rod) using multiple particle tracking microrheology (MPT) during phase transitions. In MPT, fluorescent probe particles are embedded in the sample and their Brownian motion is measured. Our system consists of a colloid (PA or HCO), a surfactant (linear alkylbenzene sulfonate, LAS), and a non-absorbing polymer (polyethylene oxide, PEO), which is used to drive gelation through depletion interactions. We measure that at  $LAS : colloid > 16$ , the diffusivity of probe particles in these systems rapidly decreases when PEO concentration is increased from 0.3 to 0.35  $c/c^*$ . The change



in diffusivity qualitatively indicates that a phase transition happens between 0.3 and 0.35 c/c\*. In contrast, the logarithmic slope of the MSD, which is an indication of restriction of particle movement, gradually decreases indicating a consistent growth of a scaffold network. Therefore, we use time-cure superposition (TCS) to quantitatively determine the critical phase transition point. Using TCS, we determine that rheological evolution depends on LAS : colloid. It is determined that the critical depletant concentration is not significantly affected by LAS : colloid. We also calculate the critical relaxation exponent,  $n$ , and it is indicated that gelation of both systems is dependent on LAS : colloid. The critical relaxation exponent for LAS : colloid = 16 is  $n_{PA} = 0.34 \pm 0.07$  and  $n_{HCO} = 0.37 \pm 0.14$ , which indicates that this scaffold is a tightly associated network. When LAS : colloid > 16,  $n_{PA} = 0.74 \pm 0.13$  and  $n_{HCO} = 0.83 \pm 0.10$ , which indicates the material loosely associated network at the gel point. This study indicates that the rheology and microstructure of monodisperse and polydisperse colloidal rod systems with similar sizes are dependent on the surfactant to colloid ratio. This provides guidance for future product design which can eliminate trial-and-error experiments to find the composition that provides the desired rheology minimizing both expense and time.

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## Mon, 14 15:20 - 16:40

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Mon-EM3-01

Detecting and distinguishing particles in heterogeneous colloidal mixtures by size, refractive index and symmetry with Total Holographic Characterization

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Spheryx, Inc.

Distinguishing and identifying different species of particles are major challenges of particle characterization technologies. By measuring particles' index of refraction, Total Holographic Characterization (THC) provides a unique tool that can be used to differentiate particle species that have overlapping size ranges. In this study, we demonstrate THC's novel ability to measure an additional particle property: symmetry. Measuring particle symmetry allows for more precise differentiation and identification of particle species that have overlapping sizes and refractive indexes. With THC's symmetry tool, protein aggregates can be more accurately distinguished from oil droplets and single spheres from particle clusters. The symmetry feature is reliable in the range of particle sizes from 800nm to 10 $\mu$ m. With this technology, over 95% of beads, such as polystyrene or silica microspheres, are identified as spherical. Similarly, over 90% of droplets in oil emulsions are identified as spherical, while over 75% of protein aggregates are identified as non-spherical. The symmetry feature provides a novel, powerful approach to particle suspension analysis. Preliminary results on the identification of rod-like particles will also be presented.

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Mon-EM3-02

Investigating the Distribution of Surface Ligands in Drop-Casted Colloidal Gold Nanoparticles Using Scanning Near-Field Optical Microscopy (s-SNOM)

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Colloidal metal nanoparticles have attracted many attentions due to their wide applications specially in localized surface plasmons and photocatalysis. Surface ligands are an inseparable part of metal nanoparticles which play an important role in adsorbate-nanoparticle interactions. Centrifugation is the most common method to remove the excess surface ligands in metal nanoparticles. However, the distribution of surface ligands in drop-casted colloidal metal nanoparticles as well as a quantitative

investigation on effectiveness of the centrifugation to remove the excess surface ligands in colloidal metal nanoparticles are not available to date. In this work, we prepare drop-casted colloidal gold nanospheres with citrate as surface ligand on as deposited and template stripped gold film with multiple rounds of centrifugation, and we use scattering-type scanning near-field optical microscopy (sSNOM) to investigate the distributions of excess citrate and quantify the effect of multiple rounds of centrifugation to remove the excess citrate. We observe that on both as deposited and template stripped gold film substrates, the excess surface ligands tend to accumulate so close to the ring boundary and as we move toward the center of the ring the amount of citrate decreases very quickly. Moreover, we see a drastic decrease in the amount of citrate after the second round of centrifugation but no significant change after third and fourth round of centrifugation was observed. We also discuss the single gold nanoparticles inside the ring as well as the correlation between the optical amplitude and phase contrast on the outer edge of the ring boundary.

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Mon-EM3-03

Self-assembly of amphiphilic fluorescent nanoparticles for bioimaging

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Self-assembly is the process of arranging molecular units into ordered structures that can be used in advanced techniques. Fluorescence imaging of biological tissues involves noninvasive visible to near-infrared radiation ranging from 440 nm to 900 nm. Although this region is well-studied, some application-based drawbacks include low stability, low water solubility of emitters, and poor biocompatibility. The challenges faced with current bioimaging systems have motivated us to study two nanosystems consisting of a hydrophobic dye, TRPZ. TRPZ possesses a rigid, linear, coplanar conjugated structure similar to pentacene, with multiple reactive sites and unique spectroscopic properties. We first coupled the propargylated dye (TRPZ) to dendritic 2,2-bis(hydroxymethyl)propionic acid (Bis MPA) alanine with protected amine groups via azide-alkyne Huisgen cycloaddition. Deprotection of tert-butyl carbamates (BOC) protected amine groups with trifluoroacetic acid afforded a cationic terminated TRPZ-bis MPA amphiphile. TRPZ-bis MPA amine was nano precipitated into water to obtain nanoparticles with sizes of 102 nm (DLS) and 130.0 nm (TEM). Secondly, TRPZ was encapsulated in pluronic-F127 (Mw=12kD) polymer surfactant to make nanoparticles with average sizes of 319.5 nm (DLS) and 323.5 nm (TEM). The photophysical properties of the nanoparticles show ideal properties for bioimaging. Size and stability studies confirm the suitability of the nanoparticles for bioimaging applications. Further evidence was provided by cell viability studies confirming the low cytotoxicity of TRPZ-bis MPA amine.

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Mon-EM3-04

Novel methods for investigating the conditions that promote formation of pathogenic biofilms

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Some pathogenic bacteria are able to attach to interfaces where they can aggregate and form a macroscopic structure with an extracellular matrix. The resultant structure is referred to as a biofilm (or plaque) and is often mechanically robust. Formation of such a biofilm makes bacteria more resistant to unfavorable environmental conditions, such as efforts to clean processing equipment or fresh produce, so

it is of interest to understand the conditions under which they form. In this presentation we describe a series of techniques to detect the formation of biofilms from pathogenic bacteria at solid-liquid and air-liquid interfaces. The results provide insight into the role of bacterial sedimentation and surface attachment on the formation of biofilms for several strains of bacteria: *Listeria monocytogenes*, *Salmonella enterica*, *Pseudomonas Aeruginosa*, *Acinetobacter baumannii*.

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Mon-GM3-01

Effect of surface wettability on the interfacial adhesion of thermosetting polymer composites

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The quality of interfaces between the polymer matrix and reinforcements can have a significant effect on the performance of polymer composites. Under most circumstances, failures at the interface region are undesirable. The formation of interfacial voids can lead to debonding, which results in inferior mechanical and physical properties and adversely affects their performance and applications. In this work, we investigate the relationship between surface wettability and interfacial fracture energy, with the goal of tailoring adhesion for polymer composites. A series of model functionalized surfaces was created using silane coupling agents with different organo-functionalities in order to alter surface wettability, then the effect of surface wettability on interfacial adhesion was evaluated. Attenuated total reflection FTIR (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) were used to characterize the surface chemistries of model surfaces. Surface energies and wettability were further determined via contact angle analysis. The 90° peel test was used to evaluate the interfacial adhesion strength between a representative thermosetting polymer network and model surfaces. A correlation between resin wettability and interfacial adhesion was observed, which suggests this approach is a promising route to select organo-functionalities to alter the interfacial interactions between polymers and reinforcements for tailorable polymer composites.

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Mon-GM3-02

Contact angle hysteresis and contact-line shape of a pendant droplet on a PDMS-coated anisotropically curved surface

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Recent studies show that the advancing or receding contact angle can depend on the geometry of contact line, but the physics behind this phenomenon is not fully revealed yet. Our study is focused on the influence of solid surface geometry on contact angle hysteresis and the shape of the contact line. We measured the droplet shape and contact angles for a pendant water droplet suspended from PDMS coated flat glass plates and 3mm-diameter cylindrical glass rods. In the advancing process, we used a pump to increase the volume of the droplet from 3 $\mu$ L to 24 $\mu$ L, with air-water-solid contact line diameters increasing from 1.7mm to 2.7mm accordingly. We found the static advancing contact angle was greater for the cylinder (about 101°) than for the flat plate (about 90°). In addition, we measured the shape of the contact line by analyzing photos of side and bottom view of the pendant droplet. For the receding process, the receding rate of the contact line along the circumferential direction was larger than along the axial direction. After measuring the shapes of the droplets and contact lines, we compare them with the equilibrium shapes computed using Surface Evolver. In addition, we will discuss the effect of the humidity on contact angle hysteresis. This

work may provide new insights into the origin of contact angle hysteresis and offer a route to calculating droplet shapes. \* We acknowledge NSF CBET-1803797 for support.

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Mon-GM3-03

Drainage from a Fluid-Handling Component with Multiple Orifices due to Inclination or Rotation

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AceMarga LLC

The onset of drainage of liquids from fluid-handling components with two or more orifices was evaluated. The components were filled with water, ethylene glycol, or ethyl alcohol and oriented vertically with their orifices facing downward. The lower end of the components was slowly raised toward the horizon. No flow occurred until a critical angle of inclination was reached. The resistance to drainage was greatest for small, closely spaced orifices and declined precipitously as the size and spacing of the orifices increased. The onset of drainage was successfully modeled as a balance between the hydrostatic pressure in the bulk liquid and the Laplace pressure of the air-liquid interfaces present within the orifices.

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Mon-GM3-04

Evaporative assembly of non-buckling shells on a superhydrophobic substrate

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Solvent evaporation in unpinned droplets of colloidal suspensions leads to the formation of porous shells which buckle under the pressure differential imposed by drying. We investigate the role of aspect ratio of rod-shaped particles in suppressing such buckling instabilities. Longer, thinner rods pack into permeable shells with consequently lower Darcy's pressure and thus avoid buckling. Our results reveal the role of particle morphology in suppressing buckling and indicate particle shape as a tunable parameter for emerging mechanical stability in unpinned droplets. From an industrial perspective, this highlights the economic advantage in exploiting the properties conveyed by shape to optimize food and drug micro-processing.

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Mon, 14 15:20 - 16:40

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Mon-KM3-01

Biomechanical measurements of a pressurized blood vessel-on-a-chip

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We use a 3D model blood vessel platform to measure the elasticity and membrane permeability of the endothelial cell layer using applied pneumatic pressure. The deformation of the mean vessel diameter is observed under varying pressures up to 300 Pa. We obtain a value for the Young's modulus of the cell layer in low strain where a linear elastic response is observed and use a hyperelastic model that describes the strain hardening observed at larger strains (pressure). Fluorescent dye is used to track the flow through the cell layer to determine the membrane flow resistance as a function of applied pressure. Finally, we

track the 3D positions of cell nuclei while pressurizing the vessel to observe local deformation and correlate inter-cell deformation with the local structure of the cell layer.

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Mon-KM3-02

## Dilatational Mechanics Evolution of Lung Surfactant Film throughout Acute Respiratory Distress Syndrome Progression Leads to Lung Collapse

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Acute respiratory distress syndrome (ARDS) is a life-threatening condition characterized by severe breathing difficulties affecting 200,000 people in the US annually with no known cure and 40% mortality. ARDS begins with trauma to the lung either by disease (including COVID-19 induced pneumonia), injury, or trauma. These underlying factors trigger an inflammatory response that leads to increased permeability of alveolar-capillary barriers. Due to the enhanced permeability, phospholipases, serum proteins, and other components of the innate immune system flood the alveolar spaces. Of particular interest is the action of phospholipase A2, which degrades bacterial, viral, and native membrane double-chain lipids into soluble single-chain lysolipids and fatty acids. The orders of magnitude increased solubility of the lysolipids cause them to dissolve out of the membranes, leading to bacterial and viral cell lysis and death. However, the resulting increased concentration of surface-active lysolipids in the alveolar fluids leads to alterations in the interfacial properties of native lung surfactants, which in turn can lead to mechanical instabilities in lung inflation. We hypothesize that this evolution of composition leads to a subsequent pulmonary collapse through lung surfactant displacement by these immune system actors. The changing composition of the interface causes an order of magnitude decrease in the dilatational modulus of the lung surfactant monolayer. This decrease in the dilatational modulus can lead to the Laplace Instability, in which smaller alveoli deflate and larger alveoli are distended, which are typical symptoms of ARDS. We find that adding a model lysolipid to our in vitro model lung surfactant monolayers, the dilatational modulus spontaneously decreases by orders of magnitude. The interfacial morphology and phase behavior also change dramatically, transitioning from solid-like to liquid-like, consistent with our initial hypothesis that the elevated concentration of these inflammatory products is one of the dominant mechanisms in ARDS progression. For sufficiently small dilatational moduli, the interfacial tension cannot adjust with changes in the interfacial area and avoid the Laplace instability. We find that the dilatational modulus is an extremely sensitive measure of the interfacial composition and this information can be invaluable in determining the effects of competing surface-active compounds in the subphase. The confirmation of this hypothesis is crucial in providing a mechanistic view of ARDS progression which can lead to new therapeutic interventions to treating ARDS.

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Mon-KM3-03

## Vesicle shape dynamics under steady and oscillatory extensional flows – insights from simulations and experiments

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We study the non-equilibrium shape dynamics of lipid vesicles using a combination of boundary element simulations and fluorescence imaging experiments under a wide range of flow conditions. Our work provides a clear understanding of the shape and stability of osmotically-deflated vesicles in steady and time-dependent, transient flows. This talk focuses on vesicle dynamics in steady and time-dependent extensional flows, which are commonly encountered in contractions, expansions, and/or suction flows. In steady flow, our results show that moderately deflated vesicles undergo different shape instabilities (asymmetric dumbbell or symmetric stretching) above a critical flowrate that are qualitatively different than droplet breakup. The physical origins of vesicle membrane shape instabilities are discussed in detail and compared with microfluidic experiments. We further discuss vesicle shape dynamics in large-amplitude oscillatory extensional (LAOE) flow, including both numerical simulations and experiments enabled by a Stokes trap, which is a new technique for particle manipulation using feedback control. Our results reveal three distinct dynamical regimes -- pulsating, reorienting, and symmetrical deformations -- based on the competition between flow frequency, flow time scale, and membrane deformation timescale. We construct phase diagrams characterizing the vesicle shapes in these three regimes in terms of the Deborah number ( $De$ , dimensionless flow frequency) and capillary number ( $Ca$ , dimensionless flow strength). Finally, we quantify the nonlinear relationship between average vesicle stress and strain rate in these oscillatory flows.

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Mon-KM3-04

## The Role of Phospholipid Headgroup in the Formation and Interfacial Rheology of Binary Phospholipid-Cholesterol Monolayers

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Lipids are major building blocks of biological membranes, with the glycerophospholipids of phosphatidylcholines (PC) and phosphatidylethanolamines (PE) being the most abundant in mammals. They undergo complicated intermolecular interactions with other lipids such as cholesterol (CHOL), impacting membrane fluidity and the formation of microdomains. In varied biological membranes from cancer cells to the myelin sheath, subtle changes in the lipid composition can have drastic impacts on membrane structure and function. PC and PE headgroups are both zwitterionic, but a key difference is PE can be both a hydrogen bond acceptor and donor while PC can only be an acceptor, leading to differences in, for example, hydration and inter-headgroup interactions. Previous studies have investigated the impacts of PE and PC headgroups on their respective monolayer formation and rheology, but our understanding of how the difference in headgroup affects monolayer formation and rheology in the presence of CHOL is lacking. Here we explore monolayer formation and rheology of binary mixtures of CHOL and either 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) or 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine (DPPE), both having the same symmetric C16:0 tails. We perform both surface pressure versus area isotherms using the pendant drop technique as well as interfacial rheology measurements using oscillating pendant drops with DPPC-CHOL and DPPE-CHOL films having varying amounts of CHOL. We demonstrate expected CHOL-induced condensation in DPPC monolayers, but more complicated condensation and expansion in DPPE monolayers depending on CHOL content. This effect is quantified using the excess Gibbs free energy of mixing, where a transition from net attraction to net repulsion between DPPE and CHOL as CHOL is increased is observed. This supports previous interpretations that stronger inter-headgroup hydrogen bonding between DPPE lipids favors immiscibility at high CHOL content compared to DPPC. In rheological results, the increased hydration and penetration into the aqueous phase results in DPPE in the absence of CHOL forming a less cohesive film with lower dilatational moduli than DPPC. However, the addition of CHOL results in stiffer DPPE-CHOL films than DPPC-CHOL. We hypothesize that this reversal in behavior is due to the combined effects of dehydration induced by the presence of CHOL coupled with stronger DPPE-DPPE interactions. Our results simultaneously add to our understanding of complicated relationships between lipids in biological films while highlighting the complexity and questions yet to be addressed in the role of lipid composition on biological membrane properties.

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# Mon, 14 15:20 - 16:40

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Mon-MM3-01

Driving energetically unfavorable dehydrogenation dynamics with plasmonics

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Nanoparticle phase transformations and their transient states underlie many technologies in energy storage, memory, and catalysis. However, modifying these intermediate states requires bridging the length-scale gap between the atomic-scale structural features (such as atomic coordination number and surface strain) that influence dynamics and the macroscale extrinsic parameters (e.g. temperature, chemical environment) that can be controlled. Optical excitation of localized surface plasmon resonances (LSPRs) offers a solution for overcoming this size mismatch. Here, we use in situ environmental transmission electron microscopy coupled with optical illumination to demonstrate how LSPRs enable spatially-modified phase transformation dynamics in nanoparticles. As a model reaction, we study the gas-phase photocatalytic dehydrogenation of a variety of Au-Pd systems, in which the Au acts as a plasmonic light absorber and Pd serves as the catalyst. Under controlled hydrogen pressures, temperatures, and illumination conditions, we study the kinetics of the desorption reaction triggered by the optical excitation of plasmons. We find that plasmons control photochemistry in three ways. First, plasmons modify the rate of distinct reaction steps differently, increasing the overall rate more than ten-fold. Secondly, plasmons open new reaction pathways that are not observed without illumination. Finally, reaction nucleation occurs at electromagnetic hot-spots – even when those hot-spots do not occur in the preferred nucleation site. Our results help elucidate the role of plasmons in light-driven phase transformations, en-route to design of site-selective and product-specific photocatalysts.

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Mon-MM3-02

Spectroscopic signatures of plasmon-induced charge separation in gold nanorods on metal-oxide semiconductors

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<sup>1</sup> Department of Chemistry, Rice University

<sup>2</sup> Department of Electrical and Computer Engineering, Rice University

Plasmon-induced charge separation, the process by which a plasmon decays into spatially separated hot-carriers, has been studied for the development of plasmonic photodiodes and solar cells. Current methods for evaluating the efficiency of a plasmon-induced charge separation device rely on having completed photodevices and are based on the bulk characteristics of the device. Here, we use single-particle darkfield scattering and photoluminescence spectroscopy and imaging to identify key spectroscopic signatures that are quantitatively related to plasmon-induced charge separation device efficiency. We identify darkfield scattering linewidth broadening and photoluminescence quantum yield quenching as two spectroscopic signatures for indirectly predicting the plasmon-induced charge separation efficiency. We find that darkfield scattering linewidth broadening is due to chemical interface damping through charge injection. The photoluminescence quantum yield quenching is indicative of space-charge separation efficiency and related to Schottky barrier formation in Au-TiO<sub>2</sub> interfaces but not in Au-ITO interfaces. Through these two spectroscopic signatures we can determine the contributions of different plasmon-induced charge separation device factors on performance such as Schottky barrier formation and height, plasmonic nanoparticle size, and effects of electron/hole transport materials prior to fabricating a completed device.

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Mon-MM3-03

## Analysis of the optical response of periodic arrays of nanostructures

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Instituto de Óptica (IO-CSIC), Consejo Superior de Investigaciones Científicas, Spain

Periodic arrays of nanostructures can support collective modes known as lattice resonances that produce strong and spectrally narrow responses. Thanks to these exceptional properties, periodic arrays are being exploited in a wide variety of applications, including ultrasensitive biosensing, nanoscale light emission, and color printing, to cite a few. In this talk, we will analyze how the arrangement of the particles within the unit cell of the array determines its optical response [1-3]. We will also discuss how the interplay between the response of the individual constituents and the collective interaction dictates the ultimate limits of the field enhancement provided by these systems [4]. [1] S. Baur, S. Sanders, and A. Manjavacas, ACS Nano (2018). [2] A. Cuartero-González, L. Zundel, S. Sanders, A. I. Fernández-Domínguez, and A. Manjavacas, ACS Nano (2020). [3] L. Zundel, A. May, and A. Manjavacas, ACS Photonics (2021). [4] A. Manjavacas, L. Zundel, and S. Sanders, ACS Nano (2019).

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Mon-MM3-04

## Plasmonic Coupling in Self-Assembled Nanocrystal Gels and Superlattices

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<sup>2</sup> Department of Chemistry, University of Texas at Austin, Austin, TX

Inorganic nanocrystals have remarkable plasmonic properties that can be tuned through nanocrystal size, shape, and chemical composition. The plasmonic response of closely spaced nanocrystals couple together, so their collective optoelectronic properties are also sensitive to structure. Materials self-assembled from colloidal dispersions of plasmonic nanocrystals take advantage of this structure-dependent behavior and are promising for scalable and highly tunable functional materials, particularly as photovoltaics, catalysts, and electrolytes. Computer simulations and statistical thermodynamics models have helped connect how the microscopic details of the nanocrystal building blocks and their environment affect the assembled morphologies, but probing the effective plasmonic properties remains a major bottleneck. The necessary optical calculations require expensive numerical solutions to many-bodied systems of equations and are therefore limited to configurations of only a handful of particles, which are not representative of large-scale structural features and heterogeneities. This limitation has hindered the rational design of self-assembled plasmonic materials. To address these shortcomings, we have developed computational tools to rapidly determine the optical response of nanocrystal materials, allowing for tens of thousands of particles to be probed at a time. We use these tools to investigate plasmonic coupling in two important classes of self-assembled materials: disordered nanocrystal gels and randomly mixed binary superlattices. The gels are assembled in molecular dynamics simulations using linker molecules to mediate bonding between nanocrystals. Gelation changes the optical response of the nanocrystals, but in qualitatively different ways depending on the physical characteristics of the nanocrystals and the linkers. Elucidating this dependence helps understand recent experimental efforts investigating plasmonic nanocrystal gels. For binary superlattices, we show how plasmonic coupling emerges excess of that expected from simple weighted mixing of pure species spectra. This excess coupling can be leveraged to create “doped” superlattices, analogous to atomic doping, by substituting dopant nanocrystals into a host superlattice to tune the effective optoelectronic properties.

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Mon, 14 15:20 - 16:40



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Mon-QM3-01

## Phase Morphology of Polymer Composites and Blends using Neutron and X-Ray Scattering

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Polymer composites and blends are tunable materials with a wide array of applications, including aerospace, organic electronic devices, pharmaceuticals, medical devices, and more. Their composition includes a dispersed material that either provides a desired functionality to the polymer matrix (e.g. increased strength) or that benefits from the presence of the matrix material (e.g. improved phase stability of the dispersed component). This enables great control of the material properties by tuning the composition or phase morphology. Our past work has focused on blends of a commodity polymer matrix with a dispersed conjugated (semi-conductive) polymer. These materials are of interest in organic electronics as the performance of the conjugated component is maintained at low concentrations while the device benefits from increased mechanical durability and extended lifetimes due to the commodity polymer. Here we first used small angle and ultra-small angle neutron scattering to characterize the phase morphology and self-assembly in model commodity/conjugated polymer composites comprised of a polystyrene matrix with a selection of dispersed polythiophenes. Wide-angle X-ray scattering and conductivity measurements were then used to understand the effects of polymer-polymer and polymer-solvent interactions on not only the final solid-state phase morphology but also the performance of the material. Our ongoing work is now focused on extending these concepts to polymer composites with a small molecule dispersed phase, i.e. amorphous solid dispersions. Most of today's drug candidates have low water solubility, which limits their bioavailability and uptake in vivo. Amorphous solid dispersions can improve drug dissolution by kinetically trapping amorphous domains of these active pharmaceutical ingredients on the order of nanometers to micrometers in a polymer matrix. However, the efficacy and stability of these formulations are dependent on the phase morphology, which is further influenced by molecular interactions between the drug and matrix phases as well as the thermal and mechanical conditions during processing. By developing a thorough understanding of this relationship, we can inform improved formulations of amorphous solid dispersions in the future.

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Mon-QM3-02

## 3D Printing and Microbial Degradation of Lignin-Zein Composite

**Jin Gyun Lee** ([jlee229@lsu.edu](mailto:jlee229@lsu.edu)), **Ahmed Al Harraq** ([aahme22@lsu.edu](mailto:aahme22@lsu.edu)), **Bhuvnesh Bharti** ([bbharti@lsu.edu](mailto:bbharti@lsu.edu))

Cain Department of Chemical Engineering, Louisiana State University

Worldwide use and disposal of plastics have reached a dramatic saturation point, polluting lands, oceans, and air across the globe. Responding to such a challenge requires, among other environmental remediation measures, the manufacture of alternative sustainable plastics. Recent studies in the area have enabled the development of degradable plastics; however, the rate and conditions required for the degradation of such materials remain under scrutiny. Here, we introduce a new class of fully plant-based, rapidly degradable lignin and zein composite blend that can be transformed into macroscopic structures using extrusion 3D printing. Corn-derived zein forms the polymeric solution, while insoluble lignin granules act as a binder for enhanced printability and facile degradation. The blend showcases a shear-thinning behavior that is ideal for rapid extrusion printing into desired 3D structures, from cuvette caps to circuit boards. Biodegradation studies show that common bacteria readily found in soil and compost are able to decompose structures made with the lignin–zein composite in shorter time frames compared to a known biodegradable plastic. The rapid biodegradability and enhanced processability highlight the potential of lignin–zein composites.

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Mon-QM3-03

## Microtensiometer Constant Surface Area Surfactant Adsorption

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University of Minnesota, Department of Chemical Engineering and Materials Science

Surfactants are an important component of many systems due to their ability to lower the interfacial tension. Applications range from stabilizing proteins in drug formulations, to emulsifying oils in enhanced oil recovery. The dynamic adsorption behavior of a surfactant is an important property when choosing a specific surfactant for an application. Common techniques to measure the adsorption behavior include capillary microtensiometers and pendant drop tensiometers; by creating a small bubble at the end of a capillary or needle, holding the pressure across the interface constant, and then measuring the change in the shape of the interface, the surface tension can be calculated as the surfactant adsorbs. However, by allowing the interface shape to change during the adsorption process, the adsorption area is also changing along with it (generally increasing) throughout the experiment. One key feature of note is an extended lag time before significant changes in the surface tension occur. The Ward and Tordai diffusion-adsorption equation, which assumes constant adsorption area, is then used to analyse the adsorption.

In order to address this experimental limitation, we designed a new capillary pressure feedback control scheme which can hold the interfacial area constant while the adsorption occurs. A model-based controller is used to dynamically regulate the pressure applied across the interface, allowing for the surface area to be held constant to gather adsorption data or even oscillated at a given change in surface area. Adsorption measurements taken at constant surface area show significantly reduced induction times before surface tension changes occur and faster overall adsorption times. The method also allows for larger differences between the maximum and minimum surface tensions that can be measured during a single adsorption, as low surface tensions no longer cause the bubble to be ejected by the capillary. We can now directly compare our results to the Ward and Tordai equation, and obtain a better understanding of the role of micelle adsorption and breakdown during surfactant adsorption.

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Mon, 14 17:00 - 19:00

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Mon-TM-01

How can we help you to advance your colloid and surface science?

**Matthias Stiemer (m-stiemer@face-kyowa.co.jp)<sup>1</sup>, Dehua Yang (dyang@ebatco.com)<sup>2</sup>**

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<sup>2</sup> Exponential Business and Technologies Company (EBATCO)

Represented by the leading nanotechnology service company, Exponential Business and Technologies Company in the USA, Kyowa is poised to support you whenever you would have a need. Kyowa's state of art instrument products include whole series of contact angle meters and surface tensiometers to allow you to study liquids, solids and their equilibrium and dynamic interactions in the colloids.



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Mon-TM-02

Nanoscience Instruments: provider of surface and interfacial analysis equipment

**MATTHEW DIXON (mdixon@nanoscience.com)**

Nanoscience Instruments

Nanoscience Instruments combines expertise in microscopy and surface science instrumentation with real-world solutions. We partner with innovative instrument manufacturers around the world to help scientists and engineers solve complex problems leading to break-through innovations. Our team of scientists and engineers are passionate about solutions and connecting our customers with the right products and services to accomplish these goals. Our customers across academia, government and industry benefit from our innovation and quality assurance. Our fast and responsive staff provides support and advice in instrumentation selection, installation, training, and service. We are committed to your success. Nanoscience Instruments' diverse portfolio consists of several novel surface science and nanoscale microscopy solutions, including desktop scanning electron microscopes, electrospinning equipment, quartz crystal microbalances with dissipation, contact angle meters and interfacial tension measuring instruments, nanoparticle generators, cathodoluminescence detectors, sample preparation for SEM and TEM, and TEM accessories such as cryoEM sample preparation, in-situ sample holders, and hybrid pixel detectors.

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Mon-TM-03

Droplet Lab: Smartphone-based Tensiometry

**Abhimanyu Bhandankar (abhandankar@dropletlab.com)**

Droplet Lab

Droplet Smart Tech is a Canadian company that develops, manufactures, and sells surface tensiometry instruments. The company was founded in 2016 as a York University spin-off from Surface Engineering and Instrumentation Lab. Its products are used in surface engineering, physical chemistry, or the chemical industry to measure the wettability of a solid surface by a liquid. The instrument is capable of measuring the below properties. 1. Surface Tension 2. Contact Angle 3. Sliding Angle 4. Surface Energy Unlike existing instruments in the market that use traditional optical technologies, its instrument uses smartphone technology to capture and analyze images that are necessary for measurement. The use of smartphones enables the company to create a small, portable, and cost-effective solution that also has comparable accuracy with the most advanced instruments in the market. The founders of the company have published papers in 2 peer-reviewed journals to establish the scientific accuracy of the instrument in comparison with established commercially available instruments. REVIEW OF SCIENTIFIC INSTRUMENTS H. Chen, Jesus L. Muros-Cobos, A. Amirfazli COLLOIDS AND SURFACES A H. Chen, Jesus L. Muros-Cobos, Juan A. Holgado-Terriza, A. Amirfazli

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Tue, 15 09:00 - 11:00-

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Tue-LGS2-01

Probing contact microstructure in dense colloidal suspensions

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The flow of dense colloidal suspensions is ubiquitous in everyday life. Engineering materials using these suspensions require understanding the microscale rearrangements associated with their flow behavior. Moreover, frictionless nature of smooth spherical colloids, used in both experiments and simulations, fail to predict complex flow phenomena such as shear thickening where the viscosity abruptly increases as a

function of applied stress. To elucidate the structure-flow relationship, we probe the contact microstructure by estimating the average nearest neighbor  $\langle z \rangle$  in suspensions of smooth and rough colloids and relate them to the respective flow phenomena. In this study, we synthesize micron-sized poly(hydroxystearic)-*grafted*-poly(methylmethacrylate) colloids, with and without surface asperities, via dispersion polymerization as model particles. Colloidal particles of diameter in the range of 1 - 2  $\mu\text{m}$  (with a narrow polydispersity of 4 - 7%) are dispersed in index matched solvent squalene to mimic nearly hard-sphere interactions. Invoking arguments of mechanical stability from granular physics, we estimate the interparticle 'contacts' between colloids in dense suspensions after normalizing spatial factors such as polydispersity, steric polymer brush length, and the surface roughness. Our studies confirmed that rough particles with rotational constraints pack less efficiently than their smooth counterparts and as a result have fewer neighbors at their maximum possible packing ( $\phi_{\text{max}}$ ). We use our understanding of estimating  $\langle z \rangle$  to explain the particle rearrangement under flow. Suspension viscosity increases with applied stress and the rate of viscosity increase is quantified by parameter  $\beta$ . We found a universal correlation between  $\beta$  and the distance of the suspension concentration ( $\phi$ ) from its respective  $\phi_{\text{max}}$  for a broad class of dense colloidal suspensions with particles of varying roughness. We built a confocal rheometer to probe the change in  $\langle z \rangle$  during shear thickening and found a linear relation between the contact deficits and the free volume available for particle rearrangement under flow. We independently verified this result using Dissipative Particle Dynamic (DPD) simulations of colloidal suspensions with same  $\phi_{\text{max}}$  as experiments. Our discovery of distance to  $\phi_{\text{max}}$  as a strong predictor for the shear thickening behavior sets design limits for a broad class of spherically-symmetric suspensions for industrial applications.

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Tue-LGS2-02

Dynamic control of active droplet propulsion in a nematic environment by an electric field.

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A water droplet that is placed in a nematic environment distorts the director field around it. When the director is perpendicularly anchored at the water-nematic interface, the director in the surrounding nematic forms either a hyperbolic hedgehog (HH) point defect of dipolar symmetry or an equatorial disclination ring, called a Saturn ring (SR) of quadrupolar symmetry. If the water droplets are crowded with micro-swimmers such as bacteria, the HH droplets with dipolar configuration propel unidirectionally along the far-field nematic director while the SR drops show only random Brownian motion. In this work, using the responsiveness of the nematic liquid crystal (LC) to the external electromagnetic fields, we demonstrate full control over the direction and speed of active drop's propulsion. These parameters could be adjusted at any desired time and location. The speed of the droplet is controlled by two methods. In one, an electric field is applied across the cell and perpendicular to the nematic director. If the nematic is of positive dielectric anisotropy, this field realigns the director along itself, thus diminishing the dipolar asymmetry, which reduces the speed. If the nematic is of a negative dielectric anisotropy, the electric field aligns the director around the droplet perpendicular to itself and enhances the asymmetry of the director and thus increases the speed. At very high field amplitudes, however, the director is firmly coupled to the field and the droplet activity cannot produce sufficient director realignments, thus the speed decreases. In the second approach, an in-plane electric field transforms the HH configuration into the SR and thus decreases the speed. The direction of the propulsion is controlled by realigning the overall director with the in-plane electric field created by segmented electrodes. Finally, we demonstrate a reversal of the propulsion direction, by using a laser beam that creates a hedgehog defect on the side that is intended to be the guiding side. The work is supported by the NSF grant DMR-1905053.

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Tue-LGS2-03

## Mechanochemistry of Inorganic Nanostructures

**Sarah Rehn (smr14@rice.edu)**

Chemistry, Rice University

Unique and fascinating chemistry occurs at surfaces that cannot take place in bulk materials, due to the presence of dangling bonds as well as strained or otherwise unusual coordination environments. As the size of an object becomes smaller, the fraction of surface atoms to bulk atoms increases. Ultimately, for nanometer-sized particles, surface effects become so large that the behavior of the system can change completely; forces that would ordinarily have little to no influence on atoms in the bulk can have an enormous impact on surface atoms and thus dictate the behavior of the system. Since all inorganic nanoparticles are capped with organic ligands that provide them stability in solution, the chemistry at the surface atom-ligand interface can be leveraged to drive new chemical processes or physical phenomena that would be impossible at any other length scale. Colloidal silver nanoplates can be readily synthesized that are several nanometers thin, maximizing the fraction of surface atoms and making them an ideal candidate for studying the effects of surface chemistry on nanoparticle properties. Their high aspect ratio renders them unusually flexible such that when draped over much small spherical nanoparticles, the plates deform, a process that can be observed via distinctive bend contours in electron microscopy images. Since the size of this bend contour can be related to the extent of the deformation in the nanoplate, we hypothesize that these bend contours might be used to study how mechanics are influenced by surface chemistry. As synthesized, the nanoplates are capped with a weakly bound ligand (citrate) that interacts with the surface through electrostatic adsorption. After replacing these native ligands with a library of other commonly used molecules, it was found that the spatial extent of the bend contour changes in proportion to the binding strength of the surface ligand. This finding demonstrates that more strongly bound surface ligands increase the mechanical stiffness of the entire nanoplate. To the best of our knowledge, this is the first demonstration of the coupling between surface chemistry and the inherent mechanical properties of a material, i.e., nanoparticle mechanochemistry.

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Tue-LGS2-04

Dynamics of polymers under extreme nanoconfinement of disordered nanoparticle packings

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Nanoparticle assemblies can be filled with polymers to create functional nanocomposites by utilizing a novel strategy of infiltration of the polymer into the nanopores through solvent-based, elastomer-aided, and thermal annealing processes. Additionally, polymer-infiltrated nanoparticle packings provide a unique platform to study the dynamics of macromolecules under extreme nanoconfinement. The degree of confinement can be tuned by appropriate choice of particle size and polymer molecular weight. By using simple yet powerful tools like microscopy and ellipsometry, we investigate the dynamics of polymers in such confined environments at unprecedented levels of confinement. In capillary rise infiltration (CaRI), the polymer film-nanoparticle packing bilayer is annealed above the glass transition temperature of the polymer leading to the polymer wicking into the pores of the packing. The dynamics of rise of the polymer into the nanoparticle packing can be studied by ellipsometric front-tracking giving a measure of the chain dynamics of polymer – effective viscosity – based on the Lucas-Washburn equation. We report that while unentangled PS show slower-than-bulk chain mobility during capillary rise into 25 nm silica nanoparticle packings, entangled chains show enhancement in mobility (average pore size is 4 nm). Reduction in viscosity with increasing size of the polymer occurs despite a segmental-level slowdown, evidenced by elevated glass transition temperature ( $T_g$ ). Increasing the degree of confinement by choosing even smaller particles such that the pore-size (1 nm) is comparable to the Kuhn length of the polymer leads to a constant, molecular-weight independent viscosity of polymers. The studies into the dynamics of high  $T_g$ , glassy polymers are complemented by studies of low  $T_g$ , mobile chains in disordered nanoparticle packings. Low  $T_g$  chains are infiltrated from an elastomer like a PDMS gel into nanoparticle packings at room temperature using

leaching-enabled capillary rise infiltration (LeCaRI). Once infiltrated into a region of nanoparticle packings using LeCaRI, these mobile chains spread out into adjoining unfilled regions. These lateral motion of the front of mobile chains can be tracked by reflection microscopy as chains move from highly filled to empty pores. We will report results on the lateral motion of PDMS chains moving inside nanoparticle packings and the effect of capillary condensed water in these systems.

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Tue-LGS2-05

### Mechanisms of Transport Enhancement for Self-Propelled Nanoswimmers in a Porous Matrix

**Haichao Wu (hwcusdu@gmail.com), Benjamin Greydanus (Benjamin.Greydanus@colorado.edu), Daniel Schwartz (daniel.schwartz@colorado.edu)**

University of Colorado Boulder, Department of Chemical and Biological Engineering

Micro/nanoswimmers convert diverse energy sources into directional movement, demonstrating tremendous promise for biomedical and environmental applications, many of which involve complex tortuous or crowded environments. Here, we investigated the transport behavior of self-propelled catalytic Janus particles in a complex interconnected porous void-space, where the rate-determining step involves the escape from a cavity and translocation through holes to adjacent cavities. Surprisingly, self-propelled nanoswimmers escaped from cavities more than 20x faster than passive (Brownian) particles, despite the fact that the mobility of nanoswimmers was less than 2x greater than that of passive particles in unconfined bulk liquid. Combining experimental measurements, Monte Carlo simulations and theoretical calculations, we found that the escape of nanoswimmers was enhanced by nuanced secondary effects of self-propulsion which were amplified in combined environments. In particular, active escape was facilitated by anomalously rapid confined short-time mobility, highly efficient surface-mediated searching for holes, and the effective abolition of entropic and/or electrostatic barriers at the exit hole regions by propulsion forces. The latter mechanism converted the escape process from barrier-limited to search-limited. These findings provide general and important insights into micro/nanoswimmer mobility in complex environments.

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## Tue, 15 09:00 - 11:00

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Tue-AT1-01

### Directed Self-Assembly of Polarizable Nanoparticles (**Keynote Lecture**)

**James Swan (jswan@mit.edu)**

Department of Chemical Engineering Massachusetts Institute of Technology

Directed assembly of dielectric and paramagnetic nanoparticles can be used to synthesize diverse functional materials that polarize in response to an externally applied electric or magnetic field. However, theories capable of predicting the self-assembled states are lacking. In the proposed work, we develop a complete thermodynamic description of such assemblies built from spherical nanoparticles. We show how an important physical feature of these types of particles, mutual polarization, sculpts the free energy landscape and has a remarkably strong influence on the nature of the self-assembled states. Modeling the mutual polarization among nanoparticles requires solving a many-bodied problem for the particle dipole moments. Typically, this computationally expensive task is avoided by neglecting mutual polarization and assuming each particle in a concentrated dispersion acquires the same dipole moment as a single, isolated particle. This constant dipole assumption leads to qualitatively incorrect predictions that fail to satisfy specific thermodynamic criteria for coexisting phases in equilibrium. Correctly accounting for mutual polarization enables a thermodynamic theory that describes the equilibrium phase diagram of polarizable dispersions in terms of experimentally controllable variables. Our theoretical predictions agree with the phase behavior we observe in dynamic simulations of these dispersions as well as that in experiments of field-directed structural transitions. In contrast to predictions of a constant dipole model, we find that dispersions of particles with different dielectric constant or magnetic permeability exhibit qualitatively

different phase behavior. This new model also predicts the existence of a eutectic point at which two crystalline phases and a disordered phase of nanoparticles all simultaneously coexist.

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Tue-AT1-02

### Liquid Crystalline Coacervates Composed of Chromonic Mesogens and Polyelectrolytes

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We report on formation of liquid crystalline (LC) coacervates composed of negatively charged polyaromatic molecules and positively charged homopolyelectrolytes. These polyaromatic molecules (such as disodium cromoglycate; DSCG) can self-assemble in aqueous solutions to form rod-like mesogens via  $\pi$ - $\pi$  interactions. At sufficiently high concentrations (300 mM), these mesogens exhibit long-range orientational order and give rise to LC mesophases. At concentrations ( $\sim$  5 mM) that are several orders of magnitude lower than the corresponding bulk LC phase, no mesophases are observed. Surprisingly, addition of polycations to 5 mM DSCG solutions leads to the formation of LC-coacervates that appear as droplets in solution. The local DSCG concentration in these droplets are significantly higher than their surroundings, leading to characteristic bipolar configuration when observed via polarized optical microscopy. We elucidate the charge-driven formation of LC-coacervates by characterizing trends in their compositions, optical textures and rheology via systematic variations of total charge, ionic strength, and temperature of the solutions.

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Tue-AT1-03

### Hybrid Hydrogels Comprising Interpenetrating Electrostatic and Covalent Networks

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Polyelectrolyte complex (PEC) hydrogels form upon spontaneous association and self-assembly of oppositely charged block polyelectrolytes in aqueous media. Their swift electrostatic self-assembly, responsiveness to changes in ionic strength of their surroundings, and self-healing attributes have led to promising avenues for their use in diverse applications ranging from drug delivery to wet adhesion to 3-D bioprinting. However, their application-specific development requires a precise tuning of their microstructure and bulk properties, as well as strategies to overcome the interdependence between their microstructures and shear response and improve their poor tensile strength. In this presentation, we will demonstrate a materials design platform for fabricating hybrid hydrogels comprising interpenetrating PEC and covalent networks. Mesoscale structure and bulk properties of a model hybrid hydrogel system comprising oppositely charged ABA triblock polyelectrolytes and UV-crosslinkable 4-arm polymers will be discussed. Minimal influence of covalent network's inclusion on PEC networks' equilibrium mesoscale structure will be demonstrated, conserving the hybrid gel's ability to encapsulate biomolecules and other charged cargo. At the same time, the hybrid hydrogels will be shown to possess superior mechanical properties, which are not achievable by either the PEC network or the covalent network. We will highlight marked improvements in the shear and the tensile strengths of the PEC hydrogels upon the incorporation of the covalent network, even as a minor component. Moreover, hybrid hydrogels will be demonstrated to exhibit enhanced resistance to salt addition and controllable swelling characteristics. The versatility of our hydrogel design platform will be established by demonstrating its compatibility with diverse covalent network formers, establishing a pathway for further broadening of the utility of the PEC hydrogels in diverse biomedical applications.

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Tue-AT1-04

## Molecular Encapsulation and Molecular Exchange in Polyelectrolyte Complex Micelles

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Polyelectrolyte complexes (PEC) form by mixing two oppositely charged polymers in solution. This phenomenon results in either complex coacervation which is a liquid-liquid phase separation or solid precipitate formation. The PEC phase separation is affected by factors such as ionic strength, chirality, hydrophobicity, and charge density. This phase separation can be restricted to the nanoscale by conjugating either one or both polyelectrolytes to a neutral hydrophilic polymeric block, forming PEC micelles with a PEC core and a neutral corona. These highly tunable nanoparticles can be applied to the encapsulation and delivery of charged molecules, particularly nucleic acids and proteins. In this work, neutral hydrophilic polymers such as the thermoresponsive polymer, poly(N-isopropyl acrylamide)(pNIPAM), and poly(ethylene glycol) (pEG) are used as the corona-forming block. pNIPAM has a lower critical solubility temperature above which a hydrophilic to hydrophobic transition occurs, which may be used as a trigger for release, while no such functionality is displayed by pEG. Encapsulation of charged molecules in the PEC core is primarily facilitated through electrostatic interactions. PEC micelles with solid cores are considered to be kinetically-trapped, while those with liquid cores are not. This work investigates the encapsulation of singly-charged molecules versus molecules with higher charge density to illustrate the potential application of PEC micelles in nucleic acid delivery. The effect of micellar core composition on encapsulation and molecular exchange is also studied. Molecular exchange is studied using Förster resonance energy transfer (FRET). Molecular exchange has been demonstrated in certain micellar systems. Here, this phenomenon is studied with a solid to liquid core transition that is assisted by the addition of salt. And increased salt concentration shields the electrostatic interactions between the polyelectrolytes, forming a less solid-like or a more liquid-like PEC phase. Additionally, the micelle morphology is characterized using dynamic light scattering, transmission electron microscopy, and small-angle x-ray scattering.

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Tue-AT1-05

## Field-driven reversible alignment and gelation of magneto-responsive soft anisotropic microbeads

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Magnetic fields offer an untethered control over the assembly, dynamics, and reconfiguration of colloidal particles. However, synthesizing 'soft' colloidal particles with switchable magnetic dipole moment remains a challenge, primarily due to the strong coupling of the dipoles of the adjacent nanoparticles. We present a way to overcome this fundamental challenge based on a strategy to synthesize soft microbeads with tunable residual dipole moment. The microbeads are composed of a polydimethylsiloxane (PDMS) matrix with internally embedded magnetic nanoparticles (MNPs). The distribution and orientation of the MNPs within the PDMS bead matrix are controlled by an external magnetic field during the synthesis process, allowing for the preparation of anisotropic PDMS microbeads with internal magnetically aligned nanoparticle chains. We study the differences in magnetic interactions between microbeads containing magnetically aligned MNPs and microbeads with randomly distributed MNPs. The interparticle interactions in the suspension of microbeads with embedded aligned MNP chains result in the spontaneous formation of percolated networks due to residual magnetization. We proved the tunability of the structure by applying magnetization, demagnetization, and re-magnetization cycles of the 2D percolated networks. The mechanical response of the microbead suspension was quantified by oscillatory rheology and correlated to the propensity for network formation by the magnetic microbeads. We also correlated experimentally the



2D alignment of the microbeads to the direction of Earth's magnetic field. Overall, the results prove that the magnetic microbeads can serve as an experimental toolbox for modeling interactions in dipolar systems leading to various percolated networks, novel magneto-rheological materials, and smart gels.

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Tue, 15 09:00 - 11:00

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Tue-BT1-01

Foams with Enhanced Rheology for Stopping Bleeding

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Bleeding from injuries in the truncal region is a leading cause of fatalities in the military and in young adults. Direct pressure cannot be applied to stop bleeding in these cases. Our lab has been particularly interested in developing foams to treat such 'non-compressible' hemorrhage. Foams can be effective because the expansion of the foam in the injured cavity can counteract blood loss without the need for compression. As an active 'hemostatic agent' in these foams, we use hydrophobically modified (hm) derivatives of biopolymers like chitosan and alginate (termed hmC and hmA, respectively). These polymers have the ability to coagulate blood cells and thus stop bleeding. In this talk, we will describe aqueous foams that can be delivered out of a double-barreled syringe by combining precursors in the two barrels that produce bubbles of gas in situ. In addition, one barrel contains hmC and the other hmA, and the amphiphilic nature of these polymers enables them to stabilize gas bubbles without the need for additional surfactants. Most interestingly, these polymer-based foams have enhanced rheological properties compared to typical foams that can be prepared in a lab. This rheological enhancement is quantified in our work, and is due to electrostatic interactions between the cationic hmC and the anionic hmA chains. Preliminary studies in animal wound models also confirm that hmC-hmA foams form effective barriers to blood loss due to their greater mechanical integrity.

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Tue-BT1-02

Drainage via Stratification in Foam Films Made with Polymer-surfactant Complexes

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Freestanding films of soft matter exhibit stratification due to confinement-induced structuring and layering of supramolecular structures like micelles. In many cosmetics, foods, pharmaceutical, and petrochemical applications, often polymers are added to surfactant solutions as rheology modifiers. Interaction between neutral polymer like PEO and monomers and micelles of anionic surfactant like SDS results in the formation of polymer-surfactant complexes and changes both interfacial properties and bulk shear rheology response. The influence of such polymer-surfactant complexes on foam formation, stability, drainage, and lifetime are not well-understood and motivate this study. In this contribution, we show foams formed with PEO-SDS mixtures exhibit three features of stratification: step-wise thinning, co-existence of thick thin regions, and formation of nanoscopic topological features like nanoridges and mesas. The nanoscopic thickness variations and transitions in foam films are characterized using interferometry, digital imaging, and optical microscopy (IDIOM) protocols, with unprecedented high spatial (thickness < 100 nm, lateral ~500 nm) and temporal resolution (< 1 ms). We characterize the variation in surface tension, shear viscosity, and extensional relaxation time as a function of surfactant concentration at fixed polymer concentration. By complementing tensiometry and rheometry measurements, we seek an understanding of the influence of added polymer on forces, flows, and fluxes that drive drainage via stratification, and model drainage via thin film equation amended with thickness-dependent disjoining pressure.

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Tue-BT1-03

## Particle-coated bubbles driven by ultrasound for high-frequency interfacial rheology

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Particles at fluid interfaces can confer emergent properties associated with the interfacial microstructure, forming the basis for the creation of functional, responsive, two-dimensional materials. In the production and application of these advanced materials, it is essential to understand the dynamic behaviour of structured interfaces at deformation timescales that are relevant in practical scenarios. For instance in processing flows, deformation rates of the order of  $10^3$ - $10^6$  s<sup>-1</sup> are often encountered, yet existing methods for interfacial rheology are usually limited to much slower timescales, between  $10^{-1}$ - $10^2$  s<sup>-1</sup>. Reliable methods are thus required to explore and characterise the high-frequency deformation of complex interfaces. We use particle-coated bubbles to probe the dynamics and interfacial rheology of structured interfaces at orders-of-magnitude higher frequency than has been possible so far. By driving a microbubble with ultrasound waves of 10-100 kHz frequencies, volumetric oscillations of the internal gas core cause the interface to undergo rapid periodic, isotropic area oscillations at frequencies of the order of  $10^4$ - $10^5$  s<sup>-1</sup>. This phenomenon enables us to use a bubble as a versatile platform to characterise interfacial mechanics at extreme timescales. We use high-speed video-microscopy, at 250,000 frames per second, to study the oscillatory behaviour of bubbles coated by microscopic, spherical colloids, as a model system, to establish a link between the macroscopic radial response of the bubble and the micromechanics of the monolayer. In comparison to bare bubble dynamics under identical conditions, the results for the coated bubbles indicate that buckling of the monolayer poses a greater resistance to compression in comparison to expansion. Overall, interfacial elasticity reduces the relative amplitude of oscillations, particularly for bubbles with radii less than 120  $\mu$ m, with the stress-strain response of the monolayer exhibiting a nonlinear trend for strain amplitudes less than 10 %. The latter response is dependent on the surface coverage, with hysteresis observed for surface coverages between 70 to 80 %. The results highlight the influence of experimental timescales on the response of complex interfaces. This paves the way for visual investigation of interfacial mechanics under extreme deformation.

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Tue-BT1-04

## Foaming and De-foaming Phenomena of Bi-phase Makeup Removers

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Bi-phase makeup remover is a category of cosmetic products associated with interesting interfacial behaviors. Made of an aqueous phase and an oil phase, a bi-phase makeup remover forms two visually distinct liquid layers when left standing. When agitated by hand shaking, foams and bubbles are created, resulting in a foamy and visually homogenous solution. A delicate balance of foaming and subsequent de-foaming has to be reached for visual appeal: while the foamy mixture must maintain visual homogeneity for an adequate amount of time, the mixture must then quickly de-foam, back to initial two separate liquid layers with complete optical clarity. We performed systematically interfacial studies to understand the foaming and de-foaming phenomena and important factors to bi-phase makeup remover formulation. Dynamic interfacial tension study was conducted to understand the evolution of the interfacial tension between two phases upon mixing. Interfacial dilational rheology was employed to understand the viscoelasticity of surfactant film subsequently formed between two liquids. By varying surfactant's ionic nature, surfactant concentration, ionic strength, as well as oil phase's polarity, we obtained further learnings of key ingredients' roles to the delicate foaming/de-foaming balance. While prior investigations on foam & bubble life cycle focused on metastable structures formed at water and air interface, our study may help

expand the understanding for foams & bubbles created at interfaces between two immiscible liquids at a short time scale.

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Tue-BT1-05

Foam and emulsion stability and its relation with surface rheology (**Keynote Lecture**)

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Laboratoire de Physique des Solides, CNRS, Université Paris Saclay

Despite its practical importance, foam and emulsion stability is not yet fully understood. This stability can be frequently related to the surface compression elasticity that characterizes surface tension gradients (Marangoni forces). We will first discuss the case of unstable foams and emulsions, where coalescence of approaching bubbles or drops readily occurs once the films formed between them are thin enough. This behavior is generally observed when the amount of surface active stabilizers (surfactant or other species) is small. It is also observed in emulsions containing larger amounts of surfactant made with microemulsions coexisting with both oil and water: these systems form very unstable emulsions when shaken. Film thinning is related to the surface compression elasticity, which is affected by the solubilization of surfactant in water (or oil). This behaviour allows explaining the observations. We will also discuss the case where stable films form between bubbles and droplets, and where coalescence proceeds via different mechanisms. Some of these mechanisms also involve the compression elasticity of the surface layers. Foam and emulsions with solid surface layers are generally very stable. In this case, the surface shear rheology might play a role, but this role is less clear.

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Tue, 15 09:00 - 11:00

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Tue-CT1-01

Fabrication and Active Propulsion of Patchy Ellipsoidal Microparticles in Electric Field

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Active colloids are a synthetic analogue of biological microorganisms that consume external energy to swim through viscous fluids. Such motion requires breaking the symmetry of the fluid flow in the vicinity of a particle; however, it is challenging to understand how surface and shape anisotropies of the colloid lead to a particular trajectory. Here, we attempt to deconvolute the effects of particle shape and surface anisotropy on the propulsion of model ellipsoids in AC electric fields. We first introduce a simple process for depositing metal patches of various shapes on the surfaces of ellipsoidal particles. We show that the shape of the metal patch is governed by the assembled structure of the ellipsoids on the substrate used for physical vapor deposition. Under AC electric field, ellipsoids show linear, circular, and helical trajectories which depend on the shapes of the surface patches. We demonstrate that features of the helical trajectories such as the pitch and diameter can be tuned by varying the degree of patch asymmetry along the two primary axes of the ellipsoids. We develop heuristics based on patch asymmetries that can be used to design patchy particles with specified nonlinear trajectories.

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Tue-CT1-02

Nonlinear Dynamics of Semiflexible Colloidal Filaments in Eccentric Time-Varying Magnetic Fields

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Chains of linked superparamagnetic particles actuated by external time-varying magnetic fields exhibit diverse dynamics that depend on the field parameters and the filament length. Their motion serves for the microscopic manipulation of fluids and as model systems of active filaments. These dynamics can be described by the competition among viscous, magnetic, and elastic forces during chain actuation. Current literature has focused mostly on studying the dynamics under symmetric (circular) time-varying fields, which have a constant strength. The colloidal chains initially coil or fold under these conditions, but eventually collapse into smaller structures that can only rotate like rigid bodies. Therefore, these fields restrict the possible configurations that the filaments can acquire. Here, we explore novel nonlinear filament dynamics by applying asymmetric (eccentric) time-varying magnetic fields, which are characterized by a time-dependent strength. When actuated with eccentric fields, the chains bend and stretch periodically, showcasing four distinct stages of motion characterized by different morphologies during a single period of the magnetic field. These stages are described in terms of the instantaneous Mason number, Magnetoelastic number, the phase lag angle between the chain and the field, and the bending energy. The extent of deformation during the bending stage is affected by the chain length, the field frequency, and the field ellipticity.

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Tue-CT1-03

Nonequilibrium shape fluctuations and motility of a droplet enclosing active particles

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Ensembles of motile colloids, driven by Quincke electrorotation to roll on a solid surface, have become a popular model of active matter since the direction of the individual colloid motion is not predetermined. We study the collective dynamics of the Quincke rollers in soft confinement by enclosing the rollers inside a liquid droplet sandwiched between two surfaces. We find that the rollers self-organize into a single vortex that uniformly fills the drop. The droplet interface exhibits strong fluctuations with power spectrum consistent with active fluctuation driven by particle-interface collisions. Broken detailed balance confirms the nonequilibrium nature of the shape dynamics. The rollers activity also gives rise to droplet net motion, which is superdiffusive. The research is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences, and NSF-DMR award 2004926.

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Tue-CT1-04

Mesoporous, Moisture-Absorbent, Temperature-Controlled Hydrogels For Atmospheric Water Harvesting

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Water scarcity is one of the greatest challenges of the 21st century. Using desiccants to harvest water from air is a promising way to address this challenge. However, most desiccants require considerable energy input to release absorbed water as vapor and then condense it. Here, we overcome this limitation by developing Moisture-Absorbent, Temperature-Controlled Hydrogels (MATCHes) that absorb water from air

at ambient conditions, and then release it in liquid form upon slight heating. Furthermore, we show that tuning the mesoscale porosity of the hydrogels dramatically impacts both the total amount and rate of water absorption and release — highlighting a previously-overlooked factor that regulates MATCH performance. Our work therefore demonstrates a new route to fabricating desiccants capable of harvesting water from air quickly, to a large extent, and with minimal energy cost.

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Tue-CT1-05

Synthesis of stimuli-responsive skins around hydrogels to regulate solute release

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University of Maryland - College Park

Many applications of hydrogels rely on their ability to deliver encapsulated solutes such as drugs or dyes to an external medium. However, a problem in many such applications is that the moment the gel is placed in contact with water, the solutes rapidly leak out by diffusion. Ideally, there should be a way to regulate the release of solutes – i.e., to ensure zero release until a desired time, and thereafter, for the release to be ‘switched on’. Moreover, it would be even better if this was a repeatable switch, i.e., if the gel could be cycled many times between the on and off states. Such a perfect, cyclical on-off release of contents from hydrogels has never been achieved to our knowledge. We address this challenge by taking inspiration from structures found in nature such as fruits and vegetables, which have a hydrophobic skin that envelops and protects their water-rich core. We have found a way to synthesize a soft hydrophobic skin around any gel. The initial skin completely prevents hydrophilic solutes from leaking out of the gel into the external solution. The skin is also equipped with redox-responsive properties. That is, in the presence of oxidants, the skin becomes hydrophilic, thereby ‘turning on’ the release of solutes out of the gel. Conversely, solute release can be ‘turned off’ at any time by adding a reducing agent that reverts the skin to its hydrophobic state. Thus, our smart skin enables regulated (on-off) release of solutes out of a gel, and this concept is likely to be useful in many applications.

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Tue-CT1-06

Manipulating Surface-Modified Cs:WO<sub>3</sub> Nanocrystals in Liquid Crystals for solar transmission control

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Highly-doped semiconductor (SC) nanocrystals have raised a special interest due to their Localized Surface Plasmon Resonance (LSPR) tunable over a large infrared range (IR). A lot of works have focused on the effect of dopant nature and its influence on LSPR response. An active modulation of these defect states, and thus of LSPR is achievable by post-synthetic redox chemistry of nanocrystals, which opens applications especially in smart windows [1]. However, like metallic nanoparticles, anisotropy or the coupling effect can affect the LSPR of SC, but haven't being studied extensively yet. It may be possible to modulate these parameters by aligning nanorods [2] or reversibly aggregate them, using an active matrix like liquid crystals. We have optimized the synthesis of Cs:WO<sub>3</sub> nanocrystals and study the impact of the particle aspect ratio on the absorption spectra [3]. We found that tungsten oxide nanocrystals are very sensitive to the surface chemistry and easily aggregate when functionalized with native oily ligands.

Because the LSPR is subject to the distance between particles, maintaining colloidal stability by ligand exchange is essential to preserve the LSPR absorption properties (cross section  $\approx 3.5 \cdot 10^{-14} \text{cm}^2$ ) for applications. By playing with surface chemistry and solvent we control the particle aggregation and assembly as well as their orientation, thereby modulating the anisotropic LSPR properties. Briefly, we found that aggregation at micron scale causes a red shift of LSPR around 250nm, a tripling of absorption band width and alters the absorption properties by 60%. After an optimization of surface chemistry, it is possible to reversibly aggregate nanoparticles in liquid crystal smectic phase defects [4] and thus tune the coupling effect and absorption with temperature. We have successfully dispersed Cs:WO<sub>3</sub> nanoparticles in isotropic phase of liquid crystal. By reducing the temperature, aggregates were formed resulting in a loss of absorption property. The aggregation was found to be partially reversible with an absorption modulation in near IR around 50%. Our finding paves the way for the development of new smart windows with active solar control. [1] Garcia & all (2011), Dynamically Modulating the Surface Plasmon Resonance of Doped Semiconductors Nanocrystals. NanoLetters, 4415-4420. [2] Liu & all (2014) Electrically and Optical Tunable Plasmonic Guest-Host Liquid Crystals with Long-Range Ordered Nanoparticles. NanoLetters, 4071-407. [3] Kim & all (2016) The interplay of shape and Crystalline Anisotropies in Plasmonic Semiconductors Nanocrystals. NanoLetters, 3879-3884. [4] Milette & all (2012) Reversible long-range patterning of gold nanoparticles by smectic liquid crystals. SoftMatter, 6593-6598.

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Tue, 15 09:00 - 11:00

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Tue-DT1-01

Microstructure and rheology of shear-thickening colloidal suspensions with varying interparticle friction: comparison of experiment with theory and simulation models, and applications to human exploration of space (**Keynote Lecture**)

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The micromechanical reasons for shear thickening in suspensions is an active area of research that benefits from novel experimental methods that interrogate microstructure as well as rheology. Two colloidal suspensions of paucidisperse, spherical silica particles with different surface chemistries leading to extreme limits of surface contact friction are studied to identify experimental differences in shear rheology and microstructure and quantitatively test theory and simulation models. The non-equilibrium microstructure in the plane of shear is measured by flow-Small Angle Neutron Scattering (SANS) for steady shear states spanning the shear thinning and shear thickening regimes. The shear rheology and microstructure are compared against predictions from theory for Brownian hard sphere suspensions and state-of-the-art simulation methods that incorporate either contact friction or enhanced lubrication hydrodynamics. The first normal stress differences are confirmed to distinguish between these micromechanical mechanisms for stress enhancement in the shear thickened regime. The nonequilibrium microstructure in the plane of shear shows more anisotropy for the suspension with higher interparticle friction. A significant four-fold symmetry is confirmed and found to be amplified with increasing surface contact friction in the shear thickened state. The differences in shear-induced microstructures between suspensions with varying contact friction demonstrate that the nonequilibrium microstructure can distinguish between nanotribological interactions in the shear thickened state. Statistical comparison of experiments with simulations indicates that better resolution of microstructures in simulation models are required to be validated by the experimental data presented. Implications for the development of theories for colloidal suspension rheology are discussed, along with the development of novel 4DRheo-SANS instruments for combined rheology and neutron scattering. (Y.F. Lee, NJW et al. Physics of Fluids, 2021). Finally, I will show how shear-thickening fluids can be used to develop advanced soft and hard composites for astronaut protection for NASA's Artemis mission and the Mission to Mars.

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Tue-DT1-02

Tunable yield stresses in suspensions of porous microcapsules *via* internal additives

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Porous capsules are an important class of soft materials characterized by a mechanically robust shell separating two liquid phases with pores that facilitate the transport of material across the interfacial boundary. These properties make porous capsules ideally suited to deliver and transport material in applications ranging from therapeutics to personal care products. Here, we produce porous capsules of cellulose nanofibrils through a simple bulk emulsification procedure and induce tunable yield stresses in their suspensions through the addition of poly(acrylic acid) (PAA) to the internal phase during production. By changing the concentration of PAA, we control the strength of attractions between particles and thereby increase the yield stress of the suspensions. The resulting clusters of particles deform and break apart under stress, resulting in hysteresis in the measured flow sweeps. Our results demonstrate that it is possible to tune the suspension rheology by only changing the composition of the internal phase without affecting the properties of the external phase, providing a novel method to tailor complex fluid rheology.

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Tue-DT1-03

Droplet-based microfluidic tool to quantify viscosity of concentrating protein solutions

**Deyu Yang (deyuy@andrew.cmu.edu)**

Carnegie Mellon University

Accurate knowledge of the viscosity of concentrated protein solutions is important for the manufacture and delivery of protein therapeutics. Conventional methods for viscosity measurements require large solution volumes, which is limiting, especially during the early stage of protein development. In this work, a droplet-based microfluidic device is developed to quantify viscosity of protein solution while concentrating using only micro-liters of sample. The corresponding viscosity is characterized by multiple particle tracking. The technique was validated using well-studied lysozyme and BSA solutions to demonstrate the applicability on protein systems. This device will further be extended to study the effect of different excipient and other additives on the viscosity of the protein solutions

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Tue-DT1-04

The hydrodynamic stresslet: representing non-equilibrium motion in a model biological cell.

**Emma Gonzalez (emmagg@stanford.edu)**, **Roseanna Zia (rzia@stanford.edu)**

Stanford University

Spherically-confined colloidal suspensions are a useful model system for representing a simple biological cell, where macromolecules interact and undergo diffusion, self-assembly, and flow. The microscopic forces between those colloids, including hydrodynamic, Brownian, and interparticle forces, are affected by confinement, and thus computational models must represent these effects. In the Stokesian dynamics framework, the fluid-mediated interactions arising from these forces are represented by a hierarchy of hydrodynamic traction moments on particle surfaces. The initial Confined Stokesian dynamics algorithm<sup>1,2</sup> paved the way to such computational methods by obtaining the hydrodynamic force and torque in a spherical cavity but was restricted to equilibrium because the stresslet coupling is required to extract suspension viscosity and osmotic pressure. Here we present the exact solution for stresslet hydrodynamic functions (including the trace components) of a colloid in a spherical cavity and its application to more concentrated suspensions via the Confined Stokesian dynamics algorithm. With this algorithm, we predict high-frequency dynamic viscosities as well as osmotic pressure of confined Brownian suspensions in and

out of equilibrium. [1]Aponte-Rivera and Zia, Phys Rev Fluids 2016 [2]Aponte-Rivera, Su, and Zia, J Fluid Mech 2018

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Tue-DT1-05

Dilatational rheological behavior of lysolipid (lung surfactant Inhibitor) in an in situ lung alveoli

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University of Minnesota-Twin Cities

The air/water interface in a lung is rheologically complex as the alveolar interfaces must be coated with a low tension surfactant film to ensure uniform lung inflation with minimal effort. The dependence of the Laplace pressure,  $\Delta P = 2\gamma/R$ , on the alveolar radius,  $R$ , means that interconnected bubbles or alveoli are at best metastable if  $\gamma$  is constant. The pressure difference between small and large alveoli can induce the Laplace Instability if the surface tension is constant during breathing, in which the smaller alveoli collapse while the larger alveoli overinflate. For  $(2\epsilon - \gamma) > 0$  (dilatational modulus,  $\epsilon = A\partial\gamma/\partial A$ ), the surface tension, and hence the Laplace pressure decreases with decreasing radius and increases with increasing radius, which reverses the Laplace instability, thereby stabilizing the alveoli against collapse. Lysolipid, a byproduct produced by the innate immune system when the lungs become inflamed due to disease or injury, competes for the alveolar interface and pushes the lung towards instability with increasing lysolipid concentration. Our previous work has shown that the dilatational modulus increases with increasing oscillation frequency, which suggests that increasing breathing frequency during mechanical ventilation may restore lung functionality by elevating the dilatational modulus of the lung interface, thereby reversing the Laplace Instability. Our bubble tensiometer allows us to perform nearly isotropic deformations on small alveolar-sized bubbles, with the dilatational modulus dominating the surface rheology. As opposed to constant area rheometry, dilatational rheometry depends more on the transport of surfactant to and from the interface, and as such, depends on the oscillation rate and the bubble size. In this work, we are going to examine the diffusion process of multiple inhibitors both above and below their critical micelle concentrations (CMC). We will show that the magnitude of the dilatational modulus peaks at the CMC. We will also discuss how  $\epsilon$  can be decomposed into elastic and viscous components and how the ratio of the elastic to viscous components changes as insoluble lung surfactant is replaced by soluble lysolipids. We find that the dilatational modulus is extremely sensitive to the detailed composition of an interfacial film.

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Tue, 15 09:00 - 11:00

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Tue-ET1-01

Tunable chiral optical properties in semiconductor nanocrystals (**Keynote Lecture**)

**Vivian Ferry (veferry@umn.edu)**

Chemical Engineering & Materials Science, University of Minnesota

Optical nanomaterials offer the ability to bend, twist, guide, and confine light in nanoscale dimensions. Among these materials, chiral nanostructures particularly show promise for applications ranging from polarization manipulation to 3D displays, sensing, and spin-selective transport. Compared to their molecular counterparts, chiral nanomaterials exhibit orders of magnitude stronger dissymmetry factors, but have only been realized in a limited set of materials systems. We have recently demonstrated different strategies to tune and manipulate the polarization state of luminescence from semiconductor nanocrystals. In one strategy, we combine films of CdSe/CdS nanocrystals with Au metamaterials, and show how the polarization and direction of the outcoupled luminescence can be controlled. However, the degree of circular polarization is limited in this geometry by the uniform arrangement of light emitters, and it is useful to create nanostructured elements comprised entirely of photoluminescent materials. We have recently developed patterning methods to transform semiconductor nanocrystals into patterned nanocrystal solids,



realizing lateral feature sizes as small as 30 nm and heights in excess of 100 nm without degradation of the photoluminescence. By designing the shape of the nanocrystal solid at this length scale and controlling connectivity between the nanocrystals, the refractive index and nanostructure absorptivity can be tailored. Chiral metamaterials comprised of these patterned quantum dot solids exhibit enhanced degrees of circularly polarized luminescence and improved angular control.

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Tue-ET1-02

Dial-a-material: precise manufacturing technology using early growth for plasmonic materials up to 100 nm

**Bruno Pinho (bp421@cam.ac.uk), Laura Torrente-Murciano (lt416@cam.ac.uk)**

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Nanoparticles present in countless critical branches of scientific research, such as virology, hyperthermia, solar cells, etc. Despite the advances in lab scale routes, there is still a significant gap between nanomaterial research and industrial deployment. Current limitations relate to the lack of continuous manufacturing technologies that combine precision, flexibility and affordability. Recent studies have proved the application of automated approaches for material synthesis and rapid characterization. However, these approaches are restricted to single-step and rapid (~minute per iteration) syntheses. Recently we demonstrated the continuous synthesis of seed-mediated growth of silver citrate-based nanoparticles with sizes ranging from 4 to 80 nm using multi-stage flow systems. Despite this technical breakthrough, the system still delivers an off-target inconsistency of  $\pm 13\%$  when performing  $>100$  characterized syntheses. Outside the controllable zone (i.e. concentration, pH, time per stage, micromixing, etc), there are uncontrollable parameters that detrimentally affect the reproducibility and repeatability, such as precursor ageing, feedstock inconsistency, flow fluctuations, fouling, speciation, metal traces, etc. In this work, we present an autonomous flow system equipped with high-throughput real-time nanoparticle sizing and shape strategy integrated into modular flow systems through low-cost spectroscopy which enables fast (within few seconds) multi-point analysis. The approach is based on real-time early growth information to a late particle size. Precise size tuneability is successfully achieved in the absence of organic capping ligands, using early growth information to mechanistically predict late particle-properties. The early access to data in long synthetic routes (beyond 10 minutes) is vital to ensure a smooth and stable operation with minor user-intervention in a dial-a-particle fashion. This is a shift from machine learning (ML) methodologies, which are restricted to trained networks with rich data sets, impractical in non-reproducible processes and limited to short residence times (e.g. few minutes). The resulting system is capable of achieving a target size in just 2-3 residence time. This approach can be extrapolated to other materials, such as quantum dots, perovskites, aluminium, etc. It probes the concept of automation for multi-stage, long (few minutes to hours) processes, paving the way to automated slow reactions. We showcase the technology for large (i.e. multi-growth stages) silver and gold nanoparticles, being applicable tofor the distributed manufacturing of materials on-demand with minor human-intervention in a self-regulated manner. This technological platform offers: materials on-demand (wide range of sizes), distributed manufacturing, minor human-intervention, controllable multi-stage synthetic protocols, real-time multi-point particle, modular flexibility, and precision.

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Tue-ET1-03

New methods to map the interfacial mobility and distribution of amphiphiles at fluid interfaces based on liquid crystals

**Sangchul Roh (sr974@cornell.edu), Nicholas Abbott (nla34@cornell.edu)**

Smith School of Chemical and Biomolecular Engineering, Cornell University  
Flow-induced non-equilibrium states of surfactant-laden interfaces play a pivotal role in interface engineering such as emulsification, foaming and spreading. Although many past studies have demonstrated that the dynamic properties of fluid interfaces decorated with surfactants are regulated by

interfacial mobility and surfactant reorganization, few methods permit simultaneous monitoring of this interplay. In this presentation, we will report on the optical responses of micrometer-thick films of liquid crystalline oils (4-cyano-4'-pentylbiphenyl, 5CB) in contact with flowing aqueous solutions with amphiphiles. We observe the flow of solutions of soluble surfactant to generate a transient and spatial optical response in the 5CB oil film, which we interpret to provide insight into interfacial mobility and interfacial surfactant concentration gradients. Experiments performed with simple salts and insoluble amphiphiles, which are placed into the context of a model of dynamic LC interfaces, are used to provide further support for our conclusions. Overall, we conclude that liquid crystalline oils provide the basis of general and facile methods to understand the dynamic behaviors of surfactants at oil-water interfaces and, potentially, to enable rapid optimization of amphiphile mixture compositions for targeted dynamical properties.

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Tue-ET1-04

### Monitoring Halide Exchange and Perovskite Nanocrystals using Diffusion Ordered NMR Spectroscopy

**Mathew Maye (mmmeye@syr.edu)**

Department of Chemistry, Syracuse University

In this presentation we'll describe our use of diffusion ordered nuclear magnetic resonance spectroscopy (DOSY) and 2D relaxation ordered spectroscopy (ROSY) to observe and probe halide exchange at CsPbX<sub>3</sub> (X = Br, I) nanocrystals and nanoplatelet interfaces. By comparing diffusion coefficient changes from DOSY with relaxation times from ROSY, an in-depth picture of the dynamic perovskite interface is possible. Halide exchange between Br- and I-rich crystals were probed, and the resulting ligand density changes provide insights into ligand binding and stability. Moreover, DOSY and ROSY were used to monitor a chemical reaction in real time at the interface, in which an organohalide could be monitored from time of addition, to interfacial coordination, to conversion to products.

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Tue-ET1-05

Does microstructure and packing of polyanions in polyelectrolyte complex coacervates depend on the conformation in the parent solution?

**Ulrich Scheler (scheler@ipfdd.de)**

Leibniz-Institut für Polymerforschung Dresden e.V.

Polyelectrolyte complex coacervates are formed mixing polycation and polyanion in solution. The conformation of polyelectrolytes depends on the repelling force between charges along the polymer chain. For a weak polyanion poly(maleic anhydride-co-ethylene) it depends on pH as well as ionic strength. The effective charge is inferred from electrophoresis NMR while diffusion NMR yields the hydrodynamic size as a measure for the conformation. The relative intensity of the acid proton signal in <sup>1</sup>H MAS spectra show the degree of dissociation. Separating solid-state <sup>1</sup>H NMR spectra in two-dimensional single-quantum-double-quantum correlation spectra distinguishes between acid protons hydrogen bonded to other acid protons from isolated acid and thus identifies polyanion-rich regions in solid polymers or complexes. Two-dimensional integration of the on-diagonal and off-diagonal signals of the acid protons enables quantification. At low pH (weak charge of the polyanion) fewer acid-acid contacts are found in the complexes. At higher pH (high nominal charge of the polyanion) with a more stretched conformation almost none acid-acid contacts are found in the complexes as expected from the more stretched conformation in the parent solution.

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Tue, 15 09:00 - 11:00

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Tue-GT1-01

## Nature-inspired structured and functional surfaces for water-energy nexus (**Keynote Lecture**)

**Zuankai Wang (zuanwang@cityu.edu.hk)**

Department of Mechanical Engineering

Water is the origin of life and also the mediator and absorber of energy. Despite its ubiquity and seeming simplicity, the water is probably the least understood matter in the world. The phase transition, transport, and manipulation, normally spanning different time and length scales, constitute the basic paradigm of numerous biological systems and industrial processes. Over the past decade, the advances in nature-inspired surfaces provide new dimensions in the fundamental understandings and control of interfacial and transport phenomena of water, especially on textured surfaces and under complicated working environments. In this talk, I will discuss our recent innovations at the nature-inspired surfaces to address one of the most important challenges facing us today, i.e., water-energy nexus. I will first describe how to rationally design, fabricate various structured structures with preferential liquid transport and mechanical properties. Then, I will discuss how to leverage the high latent heat of water and its interaction with engineered surfaces for efficient thermal management including boiling/evaporation (even completely prevent the film boiling at extremely high temperatures above 1000 degrees), condensation, radiative cooling even in high humidity conditions. Finally, I will discuss our latest efforts in water kinetic energy harvesting using transistor-like design.

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Tue-GT1-02

## Adhesion Strength and Fatigue Behavior of Single-Lap Joints Bonded with Epoxy Nanocomposite Adhesives

**Chien-Wei Chu (dscckct09@hotmail.com)**, **Ken Kojio (kojio@cstf.kyushu-u.ac.jp)**, **Atsushi Takahara (takahara@cstf.kyushu-u.ac.jp)**

Kyushu University

Single-lap joints (SLJs) of stainless steel substrates bonded with epoxy/ montmorillonite (MMT) nanocomposite adhesives, consisting of diglycidyl ether of bisphenol A and poly(oxypropylene) diamine with various weight contents of a commercialized MMT filler, were prepared. The dispersion state of MMT and bulk mechanical properties were investigated by wide-angle X-ray scattering/diffraction, uniaxial tensile test, and dynamic mechanical analysis. The lap shear strengths and failure modes were investigated based on the single-lap shear test, and the joint durability was examined using the fatigue test with various shear stress levels. Through the incorporation of the MMT fillers in epoxy resins, the lap shear strengths increased from 25 to 40 MPa, the failure modes changed from adhesive failure mode to cohesive one, and the fatigue lifetimes prolonged with the addition of a small amount of MMT.

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Tue-GT1-03

## Robust oil repellent surfaces by using microscale hyperbolic structures

**Hyunsik Yoon (hsyoon@seoultech.ac.kr)**

Seoul National University of Science & Technology

Bio-inspired liquid-repellent surfaces have been studied for decades. The research focus has moved from the fabrication of artificial microscale structures to have robustness for real applications. For instance, armored superhydrophobic surfaces have been proposed to be stable in shear friction. For the superoleophobicity, it is more complicated because re-entrant structures are necessary to repel low surface energy organic liquid. In this presentation, we suggest microscale hyperbolic structures for having oleophobicity as well as the robustness in shear forces. For the formation of hyperbolic structures, we exploited the capillary wetting on separated micropillars and the shapes can be controlled by the spacing ratio between pillars and the thickness of the liquid prepolymer. The microscale hyperbolic structures have

the advantages of easy replication for a large area fabrication and robustness due to the large surface area in the bottom region.

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Tue-GT1-04

### Effect of Polymer Concentration on Air Entrainment Dynamics under Droplet Impact

**Ziwen He (ziwen\_he1@baylor.edu), Huy Tran (huy\_tran1@baylor.edu), Min Pack (min\_pack@baylor.edu)**

Baylor University

Droplet impact dynamics is essential for achieving optimized drop deposition on surfaces including agrochemical application, spray coating and cooling processes. Recent studies have revealed that droplets tend to rebound from the surface when the ambient air decelerates the droplet and an interstitial air layer prevents contact. While this air cushioning effect has been studied under Newtonian liquid droplets, the air entrainment mechanism underneath polymeric droplets is lacking in the literature. In this study, we demonstrate that for intermediate Weber numbers,  $We = \rho U_0^2 D_0 / \sigma \sim O(1-10)$ , where the  $\rho$  is the density,  $U_0$  the impact velocity,  $D_0$  the droplet diameter, and  $\sigma$  the surface tension, the spatiotemporal evolution of the air film responds to the viscoelastic property of aqueous polymeric droplets. Herein, a submicron air layer is visualized during droplet impact of aqueous poly(ethylene oxide) and xanthan gum solutions at different polymer concentrations varied between  $O(10 - 1000)$  ppm with a total internal reflection microscopy (TIRM) technique. We observe that the slope of the air film induced by impacting droplets with PEO additives is attenuated by polymer concentrations beyond the entangled regime yet enhanced before reaching the critical overlap concentration  $c^*$ . In contrast, for xanthan gum solutions, we observe that the air film slope is enhanced beyond the entangled regime. We hypothesize that the change in the air film slope upon impact for the droplets is due to the changes in the viscoelastic properties for different concentrations.

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Tue-GT1-05

### Condensation on the Old Man Cactus spine: droplets distant coalescence

**Nicolò Giuseppe Di Novo (nicolo.dinovo@unitn.it)<sup>1,2</sup>, Lakshminath Kundanati (l.kundanati@unitn.it)<sup>1</sup>, Gabriele Greco (gabriele.greco-2@unitn.it)<sup>1</sup>, Stefano Siboni (stefano.siboni@unitn.it)<sup>3</sup>, Claudio Della Volpe (claudio.dellavolpe@unitn.it)<sup>3</sup>, Alvis Bagolini (bagolini@fbk.eu)<sup>2</sup>, Nicola Maria Pugno (nicola.pugno@unitn.it)<sup>1,4</sup>**

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Some cacti are known to have developed spines that can collect water during the condensation process and direct it to collecting areas (stomata and roots). On the Andes lives the Old Man Cactus (*Oreocereus trolli*), characterized by dense hairs and spines with micro grooves on the surface. We have analysed a particular dynamics of condensation on the spines: in addition to coalescence by contact, the droplets coalesce at a distance thanks to the presence of the grooves. In particular, a relatively smaller droplet flows into a larger one through water capillaries that form in the grooves. We found a good agreement between the experiments and an analytical model that considers the Laplace pressure difference of the two drops as the driving force. The global effect of distant coalescence is that all the smaller and re-nucleated droplets are sucked into a few large droplets. The accumulation of water in large drops could have benefited these cacti in terms of:

- delaying the evaporative cooling during the first hours of sunshine
- providing a source of water for pollinators (hummingbirds, bees)

- increasing speed in reaching the critical sliding volume of the drops that, eventually, would be harvested from the roots.

Old Man Cactus-inspired microgrooved surfaces with engineered distance coalescence may increase the efficiency of water collectors.

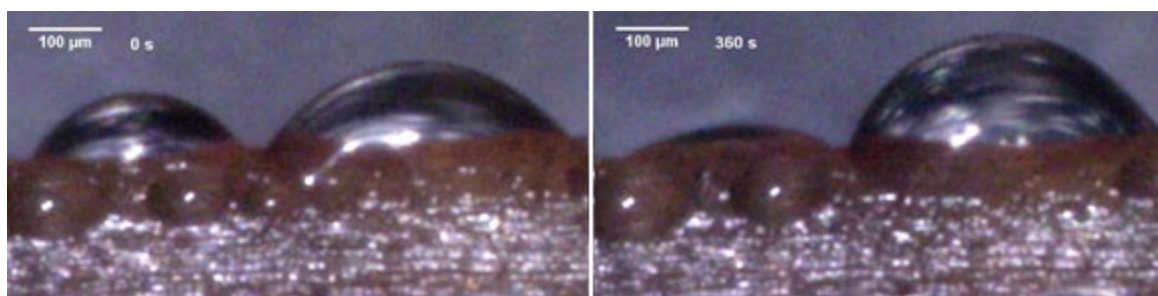


Figure 1. Beginning (left) and end (right) of a distant coalescence event captured in a condensation experiment done at  $T_{spine} = 2^{\circ}\text{C}$  and saturation ratio = 2.

Tue, 15 09:00 - 11:00

Tue-LT1-01

Catalyst design rooted in inorganic materials properties

**Zachary Ulissi (zulissi@andrew.cmu.edu)**

Department of Chemical Engineering, Carnegie Mellon University

Catalyst discovery efforts are inherently multi-objective and require an understanding of stability under reaction conditions, activity, and selectivity, among many other properties. Much current effort is devoted to screening of materials with desired descriptors, such as small molecule adsorption energies, that are expected to correlate with experimental performance. However, in many cases simpler approaches rooted in materials properties can be used to focus effort on promising materials. I will highlight three approaches from my group and collaborators: first, how to predict bulk stability under reaction conditions for oxygen evolution chemistry and lessons learned in combining and augmenting existing datasets, second, I will show that stability and crystal geometry can be used to identify catalysts that obey different scaling relations, and finally I will show how materials with specific active site environments can be enumerated and searched for selective chemistries.

Tue-LT1-02

Single-Atom Catalysis for Oxidizing Contaminants of Emerging Concern via High-Valent Fe Species

**Zhe Zhou (zhou0530@gwu.edu)**<sup>1</sup>, **Mengqiao Li (lmq123@gwmail.gwu.edu)**<sup>1</sup>, **Chunguang Kuai (chunguangk@vt.edu)**<sup>2</sup>, **Yuxin Zhang (zyx@vt.edu)**<sup>2</sup>, **Virginia Smith (vsmith@usna.edu)**<sup>3</sup>, **Feng Lin (fenglin@vt.edu)**<sup>2</sup>, **Ashlee Aiello (aiello@usna.edu)**<sup>3</sup>, **David Durkin (durkin@usna.edu)**<sup>3</sup>, **Hanning Chen (hchen@american.edu)**<sup>4</sup>, **Danmeng Shuai (danmengshuai@gwu.edu)**<sup>1</sup>

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<sup>4</sup> American University

Contaminants of emerging concern (CECs) detected at trace concentrations in water and wastewater have been threatening the public health and ecological systems. Advanced oxidation processes (AOPs) hold promising for degrading CECs, and they are continuously improved for energy efficiency and environmental

sustainability. Heterogeneous single-atom catalysts with fine-tuned coordination environment show superior activity, selectivity, and stability in AOPs for water purification. We prepared a single-atom Fe catalyst supported on oxygen-doped carbon nitride (SAFe-OCN) for degrading a broad spectrum of contaminants of emerging concern (CECs) by activating peroxides such as peroxymonosulfate (PMS). In the SAFe-OCN/PMS system, most selected CECs were amenable to degradation and high-valent Fe species were responsible for oxidation. Moreover, SAFe-OCN showed excellent performance for contaminant degradation in complex water matrices and high stability in oxidation. Specifically, SAFe-OCN, with a catalytic center of Fe coordinated with both nitrogen and oxygen ( $\text{FeN}_x\text{O}_{4-x}$ ), showed 5.13-times increased phenol degradation kinetics upon activating PMS compared to the catalyst where Fe was only coordinated with nitrogen ( $\text{FeN}_4$ ). Molecular simulations suggested that  $\text{FeN}_x\text{O}_{4-x}$ , compared to  $\text{FeN}_4$ , was an excellent multiple-electron donor and it readily formed high-valent Fe species upon oxidation. The susceptibilities of CECs to catalytic degradation in SAFe-OCN/PMS system were likely dependent on their structures and properties. By activating PMS, SAFe-OCN produced high-valent Fe species exclusively for contaminant oxidation, instead of using radicals (hydroxyl radicals, sulfate radicals, and superoxide radicals), singlet oxygen, or catalyst-mediated electron transfer. Moreover, the reactivity of SAFe-OCN was maintained in complex water matrices and for long-term oxidation. In summary, the single-atom Fe catalyst enables efficient, robust, and sustainable water and wastewater treatment, and molecular simulations highlight that the electronic nature of Fe determines the activity of the single-atom catalyst.

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Tue-LT1-03

Dilemma of activity and stability: Intrinsic photoreactivity promotes 2D nanomaterial decomposition under radical attack

**Mengqiao Li (lmq123@gwu.edu), Danmeng Shuai (danmengshuai@gwu.edu)**

Department of Civil and Environmental Engineering, The George Washington University

Knowledge about the reactivity and stability of photocatalytic nanomaterials in engineering settings is essential to advance robust catalysis. As an emerging photocatalytic nanomaterial, graphitic carbon nitride was believed to be stable, and only hydroxyl radicals ( $\bullet\text{OH}$ ), the strongest oxidant in water, could oxidize and age graphitic carbon nitride. However, our study has demonstrated that photoinduced holes significantly enhance graphitic carbon nitride nanosheet decomposition under  $\bullet\text{OH}$  attack, by using an integrated experimental and simulation approach. In the dark,  $\bullet\text{OH}$  only attack a limited amount of edge-site heptazines of graphitic carbon nitride nanosheets, resulting in peripheral etching and slow degradation. In contrast, photoinduced holes decrease the activation energy barrier of C-N bond breaking between heptazines and shift the degradation pathway to bulk fragmentation, leading to much faster degradation. This discovery not only sheds light on fundamental chemistry of photocatalytic nanomaterial aging but also provides guidelines for designing reactive, robust, and safe catalysts.

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Tue-LT1-04

Toward Single Atom Catalysis for Environmental Application (**Keynote Lecture**)

**Jaehong Kim (jaehong.kim@yale.edu)**

Yale University

Various noble metals have been employed as catalysts and co-catalysts to enhance the kinetics of reactions that are critical for environmental remediation. The need to maximize the available catalytic sites per unit mass, particularly due to noble metal scarcity and high cost, has driven the development of material architectures at the nanometer scale. Recent theoretical and experimental studies have explored noble metal catalysts on the sub-nanometer, atomic scale to maximize atomic efficiency. A single atom catalyst (SAC) or atomically dispersed catalyst is the theoretical limit in this endeavor, and previous studies have identified additional benefits such as low coordination state and strong interaction with the surrounding substrate resulting in enhanced selective catalysis. For past couple of years, our group has been exploring various SACs (Pt, Pd, Ag, and Co) anchored on different substrates ( $\text{SiC}$ ,  $\text{C}_3\text{N}_4$ , and  $\text{TiO}_2$ ) that exhibit

unique catalytic properties. This talk summarizes our recent studies to advance the water treatment catalysts from the nano-scale toward the single atom scale such as (1) single-atom Pt anchored to SiC photocatalyst (Pt1/SiC) for selective defluorination of perfluorooctanoic acid (PFOA) and selective dehalogenation of various water pollutants and (2) spatial separation of two co-catalysts by coordinating single atom cobalt at the void center of C<sub>3</sub>N<sub>4</sub> and anchoring anthraquinone at the edges of C<sub>3</sub>N<sub>4</sub> platelets to significantly enhance the catalytic synthesis of H<sub>2</sub>O<sub>2</sub>, a precursor chemical for advanced oxidation.

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## Tue, 15 09:00 - 11:10

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Tue-MT1-01

From photons to chemical bonds (**Keynote Lecture**)

**Prashant Jain (jain@illinois.edu)**

Department of Chemistry, Materials Research Laboratory, Beckman Institute for Advanced Science and Technology, and Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA.

In recent years, it has been found that noble metal nanoparticles catalyze chemical reactions when their plasmon resonances are excited by light radiation. I will discuss this emerging paradigm in chemistry and elucidate how it works. Photoexcitation of plasmon resonances in noble metal nanostructures leads to the generation of electron-hole pairs, which can be utilized as reaction equivalents in redox chemical processes. A striking example of this phenomenon is the multielectron conversion and C-C coupling of CO<sub>2</sub> to form hydrocarbons on gold nanoparticles under visible light. The lack of such activity in the dark suggests that reaction pathways are modified by optical excitation and so are the very catalytic properties of the plasmonic metal. In the case of thermodynamically uphill reactions, chemical potential is harvested from optical excitations and stored in the form of energy-rich bonds. These phenomena present a path to CO<sub>2</sub> mitigation, energy storage, and chemical manufacturing.

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Tue-MT1-02

Shape and Plasmonic Properties of Magnesium Nanoparticles

**Jeremie Asselin (ja680@cam.ac.uk)<sup>1,2</sup>, Christina Boukouvala (cb955@cam.ac.uk)<sup>1,2</sup>, Elizabeth Hopper (erh64@cam.ac.uk)<sup>1,2,3</sup>, Thomas Wayman (tmrw2@cam.ac.uk)<sup>1,2</sup>, Quentin Ramasse (qmrmasse@superstem.org)<sup>4,5</sup>, John Biggins (jsb56@cam.ac.uk)<sup>6</sup>, Emilie Ringe (er407@cam.ac.uk)<sup>1,2</sup>**

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<sup>6</sup> Department of Engineering, University of Cambridge, Trumpington Street, Cambridge, United Kingdom, CB2 1PZ

Recently, alternatives to the rare and expensive noble metals Ag and Au have been sought for more sustainable and large-scale plasmonic utilization. Mg supports plasmon resonances, is one of the most abundant elements in earth's crust, and is fully biocompatible, making it an attractive framework for plasmonics. This talk discusses the hexagonal, folded, and kite-like shapes we modelled using Crystal

Creator, our Wulff-based shape generation code for twinned nanoparticles. Nanoparticles found in colloidal syntheses are then presented and match well with predictions. Then, the optical response of Mg nanoparticles is overviewed, highlighting Mg's ability to sustain localized surface plasmon resonances across the ultraviolet, visible, and near-infrared electromagnetic ranges. The various resonant modes of hexagons, leading to the highly localized electric field characteristic of plasmonic behavior, are presented numerically and experimentally. The evolution of these modes and associated field from hexagons to the lower symmetry folded structures is then probed, again by matching simulations, optical, and electron spectroscopy data.

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Tue-MT1-03

## Manipulating Surface-modified Cs:WO<sub>3</sub> Nanocrystals in Liquid Crystal for Solar Transmission Control

**Capucine Cleret de Langavant (capucine.cleretdelangavant@saint-gobain.com)<sup>1,2</sup>, Yannis Cheref (yannis.cheref@polytechnique.edu)<sup>1</sup>, Giuseppe Boniello (giuseppe.boniello@saint-gobain.com)<sup>2</sup>, Louise Daugas (Louise.daugas@polytechnique.edu)<sup>1</sup>, Olivier Mondain-Monval (olivier.mondain@crpp.cnrs.fr)<sup>3</sup>, Virginie Ponsinet (virginie.ponsinet@crpp.cnrs.fr)<sup>3</sup>, Frédéric Mondiot (frederic.mondiot@saint-gobain.com)<sup>2</sup>, Thierry Gacoin (thierry.gacoin@polytechnique.edu)<sup>1</sup>, Jongwook Kim (jong-wook.kim@polytechnique.edu)<sup>1</sup>**

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Highly-doped semiconductor (SC) nanocrystals have raised a special interest due to their Localized Surface Plasmon Resonance (LSPR) tunable over a large infrared range (IR). A lot of works have focused on the effect of dopant nature and its influence on LSPR response. An active modulation of these defect states, and thus of LSPR is achievable by post-synthetic redox chemistry of nanocrystals, which opens new applications especially in smart windows [1]. However, like metallic nanoparticles, anisotropy or the coupling effect can affect the LSPR of SC, but haven't being studied extensively yet. It may be possible to modulate these parameters by aligning nanorods [2] or reversibly aggregate them, using an active matrix like liquid crystals. We have optimized the synthesis of Cs:WO<sub>3</sub> nanocrystals and study the impact of the particle aspect ratio on the absorption spectra [3]. We found that tungsten oxide nanocrystals are very sensitive to the surface chemistry and easily aggregate when functionalized with native oily ligands. Because the LSPR is subject to the distance between particles, maintaining colloidal stability by ligand exchange is essential to preserve the LSPR absorption properties (cross section  $\approx 3.5 \cdot 10^{-14} \text{cm}^2$ ) for applications. By playing with surface chemistry and solvent we control the particle aggregation and assembly as well as their orientation, thereby modulating the anisotropic LSPR properties. Briefly, we found that aggregation at micron scale causes a red shift of LSPR around 250nm, a tripling of absorption band width and alters the absorption properties by 60%. After an optimization of surface chemistry, it is possible to reversibly aggregate nanoparticles in liquid crystal smectic phase defects [4] and thus tune the coupling effect and absorption with temperature. We have successfully dispersed Cs:WO<sub>3</sub> nanoparticles in isotropic phase of liquid crystal. By reducing the temperature, aggregates were formed resulting in a loss absorption property. The aggregation was found to be partially reversible with an absorption modulation in near IR around 50%. Our finding paves the way for the development of new smart windows with active solar control. [1] Garcia & all (2011), Dynamically Modulating the Surface Plasmon Resonance of Doped Semiconductors Nanocrystals. *NanoLetters*, 4415-4420. [2] Liu & all (2014) Electrically and Optical Tunable Plasmonic Guest-Host Liquid Crystals with Long-Range Ordered Nanoparticles. *NanoLetters*, 4071-407. [3] Kim & all (2016) The interplay of shape and Crystalline Anisotropies in Plasmonic Semiconductors Nanocrystals. *NanoLetters*, 3879-3884. [4] Milette & all (2012) Reversible long-range patterning of gold nanoparticles by smectic liquid crystals. *SoftMatter*, 6593-6598.



Tue-MT1-04

“hot” photo-luminescence from metals - quantitative theory and application to anti-Stokes thermometry

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We provide a complete quantitative theory for light emission from Drude metals under continuous wave illumination, based on our recently derived steady-state non-equilibrium electron distribution. We show that the electronic contribution to the emission exhibits a dependence on the emission frequency which is very similar to the energy dependence of the non-equilibrium distribution, and characterize different scenarios determining the measurable emission lineshape. This enables the identification of experimentally-relevant situations where the emission lineshapes deviate significantly from predictions based on the standard theory (namely, on the photonic density of states) and enables the differentiation between cases where the emission scales with the metal object surface or with its volume. We also provide an analytic description (which is absent from the literature) of the (polynomial) dependence of the metal emission on the electric field (see Fig. 2(b)), its dependence on the pump laser frequency, and its non-trivial exponential dependence on the electron temperature, both for the Stokes and anti-Stokes regimes. Our results imply that the emission does not originate from either fermion statistics (due to e-e interactions), and even though one could have expected the emission to follow boson statistics due to involvement of photons (as in Planck's Black Body emission), it turns out to deviate from that form as well. Finally, we resolve the arguments associated with the effects of electron and lattice temperatures on the emission, and which of them can be extracted from the anti-Stokes emission. With this theory in hand, we revisit recently proposed thermometry protocols based on anti-Stokes emission from metal nanoparticles. We show that errors estimates reported so far have been underestimated and suggest an alternative thermometry protocol based on the Stokes emission which has some advantages over the existing ones.

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Tue-MT1-05

Plasmonic Mapping for Sensor Design

**Amanda Haes (amanda-haes@uiowa.edu)**

University of Iowa

Spatially resolved localized surface plasmon resonance (LSPR) and surface-enhanced Raman scattering (SERS) microscopies are used simultaneously to assess and minimize plasmonic variations of carboxylated gold nanostars on electrospun polymer films. Novel to this study, the spatial distribution and electromagnetic properties of gold nanostars deposited on the polymer are locally quantified using LSPR microscopy mapping and second derivative LSPR spectral analysis. As a result, spectral complexity arising from background variations are eliminated thus enabling quantification of local nanostar density. Next, uranyl intensities collected using SERS are shown to be insensitive to local nanostar densities that range from 140 to 200 pM-cm. This important finding provides a non-biased guideline for selecting sensing regions on electrospun polymer films. By considering interactions between gold nanostars, the polymer substrate, and the analyte and correlating spatially resolved spectral measurements at an interface, realization of a user-friendly sensor that minimizes sampling bias is possible

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Tue, 15 09:00 - 11:00

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Tue-OT1-01

Designing Colloidal Quantum Dot-Molecule Interfaces for Photocatalysis (**Keynote Lecture**)

**Francesca Arcudi (francesca.arcudi@northwestern.edu)<sup>1,2</sup>, Luka Dordevik (luka.dordevik@northwestern.edu)<sup>1,2</sup>, Samuel Stupp (s-stupp@northwestern.edu)<sup>1,2</sup>, Emily Weiss (e-weiss@northwestern.edu)<sup>1,2</sup>**

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Colloidal quantum dots have a distinct advantage as photocatalysts and photosensitizers -- the ability to chemically modify their surfaces without substantially influencing the optical and electrochemical properties associated with their cores. This talk will discuss how the surfaces of copper indium sulfide quantum dots can be designed to sequester CO<sub>2</sub> as loosely bound carbamic acid, and to assemble electrostatically with cobalt porphyrin electrocatalysts to achieve unprecedented photocatalytic activity for reduction of CO<sub>2</sub> to CO in pure water.

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Tue-OT1-02

Optical Processing of DNA-Programmed Nanoparticle Superlattices

**Leonardo Zornberg (lzornber@mit.edu), Paul Gabrys (pgabrys@mit.edu), Robert Macfarlane (rmacfarl@mit.edu)**

Department of Materials Science and Engineering, MIT

Hierarchical structural control across multiple size regimes requires careful consideration of the complex energy- and time-scales which govern the system's morphology at each of these different size ranges. At the nanoscale, synthetic chemistry techniques have been developed to create nanoparticles of well-controlled size and composition. At the macroscale, it is feasible to directly impose material structure via physical manipulation. However, in between these two size regimes at the mesoscale, structural control is more challenging as the physical forces that govern material assembly at larger and smaller scales begin to interfere with one another. In this work, the interplay of structure-directing forces at multiple length-scales is investigated by utilizing optical processing to influence both nanoscale and microscale features of self-assembled films composed of complementary DNA-grafted nanoparticles. Optical processing is used to generate heat, which causes the self-assembled particles to rearrange from a kinetically trapped, amorphous state into a thermodynamically preferred superlattice structure, which maximizes the number of complementary DNA interactions between nanoparticles. The gradient in the heat profile, however, also induces thermophoretic motion within the nanoparticle film, resulting in microscale movement at a comparable time-scale. By utilizing precise exposure times enabled by optical processing, crystallization and thermophoresis occur concurrently in the self-assembling nanoparticle system, enabling a dynamic growth mechanism whereby nucleation and growth occur in separate regions of the material. Furthermore, utilizing sufficiently short processing times allows for the formation of a fluidlike state of the DNA-functionalized nanoparticle materials that is inaccessible via typical thermal processing setups. This unique phase of the material allows for both pathway-dependent and pathway-independent growth phenomena, as appropriately tuning the experimental conditions enables the formation of morphologically equivalent nanoparticle lattices that are generated through different intermediate states (pathway-independent structures), or kinetically preprocessing a material to yield unique thermodynamic arrangements of particles once fully annealed (pathway-dependent structures).

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Tue-OT1-03

Developing colloidal interaction potentials by integrating equilibrium and non-equilibrium measurements

**Scott Fenton (scottmfenton@ucsb.edu)<sup>1</sup>, Brian Ryu (bryu@stanford.edu)<sup>2</sup>, Tuan Nguyen (tuan92@gmail.com)<sup>1</sup>, Matthew Helgeson (helgeson@ucsb.edu)<sup>1</sup>, Roseanna Zia (rzia@stanford.edu)<sup>2</sup>**

<sup>1</sup> University of California Santa Barbara

<sup>2</sup> Stanford University

Conventional approaches to model interparticle potentials for colloidal systems often utilize equilibrium experiments including scattering measurements. However, interaction potentials extracted from these approaches are limited to conditions where equilibrium can be accessed in experiment, and may not be sufficient for accurately modeling system behavior out of equilibrium, for example in kinetically arrested states under non-dilute conditions. Hence, there is a need to develop new methods to determine interaction potentials that using approaches that incorporate both equilibrium and non-equilibrium behavior simultaneously. Here, we present such an approach that involves equilibrium measurements to generate candidate families of potentials, and then non-equilibrium tests to select the most accurate model amongst the candidates. To demonstrate the new protocol, we apply the method to a thermoresponsive colloidal system involving nanoemulsions interactions mediated by temperature-responsive polymers. Candidate potential shapes are generated from dilute scattering measurements of the experimental system, and as a non-equilibrium test we compare rheological measurements of gelation kinetics rheology between the experimental system and molecular dynamics simulations involving the candidate potentials. This new protocol successfully disambiguates potentials that produce the same dilute equilibrium structure, and can be used to determine which potential best models the interparticle interactions in colloidal systems outside of equilibrium for a range of colloid densities.

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Tue-OT1-04

### Single-Particle Mapping of an $O_h$ to $T_d$ Symmetry Reduction Growth Mechanism in Metal Nanoparticle Synthesis

**Muhua Sun (ms166@rice.edu)**<sup>1</sup>, **Zhihua Cheng (Zhihua.Cheng@rice.edu)**<sup>1</sup>, **Matthew Jones (mrj@rice.edu)**<sup>1,2</sup>

<sup>1</sup> Department of Chemistry, Rice University

<sup>2</sup> Department of Materials Science & Nanoengineering, Rice University

The vast majority of single crystalline gold nanoparticles adopt shapes in the  $O_h$  point group as a consequence of the symmetry of the underlying FCC crystal lattice. Tetrahedra are a notable exception to this rule and although they have been observed in several syntheses, their growth mechanism, and the symmetry-reduction process that necessarily characterizes it, is poorly understood. Here, a novel symmetry breaking mechanism is revealed by in-situ liquid flow cell TEM observation of seeded growth in which tetrahedra nanoparticles are formed from higher symmetry seeds. Real-time observation of the growth demonstrates a kinetically-driven pathway during which rhombic dodecahedra nanoparticles transition to tetrahedra through tristetrahedra intermediates, with accompanying surface facet evolution from  $\{110\}$  to  $\{111\}$  via  $\{hhl\}$  (where  $h > l$ ), respectively. On the basis of these data we propose a symmetry-breaking mechanism that relies on rapid loss of inversion symmetry in the initial stages of the reaction, followed by differential reactivity of tips vs. faces under conditions of relatively high supersaturation and moderate ligand concentration. Application of these insights to ex-situ synthesis conditions allowed for improved yield of tetrahedra nanoparticles. This work sheds important mechanistic light on the crystallographic underpinnings of nanoparticle shape and symmetry transformations and highlights the importance of single-particle characterization tools for monitoring nanoscale phenomena.

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## Tue, 15 -09:00 - 11:00

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Tue-PT1-01

### Combinatorial Synthesis of Polyelemental Nanoparticles (**LaMer Keynote Lecture**)

**Pengcheng Chen (pcchen@berkeley.edu)**

Kavli Energy Nanoscience Institute University of California, Berkeley

The emerging potential of multimetallic nanoparticles has led to an increased demand for combinatorial and high-throughput synthesis of particles that encompass an enormous compositional and structural

parameter space. Here, we report a method termed scanning probe block copolymer lithography that integrates scanning probe lithography and polymer nanoreactors to systematically synthesize multimetallic nanoparticles. The scope of this method was demonstrated by creating nanoparticles consisting of combinations of Au, Ag, Cu, Pt, Pd, Ni, Co, and Sn. Particularly, a library of particles made by five elements, i.e., Au, Ag, Cu, Ni, and Co, was developed through the polymer nanoreactor-mediated synthesis. We show that all combinations of binary, ternary, quaternary, and quinary particles can be independently synthesized in a site-specific manner and characterized by electron microscopy. The structure of the nanoparticle is tailorable based on particle composition and metal compatibility. The ability to systematically synthesize and characterize such structures not only provides important insight into the factors that lead to alloy formation and phase segregation at the nanoscale, but also open a route to combinatorial libraries of complex nanostructures that are promising for a broad range of fields, such as catalysis, plasmonics, and magnetics.

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Tue-PT1-02

Application of machine learning to understand and predict the size of quantum dots in the hot injection syntheses

**Fabio Baum (fabiobaum.research@gmail.com)**<sup>1</sup>, **Ariadne Koche (kocheariadne@gmail.com)**<sup>2</sup>, **Tatiane Pretto (tatianepretto@gmail.com)**<sup>2</sup>, **Lilo Pozzo (dpozso@uw.edu)**<sup>1</sup>, **Marcos Jose Leite Santos (mjls@ufrgs.br)**<sup>2</sup>

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<sup>2</sup> Graduate Program of Materials Science, Universidade Federal do Rio Grande do Sul

Quantum dots (QDs) are important building blocks of nanotechnology, with applications in many technologies.[1] Despite the growth in large-scale production of QDs, controlling physical properties of these materials are still reported based on trial-and-error. The use of tools to predict QD's properties based on synthesis conditions is prone to accelerate discovery and expand its applications. Machine learning is an emerging tool in the field of chemistry and material science.[2] Here, we report the application of machine learning algorithms to a database of CdS, CdSe, PbS, PbSe, and ZnSe QDs hot injection synthetic conditions and the use of the Monte Carlo method to simulate new synthesis conditions to achieve the desired QD diameter. To create our database, we searched on Google Scholar and Web of Science, downloaded the PDF, and extracted the reaction condition parameters from the experimental and the QD diameter from the results sections of each paper. We use the caret package of the R programming language to train algorithms of multilinear regression, smoothing splines, regression trees, and random forest. The gradient boosting machine algorithm was trained using the h2o R package from the H2O.ai. A sequential deep learning model was created using the Keras API for R. The evaluation metrics of the models were R-squared, root mean squared error, and mean absolute error. Once many papers reproduce the synthetic conditions of previous works, the similarity between test and train data might cause memorization. We addressed this challenge using an HCA algorithm to split the train and test data by similarity. A 1-NN algorithm was used as a baseline for memorization. Four algorithms performed better than the memorization baseline, namely regression trees, random forest, gradient boosting machine, and deep learning. For these algorithms, the most important variable affecting the final diameter of QDs is the growth temperature. Random forest, gradient boosting machine, and deep learning were used as a model for a Monte Carlo simulation, which created new, unseen, conditions to synthesize QDs of three sizes: 2 ( $\pm 0.3$ ) nm, 5 ( $\pm 0.3$ ) nm, and 8 ( $\pm 0.3$ ) nm. Three maps were created to select the most stable regions to perform the syntheses to assure the desired size would be achieved. We show that machine learning can improve the synthesis techniques to save time and money in QDs fabrication. 1 Bera et al., *Materials*, 3, 2260, 2010. 2 Chen et al., *Adv. Energy Mater.*, 10, 1903242, 2020.

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Tue-PT1-03

Photoreduction and chemical reduction of magnetic bimetallic nanoparticles

**Francis Acquaye (fyacquaye@crimson.ua.edu)**

The University of Alabama

Using PEI polymer templates, FePt nanoparticles (NPs) with size <10 nm have been synthesized by photoreduction and chemical reduction method in aqueous media at room temperature. In the photoreduction approach, the PEI acts as both the template into which the metal ions are coordinated and as a reductant in the presence of ultraviolet light. In the chemical reduction method, PEI acts as only a template with NaBH<sub>4</sub> as the reductant. The as-made NPs were characterized using ultraviolet-visible (UV-vis) spectroscopy, powder x-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM). Starting from the same precursor state and relative concentrations, the as-made NPs from both methods are spherical and crystalline with a chemically disordered face centered cubic (fcc) structure. The as-prepared NPs in both methods are found to be superparamagnetic with soft magnetic properties. The photoreduced NPs have broad size distribution of (5 ± 1.0 nm), an expanded lattice (3.906 Å) and relatively higher coercivity (0.59 KOe) compared to a narrow size distribution (4 ± 0.7 nm), shortened lattice (3.867 Å) and a relatively smaller coercivity (0.16 KOe) of the chemically reduced NPs. The difference in reduction mechanism apparently leads to a distribution of slightly larger particles above the superparamagnetic limit and thus higher coercivity.

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Tue-PT1-04

Particle motion artifacts in equilibrium magnetization measurements of large iron oxide nanoparticles

**Shehaab Savliwala (s.savliwala@ufl.edu)**<sup>1</sup>, **Sitong Liu (liusitong@ufl.edu)**<sup>1</sup>, **Carlos Rinaldi-Ramos (carlos.rinaldi@ufl.edu)**<sup>1,2</sup>

<sup>1</sup> Department of Chemical Engineering, University of Florida

<sup>2</sup> J. Crayton Pruitt Family Department of Biomedical Engineering, University of Florida

Iron oxide nanoparticles find many applications due to their response when subjected to externally applied magnetic fields. Equilibrium magnetization measurements (commonly known as magnetization curves) are an essential characterization tool to evaluate if particles display hysteresis, and to obtain magnetic properties such as the saturation magnetization. For superparamagnetic particles, one can obtain a magnetic size distribution by fitting the data to a theoretical model, such as the Langevin function, in what is called magnetogranulometric analysis. If one wishes to use the resulting size estimates as a predictor of particle performance in applications, magnetization data must be obtained under conditions that capture the response of the particles with minimal artifacts. In this paper, we used selected iron oxide nanoparticle batches with physical size ranging from 20-45 nm to demonstrate the influence of sample preparation methods on the magnetization data obtained. We show that measurements in powder form and in liquid solvents display varying degrees of particle interaction artifacts at low fields, depending strongly on particle size and on the thickness of the surface coating. In addition, measurements in 'solid' waxy hydrocarbon matrices are shown to be susceptible to particle rotation artifacts for large particle sizes. Hard crosslinked polymer matrices are shown to restrict particle motion completely, resulting in magnetization data that follows the Langevin function if the measurement is performed above the blocking temperature of the particles. We end with a discussion of how the presence of matrix-dependent measurement artifacts influence the magnetic diameter fits obtained using magnetogranulometry, and how measuring above and below the blocking temperature can affect fit results.

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Tue-PT1-05

Optimizing superparamagnetic iron oxide nanoparticle synthesis and PEG coating for magnetic particle imaging performance and long blood circulation half-life

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Magnetic particle imaging (MPI) is a novel biomedical imaging modality that allows non-invasive, tomographic, and quantitative tracking of the distribution of superparamagnetic iron oxide nanoparticle (SPION) tracers through their nonlinear dynamic magnetization response to an alternating excitation field. As MPI directly detects SPIONs, the resolution and sensitivity of MPI is primarily impacted by the magnetic response of the nanoparticle tracers. Here, we will discuss the physics of signal generation in MPI and how they inform optimization of SPION synthesis for sensitivity and resolution in MPI. We will also discuss the requirements on particle surface coating and colloidal stability imposed by applications of MPI to blood pool imaging. Experimental results will be presented for single-core SPION MPI tracers obtained using a semi-batch thermal decomposition synthesis with controlled addition of molecular oxygen, followed by an optimized PEG-silane ligand exchange procedure. Results will show how MPI performance relates to thermal decomposition synthesis conditions and intrinsic magnetic properties of the SPIONs. The physical and magnetic properties, MPI performance, and blood circulation time of these tracers will be compared to those of the two commercially available SPIONs: ferucarbotran and PEG-coated Synomag®-D. The optimized tracers have better MPI sensitivity and much longer circulation half-life than both commercial tracers, making them ideal for use as blood pool imaging tracer in MPI.

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Tue, 15 09:00 - 11:00

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Tue-QT1-01

Factory-on-a-chip: scaling-up droplet microfluidics for large-scale materials synthesis (**Keynote Lecture**)

**Daeyeon Lee (daeyeon@seas.upenn.edu)<sup>1</sup>, David Issadore (daveissadore@gmail.com)<sup>1,2</sup>**

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Taking advantage of the precise control over the fluid flows in microchannels, droplet microfluidics has enjoyed a tremendous success in enabling synthesis of highly uniform and uniquely structured liquid droplets and gas bubbles. Although some successes in translating microfluidic-based assays and diagnostics to commercial technologies have been achieved, few examples of such translations in the domain of materials manufacturing based on microfluidics have been accomplished, largely due to the very low throughput of droplet/bubble generations. Without solving the scale-up challenge, microfluidic-based materials synthesis will continue to remain an academic exercise that may not reach its true potential in transforming various sectors of industry including medicine, personal/home care products, separations and catalysis. In this talk, I will present the recent developments that the Issadore and Lee Groups at the University of Pennsylvania have made in enabling large-scale manufacturing of materials using microfluidics. By parallelizing flow focusing generation units coupled with flow resistors in solvent-resistant materials, microfluidic generation of droplets and bubbles with precisely controlled size and morphology has been achieved at the liters-per-hr scale. Critical issues in enabling scale-up and outstanding challenges in future development of the scale-up devices will be discussed.

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Tue-QT1-02

Axisymmetric Drop Shape Analysis of Compound Droplets

**Guangle Li (guangle@hawaii.edu), Yi Y. Zuo (yzuo@hawaii.edu)**

Department of Mechanical Engineering, University of Hawaii at Manoa

A compound droplet is composed of a traditional pendant or sessile drop sharing the interface with an immiscible phase of similar sizes, which could be a solid particle, a gas bubble, or mostly another droplet of an immiscible liquid. Over the past decade, the study of compound droplets has attracted increasing attention due to extensive applications in many research fields, such as complex fluid, microfluidics, foam and emulsion, and biomedical applications. Among all technical difficulties in characterizing compound droplets, a central problem in surface science is the prediction of its equilibrium shape, which requests knowledge of complicated boundary conditions. Existing dimensionless groups, such as the Bond number traditionally used for evaluating the shape of pendant and sessile drops, largely fail in predicting the shape of compound droplets. Here we propose an alternative Bond number, termed the Neumann number, in which the droplet height ( $H$ ) is considered as an important factor in affecting droplet deformation. The Neumann number is defined as  $Ne = \Delta\rho g R_0 / \gamma$ , which can be considered as a modified Bond number with a characteristic length  $L = (R_0 H)^{1/2}$ . We will demonstrate the usefulness and advantages of the Neumann number in predicting the shape of traditional pendant/sessile drops, and four axisymmetric compound droplets, including a pendant drop with a spherical particle suspending at the droplet apex, a sessile drop with its apex disturbed by a vertical cylinder, a spherical sessile drop (no gravity) with its apex disturbed by a gas bubble or a liquid lens. We will show that the Neumann number can be readily adapted to quantitatively predict and analyze the shape of pendant/sessile drops, as well as various axisymmetric compound droplets.

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Tue-QT1-03

Osmosis-induced reversible color switching of pigmented photonic capsules

**Zhe Gong (zhengong@seas.upenn.edu)**<sup>1</sup>, **Zhuangsheng Lin (linzhuangsheng@gmail.com)**<sup>2</sup>, **Leila Deravi (l.deravi@northeastern.edu)**<sup>2</sup>, **Daeyeon Lee (daeyeon@seas.upenn.edu)**<sup>1</sup>

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Animals in nature have evolved sophisticated combinations of pigmentary color and structural color to facilitate sensing, signaling and adaptive camouflage. The dynamic coloration of cephalopod chromatophores, for example, involves intricate interplay between pigmentary and structural coloration elements. Although remarkable advances have been made in using colloidal materials to enable either pigmentary or structural colors, there rarely has been synthetic systems that can dynamically change their coloration between these two mechanisms. In this talk, we present a robust color switching platform, allowing one to reversibly toggle between pigment-dominant color and structure-dominant color by osmosis. Double emulsion droplets are fabricated via microfluidics with high uniformity and size tunability. By encapsulating cephalopod-pigment functionalized nanocolloids into double emulsion droplets, distinct pigmentary color and angle-independent structural color can be observed, depending on the packing fraction of the nanocolloids. We further investigate the synergistic relationship between the two coloration mechanisms by comparing the reflectance spectra of photonic capsules with and without pigmentary contribution, providing insights for future design of biomimetic adaptive color-changing materials utilizing both pigmentary and structural coloration elements.

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Tue-QT1-04

Multicomponent Diffusion of Interacting, Nonionic Micelles with Hydrophobic Solutes

**Nathan Alexander (npalexander@ucdavis.edu)**<sup>1</sup>, **Ronald Phillips (rjphillips@ucdavis.edu)**<sup>1</sup>, **Stephanie Dungan (srdungan@ucdavis.edu)**<sup>1,2</sup>

<sup>1</sup> Department of Chemical Engineering, University of California at Davis

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Aqueous solutions of micelles are important in many applications because they provide a means to solubilize hydrophobic solutes in water. Here, we examine diffusion in ternary, aqueous solutions of the

nonionic surfactant decaethylene glycol monododecyl ether (C12E10) and a hydrophobic solute, either decane or limonene. In solution, the surfactant molecules self-assemble to form micelles swollen by hydrophobic solutes, with essentially no free hydrophobic solute or surfactant in the surrounding solvent. The diffusive behavior of this system is very interesting in that surfactant-solute interactions are strong, and result in a highly non-diagonal diffusivity matrix  $[D]$ , which depends in part on how strongly micelles grow with an increasing amount of solubilize along the diffusion pathway. Ternary diffusion coefficient matrices  $[D]$  and morphological parameters, such as the micelle aggregation number, hydrodynamic radius, and hydration index, were measured using the Taylor dispersion method and static and dynamic light scattering techniques, respectively. The matrix  $[D]$ , for both decane and limonene solutes, was found to be highly non-diagonal, and concentration dependent, over a broad domain of solute to surfactant molar ratios, and micelle volume fractions ranging from dilute to close-packed. Measurements for the average micelle radius and aggregation number indicate a weak dependence on the micelle volume fraction but a strong linear increase with solute-to-surfactant molar ratio, at a rate dependent on the hydrophobic solute type. A recently developed theoretical model, based on Batchelor's theory for gradient diffusion in dilute, polydisperse mixtures of interacting spheres, was simplified by neglecting local polydispersity, and effectively used to predict  $[D]$  with no adjustable parameters. Even though the model originates from dilute theory, the theoretical results were in surprisingly good agreement with experimental data for concentrated mixtures, with volume fractions up to  $\phi \approx 0.47$ , indicating the effects of multiparticle hydrodynamic and thermodynamic interactions cancel, resulting in experimental and theoretical predictions that are nearly linear over the entire range of concentration. In addition, the theory predicts eigenvalues  $D^-$  and  $D^+$  that correspond to long-time self and gradient diffusion coefficients, respectively, for monodisperse spheres, in reasonable agreement with experimental data.

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Tue-QT1-05

## Synergistic Marangoni Spreading Driven by Surface Gradients of Binary Catanionic Surfactant Mixtures

**Tsung-Lin Hsieh (tsunglih@andrew.cmu.edu)**<sup>1,2</sup>, **Stephen Garoff (sg2e@andrew.cmu.edu)**<sup>1,3</sup>, **Robert Tilton (tilton@andrew.cmu.edu)**<sup>1,2,4</sup>

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<sup>4</sup> Department of Biomedical Engineering, Carnegie Mellon University

When a drop of surfactant solution is deposited at the surface of an initially surfactant-free aqueous subphase, surfactants spread out radially, and the associated radial Marangoni flow entrains particles present on the surface. Generally, the speed and extent of this Marangoni spreading depend on the spreading surface pressure, surfactant inventory (dictated by surfactant concentration and drop volume), subphase thickness, the surface tension equation of state, and the surfactant's transport properties. In the context of binary surfactant mixtures, we propose a novel concept of Marangoni spreading synergism, which describes the condition where Marangoni flow either occurs at a greater maximum velocity or persists over a greater distance after spreading a drop of a binary surfactant mixture compared to either single-surfactant system at the same total concentration. Marangoni spreading synergism differs from the well-established concept of surface tension synergism in that the latter is a purely thermodynamic phenomenon while the former is a dynamic transport process that depends not only on the surface tension equation of state but also on transport properties. The objective of this work is to test whether Marangoni spreading synergism occurs and the degree to which it is correlated with surface tension synergism. To experimentally search for Marangoni spreading synergism, a system previously verified to show surface tension synergism was used to perform the spreading experiments: anionic sodium octyl sulfate (SOS), cationic octyl trimethylammonium bromide (OTAB) and their binary catanionic mixtures. Results show that, over a wide range of compositions tested (from 0.005 to 0.995 of SOS fraction), the binary SOS/OTAB solutions at a fixed total concentration of 5 mM produce significantly faster Marangoni spreading velocities and larger maximum extents of spreading radius than both single-surfactant systems. This verifies the existence of Marangoni spreading synergism. At the concentrations and SOS/OTAB compositions considered thus far,



the system exhibits both Marangoni and surface tension synergism. Current experimental work is focused on broadening solution conditions to identify the limits, if they exist, of where Marangoni and surface tension synergism diverge. Experimental work is also complemented by ongoing numerical modeling of the spreading process to identify how transport and thermodynamic properties combine to dictate the strength of Marangoni synergism.

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Tue, 15 11:20 - 12:10

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Tue-ST1-01

Life in a Tight Spot: How Bacteria Swim, Disperse, and Grow in Complex Spaces (**2020 Unilever Award Lecture**)

**Sujit Datta (ssdatta@princeton.edu)**

Chemical and Biological Engineering, Princeton University

Bacterial motility is central to processes in agriculture, the environment, and medicine. While motility is typically studied in bulk liquid or on flat surfaces, many bacterial habitats -- e.g., soils, sediments, and biological gels/tissues -- are complex porous media. Here, we use studies of *E. coli* in transparent 3D porous media to demonstrate how confinement in a heterogeneous medium fundamentally alters motility. In particular, we show how the paradigm of run-and-tumble motility is dramatically altered by pore-scale confinement, both for cells performing undirected motion and those performing chemotaxis, directed motion in response to a chemical stimulus. Our porous media also enable precisely structured multi-cellular communities to be 3D printed. Using this capability, we show how spatial variations in the ability of cells to perform chemotaxis enable populations to autonomously stabilize large-scale perturbations in their overall morphology. Finally, we show how when the pores are small enough to prevent cells from swimming through the pore space, expansion of a community via cellular growth and division gives rise to distinct, highly-complex, large-scale community morphologies. Together, our work thus reveals new principles to predict and control the behavior of bacteria, and active matter in general, in complex environments.

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Tue, 15 12:40 - 13:30

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Tue-ST2-01

Soft friction in colloidal and polymeric materials (**2021 Unilever Award Lecture**)

**Lilian Hsiao (lilian\_hsiao@ncsu.edu)**

North Carolina State University

The need to engineer friction at the microscale is increasingly important in technologies as diverse as soft robotics and consumer products. In this plenary talk, I will describe our journey from the field of particulate materials to the realm of touch engineering. The first part of the talk focuses on the role of particle roughness in the rheology, structure, and dynamics of dense colloidal suspensions. We find that shear thickening, exemplified by the ability to run on cornstarch pools, is strongly affected by the particle shape and jamming distance. Experiments on our confocal rheometer reveal how different types of particles form different contact microstructures that give rise to viscous flows. The second part of the talk will focus on our work on haptic materials where we investigate how compression and bending of textures affect friction. A new model based on lubrication analysis predicts the sliding friction for patterned surfaces of many materials, such as elastomers, thermosets, and hydrogels in sliding conditions. The data are in excellent agreement with that collected from a bioinspired robotic fingertip and human fingers. This framework provides a foundation that informs the engineering of manufactured surfaces and automated systems, and furthermore enables the design of friction in realistic environments.

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## Tue, 15 13:40 - 15:00

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Tue-AT2-01

Dynamic Magnetochromatic Response of Concentrated Suspensions of Janus Particles

**Jinghui Gao (jig318@lehigh.edu), Samuel Wilson-Whitford (saw319@lehigh.edu), James Gilchrist (gilchrist@lehigh.edu)**

Department of Chemical and Biomolecular Engineering, Lehigh University

The promise of Janus particles as bulk additives for responsive complex fluids has been limited by the inability to scale up Janus particle functionalization. Particles having the high fidelity and monodispersity in both size and surface functionalization are fabricated utilizing particle monolayer formation and physical vapor deposition (PVD). Using Automated Langmuir Blodgett deposition, particle monolayers are fabricated on roll-to-roll substrates at meter per minute rates, overcoming the typical rate-limiting step for functionalization. Light transmittance of suspensions of Janus particles ranging from 1 - 50 microns in diameter subjected to both uniform and non-uniform oscillatory magnetic fields is measured. While larger Janus particles have faster response due to a larger magnetic force and slower relaxation due to Brownian rotation, smaller particles assembled into chains of particles give a significantly larger change in contrast due to their larger change in projected area along the light path. Their combined gravity-driven motion gives even more complexity to their orientation response. Janus particles dispersed in thermoreversible yield stress fluids also results in hysteresis response that suggests new modes of engineering of magnetically responsive complex fluids.

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Tue-AT2-02

Assembly of magnetic microspheres under combined electric and magnetic fields

**Md Ashraful Haque (mhaque@mines.edu)<sup>1</sup>, Xingrui Zhu (xzhu1@mymail.mines.edu)<sup>2</sup>, Benjamin Hanson (bhanson@mymail.mines.edu)<sup>3</sup>, Ning Wu (ningwu@mines.edu)<sup>4</sup>**

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With control over space and time, colloidal structures can remarkably enrich their prospect of being used as either model systems for scientific study or functional materials for practical application. Previous work mainly focused on the assembly of colloidal structures under specific external fields where dynamic field-particle interaction is a key ingredient. Arguably, it is difficult to control the orientational and structure of colloids under the same type of field. In this work, we take advantage of both electric and magnetic fields where almost all types of particles can be responsive to the electric field due to a mismatch in dielectric and conductive properties between particles and solvent, while the magnetic field can be conveniently manipulated in three dimensions. We can tune the magnitude of dipolar attraction and repulsion between particles independently by applying these two fields orthogonally on paramagnetic microspheres. As a result, we obtain a high density of well-aligned but individually separated long chains at low and intermediate particle concentrations. In comparison, one only obtains either non-close packed hexagonal arrays or bundles of chains under individual fields. The inter- and intra-chain spacings can be tuned by adjusting the particle concentration, relative field strengths of both fields, and the frequency of the electric field. At high particle concentrations, the microspheres form small clusters under electric fields due to anisotropic dipolar interactions. Subsequently, those small colloidal clusters, as unique building blocks, can be further assembled into hierarchical structures under magnetic fields. Overall, we demonstrate a way to reach equilibrium states of global configurations with controllable periodicity through competing forces of dipolar attraction and repulsion. Our results show the potential in using combined fields to make diversified

types of highly aligned structures for high-strength composites, optical materials, or structured battery electrodes.

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Tue-AT2-03

Magnetic assembly of micro-satellites on Janus colloids

**Ahmed Al Harraq (aahme22@lsu.edu), JinGyun Lee (jlee229@lsu.edu), Bhuvnesh Bharti (bbharti@lsu.edu)**

Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge 3307 Patrick F. Taylor Hall Baton Rouge, LA 70803

Suprastructures at the colloidal scale must be assembled with precise control over local interactions to accurately mimic biological complexes. The toughest design requirements include breaking the symmetry of assembly in a simple and reversible fashion, to unlock functions and properties so far limited to living matter. We demonstrate a simple experimental technique to program magnetic-field-induced interactions between metallodielectric patchy particles and isotropic, non-magnetic 'satellite' particles. By controlling the connectivity, composition and distribution of building blocks, we show the assembly of three-dimensional, multi-component supraparticles which can dynamically reconfigure in response to change in external field strength. The local arrangement of building blocks and their reconfigurability is governed by a balance of attraction and repulsion between oppositely polarized domains, which we illustrate theoretically and tune experimentally. The assembled supraparticles are stabilized and recovered via photo-chemical manipulation of electrostatic interactions, using a photo-acid generator. Tunable, bulk assembly of colloidal matter with predefined symmetry provides a platform to design functional microstructured materials with pre-programmable physical and chemical properties.

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Tue-AT2-04

Dynamic colloidal clusters in magnetic fields

**Ahmed Al Harraq (aahme22@lsu.edu), Bhuvnesh Bharti (bbharti@lsu.edu)**

Cain Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803

Understanding the arrangement of individual building blocks in response to changes in the free energy available is a challenge of non-equilibrium matter. The push-and-pull balance between ordered and disordered states has been described by a ratio of attraction and repulsion, yet no experimental demonstration with a dynamic energy landscape is available. Here, we uncover the 'dual nature' of ferrofluids, particulate and continuous, to design a colloidal platform that couples competitive interactions with non-equilibrium dynamics. Using a binary suspension of microspheres in ferrofluid, we describe cyclical order-disorder-order transitions, and we access a dynamic cluster state. We show that crystal and fluid states represent two extremes in the competition between attraction and repulsion, while arrangement into clusters is a pseudo-equilibrium only observed from the true balance of interaction forces.

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**Tue, 15 13:40 - 15:00**

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Tue-BT2-01

Impact of interfacial viscosity on the stability of a translating droplet

**Natasha Singh (singh567@purdue.edu), Vivek Narsimhan (vnarsim@purdue.edu)**

Purdue University

In this work, we investigate the impact of interfacial viscosity on the stability of an initially perturbed droplet translating through an unbounded quiescent fluid. The boundary-integral formulation is employed to



Understanding the role of interfacially- and self-assembled surfactants in dictating the stability and lifetime of foams and emulsions is essential towards molecular engineering of consumer product formulations as well as controlling foaming and emulsification in industrial processes. In this presentation, we will elucidate trends in the structure of surfactant self-assembly and the nanoscopic foam film thickness of ultrathin foam films containing a model surfactant sodium dodecyl sulfate (SDS) by utilizing a combination of small-angle X-ray scattering and stratification studies. We will first explicate the influence of surfactant concentrations on micellar structure evolution and interparticle interactions of aqueous SDS solutions. These trends will be compared with nanoscopic topography and thickness transitions of freely draining SDS foam films, elucidating the striking similarity on stepwise decreases between intermicellar separations in bulk solutions and stratification step sizes in thin films. Furthermore, we will highlight that increasing the ionic strength of SDS solutions results in a breakdown of the agreement between the separation distances in bulk solutions and in thin films, emerging from weakening of the micellar layering in the films and an increasing influence of the amphiphiles assembled at the air-water interfaces on the disjoining pressure in the films. Our studies will demonstrate that stratification in a foam film, driven by confinement induced layering of micelles between the liquid-air interfaces, provides a sensitive probe of non-DLVO oscillatory forces and micellar interactions.

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Tue-BT2-04

Interconnectivity of Polymerized High Internal Phase Emulsions (PolyHIPEs): Effect of Interdroplet Interactions

**Muchu Zhou (muchu@nmsu.edu), Alireza Bandegi (alirezab@nmsu.edu), Reza Foudazi (rfoudazi@nmsu.edu)**

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Polymerized high internal phase emulsions (polyHIPEs) are a good candidate for the applications such as scaffolds in tissue engineering, absorbents, and membranes, due to their high porosity and interconnectivity. The polyHIPEs are obtained through curing the organic phase of prior high internal phase emulsions (HIPEs) followed by removing the internal aqueous droplets, which generate pores. The interconnectivity is achieved through the small pores, known as windows/pore throats, on the polymer film between neighboring voids. The process of forming the windows formation is complex and it has not been well understood. In the presenting work, the attractive interdroplet interactions are manipulated by employing different surfactants, changing the van der Waals attraction between the droplets. The results show that the interdroplet attraction in HIPEs has a significant effect on the window size of polyHIPEs.

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Tue, 15 13:40 - 15:00

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Tue-CT2-01

Self-locomotion of active droplets enabled by nematic environment (**Keynote Lecture**)

**Oleg Lavrentovich (olavrent@kent.edu), Mojtaba Rajabi (mrajabi@kent.edu), Hend Baza (hbaza@kent.edu), Taras Turiv (tturiv@kent.edu)**

Advanced Materials and Liquid Crystal Institute, Department of Physics, Kent State University  
Active matter comprised of self-propelled interacting units holds a major promise for the extraction of useful work from its seemingly chaotic dynamics. Streamlining active matter is especially important at the microscale, where the viscous forces prevail over inertia, and transport requires a non-reciprocal motion. Here we report that microscopic active droplets representing aqueous dispersions of swimming bacteria *Bacillus subtilis* become unidirectionally motile when placed in an inactive nematic liquid crystal medium [1]. The random motion of bacteria inside the droplet is rectified into a directional self-locomotion of the droplet by the polar director structure that the droplet creates in the surrounding nematic through anisotropic

molecular interactions at its surface. Droplets without active swimmers show no net displacement. The active droplet trajectory can be controlled by patterning the molecular orientation of the nematic and by the external fields. The effect demonstrates that the medium's broken spatial symmetry can be the reason for and the means to control directional microscale transport. The work is supported by NSF grant DMR-1905053 (analysis of dynamics) and by the Office of Sciences, DOE, grant DE-SC0019105 (development of the alignment layers).

[1] M. Rajabi, H. Baza, T. Turiv, O.D. Lavrentovich, Directional self-locomotion of active droplets enabled by nematic environment, *Nature Physics* **17**, 260–266 (2021).

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Tue-CT2-02

Assembly and propulsion of linear colloidal chains under combined electric and magnetic fields

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The fascinating efficiency and dynamics of micromachines in bacteria cells have inspired the scientific community to search for artificial microrobots for applications in chemical sensing, cargo transport, and waste remediation. While much work has been focused on exploring new self-propulsion mechanisms, recent trends have shifted towards guided locomotion under external fields. Here, we report a strategy combining a planar magnetic field with a one-dimensional electric field to assemble and actuate linear chains made of paramagnetic microspheres. While a horizontal chain lying on the substrate is symmetric fore and aft and does not translate, a two-dimensional magnetic field can tilt the chain with an angle relative to the substrate. A superimposed alternating-current (AC) electric field leads to the propulsion of tilted chains along the substrate. Our numerical simulation and experiments confirm that the electrohydrodynamic flow along the electrode is unbalanced surrounding the tilted chain, generating hydrodynamic stresses that both propel the chain and reorient it slightly towards the substrate. Our work takes advantage of both fields where the magnetic field controls chain orientation while the electric field provides power for locomotion. Without the necessity to synthesize complex-shaped micromotors with intricate building blocks, our work reveals a propulsion mechanism that breaks the symmetry of hydrodynamic flow by manipulating the orientation of a microscopic object.

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Tue-CT2-03

Quincke oscillations of colloids at planar electrodes

**Zhengyan Zhang (zz2480@columbia.edu)**<sup>1</sup>, **Hang Yuan (hangyuan2022@u.northwestern.edu)**<sup>2</sup>, **Yong Dou (yongdou1993@gmail.com)**<sup>1</sup>, **Monica Olvera de la Cruz (m-olvera@northwestern.edu)**<sup>3,2</sup>, **Kyle Bishop (kyle.bishop@columbia.edu)**<sup>1</sup>

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Dielectric particles in weakly conducting fluids rotate spontaneously when subject to strong electric fields. Such Quincke rotation near a plane electrode leads to particle translation that enables physical models of active matter. Here, we show that Quincke rollers can also exhibit oscillatory dynamics, whereby particles move back and forth about a fixed location. We explain how oscillations arise for micron-scale particles commensurate with the thickness of a field-induced boundary layer in the nonpolar electrolyte. This work enables the design of colloidal oscillators.

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## Tue, 15 13:40 - 15:00

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Tue-HT2-01

Impact of processing and multicomponent adsorption on fluid-fluid interfaces and interfacial forces  
**(Keynote Lecture)**

**Lynn Walker (lwalker@andrew.cmu.edu)**

Department of Chemical Engineering, Carnegie Mellon University

Systems involving deformable interfaces between immiscible fluids offer a significant challenge for materials design and processing. Static interfacial/surface tension is often the only parameter considered in the design of systems with fluid-fluid interfaces. In foams, emulsions, blends, sprays, droplet-based microfluidic devices and many other applications, the dynamic nature of surface active species and deformation of interfaces requires a more detailed characterization of the interfacial transport, dynamic interfacial properties and interfacial structure. Macroscopic properties and the ability to tune and control phenomena requires an improved understanding of the time-dependent properties of the interfacial tension and interfacial mechanics. We have developed tools and approaches to quantify the impact of surface active species on interfacial behavior. Surfactant-nanoparticle complexes, polymer-surfactant aggregates and proteins show the potential of interfacial processing in controlling interfacial properties. The use of sequential adsorption, differences in transport timescales and variability in reversibility of different species allows interfaces to be engineered. This approach is appropriate for connecting interfacial properties to forces between interfaces and the impact on coalescence. This talk will provide the motivation to use microscale interfaces for efficient analysis of complex interfacial phenomena and how that relates to the material properties of interface-dominated materials.

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Tue-HT2-02

Characterizing the Hydrophobic Interactions of Fusion Peptides of Coronaviruses using Single-Molecule Force Measurements

**Cindy Qiu (xq75@cornell.edu), Miya Bidon (mrb346@cornell.edu), Susan Daniel (sd386@cornell.edu), Nicholas Abbott (nla34@cornell.edu)**

Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853

This presentation addresses the fundamental challenge of understanding how hydrophobic interactions are encoded by chemical nanopatterns, using sequences of peptides found in coronavirus (CoV) spike proteins as an important and relevant context. A critical initial step leading to fusion and infection of SARS-CoV-2 and MERS-CoV virus particles with target host membranes is insertion of the fusion peptide (FP) sequence of the spike protein into the host cell membrane. The FP sequences of SARS-CoV-2 and MERS-CoV, denoted FP1 and FP2, are largely conserved and comprise a mixture of nonpolar and charged residues hypothesized to enable fusion via hydrophobic (lipid-binding) and ionic interactions (mediated by  $\text{Ca}^{2+}$ ). Past studies have identified nonpolar motifs (e.g., leucine-leucine-phenylalanine, "LLF") of the FP and the presence of  $\text{Ca}^{2+}$  to impact fusion activity. However, the role of hydrophobic interactions, as encoded by the FP sequence, and potentially modulated by  $\text{Ca}^{2+}$ , is not well understood. To explore how the FP sequence encodes hydrophobic interactions, we have recently used single-molecule force measurements to elucidate the role of specific amino acids of FP1 and FP2 in modulating intermolecular interactions with model nonpolar surfaces.

This presentation will focus on results obtained with two peptide sequences: First, we will describe single molecule force measurements of a short peptide sequence from FP1 that contains LLF. We will use the measurements to address several key questions: 1) Does LLF play a central role in mediating hydrophobic interactions of SARS-2 FP1 with model surfaces? 2) Is there a difference in the hydrophobic interaction strength between SARS-2 and MERS, where LLF is flanked by distinct residues? Second, we

will report single molecule force measurements using a peptide sequence that spans FP1 and FP2, presenting four potential Ca<sup>2+</sup> binding sites. We will use the measurements to address the question of whether or not binding of Ca<sup>2+</sup> to FP impacts hydrophobic forces encoded by the sequence. The results of our single-molecule force measurements will be placed into the context of independent measurements of fusion peptide activity.

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Tue-HT2-03

Nanomechanical measurements of microcapsules and microparticles

**Joseph Berry (berryj@unimelb.edu.au), Matthew Biviano (mattbivi@gmail.com), Ray Dagastine (rrd@unimelb.edu.au)**

Department of Chemical Engineering, University of Melbourne, Parkville 3010, Australia

Soft materials have critical application in paints, food processing, biology and medicine. The function of these materials depends upon responses to external stimuli that may be orders of magnitude different in length and time-scales. A change in something as simple as size or material stiffness of a drug delivery particle can mean the difference between successful transport & release of a drug to a specific disease site in the body or expulsion; and a change in elastic modulus can determine if capsules containing flavour, fragrance or paint survive processing & handling. These widely varying but poorly understood characteristics are fundamental to the future design of advanced materials. However, there is a lack of robust, quantifiable models that can capture multi-scale phenomena in complex microscale soft matter systems to make accurate predictions and guide the design process. Measurements are typically carried out on larger samples under the assumption that materials made from the same components have the same properties regardless of size and shape. For example, interfacial rheology of complex interfaces is commonly carried out on flat interfaces, and material property measurements of hydrogels are undertaken on large, thick films. Here we show that size and shape do matter, and present new models required to interpret data resulting from experiments directly undertaken with micro-capsules and micro-particles. The new models open up the possibility of testing the rheological and/or mechanical properties of capsules and particles directly at the length-scale and geometry relevant to the required application

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Tue, 15 13:40 - 15:00

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Tue-JT2-01

Leveraging Colloid Properties for Efficient and Targeted Foliar-applied Agrochemicals (**Keynote Lecture**)

**Gregory Lowry (glowry@cmu.edu), Yilin Zhang (yilinz1@andrew.cmu.edu), Juan Pablo Giraldo (juanpablo.giraldo@ucr.edu), Robert Tilton (tilton@cmu.edu)**

Agrochemical application practices are inefficient and require more sustainable approaches. Foliar application of engineered colloidal carriers could provide highly efficient and controlled delivery of agrochemicals into plants, but the colloidal properties controlling leaf uptake and translocation in plants are not yet elucidated. I will present an overview of the opportunities for targeted particle-based agrochemical delivery, and discuss what is known, and what is not known about the how the colloid properties of polymer nanoparticles and metal and metal oxide nanoparticles influence their uptake in leaves, phloem loading, and translocation to other plant compartments. Application of biorecognition molecules for targeted delivery to plant organelles, and potential approaches for providing plant-activated agent delivery are also discussed. Results indicate that the colloidal properties (size, charge content, and hydrophobicity) can determine their behaviors in plants, including uptake through the leaf cuticle and epidermis into the leaf mesophyll, rate of phloem loading, and distribution in plant tissues. Our results also indicate that both temperature and ROS may be viable triggers for release of encapsulated agents in polymer nanocarriers. Importantly, behaviors determined from star polymer nanoparticles are consistent with those determined



for metal nanoparticles, suggesting that the colloidal interactions may be generalizable to a range of particle types used across agriculture. These results can promote rational design polymer nano-carriers and metal/metal-oxide nutrient nanoparticles for more efficient and targeted agent delivery in plants, and more sustainable agricultural practices.

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Tue-JT2-02

Liquid sheet breakup and droplet evolution in agricultural sprays

**Iaroslav Makhnenko (makhn003@umn.edu)<sup>1</sup>, Cari Dutcher (cdutcher@umn.edu)<sup>1</sup>, Elizabeth Alonzi (ERAlonzi@landolakes.com)<sup>2</sup>, Christine Colby (CColby@landolakes.com)<sup>2</sup>, Steven Fredericks (SFredericks@landolakes.com)<sup>2</sup>**

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Spraying is a common process in everyday life with applications in agriculture, drug administration, printing, and painting. For agriculture purposes, small droplets are needed to enhance coverage and deposition of agricultural sprays, but not so small that they cause drift of the sprayed pesticides. Spray drift can cause the deposition of chemicals to undesired areas with a negative impact on livestock, ecosystems, and human health. In this work, different factors influencing spray breakup and droplet size distributions are studied, so the mechanism of spray formation can be explained, and droplet size can be optimized. In addition, dynamic surface and interfacial tension measurements are performed to understand the behavior of a liquid sheet during a breakup process. Here, we use a wind tunnel to find a droplet size distribution (DSD). The usual way to define the number of drift-prone droplets is the volume mean diameter (VMD) and the number of small droplets (typically below 100-150  $\mu\text{m}$ ). The VMD is the average droplet diameter with half of the spray volume contained in droplets larger than the VMD. It is hypothesized that the VMD and the number of fine droplets can be regulated by the presence of surfactant and oil emulsions in the sprayed liquid. The results of this work will help to understand the factors affecting a droplet size during a spraying process, towards increased efficacy of spraying pesticides.

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Tue-JT2-03

Under pressure: Hydrogel swelling in a granular medium

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<sup>1</sup> Princeton University

<sup>2</sup> University of Nevada, Las Vegas

Hydrogels hold promise in agriculture as reservoirs of water in dry soil, potentially alleviating the burden of irrigation. However, confinement in soil can markedly reduce the ability of hydrogels to absorb water and swell, limiting their widespread adoption. Unfortunately, the underlying reason remains unknown. By directly visualizing the swelling of hydrogels confined in three-dimensional granular media, we demonstrate that the extent of hydrogel swelling is determined by the competition between the force exerted by the hydrogel due to osmotic swelling and the confining force transmitted by the surrounding grains. Furthermore, the medium can itself be restructured by hydrogel swelling, as set by the balance between the osmotic swelling force, the confining force, and intergrain friction. Together, our results provide quantitative principles to predict how hydrogels behave in confinement, potentially improving their use in agriculture as well as informing other applications such as oil recovery, construction, mechanobiology, and filtration.

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Tue, 15 13:40 - 15:00

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Tue-KT2-01

Bi-disperse multiple particle tracking microrheology measures length scale dependent re-engineering of polymer-peptide hydrogels by human mesenchymal stem cells

**John McGlynn (jam217@lehigh.edu), Kilian Druggan (kid220@lehigh.edu), Kiera Croland (kjc222@lehigh.edu), Kelly Schultz (kes513@lehigh.edu)**

Department of Chemical and Biomolecular Engineering, Lehigh University, Iacocca Hall, 111 Research Drive, Bethlehem PA 18015

Human mesenchymal stem cells (hMSCs) migrate to wounds to coordinate repair. During migration, hMSCs remodel their surroundings, secreting matrix metalloproteinases (MMPs), which chemically degrade the matrix, and exerting cytoskeletal tension on the network. These components of migration impact the structure and rheology of the material at multiple length scales, from breaking of individual cross-links to bulk degradation of the material. To understand how cellular remodeling occurs on multiple scales, we encapsulate hMSCs in a well-defined synthetic hydrogel and characterize scaffold remodeling. Our scaffold is composed of 4-arm poly(ethylene glycol) molecules end-terminated with norbornene. These react with a peptide cross-linker to form a gel. The peptide is cleaved by MMPs resulting in scaffold degradation. Microstructural changes are measured using bi-disperse multiple particle tracking microrheology (MPT). Bi-disperse MPT measures the Brownian motion of two differently sized fluorescently labeled probe particles (0.5 and 2.0  $\mu\text{m}$ ) to simultaneously characterize changes on different length scales. When our material is degraded by enzymes without cells, the material evolves the same on both length scales. When cells actively remodel the network, the 2.0  $\mu\text{m}$  particles are more mobile than the 0.5  $\mu\text{m}$  particles indicating that larger length scales are more heavily remodeled. We hypothesize that cytoskeletal tension is the source of this difference in degradation since it was not present during the non-cellular enzymatic degradation. We inhibit cytoskeletal tension and measure that the difference in particle mobility between the 0.5 and 2.0  $\mu\text{m}$  probes is significantly reduced, indicating that the larger particles are measuring tension applied to the network. In separate experiments, we use a third particle size, 4.5  $\mu\text{m}$ , and measure greater particle mobility than the 0.5 and 2.0  $\mu\text{m}$  particles. We measure that cell speed correlates with material state on each length scale. Differences in particle mobility are greater at higher cell speeds ( $> 50 \mu\text{m/hr}$ ) and on the third day post-encapsulation when cells exert tension and move rapidly and material is degraded. In tension-inhibited populations, material must be more degraded by MMPs to achieve similar cell speed as untreated hMSCs, emphasizing the importance of tension on migration. On later days post-encapsulation, cell speeds increase indicating cells are migrating more effectively in their re-engineered microenvironment. These relationships between cytoskeletal tension and degradation on various length scales are important when designing implantable wound healing scaffolds. These new materials can exploit length scale dependencies in their structure to inform cell behavior to achieve a specific delivery goal.

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Tue-KT2-02

Designed Interfaces Between Proteins and Inorganic Crystals for Templated Assembly and Co-Assembly

**Sakshi Yadav (sakshi.yadav@pnnl.gov), Shuai Zhang (zhangs71@uw.edu), Harley Pyles (pylesh@uw.edu), David Baker (dabaker@uw.edu), James de Yoreo (James.DeYoreo@pnnl.gov)**

Pacific Northwest National Lab

Previously we have shown we could use Rosetta to design proteins that exhibited a lattice match to mineral surfaces (1Pyles, H., Zhang, S., De Yoreo, J.J., Baker, D.; Nature 2019. DOI: 10.1038/S41586-019-1361-6). We discovered that we could exploit those interactions to generate a variety of ordered 2D phases (micrometer-long wires and extensive honeycomb arrays) that were strongly dependent on electrolyte type and concentration and several other factors. Comparison to Monte Carlo simulations of non-interacting colloidal rods demonstrates that these phases are not predicted and thus must result from the competition between the designed interfaces (protein-protein and protein-substrate) and the colloidal forces, while machine learning analysis shows that the orientation dependent energy landscape is both complex and

also dependent on electrolyte type and concentration. Moving beyond a system of homogeneous protein building blocks, we are now using the power of co-assembly to both investigate the role of complementarity and frustration in defining order and to generate higher-order assemblies.

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Tue-KT2-03

### Fluorescent Quantum Defect Based Nanosensors for Biomedical Applications (**LaMer Keynote Lecture**)

**Mijin Kim (kimm7@mskcc.org)**<sup>1,2</sup>, **Daniel Heller (hellerd@mskcc.org)**<sup>1</sup>, **YuHuang Wang (yhw@umd.edu)**<sup>2</sup>

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<sup>2</sup> Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, United States

Organic color centers (OCCs) are molecularly tunable quantum defects, which are covalently incorporated into a single-walled carbon nanotube (SWCNT). OCCs efficiently harvest mobile excitons through the SWCNT antenna, producing a distinct fluorescence band in the near-infrared. The OCC fluorescence confers new biochemical sensitivities determined by the chemical nature of the defect, making OCCs the molecular focal point for local environmental responses. To benefit from the unique chemical sensitivity and specificity of OCC fluorescence for biomedical applications, we developed methods that systematically control the biological interactions and solvatochromic behavior of OCC-based nanosensors via surface chemistry. The resulting nanosensors can real-time monitor local intracellular events in live cells and in vivo. Our results support the feasibility of using OCCs as biosensors for disease detection and biomedical research.

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## Tue, 15 13:40 - 15:00

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Tue-LT2-01

### What makes for a well-defined or 'single-site' oxidation catalyst? (**Keynote Lecture**)

**Justin Notestein (j-notestein@northwestern.edu)**

Chemical and Biological Engineering Center for Catalysis and Surface Science Northwestern University  
A material's long-range order may or may not be related to uniformity of its active sites, especially for complex reactions like selective oxidation, and the phrase 'single-site' is not necessarily synonymous with 'single-atom'. This talk will discuss progress in understanding oxide-based selective oxidation catalysts in the Notestein research group. In our group, oxidation catalysts span the range from highly crystalline bulk materials like MoS<sub>2</sub>, to porous crystalline metal organic frameworks with redox-active nodes, to supported oxides with no long-range order. The first two materials classes may have catalytically-relevant 'defect sites', but the latter is all 'defect', and they will be the focus of this talk. For these materials, in spite of expectations for low levels of control, bulky precursors, low loadings, designed supports, or specific materials pretreatments can give rise to 'single-site' behavior, both kinetically and spectroscopically. Here, 'single-site' is used to indicate materials that have a single kinetically relevant population of atoms, which aids scientific understanding and can lead to improved selectivity. In this definition, materials that mix isolated atoms with larger clusters are not 'single-site', even if the catalytically relevant species are the single atoms. Many studies on supported oxides focus on identifying the active sites out of a large distribution of surface atoms. In contrast, critical aspects in assigning 'single-site' behavior are using kinetic and spectroscopic tools to verify that materials properties are uniform or do not change with surface density, and in developing new tools to identify and count active sites. Two specific examples of 'single-site' catalysts in the group are highly dispersed M-SiO<sub>2</sub> catalysts (M=Ti, Nb, or Ta) for activation of H<sub>2</sub>O<sub>2</sub>. In these, 'single-site' behavior proven by titration methods, spectroscopy, and kinetic studies. The 'single-site'

nature of these materials then enables systematic modification of the active sites in a rational way. In another example, we observed that highly loaded CuOx catalysts on hydrated supports give CuO clusters with low activity in oxidative dehydrogenation (ODH), somewhat as expected. However, loadings below a certain threshold on highly dehydroxylated or Lewis acidic supports give rise to a single population of well-defined Cu(II) dimers active in ODH, which opens up new avenues for ODH, and is a good example of a 'single-site' catalyst that is not 'single-atom'.

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Tue-LT2-02

## A Functional Model of Single Cobalt Sites on C-doped Carbon Nitride for Solar CO<sub>2</sub> Reduction

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University of New Hampshire

Single Co<sup>2+</sup> sites in graphitic carbon nitride (C<sub>3</sub>N<sub>4</sub>) demonstrated superior photocatalytic activity in selective CO<sub>2</sub> reduction. Doping C<sub>3</sub>N<sub>4</sub> with carbon was found to be key for the observed activity. We combine experimental and computational tools to explore the origin of such enhancement effect of C doping. In this single atom catalyst, each Co<sup>2+</sup> site exists in the Co-N<sub>2</sub>+2 coordination at C<sub>3</sub>N<sub>4</sub> edge sites. In addition to improving the photophysical properties of C<sub>3</sub>N<sub>4</sub>, C doping was found to alter the Co-N bond length and binding energy by replacing some N atoms near the metal center. The stronger Co-N binding upon C doping subsequently promotes electron transfer from photoactivated C<sub>3</sub>N<sub>4</sub> to the Co<sup>2+</sup> sites for improved CO<sub>2</sub>-reduction catalysis.

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Tue-LT2-03

## Single Pt atom catalyst synthesis and its application for selective propane dehydrogenation to propylene

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Catalysis is crucial for our modern life and approximately 35% of world's GDP is influenced by catalysis. High efficiency heterogeneous catalysis plays a vital role in modern chemical industry, contributing ~90% chemical production. Comparing to heterogeneous catalysis, homogeneous has the advantage of high selectivity for some reactions because it features uniformly distributed active sites and low reaction temperature. On the contrary, after catalyst calcination and activation many different metal species are present on the support which hinders active sites identification and thus the development of highly efficient catalyst. Single atom catalysts featuring homogeneously dispersed metal atoms on high surface solid support that have both advantages of uniform sites and high efficiency. However, it remains a challenge to achieve this goal due to limitations in tools kit for atomically dispersed catalysts synthesis that usually requires multiple steps, unique supports, and extreme low metal loading. Mixed metal oxides are widely used in developing catalyst and the role of adding one more metal oxide is intriguing but complex. Here, we show that grafting one reducible metal oxide to a high surface area inert support to form hetero-metal oxides can effectively anchor a Pt atom through a bridging oxygen, metal, or both after reductive gases treatment. The variety of binding sites yield atomically dispersed metals with various coordination environments, which is demonstrated by in-situ CO IR, EXAFS, and STEM. Propane dehydrogenation was carried out over the Pt based catalysts. The atomically dispersed Pt on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> shows higher activity and selectivity to propylene and better stability than the conventional Pt/Al<sub>2</sub>O<sub>3</sub>. The coke formation and cracking products are suppressed. This methodology sheds light on design and synthesis of highly efficient catalysts for C-H activation reactions.

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Tue, 15 13:40 - 15:00

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Tue-MT2-01

### Predicting and Controlling Correlated Light-Matter Interactions at the Atomic-Scale

**Prineha Narang (prineha@seas.harvard.edu)**

Harvard University

Our work focuses on how quantum systems behave away from equilibrium and how we can harness these effects<sup>1</sup>. By creating predictive approaches to study dynamics, decoherence and photo-induced correlations in molecules, our work could enable technologies that are inherently more powerful than their classical counterparts ranging from quantum information science, to ultra-high efficiency optoelectronic and energy conversion systems. In this talk, I will present work from my research group on describing from first principles approaches microscopic dynamics and optically-excited collective phenomena at finite temperature. Capturing these dynamics poses unique theoretical and computational challenges. The simultaneous contribution of processes that occur on many time and length-scales have remained elusive for state-of-the-art calculations and model Hamiltonian approaches alike, necessitating the development of new methods in theoretical and computational quantum chemistry<sup>2-5</sup>. I will introduce our work at the intersection of ab initio cavity quantum-electrodynamics and electronic structure methods to treat electrons, photons and phonons on the same quantized footing, accessing new observables in strong light-matter coupling. Building on this, I will present selected examples on optically driving quantum chemical systems far out-of-equilibrium to control the coupled electronic and vibrational degrees-of-freedom<sup>6-8</sup>. References: 1. Head-Marsden, K., Flick, J., Ciccarino, C. J. & Narang, P. Quantum Information and Algorithms for Correlated Quantum Matter. *Chem. Rev.* (2020) doi:10.1021/acs.chemrev.0c00620. 2. Rivera, N., Flick, J. & Narang, P. Variational Theory of Nonrelativistic Quantum Electrodynamics. *Physical Review Letters* 122, 193603 (2019). 3. Flick, J., Rivera, N. & Narang, P. Strong light-matter coupling in quantum chemistry and quantum photonics. *Nanophotonics* 7, 1479–1501 (2018). 4. Flick, J. & Narang, P. Cavity-Correlated Electron-Nuclear Dynamics from First Principles. *Physical Review Letters* vol. 121 (2018). 5. Schäfer, C., Flick, J., Ronca, E., Narang, P. & Rubio, A. Shining Light on the Microscopic Resonant Mechanism Responsible for Cavity-Mediated Chemical Reactivity. *arXiv [quant-ph]* (2021). 6. Juraschek, D. M., Meier, Q. N. & Narang, P. Parametric Excitation of an Optically Silent Goldstone-Like Phonon Mode. *Physical Review Letters* vol. 124 (2020). 7. Juraschek, D. M., Narang, P. & Spaldin, N. A. Phono-magnetic analogs to opto-magnetic effects. *Phys. Rev. Research* 2, 043035 (2020). 8. Juraschek, D. M., Neuman, T., Flick, J. & Narang, P. Cavity control of nonlinear phononics. *arXiv [cond-mat.mtrl-sci]* (2019).

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Tue-MT2-02

### Dielectric Resonance-Enhanced Photocatalysis on High Refractive Index Semiconductor Nanostructures

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Plasmonic metal nanostructures (PMNs) have gotten a lot of attention in recent years for their potential to convert solar energy into chemical energy. PMNs exhibit a special property called localized surface plasmon resonance (LSPR), which results in strongly enhancing the incoming electromagnetic radiations. In hybrid nanostructures made of PMNs and semiconductors, this property has been shown to improve the photocatalytic efficiency of nearby semiconductors. In this talk, we will demonstrate a new class of materials known as high refractive index nanostructures that can exhibit high Dielectric Mie resonance in the UV-Vis-near-IR region. The electromagnetic field enhancements observed over high dielectric nanostructures are up to an order of magnitude higher than those observed over PMNs, according to our findings. This latest

class of non-plasmonic metal oxide semiconducting nanostructures having a high refractive index ( $> 2$ ) and is dielectric in nature. Our findings also show that by manipulating the geometry of the nanostructures, the Mie resonance on these high-dielectric nanostructures can be tuned anywhere from UV-Vis to near-IR. To create optically resonant nanostructures with tunable Mie resonance, we used size- and shape-controlled synthesis techniques. A variety of spectroscopic techniques and photo-reduction-oxidation (photoredox) studies have been used to validate the Dielectric Mie resonance-induced energy transfer (DRET) pathways in these nanostructures. The design rules developed in our study for optically resonant nanostructures could be used in a variety of applications, including solar light-driven photocatalysis and dye-sensitized solar cells.

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Tue-MT2-03

## Plasmonics or Dielectrics? Light with a Phase Transition

**Gururaj Naik (guru@rice.edu)**

Electrical & Computer Engineering, Rice University

Plasmonics has enabled focusing light down to the nanoscale, but at the cost of absorption losses. On the other hand, dielectrics are nearly lossless, but poorly confine light at the nanoscale. A way to achieve the best of both these worlds can be a gamechanger to many optical applications, and here, we demonstrate it. If absorption losses or imaginary index can be considered as a design parameter, clever designs based on non-Hermitian physics allow the best of plasmonics and dielectrics. Non-Hermitian systems based on coupling lossy resonators to lossless resonators exhibit a phase transition at an exceptional point. The phase transition arises from the split in the system eigenvalues going from the real plane to the imaginary plane. Controlling the imaginary eigenvalue of the system, thus allows a new tool to engineer the losses in the system. We demonstrate non-Hermitian physics in a plasmonic-dielectric hybrid for creating bright and spectrally narrow thermal emitters. Such thermal emitters could be revolutionary for thermophotovoltaic energy conversion where solar conversion efficiencies greater than 50% are possible. In another such demonstration of a phase transition, we couple light to a correlated electronic system. The phase transition in the correlated material, 1T-TaS<sub>2</sub> gives it a large optical tunability. We observe a unity order index change at room temperature when illuminated with a low-intensity (1-Sun) incoherent white light. We probe the material to find that the charge density wave (CDW) domains in this layered material stack differently upon illumination. The resulting phase transition manifests in a unity-order change in the refractive index. Using plasmonic structures on dielectric 1T-TaS<sub>2</sub> films, we demonstrate tunable optical devices with 100% modulation depth, MHz bandwidth, and ultralow-power operation. Such tunable optical devices could be disruptive for emerging imaging and display applications.

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Tue-MT2-04

## Near- and Far-Field Response of Thin Metallic Nanodisks

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Metallic nanostructures are able to support surface plasmons, the collective oscillations of their conduction electrons, which produce large degrees of field confinement and enhancement. In recent years, there has been significant interest in studying the plasmons supported by thin nanostructures. These structures provide a stronger degree of field confinement and enhanced light-matter interaction compared to conventionally-shaped nanostructures. Here, we provide a comprehensive analysis of the optical response of metallic nanodisks under near- and far-field excitation as their thickness is changed. We find that thicker disks have a stronger far-field response, while the opposite is true of the near-field behavior, a result that we attribute to the more efficient excitation of thinner disks by a localized source. Our results provide fundamental insight into the plasmonic properties of thin metallic nanostructures.

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## Tue, 15 13:40 - 15:00

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Tue-NT2-01

### Complex Colloidal Micro-transducers for Bacteria Activity Sensing

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The development rapidly deployable, point of care sensors for detecting and monitoring bacteria is necessitated by the ever-present and serious public health threat they continue to pose. However, the ability to discern between dead and live populations or quantifying the viability of the bacteria involved remains a non-trivial challenge to address. Here, we develop simple droplet based optical micro-transducers that can not only readily distinguish between live and dead bacteria but are also capable of gauging the metabolic levels of individual cells by tracking the time dependent force generated by a bacterium with sub piconewton resolution. We utilize complex colloidal droplets comprising of immiscible liquid crystal and fluorocarbon phases, where we control the LC anchoring to create topological singularities for selective localization of mannose functionalized surfactants for conjugation with Escherichia coli cells. The asymmetry in density induced by the two-phase morphology induces a dynamic tug-of-war between the swimming bacteria and opposing gravitational forces on the droplet. The interaction and the underlying mechanism are investigated through controlled experiments and modelling. These results provide a demonstration of tunable liquid systems that can facilitate efficient mechano-optical responses via chemical coupling with biological organisms which finds important utility in the development of both rapidly deployable pathogen sensing systems and biologically powered micro-actuator systems.

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Tue-NT2-02

### Studies of hierarchical nanoporous gold as a promising nanomaterial for biosensor applications

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Department of Chemistry and Biochemistry, University of Missouri, Saint Louis (UMSL)

Nanobiotechnology is an emerging interdisciplinary branch of science that deals with the integration of nanomaterials with biological moieties such as antibodies, enzymes, lipids, carbohydrates, and aptamers. The surface-modified nanomaterial serves the purpose of signal amplification when the binding event takes place. To create a sensitive and highly specific sensor the need of the hour is to fabricate a biosensor with structural details meeting the desired requirements in material design. A biosensor is composed of three units namely, recognition element, transduction unit, and signal analyzer. Nanomaterials are promising candidates to be used as transduction elements due to their high specific area that helps to amplify the quantity of bioreceptor units that can be immobilized thereby increasing the sensitivity of the sensor. In recent years, the use of metal-based nanomaterials has expanded in various biomedical applications due to the scope of facile synthesis and functionalization, ease of detection, high surface area, and extensive stability towards heat. Nanoporous gold (NPG) is one of the emerging nanostructured materials fabricated by the removal of a less noble element from the bulk alloy and the self-assembly of the remaining element (Au) giving rise to pores and ligaments. It has demonstrated significant scope in the biosensor domain owing to its unique properties of good biocompatibility, adjustable pore and ligament size, and facile functionalization which are highly dependent on its microstructure and feature size. Significant research has been done to look into the strategies to control the morphology of NPG and considerable efforts are being investigated to ameliorate the current design as the morphology. Material design is based on two pillars which include a large surface area exploited for immobilizing molecules of interest and incorporating

pathways for easy movement of molecules. These two key aspects are inherently competing since restricted transport comes into the picture when the sensor has exceedingly small pores. The solution to this problem is to create a structural hierarchy. We have chosen to take advantage of the surface architectures of hNPG due to the presence of a large specific surface area for functionalization and rapid transport pathways for faster response. Here small-sized pores are exploited for immobilization and a network of larger pores helps in transport. The precise control of the structure, composition, and surface functionalization reveals the importance of the structure-property relationship to designing efficient platforms for biosensing applications.

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## Tue, 15 13:40 - 15:00

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Tue-OT2-01

Prediction of Structure in Binary Superlattices with Perovskite Nanocubes (**Keynote Lecture**)

**Alex Travesset (trvsst@ameslab.gov)**

Department of Physics and Astronomy, Iowa State University  
Ames Lab

I will present our results in predicting the structure of superlattices consisting of two nanocrystal species within the Orbifold Topological Model (OTM), where ligands determine bonding akin to electrons in crystals with simple atoms. The OTM is validated from hundreds of independent experiments and from all atom explicit free energy calculations. I will also describe our new results consisting of binary systems of Perovskite Nanocubes and spherical nanocrystals.

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Tue-OT2-02

Nanoparticle Assembly in High Polymer Concentration Solutions Increases Superlattice Stability

**Margaret Lee (mlee22@mit.edu), Alfredo Alexander-Katz (alexand@mit.edu), Robert Macfarlane (rmacfarl@mit.edu)**

Massachusetts Institute of Technology

Polymer nanocomposites are made by combining a nanoscale filler with a polymer matrix, where polymer-particle interactions can enhance matrix properties and introduce behaviors distinct from either component. Manipulating particle organization within a composite potentially allows for better control over polymer-particle interactions. However, self-assembly of ordered particle arrays using building blocks such as the recently developed Nanocomposite Tectons (NCTs, polymer brush particles that use supramolecular bonding to drive their assembly) typically requires weak interparticle interactions to prevent kinetic traps, making these assemblies incompatible with most conventional processing techniques. As a result, investigations are needed into methods to provide additional stability to these lattices without disrupting their internal organization. The addition of free polymer chains to the assembly solution is a simple means to increase the stability of nanoparticle superlattices against thermal dissociation. By adding high concentrations (>50 mg/mL) of free polymer to NCT superlattices, it is possible to significantly elevate their thermal stability without adversely affecting their ordering. Moreover, polymer topology, molecular weight, and concentration can also be used as independent design handles to tune this behavior. This allows for a wider range of processing conditions for generating future nanocomposites with control over particle organization within the material.

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Tue-OT2-03



## On the Thermodynamic Stability of Binary Superlattices of Polystyrene Functionalized Nanocrystals

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<sup>2</sup> University of Chinese Academy of Sciences

<sup>3</sup> Department of Physics and Astronomy and Department of Materials Science and Engineering, Iowa State University and Ames lab

Assembly of two types of functionalized nanocrystals by tuning solvent quality always leads to phase separated single component superlattices, while if directed by solvent evaporation, it may result in cocrystallization into binary superlattices, thus raising the obvious question of what phase is the thermodynamic equilibrium. We address this fundamental problem by evaluating the free energies of single component and binary superlattices of nanocrystals functionalized with polystyrene. We show that most binary superlattices reported in the literature are metastable against phase separation. We also characterize the structure of the different superlattices and show that they are accurately described by the Orbifold Topological Model (OTM). We discuss the implications of the results for ongoing experiments and for the general assembly of nanostructures.

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## Tue, 15 13:40 - 15:00

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Tue-PT2-01

### An Easy-to-use Method for Quantitatively Determining the Hydrophobicity of Nanoparticles

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Department of Mechanical Engineering, University of Hawaii at Manoa

The hydrophobicity of nanoparticles is an important physicochemical property that plays a predominant role in controlling the transportation, aggregation, dispersion, and sedimentation of nanoparticles, thus directly determining their biomedical and industrial applications, and their environmental, health, and safety (EHS) impacts. Quantitative characterization of the hydrophobicity of nanoparticles, however, is not an easy task. At present, most analytical methods for characterizing the hydrophobicity of nanoparticles are qualitative, such as the Rose Bengal and liquid partitioning methods, which determine the relative hydrophobicity of particles studied under the same experimental condition. It is technically difficult, if not impossible, to directly compare the hydrophobicity results reported across literature. Here we present a novel optical method, called the maximum particle dispersion (MPD) method, which is capable of directly determining the surface free energy (SFE) of nanoparticles. The MPD method relies on a novel measuring principle that analyzes the colloidal stability using the DLVO theory. We will show that the MPD method is capable of determining the SFE of a range of micro- and nanoparticles of various chemistries, sizes, shapes, and morphologies. The MPD method has the potential to be developed into a standard, low-cost, and easy-to-use method for quantitatively characterizing the hydrophobicity of particles at the micro- and nanoscale.

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Tue-PT2-02

### Neutrally Charged Nanosilver Antimicrobial Effects: A Surface Thermodynamic Perspective

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Antimicrobial effects of nanosilver are affected by the nanosilver's size. Nanosilver has a large surface area available that contributes to enhanced interactions with bacteria as well as silver ion release. Nanosilver with smaller diameters showed better antimicrobial effects because smaller nanosilver had larger surface areas, which led to greater silver ion release and stronger attachment to bacteria. The attachment of nanosilver to bacterial surfaces is attributed to the interaction surface energy between the nanosilver particles and bacteria, which is also a function of the size of nanoparticles. Although antimicrobial activity of nanosilver has been extensively studied, there is gap between the antimicrobial effects with nanosilver interactions with bacteria and subsequent attachment. With the more interest in the usage of stabilizing agents in nanosilver manufacturing, natural charged nanosilver is attracting more and more attention. Especially, the impact of surface-active agents, which are commonly used in in situ remediation, on nanosilver aggregation and nanosilver-bacteria interaction has not been fully investigated. The surfactants affect nanosilver aggregation and nanosilver-bacteria interactions by changing their interfacial interactions. The objectives of this study were to evaluate nanosilver aggregation and attachment to bacteria and subsequent antimicrobial effects under different solution chemistry conditions. Nanosilver-nanosilver and nanosilver-bacteria interactions were quantified based on the DLVO and surface chemistry theories and were used to interpret subsequent nanosilver aggregation, nanosilver-bacteria attachment and nanosilver antimicrobial effect observations.

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Tue-PT2-03

A new class of biodegradable, tough, and clear polysaccharide films reinforced with chitosan dendricolloids

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We will report a new class of biopolymer composite films, which are envisioned as sustainable high-performance packaging material. These films are based on the recently discovered soft dendritic colloids (SDCs) in our group. The SDCs are highly branched polymeric particles surrounded by a nanofibrillar corona produced from polymer precipitation in a turbulently sheared non solvent medium. They are characterized by their large surface area and excluded volume and they provide excellent structure building properties due to fibrillar entanglement and vdW interactions. The biocomposite films that we developed are based on an agarose (AG) polysaccharide matrix reinforced with chitosan (CS) SDCs. The composite films are prepared through solvent mixing and subsequent solution casting. The hierarchically branched CS reinforcement network endow superior properties to the films such as mechanical toughness and hydrophobicity. The ductility and toughness modulus of films containing 15 w/w% of CS SDCs increase 3-fold compared to their unreinforced counterpart. Due to a dense network formation and intermolecular interactions between the SDCs and the matrix, the films become hydrophobic, which may overcome the most common limitation to biodegradable packaging materials. Due to the abundance of polar functional groups along both AG and CS molecules, which can form intermolecular hydrogen bonds, the interactions of the SDCs and their matrix were characterized using infrared spectrum analysis (FT-IR). Morphological analysis showed that SDCs are well incorporated in the AG matrix with no obvious signs of agglomeration in the composite films. The swelling of the films and their oxygen and water vapor permeability showed synergistic effects due to the SDCs inclusion. These films can find application as sustainable food packaging materials with comparable or superior properties to the commercial petroleum-based films.

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Tue-PT2-04

Multidimensional free energy landscapes for the binding of functionalized nanoparticles to lipid bilayers

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University of Wisconsin-Madison

Nanoparticles (NPs) functionalized with organic ligands offer a potential nanotechnology platform for drug/gene delivery and phototherapy. These applications require specific interactions with cell membranes to facilitate efficient cell uptake or membrane adsorption while minimizing cytotoxicity. These interactions can be tuned by varying the properties of the ligand coating. However, nanoparticle interactions with the cell membrane remain difficult to predict a priori, hindering nanoparticle design. To address this challenge, previous experiments have correlated NP binding to model lipid bilayers with the octanol/water partition coefficient of the grafted ligand, yet the mechanism for this binding process is still largely unexplored. Molecular dynamics (MD) simulations offer the capability to understand these processes, explore the impact of new design motifs, and predict binding behavior. A challenge for molecular simulations is modeling the free energy landscapes underlying the binding of large NPs. Past simulation studies of NP-bilayer binding have utilized the center-of-mass (COM) distance between the NP and the bilayer to calculate free energy differences for the binding of NPs with short ( $< 1\text{ nm}$ ) ligands. Recently, atomistic MD simulations of NPs grafted with longer functionalized ligands have shown hysteresis in the COM-based measurement and suggest that the number of contacts between the ligands and the bilayer must contribute to binding. Sampling contacts in simulations that only bias the COM distance is challenging, indicating that the number of contacts must be simultaneously biased to obtain accurate binding predictions. In this work, we parameterize coarse-grained (CG) simulation models of functionalized NPs based on prior atomistic calculations. We utilize the CG models to determine the free energy for binding NPs to model lipid bilayers as a function of both COM distance and the number of contacts. Using the string method, we then efficiently find minimum free energy pathways for binding and compare the binding properties of several functionalized NPs. We find the lipid tails partition to the core of the NP and can be extracted from the bilayer. These predictions offer new mechanistic insight into binding for these NPs, allowing us to better understand which NP features contribute to enhanced binding to guide further NP design.

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Tue, 15 13:40 - 15:00

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Tue-QT2-01

Analysis of sodium dodecyl sulfate contamination via dilational rheology measurements

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Chemical, Biological and Materials Engineering, The University of Oklahoma

The presence of contamination in sodium dodecyl sulfate (SDS) solutions is known to drastically affect the resulting interfacial properties such as surface tension and viscoelasticity. Dodecanol molecules, which are a product of SDS hydrolysis and are inherently present in SDS solutions, have a higher surface activity than SDS itself. For example, even trace amount of dodecanol in the bulk solution, three orders of magnitude lower than SDS concentration, contributes to more than 80% of the total surface coverage and yields a reduction in the surface tension down to  $\sim 20\text{ mN/m}$ . A characteristic dip in the surface tension isotherm is an indicator for the presence of dodecanol in the sample and the shape of surface tension isotherm has been used to estimate the bulk concentration of dodecanol. However, in the presence of electrolytes, the electrostatic repulsion between the negatively charged head groups of SDS molecules is screened, which leads to a higher surface activity of SDS molecules and a lower CMC value. This increase in surface activity of SDS may cause the surface tension isotherm to match a pure sample isotherm, leading one to believe the surface is free of dodecanol and exclusively populated with SDS. In this work, we have examined the surface tension isotherms for SDS solutions in presence of various electrolyte concentrations and fitted the isotherms to a thermodynamic model to estimate the amount of dodecanol present in the sample. We compared these results with interfacial rheology measurements that we used to probe a contaminated interface. Our findings demonstrate that presence of impurities can be captured under dynamic expansion and contractions, even for solutions of high electrolyte concentration. The results obtained from these studies provide valuable insights for more complex interfacial systems in which interfacial activity of SDS molecules under dynamic conditions is of interest.

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Tue-QT2-02

Thermoreversible gels composed of hollow adhesive silica nanorods with short-range attractions

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Colloidal suspensions composed of anisotropic particles are widely utilized in consumer products, coatings, cements, food products, and pharmaceuticals. However, the effect of particle shape on the gel and glass transition boundaries is not well-understood for anisotropic particle suspensions, particularly for colloids with lower aspect ratios ( $L/D \sim 1-10$ ). A new thermoreversible colloidal system has been developed, which is composed of hollow, octadecyl-coated silica rods with dimensions of 30-200 nm, tunable aspect ratios, and short-range attractions. These particles are also termed as adhesive hard rods (AHR) and their hollow-core structures have shown to mitigate the effects of gravitational settling on the suspension fluid and gel microstructure. The hollow AHRs are suspended in tetradecane, which enables thermoreversible gel transitions from fluid-like to solid-like states. While this temperature-driven change visually appears like a liquid-soft solid transition, we investigate the precise microstructure responsible for the soft solid state. The gelation behavior is studied at different aspect ratios and attraction strength of the AHR. We also study the flow behavior of AHR gels under deformation and correlate it with the local microstructural changes. Small-angle neutron scattering methods provide critical information including the form factor of primary particles (shape, core and shell dimensions, brush conformation, size dispersity) as well as the interparticle attraction strength ( $\tau$ ) and fractal dimension ( $D_f$ ) of the fluid and gel microstructure. The flow behavior of AHR system can guide in understanding the response of complex anisotropic biological systems.

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Tue-QT2-03

Exploring Nonadditive Ion Effects on Protein Stability in Aqueous Solutions

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Nonadditive behavior was studied for salt mixtures containing a weakly hydrated anion, iodide, and a strongly hydrated anion, sulfate, on the solubility of poly(*N*-isopropylacrylamide) (PNIPAM) with sodium being the common cation. The lower critical solution temperature (LCST) of PNIPAM in the presence of a fixed concentration of  $\text{Na}_2\text{SO}_4$  and increasing concentration of NaI showed a non-monotonic trend that was markedly different from the effects of the individual salts. Specifically, at low NaI concentration,  $\text{Na}^+$  ions preferentially partition to the counterion cloud around sulfate, leaving iodide more hydrated. This resulted in an enhanced salting-out effect for the initial decrease in the LCST of PNIPAM. Upon further increase in NaI concentration, the LCST began to increase and reached a maximum due to the saturable interaction of iodide with the hydrophobic moieties on the polymer surface. At high NaI concentration, a decrease in the LCST was again observed. This salting-out effect was attributed to an excluded volume effect. These observations can be extended to the nonadditive behavior of iodide/sulfate salt mixtures for other common cations, namely  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ . Nonadditivity was observed for all the cations that were studied and following the series  $\text{Cs}^+ < \text{Li}^+ < \text{Na}^+ < \text{K}^+$ . By utilizing a competitive binding model and ion-pairing constants for the cations with sulfate and iodide, it was demonstrated that  $\text{K}^+$  had the tightest binding affinity to sulfate. As such it was most effectively swiped from iodide, leaving the largest concentration of iodide ions more hydrated. By contrast,  $\text{Cs}^+$  had the weakest binding affinity to sulfate and the strongest binding affinity to iodide, resulting in fewer “more hydrated” iodide ions and the least pronounced nonadditivity. Taken together, this work suggests that the identity of counter cation plays an important role in the nonadditivity

of salt mixtures and should be considered when discussing the behavior of electrolytes in aqueous solutions.

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Tue-QT2-04

Specific effects of ionic liquid constituents on the stability of particle dispersions

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Ionic liquids (ILs) represent novel types of solvents with many advantageous properties such as low vapor pressure, high electrochemical window as well as tunable structure and composition. The latter properties can be utilized to functionalize solid/liquid interfaces by applying task specific ILs adsorbed physically or grafted chemically to the solid surfaces. Once colloidal or nanoparticles are dispersed in ILs or in their aqueous solutions, the interfacial assembly of the constituents and the resulting solvation of the surfaces play crucial roles in the colloidal stability of the particle dispersions [1]. Therefore, the present study aims at studying the charge and aggregation properties of clay and polystyrene latex particles in the presence of ILs. Results of time-resolved light scattering measurements performed in aqueous IL solutions revealed that the particle aggregation mechanism is governed by electrostatic forces in the diluted IL samples, where dissociated and hydrated IL constituent ions are present [2]. The aggregation rates of both clay and latex particles were sensitive to the composition of ILs leading to IL-dependent critical coagulation concentration values obtained. Such an ion specific effect on the colloidal stability could be masked by coating the particle surfaces with a polyimidazolium-based IL polymer [3]. The particle aggregation slows down at higher IL concentrations due to the increase in the viscosity of the medium. Besides, the particles were highly stable in pure ILs, where only trace amount of water was present. Under the latter experimental conditions, no particle movement could be detected by applying an electric field in phase analysis light scattering experiments. This fact indicates that the origin of the stabilizing forces is not electrostatic as in diluted solutions and that the dispersions are stable rather due to repulsive oscillatory forces resulting from the layered assembly of the IL constituents on the particle surface. These results shed light on the origin of the main interparticle forces responsible for the colloidal stability of particles in both pure ILs and in their aqueous solutions. References [1] I. Szilagyi, T. Szabo, A. Desert, G. Trefalt, T. Oncsik, M. Borkovec, Phys. Chem. Chem. Phys. 16 (2014) 9515-9524. [2] B. Katana, D. Takacs, E. Csapo, T. Szabo, A. Jamnik, I. Szilagyi, J. Phys. Chem. B 124 (2020) 9757-9765. [3] B. Katana, D. Takács, F.D. Bobbink, P.J. Dyson, N.B. Alsharif, M. Tomšič, I. Szilagyi, Phys. Chem. Chem. Phys. 22 (2020) 24764-24770.

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Tue, 15 15:20 - 16:40

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Tue-AT3-01

Networks of Anisotropic, Magnetically-Polarized Colloidal Particles Reversibly Reconfigure under the Influence of an External Magnetic Field

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In recent work, Velev and coworkers have developed a new class of engineered materials that interact, assemble, reconfigure, and propel in response to external magnetic and electric fields. Cubic microparticles with a ferromagnetic-metallic coating on one or two opposing faces retain residual polarization when exposed to an external magnetic field, even after the field is turned off. The many different interactions that exist when anisotropic, magnetically-polarized colloidal particles are placed in tunable external fields creates numerous design variables that are challenging to fully explore in vitro. The search for potentially useful structures formed by this colloidal material can be enhanced by simulations of colloidal particle

assembly. We have simulated large systems of cubic microparticles with one magnetic dipole under the influence of an external magnetic field using Discontinuous Molecular Dynamics (DMD). DMD is a fast variant of standard molecular dynamics that is applicable to systems of molecules interacting via discontinuous potentials (e.g., hard sphere, square well potentials). DMD is best suited for exploring phenomena that occur at long time scales. Microcubes were represented in quasi-2D as groupings of hard circles bonded together to create a rigid square geometry. Magnetic dipoles were mimicked in silico by embedding opposite electrostatic charges along one cubic face. A modified Anderson thermostat was employed to simulate the force that an external magnetic field exerts on a magnetically-polarized microcube while keeping the system's temperature constant. Annealing DMD simulations performed using the model described above have revealed that highly percolated structures form at high surface densities as the temperature is reduced and the strength of the dipolar interactions overcome thermal fluctuations. Order parameters quantifying the different types of particle clusters that can form were used to characterize the phase behavior (fluid, string-fluid, gel, etc.) of these colloidal systems. Our studies differentiate between structures that the colloidal aggregates form in the presence of, and in the absence of, an external magnetic field. The formation of chain-like structures was seen to a larger degree in networks formed under the influence of an external magnetic field. Additionally, diverse field-on and field-off time evolution patterns revealed the ability of networks formed under the influence of an external magnetic field to reversibly reconfigure, whereas irreversible jamming was seen in networks formed in the absence of an external magnetic field. Our results highlight the conditions under which reversible, reconfigurable networks form, adding to the fundamental knowledge base for directed assembly of colloidal particles.

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Tue-AT3-02

### Anisotropic Colloidal Assembly in AC Electric Fields

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Anisotropic colloidal building blocks enable diverse microstructured materials with directional properties not achievable by spherical colloids. Ongoing challenges exist in reliably assembling different microstructures without defects that influence their final properties. As part of addressing this challenge, we aim to understand the connections between particle shape, interaction potentials, and microstructure for assembly in high frequency AC electric fields. By comparing ensemble average equilibrium microstructures in experiments and simulations, we obtain via an inverse analysis particle-particle and particle-field potentials of different shaped epoxy particles. Using of the resulting accurate interaction potentials, we then systematically investigate in both microscopy and computer experiments the assembly of prism particles with cross-sections of circles, squares, hexagons, ellipses, and rectangles. We characterize the resulting liquid, liquid crystal, and crystal microstructures including local symmetry from particle coordinates using order parameters. Our findings show how particle shape (aspect ratio, curvature) and dipolar potentials together drive the formation of different microstructures. Understanding the connections between colloidal shapes, potentials, and microstructures provide the ability to design microstructured materials and the information necessary to control dynamic assembly processes to remove defects and reconfigure between microstructures.

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Tue-AT3-03

### pH mediated colloidal aggregation to separation transitions in low frequency oscillatory electric fields

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Colloids in low frequency ( $< 1$  kHz) oscillatory electric fields near planar electrodes aggregate in neutral pH electrolytes due to electrohydrodynamic (EHD) flow but separate in alkaline pH electrolytes. Colloid zeta potential and electrolyte ion mobilities are thought to play roles in the underlying mechanism for this phenomenon, but a unifying theory for why particles aggregate in some electrolytes and separate others remains to be established. Here we show that increasing local pH near the electrode via electrochemical reduction of benzoquinone causes a colloidal aggregation to separation transition in oscillatory electric fields that induce strong attractive EHD flows. Counterintuitively, decreasing frequency, which increases attractive EHD drag forces, caused a similar aggregation to separation transition. Even more interesting, multiple transitions were observed while varying the oscillatory potential at constant electrochemical potential and frequency. Taken together these results suggested the oscillatory potential induced an extensile electrokinetic flow and repulsive hydrodynamic drag force on colloids. Scaling arguments for the recently discovered asymmetric rectified electric field (AREF) showed that a repulsive AREF induced EO flow was sufficiently strong to compete with attractive EHD flow. A pairwise colloidal force balance including a repulsive AREF induced EO flow and attractive EHD fluid flow exhibited flow inversions qualitatively consistent with experimentally observed aggregation to separation transitions. More broadly, these results emphasize the importance of AREF induced EO flows in colloid aggregation and separation in low frequency oscillatory electric fields.

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Tue-AT3-04

## Endoskeletal Droplets under Standing Surface Acoustic Waves: Effects of Acoustic Radiation Forces

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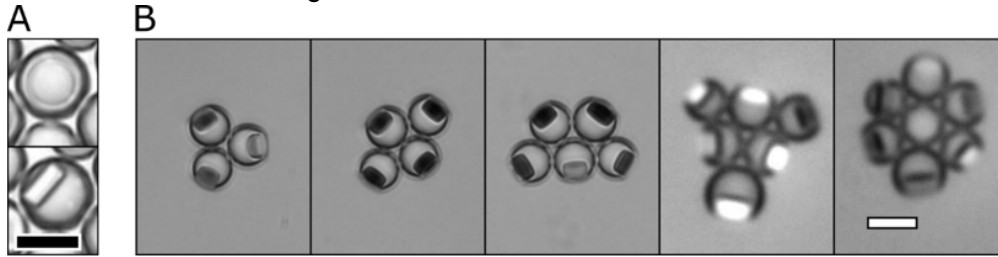
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Primary and secondary radiation forces play an important role in the manipulation and interaction of particles under acoustic fields. A major parameter affecting the interactions is the acoustic contrast factor, which depends on the particle and medium density and compressibility. Here, we incorporate endoskeletal droplets to integrate both positive and negative contrast factors into one system. This allows us to bring about interesting particle patterning behavior in the liquid droplets as well as the solid disks and study the effect of radiation forces on them. We employed microfluidics to generate uniform endoskeletal droplets (perfluorododecane solid inside perfluorohexane liquid droplets). Standing acoustic waves were generated using surface acoustic wave (SAW) devices which consists of interdigitated transducers patterned on a piezoelectric substrate (Lithium Niobate, LiNbO<sub>3</sub>). Particle aggregation behavior under standing SAW were observed at 10 and 20 MHz frequency. Comsol simulations were performed for theoretical modeling of the interaction behavior as well as to verify the experimental observations. We show that these complex emulsions could be generated using a microfluidics technique. In a standing acoustic field, we also show that endoskeletal droplets are forced to the pressure antinodes by the primary radiation force. Whereas the secondary radiation force forms clusters of these droplets because of its negative contrast factor (as opposed to chains for positive contrast factor particles in nodes). Interestingly, we observe that the solid disks, which has a positive contrast factor in reference to the liquid environment and are initially randomly oriented, are forced to align perpendicular to the surface under the acoustic field. This phenomenon forms fascinating clusters as seen in figure 1. Moreover, the orientation of the disks can be manipulated on demand by changing the frequency of the acoustic waves as the equilibrium state of the droplets depends on the interplay between the primary and secondary radiation forces. Additionally, we provide simulation results showing the equilibrium position of the droplets and the disks under the standing acoustic field. Better understanding of the primary and secondary radiation forces is necessary for understanding particle behavior under acoustic waves. In our work, we show the effects of these forces on the clustering and patterning behavior of liquid droplets with a negative acoustic contrast factor as well as solid disks inside

the droplets with a positive contrast factor. This peculiar mixture of two contrast factors in one system allowed us to observe fascinating behaviors not seen elsewhere.



**Fig 1:** Optical microscopic images of endoskeletal droplets. **A.** Different orientations of the solid disks seen on the same droplet. Top - parallel to the surface, Bottom - perpendicular to the surface. Scale bar 10  $\mu\text{m}$ . **B.** Clustering behaviour of the disks and the droplets seen in different sized clusters. SAW waves propagating from +ve and -ve x-direction. Scale bar 15  $\mu\text{m}$ .

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Tue-BT3-01

Fluid-like interfacial dynamics of sodium dodecyl sulphate stabilized hexadecane nanodrops

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A long-standing challenge to resolve electrokinetic and thermodynamic measurements of sodium dodecyl sulphate (SDS) decorated oil–water interfaces is addressed to better understand the contemporary literature on nanoemulsions. In this study, we measured dynamic mobility spectra of SDS-stabilized hexadecane nanodrops (in aqueous NaCl electrolytes) using the electrokinetic sonic amplitude. Spectra were interpreted using a recent electrokinetic theory that draws on an interfacial isotherm linking interfacial charge and surface tension to surfactant and added salt concentrations. According to this unified model, emulsion drops exhibit fluid-like dynamics at megahertz frequencies, whereas such drops are conventionally assumed to behave as rigid spheres because of the interfacial “freezing” effects attributed to Maxwell and Marangoni stresses. SDS-decorated emulsion drops are concluded to be very highly charged, in a regime for which the standard electrokinetic model predicts two zeta-potentials for a single steady electrophoretic mobility. Thus, the conventional Smoluchowski  $\zeta$ -potential with Guoy–Chapman interpretation will misinterpret the interfacial charge.

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Tue-BT3-02

The impact of viscous stress and surfactant concentration on the micro-scale droplet coalescence

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Liquid-liquid droplet emulsions are widely observed in various applications such as bilgewater, food processing, and water-entrained diesel fuels. The dispersed droplets are usually stabilized by the surfactant molecules that are adsorbed onto the droplet interfaces. The adsorbed surfactants reduce the interfacial tension force, and therefore, inhibit the droplet coalescence. In addition to the interfacial tension, other factors will also have major impacts on droplet stability. When two droplets are moving close to each other, a thin film forms between the two droplets and must drain before they can coalesce. In this scenario, the time scale for the film drainage is significant to quantify the emulsion stability. Studies have shown that this film drainage time can be influenced by the viscous stress and Marangoni stress at the droplet interface. The viscous stress at the interface is determined by the viscosity ratio between the dispersed and continuous phases, while the Marangoni stress is induced by the surfactant gradient along the interface.



Based on the conditions of the liquid-liquid systems, both viscous stress and Marangoni stress will inhibit the film drainage to a certain extent, which will be the focus of this work. In this presentation, systematic droplet coalescence experiments will be presented. In particular, systems with different viscosity ratio between the dispersed and continuous phases are studied to understand the impact of the viscous stress. In addition, the film drainage time is also characterized for surfactants with different concentrations to understand the effect of the Marangoni stress on the droplet coalescence.

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Tue-BT3-03

Peeling back the layers: Understanding how the surface structure and stability of oil-in-water nanoemulsions are impacted by interfacial polymer layering

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University of Oregon

Many applications surrounding biopharmaceuticals, cosmetics, and food sciences involve the use of nanoemulsions and layer-by-layer deposition techniques to provide stability and functionality to the droplet surface. Nanoemulsions are kinetically stable, nano-sized oil droplets dispersed in water, which can serve as a vehicle for water-insoluble active ingredients or drugs. Because nanoemulsions are kinetically stable, efforts to understand molecular factors that contribute to their stability are highly beneficial for enhancing the product's shelf life and response to an external stimulus. Thus, investigating both the long-term stability and the interfacial details of polymer-coated nanoemulsions allows for better understanding of structure-function relationships within these systems. Although previous work has studied layer-by-layer self-assembly on flat substrates, less is understood about the structural information of adsorbed polymer layers at a droplet oil/water interface due to experimental difficulties in probing spherical dispersed droplets.

In this work, we investigate both the macroscopic and molecular-level surface properties of nanoemulsions stabilized by a cationic surfactant and two different polymers: anionic poly(styrene sulfonate) (PSS) and partially cationic polyethylenimine (PEI). We use dynamic light scattering to measure and monitor the nanoemulsion size distribution, average diameter, polydispersity index, and zeta potential over a 30-day span. In tandem with these macroscopic studies are molecular-level interfacial studies using vibrational sum frequency scattering spectroscopy, which provides us with structural information on the surface adsorbates. Our results reveal that although electrostatic interactions contribute greatly to enhancing the net alignment of the PSS layer, a balance between hydrophobicity and electrosterics is critical for long-term nanoemulsion stability. This study provides valuable macroscopic and molecular-level insights into these polymer-coated nanoemulsions, allowing for guided efforts towards the design of stimuli-responsive nanoemulsions to be made.

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Tue-BT3-04

Comb-polyelectrolyte Stabilized Polyelectrolyte Complex Coacervate Emulsions

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Polyelectrolyte complex (PEC) coacervates form upon electrostatic complexation of oppositely charged macromolecules and their subsequent condensation into aqueous macromolecule-rich phases. These aqueous two-phase systems have been demonstrated to possess unique capabilities to achieve dynamic spatial compartmentalization and spontaneous sequestering of biological molecules. Despite such exciting prospects, their use has been limited owing to our inability to stabilize coacervate droplets and prevent their macro-phase separation. Inspired by pioneering work on stabilization of water-water emulsions by block polyelectrolytes, in this contribution, we will highlight our research progress on coacervate emulsions stabilized by comb-polyelectrolytes (cPE) commercially used as dispersants. We demonstrate that the stable complex coacervate emulsions exhibit long-term (>4-month) stability, composed of oppositely

charged linear polyelectrolytes and stabilized by the polycarboxylate ether-based comb-polyelectrolyte interfacially adsorbing at the coacervate-water interfaces. The microdroplet size remains relatively constant with time and is shown to be regulated by the concentrations of the comb- and linear polyelectrolytes. The emulsion properties can be optionally tuned by the addition of water and salt while the stability is not influenced. This stabilization strategy provides steric stabilization to the droplets while allowing the transport of small molecules in and out of the coacervate droplets and retaining the tendency to sequester proteins and other charged molecules from solution, paving the way for them to be immensely employed as multifunctional bioreactors and encapsulants in agricultural, cosmetics, food, and pharmaceutical formulations.

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Tue-HT3-01

### Growth and Coalescence of Nanoscopic Mesas in Stratifying Micellar Foam Films

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Freestanding films of soft matter exhibit stratification due to confinement-induced structuring and layering of supramolecular structures like micelles. Stratification in micellar films proceeds by the growth of thinner domains at the expense of surrounding thicker film, and local volume conservation leads to the formation of nanoscopic ridges at the moving front. The ridge often undergoes an instability leading to nucleation of nanoscopic mesas, that grow and coalesce over time. The shape and size of ridges and mesas in stratifying films are visualized and analyzed using interferometry, digital imaging, and optical microscopy (IDIOM) protocols, with unprecedented high spatial (thickness < 100 nm, lateral ~500 nm) and temporal resolution (< 1 ms). In this contribution, we analyze the shape evolution and coalescence of mesas in an effort to develop a comprehensive understanding of drainage by stratification in micellar foam films, including the role played by the contribution of supramolecular oscillatory structural forces to disjoining pressure.

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Tue-HT3-02

### Multiscale dynamics of colloidal deposition and erosion in porous media

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Diverse processes—e.g., environmental pollution, groundwater remediation, oil recovery, filtration, and drug delivery—involve the transport of colloidal particles in porous media. Using confocal microscopy, we directly visualize this process in situ and thereby identify the fundamental mechanisms by which particles are distributed throughout a medium. At high injection pressures, hydrodynamic stresses cause particles to be continually deposited on and eroded from the solid matrix—notably, forcing them to be distributed throughout the entire medium. By contrast, at low injection pressures, the relative influence of erosion is suppressed, causing particles to localize near the inlet of the medium. Unexpectedly, these macroscopic distribution behaviors depend on imposed pressure in similar ways for particles of different charges, although the pore-scale distribution of deposition is sensitive to particle charge. These results reveal how

the multiscale interactions between fluid, particles, and the solid matrix control how colloids are distributed in a porous medium.

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Tue-HT3-03

DLVO energy landscape of a Janus particle with a nonuniform cap

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A colloidal particle is often termed “Janus” when some portion of its surface is coated by a second material which has distinct properties from the native particle. These coated regions are typically nonuniform as a result of the fabrication process. Here we develop simple, computationally facile, semianalytic equations to accurately calculate the DLVO potential landscape of a Janus particle with nonuniform coating thickness above a solid boundary. Furthermore, we characterize the role of van der Waals interactions, which have not previously been considered, in Janus particle dynamics. The effects of both nonuniform coating thickness and van der Waals interactions significantly influence the potential landscape of the particle, particularly in high ionic strength solutions, where the particle samples positions very close to the solid boundary. As such, equations developed herein facilitate accurate characterization of conservative interactions experienced by a confined Janus particle in a broader range of experimentally relevant systems.

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Tue-JT3-01

Dispersing Crude Oils of Varying Viscosities Using a Food-Grade Dispersant

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The mitigation of crude oil spills in the ocean is generally done using chemical dispersants, which convert the oil slick into small droplets. These dispersants are mixtures of surface-active molecules (surfactants) dissolved in a solvent. Questions regarding the toxicity of current commercial dispersants have prompted our lab to develop an eco-friendly alternative based on the food-grade surfactants, soy Lecithin (L) and Tween 80 (T). In previous studies, the roles played by L/T and the solvent in a typical dispersant have been studied, but all those studies were done with a light crude oil, i.e., one with a low viscosity. In this study, we examine if our food-grade dispersant remains effective at dispersing heavier crude oils, i.e., crudes of higher viscosity. We study a light, a medium, and a heavy crude and compare their dispersion into seawater using a fixed L/T blend in various solvents. We find that the efficiency of dispersion is lower when the crude is more viscous. Moreover, in line with our previous findings, simply varying the solvent can alter the dispersion efficiency from poor to good. The solvents that promote dispersion can be identified systematically by using a plot of Hansen Solubility Parameters (HSPs). However, there do exist several key differences between the solvents most effective for the three crudes. Our analysis suggests that crude oil composition must be taken into account when optimizing the formulation of a dispersant.

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Tue-JT3-02

Effect of nanoparticle addition on oil spill bioremediation by hydrocarbonoclastic bacterium *A. borkumensis*

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Oil seepage and spills present severe environmental and health hazards, so prompt and thorough remediation is a necessity. Bioremediation is an oil spill remediation method where naturally occurring microbial species metabolize hydrocarbons, removing spilled oil from the environment. Unfortunately, complete bioremediation can take decades, so methods for enhancing the process are continually being sought. Recent studies have introduced nanoparticles to enhance biodegradation rates. These nanoparticles typically serve as emulsifiers to improve the bioavailability of the oil or to release growth-limiting nutrients at the oil-water interface to increase proliferation. In this study, we investigate the effect of the presence of three model nanoparticles namely silica, silver, and lignin, on the hydrocarbon-degrading properties of a model bacterium, *Alcanivorax borkumensis*. We study the impact of the surface charge of nanoparticles on their adsorption onto the bacterium surface and the subsequent binding of the bacteria-nanoparticle composite on the oil-water interface. The surface charge of the nanoparticles was controlled by selective adsorption of positively charged polyelectrolyte chitosan on their surface. No significant change in cell growth was observed in the presence of chitosan coated and uncoated silica nanoparticles. Silver nanoparticles had no impact on the growth rate or adherence of the bacteria to hydrocarbons, but the addition of chitosan coated silver nanoparticles resulted in a more than three-fold decrease in the growth rate of the bacteria. Interestingly, we find a nearly 50% increase in the number of bacteria adhered to hexadecane in the presence of chitosan coated lignin compared to cells grown in the absence of nanoparticles. We correlate the observed growth rate of bacteria in presence of nanoparticles with the interfacial tension measurements which suggest that lignin nanoparticles not only facilitate the proliferation of *A. borkumensis* but likely assist in the increase of biosurfactant production by the bacterium. These findings indicate that naturally derived nanoparticles can be used in enhancing the bioremediation of spilled oil, thus providing a new sustainable alternative to large-scale oil spill remediation.

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Tue-JT3-03

Colloidal Interactions of Microplastics at Interfaces of Liquid Crystals: A Soft Matter Platform for Rapid Characterization of Microplastics

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A key environmental challenge is the clean-up of “microplastics”, dispersed particulate polymer debris that has accumulated in the oceans and freshwater systems. Microplastics are highly heterogeneous, both in terms of size, composition and surface properties. Strategies to efficiently collect and treat (e.g., degrade via microbial processes) microplastics thus require characterization at the site of collection. This presentation will address efforts to develop novel methods for characterization of microplastics based on their adsorption and assembly at aqueous interfaces of liquid crystals. The approach is motivated by our prior studies that have revealed that macromolecules/nanoparticles/microparticles adsorbing at aqueous interfaces of a liquid crystal are able to form interfacial assemblies with characteristic optical patterns (optical fingerprints) that are strongly dependent on adsorbate surface chemistry and shape. This presentation will describe experiments performed with polyethylene (PE) and polystyrene (PS) microparticles, representative of two of the most common microplastic pollutants. Overall, our results reveal that liquid crystals provide a promising soft matter platform for characterizing colloidal interactions of microplastics at interfaces and for rapid identification of microplastics.

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Tue-JT3-04

Soft dendritic colloidal particles as novel environmentally-friendly microcleaners for microplastic remediation

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The exponential increase in plastic usage and the lack of proper disposal or conversion into reusable resources, has created the world-wide problem of accumulation of microplastics in freshwater and marine environments. The current methods for the removal of these highly undesirable colloidal dispersions through filtration or centrifugation may be resource-heavy, time-consuming, and cost-prohibitive. As an alternative, we will present a novel solution of using soft dendritic colloids (SDCs), or dendricolloids, as a physical method to remove microplastics from aquatic environments. The SDCs represent a new class of soft matter systems introduced in our group, which have a unique polymeric morphology with a hyperbranched, nanofibrous corona and large excluded volume. The SDC possess adhesive and gelation properties which enable capabilities of highly efficient capture of large amounts of microplastics in polluted water. Here, we will discuss how interfacial properties of the dendricolloids and microplastics can affect their heterocoagulation in various ionic strength and pH conditions. In addition to understanding the role of the unique morphology of the particles, we theorize that both van der Waals and electrostatic interactions play a role in microplastics adsorption.

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Tue, 15 15:20 - 16:40

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Tue-KT3-01

Foliar applied reactive oxygen species (ROS)-responsive star polymers protect plant photosynthesis under abiotic stress

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Climate change induced extreme weather is increasing the severity of plant abiotic stress, which causes reactive oxygen species (ROS) accumulation and inhibits plant photosynthesis. We synthesized a 20 nm diameter ROS-responsive star polymer (RSP) poly(acrylic acid)-block-poly((2-(methylsulfinyl)ethyl acrylate)-co-(2-(methylthio)ethyl acrylate)) (PAA-b-P(MSEA-co-MTEA)) with ROS scavenging and controlled Mg release functionalities and demonstrated that it alleviated abiotic stress (heat, light and nutrient deficiency) after foliar delivery to tomato (*Solanum lycopersicum*) plants. RSP scavenged up to 10  $\mu\text{mol mg}^{-1}$  ROS in vitro, and significantly suppressed ROS in vivo among stressed tomato leaf mesophyll. Mg release from RSP was also enhanced by ROS under plant-relevant pH conditions (4.5 and 7.5). RSP exhibited uptake into the foliar mesophyll and distribution around chloroplasts, as observed by Hyperspectral-Enhanced Darkfield Microscopy. Relative to a similar but non-responsive star polymer control, RSP foliar application increased the tomato plant carbon assimilation rate by 67%, quantum yield of CO<sub>2</sub> assimilation by 59%, RuBisCo carboxylation rate by 81% and photosystem II quantum yield by 57% after heat and excess light stress (T=40 °C, 2000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  PAR). Mg-loaded RSP enhanced carbon assimilation of Mg-deficient plants by 29% and increased RuBisCo carboxylation rate by 118%, improved photosynthesis of Mg-deficient plants mainly by promoting RuBisCo activity. These results underline the potential of ROS-scavenging nanocarriers to protect plant photosynthesis and crop yield under severe stress conditions, which allow plants to be more resilient to climate change-induced extreme weather.

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Tue-KT3-02

## Chemotactic smoothing of bacterial populations

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Collective migration -- the directed, coordinated motion of many self-propelled agents -- is a fascinating emergent behavior exhibited by active matter that has key functional implications for biological systems. Extensive studies have elucidated the different ways in which this phenomenon may arise. Nevertheless, how collective migration can persist when a population is confronted with perturbations, which inevitably arise in complex settings, is poorly understood. Here, by combining experiments and simulations, we describe a mechanism by which collectively migrating populations smooth out large-scale perturbations in their overall morphology, enabling their constituents to continue to migrate together. We focus on the canonical example of chemotactic migration of *Escherichia coli*, in which fronts of cells move via directed motion, or chemotaxis, in response to a self-generated nutrient gradient. We identify two distinct modes in which chemotaxis influences the morphology of the population: cells in different locations along a front migrate at different velocities due to spatial variations in (i) the local nutrient gradient and in (ii) the ability of cells to sense and respond to the local nutrient gradient. While the first mode is destabilizing, the second mode is stabilizing and dominates, ultimately driving smoothing of the overall population and enabling continued collective migration. This process is autonomous, arising without any external intervention; instead, it is a population-scale consequence of the manner in which individual cells transduce external signals. Our findings thus provide insights to predict, and potentially control, the collective migration and morphology of cell populations and diverse other forms of active matter.

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Tue-KT3-03

## Thermodynamic and Rheological Consequences of Healthy versus Diseased Model Myelin Monolayers and Implications for Demyelination

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The myelin sheath is a critical component of the central nervous system (CNS) and peripheral nervous system (PNS). It is a multilamellar membrane consisting of a coiled bilayer that acts as an electrical insulator for nerve impulses traveling along axons between nerve cells. Myelin's effectiveness as an electrical insulator is correlated with its thickness and compactness, and its ability to closely pack both the cytoplasmic faces within and the extracellular faces outside of each layer is critical for proper function, otherwise leading to serious neurological diseases including multiple sclerosis. Compared to other membranes in the body, the myelin sheath contains a large lipid fraction in the range of 75-80% of the dry mass, compared to about 50% in other membranes, consisting of many different lipids falling primarily within the classes of glycerophospholipids, sphingolipids, and sterols. The lipids in the myelin sheath play a critical role in membrane stability and compaction, and it has been shown that the lipid composition differs significantly between healthy specimens and those sensitized with experimental autoimmune encephalomyelitis (EAE). While previous investigations have used model lipid bilayers and monolayers to study their interactions with important proteins including myelin basic protein (MBP) and proteolipid protein (PLP), our understanding of the role of lipid composition on membrane formation thermodynamics and rheology, particularly when comparing healthy versus diseased membranes, is lacking. In this presentation we study the formation and interfacial dilatational rheology of lipid monolayers modeling the cytoplasmic and extracellular sides of healthy and EAE myelin. We use a Langmuir trough for both surface pressure versus area isotherms and oscillating area interfacial rheology measurements, all performed at approximately body temperature (37°C). From isotherm data, we calculate differences in the Gibbs free energy of mixing between the four monolayers to show differences in intermolecular interactions and miscibility. These results are used to support observations in interfacial rheology results, where EAE

extracellular monolayers are substantially stiffer than their healthy counterparts, and both cytoplasmic monolayers are significantly softer than the extracellular side. We also analyze the nonlinear rheological behavior of the monolayers, for example observing in general film softening during compression and expansion. These first oscillatory interfacial rheology measurements of model myelin monolayers, coupled with the thermodynamic analysis of film formation, improve our understanding of the implications of the different lipid compositions on the film properties, and provide clues to how the changes in lipid composition may lead to demyelination.

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Tue-KT3-04

Biophysical properties of the model tear film lipid layer

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Tear film lipid layer (TFLL) is the outmost layer of the tear film. It plays a crucial role in stabilizing the tear film by reducing surface tension and retarding evaporation of the aqueous layer. Dysfunction of the TFLL leads to dysfunctional tear syndrome (DTS), with the dry eye disease (DED) being the most prevalent eye disease affecting 10-30% of the world population. To date, except for treatments alleviating the dry eye symptoms, effective therapeutic interventions in treating the DED are still lacking. Therefore, there is an urgent need to understand the biophysical properties of the TFLL with the long-term goal to develop translational solutions in effectively managing the DED. Here we studied the biophysical properties of a model TFLL using a novel experimental methodology called the constrained drop surfactometry (CDS), recently developed in our laboratory. The model TFLL was composed of 40% behenyl oleate and 40% cholesteryl oleate, representing the most abundant wax ester and cholesteryl ester in the nature TFLL, respectively, and 15% phosphatidylcholine and 5% palmitic-acid-9-hydroxy-stearic-acid (PAHSA) that represent the two predominant polar lipid classes in the natural TFLL. Using CDS and atomic force microscopy (AFM), we have systematically studied the surface activity, interfacial rheology, lateral structure and topography of the model TFLL. It is found that the major biophysical function of phospholipids in the TFLL is to reduce the surface tension; while the primary function of PAHSA is to regulate interfacial rheology of the TFLL, thus optimizing the viscoelastic properties of the TFLL under physiologically relevant conditions. These findings have novel implications in better understanding the physiological and biophysical functions of the TFLL, and may offer new translational insight to the treatment of DED.

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Tue, 15 15:20 - 16:40

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Tue-MT3-01

Plasmonic Metal Oxide Nanocrystals

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Metal oxide nanocrystals doped with a few percent of aliovalent dopants become electronically conducting and support strong light-matter interactions in the infrared due to localized surface plasmon resonance (LSPR). In the prototypical material tin-doped indium oxide ( $\text{Sn:In}_2\text{O}_3$ ), we have found that the strength and spectrum of light absorption depend nontrivially on nanocrystal doping, size, and the radial distribution of dopants. Localizing tin dopants in the outer shell of the nanocrystals makes them more sensitive to changes in the refractive index of their surroundings. The associated compression of the near-surface depletion region also enhances conductivity in nanocrystal films. Doping with fluorine, as a substitutional dopant for oxygen, plays a dual role as an electron donor and a shape-directing agent, leading to well-faceted nanocrystal cubes. Co-doped  $\text{F,Sn:In}_2\text{O}_3$  nanocrystals have strong coupling between the near-infrared LSPR of individual cubes in 2-D arrays. Overall, this new class of plasmonic nanomaterials offers opportunities for synthetic tuning of optical properties beyond what's possible with conventional metals.

Emerging applications in sensing, smart windows, and catalysis may take advantage of their unique ability to concentrate and direct energy flow from infrared light.

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Tue-MT3-02

## Plasmonic Substrates for Modified Reaction Chemistry via Vibrational Strong Coupling

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Vibrational strong coupling has been increasingly explored recently as a means to alter chemical reactions. When molecules are placed near an optical cavity that is tuned to the vibrational frequency, the two systems can resonantly exchange energy. If the energy exchange occurs faster than losses to the environment, the strong coupling regime is reached, primarily characterized by Rabi splitting of the original eigenstates to upper and lower polariton modes, with subsequent modification of the bond-energy. Usually, Fabry–Pérot (F.P.) cavities are used for coupling due to their high Q-factors; however, these cavities are intrinsically limited because the coupling strength is directly proportional to both the electric field mode density and the angle between light and the molecular dipole. Because of this, a continuum of “dark”, unperturbed states exist near the original vibrational mode, limiting the total chemical modification. To address this problem, we have shown that plasmonic nanodisk substrates can be used as a new optical platform for increasing the coupling strength to molecules in sub-diffraction limited volumes. Because the electric field strength is so large in extremely small volumes, the plasmonic nanodisks are able to overcome their intrinsic losses in order to reach the strong coupling regime. Furthermore, the plasmonic substrates are completely angle-independent, which allows for coupling to an entire ensemble of molecules spread across the surface of the substrate, regardless of molecular orientation, which helps to decrease the number of dark states in the system. Additionally, the large plasmon linewidth allows for strong coupling to multiple, closely spaced vibrational modes simultaneously, opening the door for coherent energy exchange between previously orthogonal vibrational modes. We hypothesize that the alleviation of dark states will lead to new chemical modifications beyond what has previously been observed in F.P. cavities.

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Tue-MT3-03

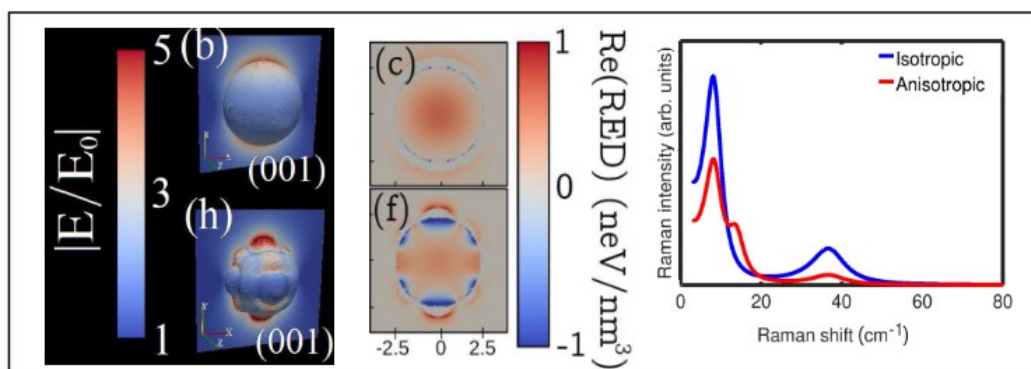
## Acousto-Plasmonic Coupling: The Raman Energy Density (RED)

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Interactions between elementary excitations, such as plasmon-exciton and plasmon-phonon, are of great interest from a fundamental point of view and for applications. While plasmon-exciton interactions have been extensively studied both experimentally and theoretically [1], the interaction mechanisms between acoustic vibrations (phonons) and localized surface plasmons (LSPs) remain largely unexplored [2]. Here we present a theoretical investigation of the interactions between confined acoustic vibrations and LSPs in the framework of resonant acoustic Raman scattering. We express the Raman scattering process in the framework of Fermi golden rule and introduce for the first time the concept of Raman energy density (RED). Similarly to the Raman-Brillouin electronic density (RBED) introduced for semiconductors [3–4], this new physical quantity is used as a theoretical tool for the interpretation of resonant Raman scattering mediated by LSPs in metallic nanoparticles. The RED represents the electromagnetic energy density excited by the Raman probe and modulated by the acoustic vibrations of the nanoparticle. We show that, similarly to the local density of optical states (LDOS) and the RBED, the RED is a local physical quantity that can be mapped in the near-field region. It provides a clear picture of the interaction between LSPs and acoustic vibrations which give rise to inelastic scattering measurable in the far-field. Here, we use the newly introduced RED concept to investigate elastic (an)isotropy effects and calculate the Raman selection rules of spherical nanoparticles in a dielectric environment.





**Fig. 1** Left: Isotropic ( $l=0$ ) and Anisotropic ( $A_{1g}$ ) breathing acoustic mode of a AuNP modulating the near electric field induced par the dipolar localized surface plasmon (LSP). Center: Raman energy density (RED) resulting from the interaction of the  $l=0$  and  $A_{1g}$  vibration mode with the dipole LSP. Right: Calculated acoustic Raman spectra for the isotropic and anisotropic nanoparticles.

**References** [1] Schlather, A. E.; Large, N.; Urban, A. S.; Nordlander, P. and Halas, N. J. "Near-Field Mediated Plexcitonic Coupling and Giant Rabi Splitting in Individual Metallic Dimers," *Nano Lett.*, 2013, 13, 3281 [2] Large, N.; Saviot, L.; Margueritat, J.; Gonzalo, J.; Afonso, C. N.; Arbouet, A.; Langot, P.; Mlayah, A. and Aizpurua, J. "Acousto-plasmonic Hot Spots in Metallic Nano-Objects," *Nano Lett.*, 2009, 9, 3732 [3] Large, N.; Huntzinger, J. R.; Aizpurua, J.; Jusserand, B. and Mlayah, A. "Raman-Brillouin electronic density in short period superlattices," *Phys. Rev. B*, 2010, 82, 075310 [4] Mlayah, A.; Huntzinger, J.-R. and Large, N. "Raman-Brillouin light scattering in low-dimensional systems: Photoelastic model versus quantum model," *Phys. Rev. B*, 2007, 75, 245303

Tue-MT3-04

Plasmon-Coupled Gold Nanoparticles in Stretched Shape-Memory Polymers for Mechanical/Thermal Sensing

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The organization of plasmonic nanoparticles (NPs) determines the strength and polarization dependence of coupling of their surface plasmons. In this study, plasmon coupling of spherical Au NPs with an average diameter of 15 nm was investigated in shape-memory polymer films before and after mechanical stretching and then after thermally driving shape recovery. Clusters of Au NPs form when preparing the films that exhibit strong plasmon coupling. During stretching, a significant polarization-dependent response develops, where the optical extinction maximum corresponding to the surface plasmon resonance is redshifted by 19 nm and blueshifted by 7 nm for polarization parallel and perpendicular to the stretching direction, respectively. This result can be explained by non-uniform stretching on the nanoscale, where plasmon coupling increases parallel to the shear direction as Au NPs are pulled into each other during stretching. The polarization dependence vanishes after shape recovery, and structural characterization confirms the return of isotropy consistent with complete nanoscale recovery of the initial arrangement of Au NPs. Simulations of the polarized optical responses of Au NP dimers at different interparticle spacings establish a plasmon ruler for estimating the average interparticle spacings within the experimental samples. An

investigation of the temperature-dependent recovery behavior demonstrates an application of these materials as optical thermal history sensors.

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## Tue, 15 15:20 - 16:40

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Tue-NT3-01

Oil-infused Rough Elastomers as Water and Ion Barriers for Implantable Flexible Bioelectronics

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Implantable bioelectronics have a wide range of applications in basic biomedical research and clinical medicine. The encapsulation of these systems represents a key challenge as they demand robust isolation of electronics from surrounding biofluids to prevent current leakage and the degradation of underlying devices. To date, all the barrier materials for flexible bioelectronics, including polymer layers, inorganic coatings, and transferred barriers, are solid materials. These solid materials suffer from limited barrier lifetime due to pinholes, cracks, and nanopores or from complicated fabrication processes and limited stretchability for interfacing with complex biological tissues. This paper reports a solution to this materials challenge by introducing an oil-infused rough silicone elastomer as a transparent, flexible, stretchable, slippery, and damage-tolerant biofluid barrier material. Accelerated lifetime tests suggest robust water barrier characteristics that approach 226 days at 37 °C, even under severe mechanical damage using a knife. A combination of temperature- and thickness-dependent experimental measurements and reaction-diffusion modeling reveal the key water-proof property. In addition to serving as a barrier to water, oil-infused rough elastomer demonstrates an attractive ion prevention property. All these exceptional properties suggest the potential applications in flexible bioelectronics implants for emerging applications ranging from chronic neural recording to bioelectronic medicine.

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Tue-NT3-02

Biocompatible cellular coatings to improve the oxygen tolerance of anaerobes

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Microbial probiotics are becoming increasingly important for maintenance of health, but several challenges remain in their manufacture, storage and transport. Specifically, many anaerobic bacteria lack oxygen scavenging mechanisms, leading to reactive oxygen species-mediated damage and cell death within minutes of ppm level oxygen exposure. To address these challenges, we have developed a self-assembling cellular coating made from non-toxic metal ions and natural organics, to improve the oxygen tolerance and stability of these anaerobes. By optimizing these coatings, we have successfully encapsulated microbes. Because of the high biocompatibility of these coatings, the anaerobes demonstrated negligible viability loss after encapsulation and improved oxygen tolerance. This coating strategy will shed light on interfacial interactions of biotic and abiotic hybrid materials.

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Tue-NT3-03

Flexible and Robust Polymer Gel-Sheet with Ideal Properties for Hemostasis

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Superabsorbent polymer gels that can absorb a significant amount of water are widely used in materials such as diapers and for keeping soil moist. These gels are typically in the form of microscale beads. The same gels can also be made as macroscopic solids (e.g., a sheet or cube), but these solids take a long time (~ 24 h) to swell in water. For a large, solid gel to swell rapidly, it is necessary to make it porous, but porous gels tend to be fragile. Here, we present a simple and low-cost approach to create solid gels that are both porous and highly robust. Our approach involves the polymerization of a foamed monomer solution, with the bubbles of the foam being stabilized by novel polymers. The final dried material is typically in the form of a sheet (thickness ~ 1 mm, length and width from 1 to 100 cm). The sheet is flexible and robust; it can be rolled up like a paper towel and cut into patches of desired size. When added to water, the gel-sheet absorbs 150 times its weight in water within 30 s, and the swollen sheet can be lifted up by hand. We expect this type of superabsorbent material to have applications in many applications, one of which is in stopping bleeding from severe wounds. In that regard, our gel-sheet is able to rapidly absorb whole blood – up to 60 times its weight within a minute. Moreover, due to the presence of the polymer stabilizers, the blood tends to remain immobilized in the swollen gel. Data from experiments with bleeding models in animals will be presented.

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Tue-NT3-04

Cuprous oxide/polyurethane surface coating that inactivates the SARS-CoV-2 virus

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As of April 2021, the COVID-19 pandemic has infected about 130 million people and caused 3 million deaths. The disease is caused by SARS-CoV-2 virus. The main route for virus spread is believed to be through inhalation of contaminated respiratory droplets. Additionally, the disease can also spread by fomites, i.e. a healthy person making contact with a contaminated object and subsequently touching their face. Studies have shown SARS-CoV-2 can remain infectious on solids for up to a week. In this talk, we present an inexpensive surface coating that rapidly inactivates the SARS-CoV-2 virus, to help stop the spread of disease by fomites. To have high applicability, we utilized commercial polyurethane to fix cuprous oxide (Cu<sub>2</sub>O) particles on solid surfaces. This coating dramatically reduced the viability of SARS-CoV-2 (i.e. >99.9% within 60 minutes). This coating can be made on different solids, such as glass, stainless steel, plastic, wood, et. Also, the surface coating is durable and remains active against the virus after repeated exposures to it. Additionally, our tests indicated the coating is potent to the virus after immersion in water for 13 days.

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## Tue, 15 15:20 - 16:40

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Tue-OT3-01

The Nanoscale Caterpillar : or how to achieve precise motion and assembly with random sticky feet

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Particles with sticky feet - nanoscale caterpillars - in biological or artificial systems, beat the paradigm of diffusion to achieve complex functions. Some cells (like leucocytes) use ligand-receptor contacts (sticky

feet) to crawl and roll along vessels. Sticky DNA (another type of sticky feet) is coated on colloids to design programmable interactions and self-assembly. Predicting the dynamics of such sticky motion is challenging since sticky events (attaching/detaching) often occur on very short time scales compared to the overall motion of the particle. Even understanding the equilibrium statistics of these systems (how many feet are attached in average) is largely uncharted. Yet, controlling the dynamics of such particles is critical to achieve these advanced functions. Here we present advanced theory and experimental results on a model system. We rationalize what parameters control average feet attachment and how they can be compared to other existing systems. We investigate furthermore how various motion modes (rolling, sliding or skipping) may be favored over one another.

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Tue-OT3-02

Construction of diamond lattice and chiral assembly using gold tetrahedral nanoparticles

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Self-assembly of tetrahedral particles and their packing problems have been extensively studied in simulations for many years. Despite the progress in mathematical constructions of tetrahedral packings, only limited tetrahedra self-assembly structures have been successfully demonstrated in experiments. For example, diamond lattice, an open structure with interesting optical and mechanical properties, has only been recently achieved in the assembly of colloidal particles by utilizing tetrahedrally coordinated sticky patches; as another example, chiral assemblies of tetrahedral nanoparticles have only been showcased in 1D chain-like helical structures but not in a largescale superlattice. Here, by using highly uniform gold tetrahedral nanoparticles as the building blocks, we observe their self-assembly into diamond structure on a supported substrate simply relying on their shape anisotropy without introducing tip patchiness as the directional force. More interestingly, these diamond lattices can undergo a spontaneous symmetry-breaking event to form into chiral assemblies, when the size of tetrahedral building blocks increases. A similar trend has also been observed when we fine tune the interparticle interactions, and the as-formed chiral structures can eventually transform into a decahedral packing. We further demonstrate the performance of different assembly structures in enhancing the surface-enhanced Raman scattering (SERS) signal. Our study can provide interesting insights into the largescale self-assembly of anisotropic nanoparticles to enrich the diversity in their structures and functionalities.

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Tue-OT3-03

Separation of gold single-crystalline and penta-twinned seeds through difference exaggeration overgrowth and purification

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Seed-mediated growth of nanoparticles (NPs) is widely used to achieve the size, shape and symmetry control of NPs, where the starting seeds are regarded as the templates for the products. Although a library

of NPs with different shapes have been controlled via various synthetic conditions, the quality of these NPs is always limited because the purity and uniformity of a specific type of seeds (i.e. single-crystalline, single-twinned or penta-twinned seeds, SC, ST and PT seeds, respectively) with well-defined crystallinity is extremely hard to achieve. The reason for this is that the unavoidable twinning behavior during the seed formation when only several layers of packing faults happen spontaneously. This small differences in seeds is so subtle that it is extremely difficult to separate them based on their crystalline features. Herein, for the first time, we reported a new method called difference-exaggeration overgrowth and purification and achieved high purity and uniformity of gold (Au) SC, PT seeds (>95% yield). These highly pure Au seeds can be achieved by the overgrowth of silver (Ag) NPs on Au seeds to magnify the difference between SC and PT seeds, during which the Au SC seeds will turn into core-shell Au SC seed@Ag nanocubes and Au PT seeds will turn into core-shell Au PT seed@Ag nanowires exclusively. By exaggerating the differences larger enough, we were able to separate them and then obtain purified SC and PT seeds by selectively etching Ag shell. With these purified seeds, a library of NPs with high uniformity and purity and even several new types of NPs that never be achieved previously, which demonstrated the advances of this method for achieving highly pure seeds. This method opens new avenue for precisely control over the shape, size and symmetry of NPs by improving the quality of seeds, which will provide more possibility for future understanding of growth behavior of NPs and their potential applications which require better control of NPs.

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Tue-OT3-04

#### Assembly of Nanoparticle-Polyelectrolyte Membranes at Water-water interfaces

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University of Pennsylvania

Complexation between polyelectrolytes (PEs) and nanoparticles (NPs) have been used to assemble functional films and membranes that respond to multiple inputs and stimuli. Interfacial complexation between oppositely charged polyelectrolytes and nanoparticles at the interface of aqueous two-phase systems has emerged as a powerful method to assemble these functional membranes. Remarkably, these membranes can grow continuously to thicknesses approaching 1 cm, naturally raising the question as to what is the underlying mechanism for the growth of these membranes. By taking advantage of a microfluidic setup, we study the growth mechanism behind interfacial complexation between silica (SiO<sub>2</sub>) nanoparticles and Polydiiallyldimethylammonium chloride (PDADMAC). The sequential insertion of PDADMAC and fluorescently labelled PDADMAC has shown that the membranes grow through a permeation mechanism, in which PEs diffuse and permeate continuously to the growing front of the membrane. Taking advantage of this growth mechanism, we demonstrate that PDADMAC/SiO<sub>2</sub> nanoparticle membranes can be spatially structured to embed specific functionality, which could potentially be useful for programmed delivery of actives from the membrane.

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## Tue, 15 15:20 - 16:40

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Tue-PT3-01

#### Fabrication of microstructured electrodes via electroless metal deposition onto polydopamine-coated polystyrene substrates and thermal shrinking

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The ability to provide high sensitivity with small footprints makes miniaturized electrodes key components of biosensing, wearable electronics and lab-on a-chip devices. Recently, thin film deposition onto

polystyrene films, followed by thermal shrinking has been used to produce microstructured electrodes (MSEs) with high electroactive surface area (ESA). Nevertheless, the high cost associated with film deposition through evaporation used in microfabrication and the variability in performance of screen-printed electrodes (SPEs) remain key barriers that limit their widespread deployment. Here, a simple and inexpensive method is developed for the solution-based patterning of high-quality metallic films on polystyrene substrates for MSE fabrication. The ESA of electrodes produced through this method is 2 × and 12 × larger than that of microstructured and planar electrodes produced through sputtering, respectively, and their cost is only 20% of sputtered ones. This methodology allows the fabrication of on-chip microstructured electrochemical cells (SMECs) with excellent analytical performance (3% RSD inter-day reproducibility and 0.3% RSD repeatability), superior to that of commercially available SPEs. In addition, the ESA of SMECs is significantly higher than that of SPEs, and they show excellent response toward dopamine detection. We anticipate that this solution-based fabrication approach will expedite the development of miniaturized sensing platforms for point-of care applications.

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Tue-PT3-02

Ultra-high throughput on-chip synthesis of microgels with tunable mechanical properties

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Hydrogel particles (microgels) generated using microfluidic methods have superb properties such as high size uniformity and precise control over degradation and release profiles, making them useful for applications in wound healing and injectable drug delivery. However, the throughput of microfluidics is constrained by the physics governing the flow of immiscible fluids confined within microchannels. This throughput tends to be several orders of magnitude lower than what would be necessary for commercial and clinical applications. Here, we demonstrate the scaling up of on-chip synthesis of microgels by parallelizing the microfluidic channels. Taking advantage of the established fabrication technologies developed by the semiconductor industry and a high flow control system, a 4-inch silicon microfluidic chip integrating more than 4,000 microfluidic devices is developed. By incorporating a high energy flood UV source, this chip allows the synthesis of poly (ethylene glycol) diacrylate microgel particles with diameter down to 30 μm at a throughput above 1kg/hr. By using photomasks that enable milli-second scale control of the UV exposure, the stiffness of microgels can be varied between 103 to 104 Pa. Large-scale production of microgels will enable construction of large-scale tissue scaffold with well-defined physiochemical properties, and will provide scalability for translation to clinical settings.

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Tue-PT3-03

Complexity and Dynamics in Nanoporous Materials: How to Cut, Insert, Edit, and Animate Their Modules (**LaMer Keynote Lecture**)

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A central goal in chemistry is to synthesize solid functional materials capable of addressing the current energy, environmental, and health challenges. The achievement of this objective requires the management of complexity and dynamics within materials. However, one of the most significant challenges facing materials science and pore engineering is introducing complexity and dynamics into chemical structures, especially extended materials, without creating chaos and losing control due to the inevitable result of

uncharacterizable disorder systems.<sup>1</sup> In the first part of my talk, I will describe my efforts in introducing compositional and spatial complexity into crystals of extended structures such as metal-organic frameworks (MOFs) and polymers for manipulating molecular diffusion, maximizing catalytic cooperativity, and selectivity (Figure A).<sup>2-9</sup> I will discuss synthetic strategies to cut, insert, migrate, modify and assemble the building blocks in these porous materials to improve its performance metrics. By utilizing the intrinsic order of MOFs' backbone, constituents including inorganic clusters and organic linkers can be selectively extracted or added without affecting the overall crystallinity of the material. In the second part of my talk, modular animation of MOF/polymer composites by artificial molecular machines will be introduced, forming a molecular factory capable of undergoing repeated collection of cargoes from solutions and selective unloading at a targeted location (Figure B).<sup>10</sup> By combining the robustness of MOF materials and responsive dynamics of polyrotaxanes, an integrated system with amplification effects in two and three dimensions can be achieved to realize a sustainable future. These molecular logistics factories serve as a basis for developing more complex molecular integrated systems with diverse functions. Overall, the fabrication of these multicomponent mesoscale architectures with sophisticated geometries and compartmentalization patterns is critical in creating artificial lives in the future. Such synthesis, transportation, and separation studies open up new opportunities to prepare novel functional materials and systems essential in fundamental research and industry. References 1. Feng et al., Chem. Rev. 2020, 120, 13087–13133; 2. Lo, Feng et al., Nat. Chem. 2020, 12, 90–97; 3. Feng et al., J. Am. Chem. Soc. 2018, 140, 2363–2372; 4. Feng et al., Matter, 2019, 1, 156–167; 5. Feng et al., Matter, 2020, 2, 988–999; 6. Feng et al., Chem, 2019, 5, 1265–1274; 7. Feng et al., Chem, 2020, 6, 460–471; 8. Feng et al., J. Am. Chem. Soc., 2020, 142, 3069–3076; 9. Feng et al., J. Am. Chem. Soc. 2019, 141, 14524–14529; 10. Feng et al., in preparation.

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## Tue, 15 17:00 - 19:00

Poster session

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Tue-RT-01

Data Analysis for Process Control of Highly Monodispersed sub-10 nm ZrO<sub>2</sub> Nanocrystals

**Amy Stabell (astabell@pixelligent.com)<sup>1</sup>, Sheri Johnson (sjohnson@pixelligent.com)<sup>1</sup>, Ulf Nobbmann (ulf.nobbmann@malvern.com)<sup>2</sup>, Ana Morfesis (ana.morfesis@malvern.com)<sup>2</sup>**

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As manufacturing of nanomaterials becomes more mature, one direction of advancement will be towards the production of small nanoparticles (<10 nm) with tight size distribution (low polydispersity). Such nanomaterials are being achieved today by Pixelligent Technologies, which produces monodisperse colloidal zirconium dioxide particles 4-6 nm spherical inorganic cores with organic capping agents. These materials are finding commercial success in OLED and HD display, OLED and LED lighting, and optical coating and film applications. The particle size distribution quality parameters of sub-10 nm capped ZrO<sub>2</sub> particles and NIST gold standard particles have been compared by Dynamic Light Scattering (DLS). Z-average, PDI, Intensity, Volume, and Dv(0.9999) have been measured and indicate that very high quality reproducible sub-10 nm ZrO<sub>2</sub> nanocrystals require the use of multiple narrow mode data analysis to resolve changes to dispersion quality. The data is presented from production lots over multiple years. The measurement of such small sizes and tight size distributions can be a challenge for many commercial DLS instruments. Malvern's Zetasizer Nano-S DLS instrument can measure the particle size of next generation nanomaterials such as Pixelligent's ZrO material. Herein we discuss the measurement of these nanocrystals in non-aqueous solvents by the Zetasizer Nano-S, which not only shows the high quality of the material but also of the measurement system.

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Tue-RT-02

## Improvement of montmorillonite surface properties for pollutants adsorption

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Montmorillonite (Mt) is an eco-friendly clay mineral commonly used as adsorbent material of several kinds of pollutants. Despite its adequate adsorption properties for cationic pollutants, abundance and low cost, this mineral has presented limitations from a technological point of view due to its low flocculation degree. Besides, its negative charge density prevents the adsorption of anionic pollutants, decreasing its efficiency as adsorbent material. Surface modifications of this raw material result crucial to extend its technological applications. In this sense, modifications of surface charge by surfactant loading have been performed, while magnetic response have been conferred by the surface grown of magnetite nanoparticles, which allow an operator-free sludge manipulation with external magnetic field application. In this work, hexadecyl trimethyl ammonium bromide molecules have been incorporated by cationic exchange reactions at several percentages of the cationic exchange capacity of montmorillonite (CEC). The resultant hybrids have been used as supporting materials for magnetite nanoparticles. The surfactant incorporation produced changes on the adsorbents' electric surface charge properties, determined by zeta potential measurements, and its inclusion has been followed by the modification of the basal space determined by X-ray diffractograms (001 diffraction peak). Magnetic properties have been analyzed using a Vibrating Sample Magnetometer. This technic allowed determine the saturation magnetization of the magnetic hybrids, a relevant parameter to be considered for the technological application of adsorbent materials. Besides, Mössbauer Spectroscopy permitted the study of the iron oxide phases and the total magnetite content of each sample. The results have shown that, on the one hand, the hybrid with surfactant load corresponding with the inclusion at 100% of the CEC (O100MtMag) presented the highest magnetization saturation value among the other samples ( $20.3 \pm 0.5 \text{ Am}^2 \text{ Kg}^{-1}$ ). In addition, this material presented an As(V) removal efficiency of  $7.8 \pm 0.8 \text{ mg g}^{-1}$  and adequate performance after two adsorption cycles. On the other hand, the synthesis of the magnetic composite on raw Mt (MtMag) was relatively simple and the adsorbent showed a relevant adsorption capacity of As(V) ( $9 \pm 1 \text{ mg g}^{-1}$ ) and Bovine Serum Albumin protein ( $4.3 \cdot 10^{-6} \pm 0.4 \cdot 10^{-6} \text{ mol g}^{-1}$ ). Both materials have shown the possibility to be attracted from an aqueous matrix by an external magnetic field application.

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Tue-RT-03

## BiO/CNT heterostructure with enhanced performance towards electrocatalytic nitrogen reduction reaction

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POSTECH(Pohang University of Science and Technology)

Ammonia has great attention because it is a raw material for artificial fertilizers and fine chemicals. Recent years, it is becoming more and more important as the possibility of using it as a hydrogen storage and carrier. Electrochemical nitrogen reduction reaction has received many attentions as eco-friendly method of producing ammonia. Therefore, increasing activity and selectivity of electrochemical nitrogen reduction catalysts are important. In this study, an electrocatalyst composed of carbon nanotube (CNT) and bismuth oxide was developed. CNT, which is synthesized by annealing melamine, is expected to increase activity. Furthermore, bismuth oxide, deposited on the CNT by electrodeposition, is expected to increase selectivity because previous calculation result shows its 6p orbital helps nitrogen adsorption. The synthesized nitrogen reduction reaction catalyst has high selectivity and high productivity.

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Tue-RT-04

## Phosphorus Removal from Recirculating Aquaculture System Water

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Recirculating aquaculture systems (RAS) have grown in popularity in recent years due to their potential to provide a high-quality protein source in a contained environment. With increased production comes the need for RAS wastewater treatment to remove waste products such as phosphorus. Discharged phosphorus can contribute to algae blooms in surrounding water bodies, harming other aquatic life in the area. Additionally, there is potential to harvest the wasted phosphorus for use as a fertilizer and combat nutrient scarcity. This study investigates a phosphorus sorbent made by Phospholutions for its applicability in RAS use under fresh and simulated seawater conditions. Batch tests were performed to investigate the behavior of the sorbent in both kinetic and equilibrium experiments. These showed that the sorbent does not have a high selectivity towards phosphorus, as more phosphorus was removed under fresh water conditions than simulated seawater conditions. The controlling adsorption mechanism for the rate of binding was investigated by modeling kinetic data using five different models: the first and second order rate models, the Elovich model, the Weber-Morris model, and the intraparticle diffusion model. It was found that the sole limiting rate step is intraparticle diffusion. Adsorption isotherms were also investigated, and it was found that the Freundlich isotherm fit the data better than the Langmuir isotherm, though both were suited to model the data. Column studies were performed in order to test the sorbent's performance in a plug-flow system, and four different models including the Adams-Bohart, the Clark, the Thomas, and the Yoon-Nelson models are currently being investigated for their suitability for modeling the breakthrough curve data. The mass transfer zone and dynamic adsorption capacity for each column test will also be analyzed. These models will provide an understanding of the sorbent's behavior under changing salinity levels, the potential for the sorbent to be used for harvesting phosphorus from water, and the potential for serving as a part of the RAS wastewater treatment process.

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Tue-RT-05

## Exploring the relationship between temperature activated hydrogen-deuterium exchange and protein stability with SANS

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Hydrogen deuterium exchange, (HDX) is of increasing interest for characterization of protein dynamics in solution. In particular, the fast development of HDX mass spectrometry (HDX-MS) has helped to provide insight into protein flexibility and conformational changes by investigating the exchange of amide hydrogens with deuterium. Due to the very large difference of the neutron scattering cross section between H and D, neutron scattering techniques, and particularly small angle neutron scattering (SANS), offer a sensitive technique to study the HDX in solution. Unlike HDX-MS, SANS allows for the continual measurement of HDX over time and is a non-invasive way to probe the HDX in solution. Even though SANS does not have the sensitivity to study the sequence specific exchange kinetics, it could provide the spatial distribution information of exchangeable protons in a protein, as a function of the exchange time. By using SANS with elevated temperature conditions, we probed the HDX of globular proteins, such as bovine serum albumin, (BSA) with aim of making discovery transferrable to pharmaceutical globular proteins, such as monoclonal antibodies. The detailed analysis of the SANS data will be discussed. The exchange kinetics and the spatial distribution of exchangeable protons are determined using SANS. Also, the effect of the sample conditions, such as the temperature and buffer conditions, on the HDX will be presented.

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Tue-RT-06

Ultra-thin phthalocyanine layer deposition on TiO<sub>2</sub> nanoparticles to simultaneously enhance charge separation and light absorption in photocatalysts

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In the present study, 2-nm copper phthalocyanine (CuPc) layer was deposited on TiO<sub>2</sub> nanoparticles by a facile solution reaction. As-prepared photocatalyst composites exhibited the standout hydrogen generation ability under visible-light irradiation. An ultra-thin CuPc layer on the surface of TiO<sub>2</sub> harvested visible-light, as well as facilitated the charge migration at the interfaces. This enhancement led to the high AQY of 1.48 % at 680 nm. In addition, the CuPc/TiO<sub>2</sub> composite has been used to demonstrate high durability through multiple consecutive hydrogen generation. The enhanced light absorption and charge transfer were investigated by DRS and TRPL, respectively. Under the visible-light irradiation, the photoexcitation occurs only in CuPc and the electrons are transferred to TiO<sub>2</sub>. These electrons can be securely involved in the surface reaction, avoiding internal recombination. This study suggests that the ultra-thin CuPc layer greatly enhances the hydrogen evolution activity of TiO<sub>2</sub> photocatalyst.

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Tue-RT-07

Biomimetic Electrocatalysts of metal-doped NiP for Efficient Water Splitting

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The design of efficient nanostructured electrocatalysts is highly desirable for promoting the hydrogen/oxygen evolution reactions (HER/OER), which are key processes of ecofriendly H<sub>2</sub> production in water splitting systems. In this study, we present novel biomimetic hierarchical nanocoral reef materials as efficient and durable electrocatalysts for alkaline water splitting. Our nanocoral reef catalyst has a unique structure consisting of Ni(Co,Fe)P nanosheet (NS) algae and WO<sub>x</sub> nanowire (NW) corals. The WO<sub>x</sub> NW corals effectively transport charges (e<sup>-</sup>/h<sup>+</sup>) to the Ni(Co,Fe)P NS algae through a 1D directional structure. The ultrathin 2D Ni(Co,Fe)P NS algae grown on the WO<sub>x</sub> NW corals provide an abundance of active sites for splitting water molecules into H<sub>2</sub> and O<sub>2</sub>. As a result, our hierarchical 2D-NS/1D-NW-structured NiCoP-WO<sub>x</sub> (HER) and NiFeP-WO<sub>x</sub> (OER) catalysts demonstrate excellent activities, requiring low overpotentials of 49 and 270 mV, respectively, to generate a current density of 10 mA/cm<sup>2</sup>. Additionally, they exhibit high electrochemical stability for over 50 h in 1 M KOH. In addition, the overall water splitting (OWS) system of NiCoP-WO<sub>x</sub> (HER)/NiFeP-WO<sub>x</sub> (OER) can provide a current density of 10 mA/cm<sup>2</sup> at a cell voltage of 1.51 V, which is outstandingly low among other reported transition metal phosphide catalysts. The biomimetic engineering presented in the current study provides not only efficient electrocatalysts but also a promising, useful strategy to develop functional 1D/2D hierarchical materials for advanced energy applications.

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Tue-RT-08

Enhanced Visible Light Photocatalytic Activity of g-C<sub>3</sub>N<sub>4</sub> by Using Heterojunction and Electron Mediator

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When ZnO and g-C<sub>3</sub>N<sub>4</sub> are in intimate contact with each other, a heterojunction structure forms on the interface. Heterojunction helps not only efficient separation of charge carriers but also maintenance of their strong redox abilities, simultaneously. The enhanced separation of electron hole pairs increased

photocatalytic activity and the photocatalytic activity further increased by using an electron mediator on the interface of these materials under visible light irradiation.

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Tue-RT-09

## Topological Defect Dynamics in Curved Colloidal Crystals

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Colloidal crystal assembly on curved surfaces is important to numerous natural and technologically important materials without flat interfaces. Crystallization and assembly of ordered structures on curved surfaces present a number of unique issues connected to geometric frustration and topological defects. While the thermodynamics and kinetics of defects in crystals are well understood on flat surfaces, there are many open fundamental questions about the connections between interactions, dynamics, and microstructure leading to crystallization on curved surfaces. In this work, we aim to understand how curvature perturbs and introduces qualitatively new aspects in the stability and dynamics of topological defects in curved crystals. We use Brownian Dynamic simulations to investigate a model system of colloidal particles at a drop surface with tunable dipolar interactions mediated by high frequency AC electric fields. We systematically vary crystal size, surface curvature, and field amplitude and characterize microstructures using unique order parameters adapted to curved surfaces. Microstructure evolution in order parameter space is quantified by low dimensional Smoluchowski equations, producing diffusivity and energy landscapes for each condition investigated. Our results show important qualitative differences in the assembly of crystals as curvature increases. The resulting quantitative dynamic models are being used in ongoing research to enable formal design, control, and optimization of dynamic assembly processes towards desired target structures.

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Tue-RT-10

Thermochromic Fibers Via Electrospinning and In Situ Phase Separation

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Cholesteryl ester liquid crystals are a class of unique soft materials with thermochromic properties arising from their helical structure with a temperature-dependent pitch length. Near the mesophase transition temperature, the liquid crystal first reflects blue light ( $\lambda = 450$  nm) at relatively short pitch lengths. As the temperature decreases, the wavelength reflected shifts to the red end of the spectrum ( $\lambda = 760$  nm) due to the increase in pitch length. Such materials have been used in thermal mapping and analysis in medical, industrial, and engineering applications. Electrospinning is a useful approach to incorporate such functional additives into fibers. In this work, we aim to achieve thermochromic fibers in a single-step, single nozzle electrospinning process using solvent induced phase separation. Specifically, we blend the liquid crystal with spinnable polymer solutions (one-phase). During the fiber spinning process, as the solvent evaporates and the polymer concentration increases, phase separation of the liquid crystal will occur by spinodal decomposition or nucleation and growth process. Three polymer systems were examined with chloroform as the solvent: polystyrene (PS), polyethylene oxide (PEO), and polycaprolactone (PCL). The fibers were analyzed using polarized light microscopy (PLM) on a temperature-controlled stage. All of the blend systems formed fibers with fiber diameters  $\sim 15$ -30 microns depending on the polymer. Liquid crystal loadings (mass of LC/(mass of LC + mass of polymer)) between 60 and 97% could be achieved. These results indicate the liquid crystal did not disrupt the polymer entanglement required for fiber formation. Interestingly, the liquid crystal containing fibers spun from PEO and PCL produced thermochromic fibers with a core-shell structure (liquid crystal core/polymer shell) whereas the fibers spun from PS were not

thermochromic. Thus, polymer-liquid crystal compatibility is an important consideration to achieve phase separation and thermochromic fibers.

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Tue-RT-11

Solution-based electroless deposition of gold electrodes on cotton fabrics for wearable heaters and supercapacitors

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Cotton fabrics have received substantial attention as promising substrates for wearable electronics due to their large surface area and flexibility. Although the majority of studies have been devoted to fabricating electrodes utilizing cotton, simple fabrication process of highly-conductive metal electrodes inserted in fabrics has yet to be achieved. Herein, we demonstrate the facile, electroless deposition of Au electrodes inserted in cotton by a seed-mediated, metal-growth strategy. The sequencable deposition of Au was achieved by the autocatalytic reduction of Au ions with Au nanoparticle seeds which were electrostatically deposited on cotton. The deposition efficiency was significantly improved by effectively removing physisorbed silane molecules on amine-modified cotton. The design was applied to various E-textiles, i.e, wearable heaters, and energy storage devices. The cotton-based, wearable heater exhibited excellent Joule heating properties up to 120 °C at 1 V within only 2 s. The wearable supercapacitor with cathode-deposited MnO<sub>2</sub> also demonstrated a promising, pseudo-capacitive performance of 167.55 F g<sup>-1</sup> at 0.3 A g<sup>-1</sup>.

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Tue-RT-12

Mo doping on Ni<sub>2</sub>P nanowire promote hydrogen evolution reaction in alkaline condition.

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POSTECH

NiMoP are synthesized through simple two process: cation exchange and phosphorization. ZnO nanowire is growing up at Ni Foam by hydrothermal method. NiMoO nanowire are formed by cation exchange process of ZnO nanowire. NiMoP are synthesized through furnace at 450 °C for 2 hours. NiMoP maintain nanowire structure during phosphorization. Many kinds of other element doping have also been tried. Mo was the best dopants on Ni<sub>2</sub>P. Transition metal based NiMoP is cheap and sustainable electrocatalyst. This material shows high hydrogen evolution activity in alkaline media.

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Tue-RT-13

Highly transparent electrodes based on the web-like networked AgNW film by controlling dewetting phenomena

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We report the web-like structured silver nanowires (AgNW) bundle networks by dewetting liquid thin films to produce highly transparent electrodes. Such AgNW-web structures were formed by dewetting the thin films of AgNW suspension in a mixture of isopropyl alcohol (IPA) and ethylene glycol (EG) on hydrophobized coating substrates by using meniscus-dragging deposition (MDD) technique. Length and diameter of the AgNW bundles and the open space area in the AgNW-web network can be finely controlled by varying contact angle, EG concentration, and coating parameters of the MDD process. The formation

of such AgNW-web structures was well analyzed by calculating dewetting and drying times of the liquid thin films. The transparent thin films with AgNW-web structures exhibit the superior optical and electrical properties compared to the electrodes with random network of AgNW, which is well described by the high ratio of DC to optical conductivity and percolation theory in a two-dimensional matrix model. Our simple coating technique enables the deposition of AgNW-web network with high optical transparency, flexibility, and stretchability directly on rigid or plastic substrates.

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Tue-RT-14

Water droplet-based triboelectric nanogenerator with controllable nanowire structure

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POSTECH

Triboelectric nanogenerators (TEGs) is considered as a sustainable power source that convert mechanical energy into electric energy. Water droplet-based TEGs (WD-TEGs) harvest energy from triboelectrification between water and solid. This work introduces controllable surface with nanowire structure as a triboelectrification layer. WD-TEGs are simple structures in which layers of insulators are placed directly in contact with droplets on the electrodes. We prepared cobalt-PDMS layer with response to magnetic field and high electron-withdrawing capability as an insulator layer. Low surface energy and nanowire structure improve hydrophobicity to get stable electrical output. Open-circuit voltage was measured for structures with bare PDMS TENG and cobalt-PDMS nanowire TENG to compare TENG performance. This TENG shows a maximal open-circuit voltage of 2.2 V per a 0.5ml droplet. This work provides a method for optimizing nanowire structure for controllable performance of WD-TENG.

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Tue-RT-15

pH-stimuli viscoelastic gel based on betaine-based complexes as viscosifier for hydraulic fracturing fluid

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Petroleum and natural gas production through the unconventional reservoir rapidly increase in recent years to achieve more than 50 percent of the total production in the United States. Production from the unconventional reservoir now mostly relies on the horizontal drilling and hydraulic fracturing technique. The hydraulic fracturing process involves injecting fracturing fluid with proppant to the reservoir to open the cracks and failures. The critical key for improving the production by fracturing relies on the proppant transport to the cracks following the fluid to keep the cracks open and let the natural gas and oil flow freely during the pumping back process. Thus, one of the most important factors that impact the fracturing process is the viscosifier of the fracturing fluid, which drives the proppant to the cracks. Herein, we reported a novel viscosifier based on a binary complex including pH-stimuli viscosity. The novel viscosifier is a complexation of a long chain zwitterionic type surfactant and diethylenetriamine. At a two wt.% of viscosifier in fluid, the fluid displayed a zero viscosity from 9 Pas to 200 Pas with different pH. Moreover, the viscosity measurement of the fluid with varying concentrations of salt, different temperature, and pH reversibility was carried out. To know the potential application of proppant transportation, the sand settling test was performed at both room temperature and 90oC. Compared to the polyacrylamide solution, the novel viscosifier system displayed better sand stability at room temperature and similar performance at 90 oC. Compared to the conventional fluid, which needed to be broken by breakers without reusability. Adjusting the pH back and forward from 4 to 8 helps deform and rebuild the gel's network that improves the reusability of the fluid.

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Tue-RT-16

## Adsorption of Phenols on Surfactant-Modified Ion Exchange Resins

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Various adsorption techniques can be used to remove phenolic compounds from wastewater. In this work, the adsorption of 4-chlorophenol and phenol on surfactant-modified ion exchange resins were studied. Ion exchange resins were treated with oppositely-charge surfactant, and the modified resins were brought into contact with solutions containing one of the phenolic compounds. Adsorption isotherms were calculated from concentration measurements and then modeled with the Langmuir and Freundlich equations. Results are compared with those from other adsorption techniques including surfactant-modified clays.

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Tue-RT-17

## Emulsion systems for encapsulation of iron for food fortification

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Iron is a vital micronutrient in human nutrition. Prevalence of the diseases caused by iron deficiency such as anaemia emphasizes the need to consider strategies for the fortification of food products with this micronutrient. Among the strategies that received attention for food fortification during recent years, emulsion systems show promising potential for delivery of iron as they can contribute to masking the undesired metallic taste of most iron compounds, and reduce their interaction with other food ingredients such as polyphenols that limit iron bioavailability. Emulsions stabilized with polysaccharides and protein-based emulsifiers can be used for encapsulation of iron and enhance delivery and uptake during digestion based on variations in environmental factors such as pH, presence of bile salts, and enzymes. The application of emulsion systems for enhanced delivery of iron through processed foods is a novel alternative technology for addressing the pressing public health challenge of iron deficiency.

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Tue-RT-18

## Extensional Rheology of Colloid-Polymer Mixtures with Depletion Attractions

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Extensional deformation of particle-laden complex fluids is ubiquitous in industrial processes such as fiber-spinning, extrusion, and injection molding. Prior studies in a mixture of colloids and non-adsorbing polymer, a model for interparticle attractions, revealed that polymer size and dispersity can affect the shear rheology of colloid-polymer mixtures. Here, we study the extensional rheology of depletion system using a dripping-onto-substrate (DoS) protocol. In this protocol, we characterize the capillary-driven thinning and pinch-off dynamics of liquid bridge neck formed between a nozzle and a sessile drop. From the filament-thinning dynamics, the extensional viscosity and suspension relaxation time can be obtained. We use a model colloidal system of methacrylate copolymer particles with dimethylacrylamide copolymer brushes. The particles are suspended in refractive index and density matched glycerol-water mixtures with added NaCl for electrostatic screening to achieve nearly hard-sphere interactions. Depletion attractions between the colloids are introduced by adding polyacrylamide at different polymer concentration to control the attraction strength. We compare the extensional properties of depletion suspensions with different depletant size and dispersity at similar normalized concentration. This will allow us to explore the role of polymer size

distribution in the extensional rheology of colloid-polymer mixtures, which represent simplified models of suspensions used in practical applications.

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Tue-RT-19

## The interesting phenomena of the "Coffee Stain Effect"

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Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati-781039, India. When a droplet containing solute particles evaporate, the droplet eventually disappears but leaves behind a stain on the surface, which is termed as "Coffee Ring." These coffee rings are nothing but the deposition occurring on the pinned contact line during evaporation. When evaporated liquid from the droplet periphery is replenished by the flow of bulk liquid from its central location; along with the liquid, solute particles also travel toward the contact line and settle there. Based on the interactions amongst solute, solvent, and substrate, structures like faint coffee ring, coffee ring, irregular disk-like deposition, and uniform disk-like deposition can be generated. Analytically, from the factors like total time of deposition ( $t_d$ ) and the geometric shape of the droplet ( $L_c = \text{Initial footprint diameter/Height}$ ), one can predict the evaporative deposition patterns from a proposed deposition map. Moreover, predictive uniform disk-like deposition can be transformed into a coffee ring by appropriate tuning of the Marangoni flow.

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Tue-RT-20

## Nanoparticle dynamics in semidilute polymer solutions: rings versus linear chains

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Understanding the dynamics of nanoparticles in polymer solutions is immensely important for their applications in targeted drug delivery, enhanced oil recovery, and polymer composite processing. The dynamics of nanoparticles are well described by the generalized Stokes-Einstein (GSE) relation, when the nanoparticles are much larger than the polymers. However, deviation from the GSE is observed when the nanoparticle's size is comparable to the length scale in polymer solutions. We investigate the microscopic origin of this anomalous behavior using multiparticle collision dynamics (MPCD) simulations, an advanced algorithm for rigorously modeling solvent-mediated hydrodynamic interactions in coarse-grained, mesoscale simulations. We apply hybrid MD-MPCD simulations to study dynamics of nanoparticles in semidilute solutions of ring and linear polymers in the presence of many-body hydrodynamic interactions. The dynamics of the monomers, the polymer centers-of-mass, and the nanoparticles coincide for these two architectures for solutions of the same monomer concentration. The long-time diffusivities of the nanoparticles follow the predictions of a polymer coupling theory, [L.-H. Cai, S. Panyukov, and M. Rubinstein, *Macromolecules*, 44, 7853–7863 (2011)] suggesting that nanoparticle dynamics are coupled to segmental relaxations of both ring and linear polymer architectures. At intermediate time scales, the nanoparticle dynamics are characterized by subdiffusive exponents, which markedly deviate from coupling theory and closely follow those of the polymers. Instead, the nanoparticle dynamics are strongly coupled to the polymer center-of-mass motions for both architectures rather than their segmental dynamics. We show that this disagreement is due to the tight coupling of the translational motions of the nanoparticle and polymer centers-of-masses, which is not accounted for in current theories. We also investigate the influence of polymer morphology on this coupling behavior. Surprisingly, we find that the dynamic coupling observed

in ring and linear polymer chains solutions is remarkably similar, even in systems with large fractions of ring concatenation defects.

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Tue-RT-21

### *In vivo* pharmacokinetics of microbubbles: A direct blood characterization study

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Blood–brain barrier disruption (BBBD) induced by ultrasound-stimulated microbubbles (MBs) represents an attractive intracerebral delivery approach. Variations in MB concentration, gas composition, and size distribution introduce high variability in BBBD effects. To reduce this variability, previously we proposed to use microbubble volume dose (MVD) as a unified dose metric. To study the role of MB on BBBD efficiency, it is necessary to study the *in vivo* pharmacokinetics of MB to determine the gas volume fraction ( $\phi_{MB}$ ) and half-life ( $t_{1/2}$ ) for different MBs and MVDs. *In vivo* studies have measured the pharmacokinetics of MBs using indirect methods such as ultrasound contrast, however, the purpose of pharmacokinetics is to measure directly in blood the concentration of drugs. Hence, the goal of this work was to demonstrate the feasibility to measure directly the *in vivo* pharmacokinetics of different MB sizes in blood. 2–5  $\mu\text{m}$  DiO-labeled microbubbles (DSPC: PEG40S and PFB gas) were used. The  $\phi_{MB}$  value was calculated plotting MB concentration vs MB volume and integrating the area under the curve. For *in vivo* pharmacokinetic studies, three Wistar rats (300–400 g) were injected with a fixed MVD = 5  $\mu\text{L}/\text{Kg}$  of each MB size via jugular vein catheter. Then, 150  $\mu\text{L}$  of blood were collected at 1–5 and 10 min after MVD administration. Blood samples were analyzed using a hemocytometer and MB concentration was obtained by image analysis. Pharmacokinetics curves and  $t_{1/2}$  were obtained plotting MB concentration vs time. Isolated MBs obtained had median diameters of 2, 3, and 4.6  $\mu\text{m}$ . The corresponding  $\phi_{MB}$  was  $116 \pm 22$ ,  $341 \pm 75$ , and  $386 \pm 68$   $\mu\text{L}/\text{mL}$  (Figure 1A). Intravenous injection of MVD = 5  $\mu\text{L}/\text{Kg}$  showed first-order elimination kinetics (Fig. 1B), the exponential decay curves demonstrate that MBs were eliminated from the circulation 10 min after administration. Also, we showed that  $t_{1/2}$  increases for 3 and 4.6  $\mu\text{m}$  ( $1.5$  and  $1.6 \pm 0.1$  min) compared with 2  $\mu\text{m}$  ( $0.9 \pm 0.1$  min) (Fig. 1C). These results suggest that by increasing the MVD, the persistence of MBs in circulation also could be increased. In conclusion, we present the first novel direct MB pharmacokinetics study that allows us to estimate accurately the MBs persistence in an *in vivo* circulation and establish the bases to study the MVD metric in BBBD efficiency studies.

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Tue-RT-22

### Surface characterization of outer membrane vesicles, naturally-produced colloids, from bacterial biofilms

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Outer membrane vesicles (OMVs) are nano-sized lipid envelopes produced from the outer membranes of Gram-negative bacteria. These natural colloids may contain proteins, lipopolysaccharide, enzymes, DNA, and RNA. Previous OMV studies by our research group have observed OMV aggregation in atomic force microscopy images of biofilms and isolated OMVs of the plant-health-promoting bacterium, *Pseudomonas chlororaphis* O6 (*PcO6*). In *Myxococcus xanthus* and *Xyella fastidiosa*, OMV aggregation appears to serve a structural role, allowing OMVs to create scaffolds to form and support the biofilm matrix. These studies aimed to characterize OMV surface properties and how these properties affect OMV and cell aggregation in *PcO6* biofilms. *PcO6* biofilm cells and OMVs isolated from *PcO6* biofilms were suspended in buffers at pH values of 6.0, 7.0, and 8.0. Surface charges at these pH values were measured with zeta potential. Cell and OMV aggregation were quantified with dynamic light scattering and qualitatively assessed with atomic



force microscopy. These results show the importance of OMV surface chemistry in biofilm formation by *PcO6*.

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Tue-RT-23

### The Kitchen Pot Thickens, Drop by Drop

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Many food formulations contain sugars and polysaccharides as thickeners that influence flow behavior, stability, processability, texture, and mouthfeel. Interfacial and rheological properties of key ingredients including polysaccharides influence production and processing of various foods, as well as the consumer perception and bioprocessing that begin with every bite. Typically, chefs, formulators and regular cooks in kitchens judge stickiness, stringiness, spinnability, ropiness, and flowability by dripping a sauce or a mixture from a ladle, stretching a liquid bridge between finger and thumb, or by dispensing from a nozzle/bottle onto a substrate. Stream-wise velocity gradients associated with extensional flows spontaneously arise during these operations associated with dripping, dispensing or stretching liquid bridges. In spite of great advances in quantitative characterization of shear rheology response, elucidating, measuring and harnessing the extensional rheology, there remain well-known challenges associated with robust, reliable and affordable measurement of extensional rheology response. In this contribution, we present a range of experiments that emulate the kitchen flows and survey the influence of typical thickeners by quantitative studies relying on visualization and analysis of pinching flows encountered in dripping, dispensing, and stretched liquid bridges. In addition to dripping, we rely on dripping-onto-substrate (DoS) rheometry protocols that we developed that rely on analysis of capillary-driven thinning and break-up of liquid necks created by releasing a finite volume of fluid onto a substrate. Additionally, we devise a portable stretched liquid bridge that emulates the commercially available capillary break-up extensional rheometer (CaBER). Finally, we describe our efforts to experimentally examine and characterize the flow behavior of sugar and polysaccharide-based recipes considered desirable by chefs and sweet makers.

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Tue-RT-24

### Structure and Phase Behavior of Polyelectrolyte–Nanoparticle Complexes

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Aqueous mixtures of oppositely charged polyelectrolytes (PE) and nanoparticles (NP) self-assemble into dense complexes. This self-assembly forms the basis of diverse phenomena ranging from flocculant action in water treatment, where the PE-NP flocs phase separate and sediment, to DNA compaction around histone proteins into chromatin. Factors such as the PE concentration, length, architecture and concentrations; NP charge, morphology and concentrations; and solution conditions (pH and ionic strength) play key roles in directing these PE-NP assemblies. In this presentation, we will delineate fundamental investigations into the phase behavior and structure of polyelectrolyte-NP assemblies using small angle X-ray scattering, turbidimetry and rheology with systematic variation of PE sizes and flexibility, NP sizes, and a wide range of concentrations of both components. Trends in interparticle spacings correlations as well as fractal dimensions of assemblies with varying PE and NP concentrations will be discussed, presenting a comprehensive narrative of the hierarchical structure of PE-NP self-assemblies. A general collapse of these trends on a master curve will be highlighted, providing universal guidelines for tailoring the microstructure of these assemblies.

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Tue-RT-25

## Exploring The Nanoarchitecture and Rheological Properties of Zwitterionic Surfactant Based pH-tunable Dynamic Binary Complex

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Supramolecular chemistry entails a fascinating area of materials science wherein the constituents are held together by non-covalent interactions. This enables them to be sensitive to an application of an external stimuli like pH, temperature, salinity, light, etc. Surfactants in particular have potential to be used in this respect. There are several surfactants commercially available and several more are developed each year. Herein, we report a novel long-chained zwitterionic surfactant synthesized by a facile condensation reaction. NMR analysis was done to analyze the reaction taking place. This surfactant has the potential to form pH-tunable dynamic binary complexes upon dissolution with a complexing agent. Several studies were conducted in order to explore the corresponding nanoscale architecture that spans the solution. The viscosity and viscoelastic properties of the resulting solutions were measured as a means to characterize the changes in properties with pH. The effect of temperature on the rheological properties were also taken into consideration. Furthermore, to comprehend the microstructure that actually contributes to the unique properties, a microscopic analysis was also done. In conclusion, the use of such dynamic binary complexes may have several important applications. Response to a stimulus opens up the potential for careful shaping and structuring of the gels in applications like 3D printing and drug delivery. They may also find use in areas such as nanoscale electronics and robotics. It is the need of the hour to better comprehend the assembly of these tunable soft materials so that they may be effectively applied in various fields.

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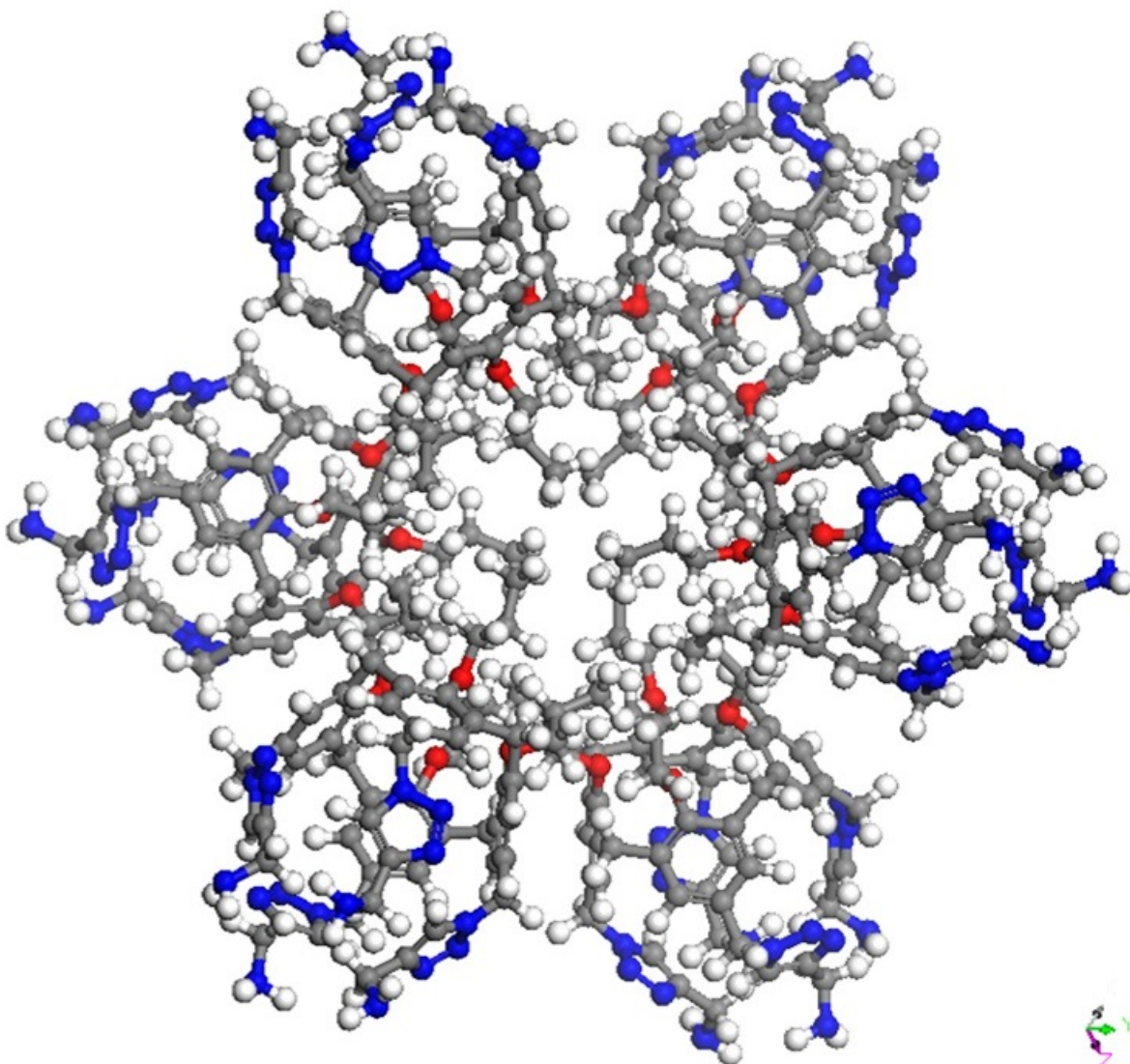
Tue-RT-26

## Platonic Micelles: Exploration of Micelle Stability at Different Discrete Aggregation Numbers

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DEVCOM Soldier Center, Natick, MA

Spherical micelles of discrete aggregation numbers, called Platonic micelles, have been proposed in the literature by the Sakurai group for specific combination of tail length and head volume of calix(n)arene amphiphiles. The selection of the preferred aggregation number is related with the formation of a closed packed configuration of the headgroups in an ideal sphere, as described in the Tammes problem. In this work, we explore the role of the tail and head groups in the structural properties of the micelle and in the selection of the discrete aggregation number. We modeled the calix[4]arene-based micelle with a primary amine headgroup and a propyl tail (PACaL3) with aggregation numbers 4, 5, 6, 7 and 8 using density functional theory. We consider a closed packed configuration for the headgroups and modeled the PACaL3 micelle in a polyhedral like structure. We found that the arrangement of the headgroup can determine the stability, structure and specific aggregation number that spherical micelles adopt. A combination of binding energy and structural parameters calculated for PACaL3 suggest that this micelle has a preferred aggregation number of 6, but the energy parameters calculated suggest that the formation of spherical micelles with aggregation numbers 5 and 7 may also be possible.



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Tue-RT-27

Phase Morphology of Conjugated Polymer Blends with an Elastomeric Tri-block Matrix.

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University of Washington

Blends of conjugated and commodity polymers allow for a refinable balance between the conjugated polymer's electronic properties and the commodity polymer's variable physical properties. This balance is vital in organic electronics such as electronic skin or haptics, which require increased flexibility and durability, while still maintaining high electronic performance. Understanding the fundamental interactions between conjugated polymers and commodity matrix polymers is essential for designing and optimizing organic electronic devices. Previous research using conjugated polymer blends has shown a strong relationship between the morphology of the blends, with consideration of degree of phase separation and degree of crystallization, and the resulting electronic properties. Using X-ray scattering, we examine the phase separated structure of an elastomeric tri-block matrix polymer as well as changes in the spacing and structure that occur with the addition of a conjugated polymer. When these films were analyzed, a significant shift in the characteristic peaks of the tri-block was observed, indicating that the addition of the conjugated polymer forced the swelling of the tri-block's phase-separated lattice structure. Experiments are being conducted to determine the extent of swelling and the final conformation of these films. The goal of

this work is to develop a schematic for the phase separation of elastomeric tri-block based polymer blends, focusing on the morphological and electronic impact of the addition of conjugated polymers on the existing structure of elastomeric tri-blocks.

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Tue-RT-28

### Phase Behavior of Colloids with Polymer-Mediated Attractions

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University of Houston, Department of Chemical and Biomolecular Engineering

Tailoring the interaction between colloidal particles and polymers in solution can result in different types of attractions between particles, thereby affecting phase behavior. Polymers that adsorb to the particle surface create physical bridges between the particles, which can drive the formation of clusters or flocs. Here, we investigate the phase behavior of a colloid-polymer mixture with attractive bridging interactions in which the strength of the polymer adsorption can be tuned through the pH of the solution. Bridging interactions were induced between trifluoromethyl methacrylate-co-tert-butyl methacrylate (TtMA) particles of diameter 1.7  $\mu\text{m}$  by introducing poly(acrylic acid) (PAA) of molecular weight 450 kDa to the system. The bridging attraction is likely driven by hydrogen bonding of PAA with either or both of the steric and electrostatic stabilizers on the surface of the particles. The steric stabilizer on the particles, poly(vinylpyrrolidone), forms strong hydrogen bonds with PAA at low pH. Likewise, the electrostatic stabilizer, dimethylacrylamide-co-sulfopropyl acrylamide, can strongly hydrogen bond to PAA in acidic conditions in the presence of a co-polymer. The formation of hydrogen bonds between TtMA particles and PAA decrease as pH is increased. The structure and dynamics of the TtMA particles as a function of solution pH and polymer concentration were determined using confocal microscopy for particle volume fractions  $\Phi = 0.15$  and  $0.40$  and polymer concentrations (relative to the overlap concentration  $c^*$ ) of  $0$ ,  $0.7$ , and  $2.4 \text{ mg mL}^{-1}$ . We find that the particles form flocs and networks at low pH but largely remain dispersed at high pH. By quantifying the dynamics (MSD & van Hove correlation) and structure ( $g(r)$  and NDF), we confirmed gel and fluid systems within our bridging samples. The results of this model may be useful for investigating mechanisms of flocculation as seen in processes such as wastewater treatment.

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Tue-RT-29

### Sodium Alginate Alters Protein Folding Stability and Structure

**Roger Chang (rogerc2@illinois.edu)**

Department of Chemical Engineering at University of Illinois at Urbana-Champaign

This study demonstrates that soluble sodium alginate alters the thermodynamic stability of proteins and stabilizes their unfolded states. Sodium alginate is a biocompatible polysaccharide used for drug delivery and tissue engineering applications. Although proteins are often encapsulated in sodium alginate gels, there are limited studies of the interactions between alginate and biomacromolecules or the impact on protein stability. Here, spectro-fluorometer measurements were used to test how sodium alginate affects protein folding stability. Studies focused on the model protein phosphoglycerate kinase, modified with a FRET pair. The experimental results demonstrate that soluble alginate increases in folding stability of PGK, based on increases in the melting temperature,  $T_m$ . Moreover, the stabilization depends non monotonically on the wt.% of alginate in solution. Results also show that sodium alginate prevents protein aggregation, suggesting irreversible protein-alginate interactions with the unfolded protein. These results reveal concentration dependent interactions between sodium alginate and proteins that alter protein stability and structure, thus challenging the assumed benign effects of alginate systems on biomacromolecular functions.

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Tue-RT-30

## Molecular Simulation of Poly(methacrylic acid) and Poly(acrylic acid) Adsorbed at Oil-Water Interface : Effect of Tacticity and Interface Concentration of Polymer

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The structure and interactions of polyelectrolytes adsorbed at oil-water interface determine the stability of emulsion droplets. The molecular level structural details of polyelectrolytes at oil-water interface is important to applications related to emulsion stability and for the design of separation processes based on selectivity of adsorbed films at such interfaces. The dissociation and deprotonation of Poly(acrylic acid) PAA and Poly(methacrylic acid) PMA results in anionic polyelectrolytes that are industrially important. The effect of stereo-chemistry (i.e. tacticity) of the chain on the conformations, orientations and intermolecular structure of PMA adsorbed at CCl<sub>4</sub>-water interface was studied by atomistic molecular dynamics (MD) simulation. The effect of the interface concentration on the structure of the adsorbed layer was studied for syndiotactic chains (s-PAA, s-PMA) by all-atom explicit-solvent MD simulations. 30 repeat unit oligomeric polyelectrolyte chains in un-dissociated state (i.e. uncharged) were studied in all systems. PMA adsorbs in a planar conformation at CCl<sub>4</sub>-water interface irrespective of its chain tacticity. The radius-of-gyration ( $R_g$ ) of adsorbed PMA showed that isotactic chains are more coiled as compared to syndiotactic chains. The density distribution of PMA along the direction normal to the interface shows that PMA adsorbs in an ordered conformation in agreement with experimental results [1]. The orientation of different types of bonds such as C-CH<sub>3</sub>, C=O and O-H with respect to the interface-normal was obtained. Orientation distribution curves indicate greater hydrophobicity of i-PMA and there is evidence of a greater degree of hydrophobicity of i-PMA in agreement with experimental results [2]. The hydration state of COOH was calculated in terms of H-bonds with water. The variation of the concentration of s-PMA and s-PAA up to monolayer coverage showed that both polymers undergo conformational transition with increase in interface concentration. The  $R_g$ , backbone torsion angle distribution, and the orientation distribution of different groups of the polymer indicate a change in the conformational characteristics of polymer chain, in going from a planar-ordered to a non-planar disordered structure with increase in concentration for both polymers. The variation interface coverage and thickness of adsorbed layers with concentration was calculated. Our study provides molecular level structural details of polar polymers adsorbed at oil-water interface which are otherwise difficult to determine from experiments. References: 1. Robertson, E. J.; Richmond, G. L. J. Phys. Chem. C 2014, 118(49), 28331. 2. Valley, N. A.; Robertson, E. J.; Richmond, G. L. Langmuir 2014, 30(47), 14226.

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## Wed, 16 09:00 - 11:00

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Wed-AW1-01

Acoustophoretic assembly of millimeter-scale Janus fibers

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This talk presents a method for the directed assembly of millimeter-scale Janus fibers using acoustophoresis as an assembly mechanism. An acoustic flow cell mounted to a 3D printer combines acoustophoresis and additive manufacturing in a unique approach that allows for the assembly of textured Janus fibers. A dispersion consisting of polymethylmethacrylate (PMMA) filler particles in a UV curable polymer resin is passed through an acoustically excited capillary tube. To fundamentally understand this process, we develop a suspension balance model that accounts for acoustophoresis and concentration-driven shear-induced diffusion. Once assembled, the particle-polymer dispersion is cured using UV illumination to create a polymer composite fiber with particles immobilized on one side in a Janus-like configuration. The Janus fiber is observed to modify the light transmission profile when rotated on an optical microscope stage. Tensile measurements of the fiber show that the Young's modulus of the Janus fiber

(50.5 MPa) is approximately twice that of a fiber fabricated from the polymer alone (24.7 MPa). The process we describe here could serve as a pathway for the fabrication of a variety of functional Janus fibers with possible applications to wearable textiles, soft robotics or surgical sutures.

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Wed-AW1-02

### Self-limiting Assembly of Curved Colloidal Particles

**Nabila Tanjeem (nabila.tanjeem@colorado.edu)**<sup>1</sup>, **Doug Hall (dhall@mail.pse.umass.edu)**<sup>2</sup>, **Greg Grason (grason@mail.pse.umass.edu)**<sup>2</sup>, **Ryan Hayward (Ryan.Hayward@colorado.edu)**<sup>1</sup>

<sup>1</sup> University of Colorado Boulder

<sup>2</sup> University of Massachusetts Amherst

Geometric constraints limit the self-assembly of colloidal particles when local order in the assembly fails to propagate globally. We study an example of such geometrically frustrated self-assembly and show that the equilibrium size of the assembled structures is self-limited and can be designed. In our system, plate-like particles with a preferred curvature stack due to an attractive face-to-face interaction. Achieving perfect contact between the curved particles ('curvamer') forces them to bend, resulting in an elastic energy cost. Our analytical model shows that the equilibrium size of the self-assembled stacks is finite and determined by the ratio of the bending energy to the adhesive energy. We developed a bead-spring model of a curvamer that bends like a linear elastic material. We design the adhesive energy between two curvamer by applying a Lennard-Jones potential between the beads on the opposite faces of each curvamer. We perform energy minimization of a curvamer stack and characterize the curvature of each curvamer in the stack. As we plot the average energy of a curvamer in a stack as a function of the stack size, we observe a reduction and a subsequent increase in energy with increasing stack size -- showing an energy minimum at a particular stack size ( $N_{\min}$ ). This behavior of the energy curve indicates that the assembly of a curvamer stack is self-limited to a size ( $N_{\min}$ ) due to the elastic energy cost required for bending. We show that the self-limiting size ( $N_{\min}$ ) can be designed by tuning the ratio of the bending energy to the adhesive energy, as predicted by the analytical model. We demonstrate that this relationship between stack size and energy ratio holds for curvamer with different preferred curvature. Additionally, we find that when the adhesive energy is represented by a long-ranged attractive potential, the self-limiting stack size ( $N_{\min}$ ) takes a larger value due to the gap-opening and curvature relaxation of the curvamer in the stack. Finally, we explore certain conditions of self-assembly that can escape the geometric frustration by producing a zigzag-shaped stack. In conclusion, our model helps to elucidate the role of geometric frustration in determining the size and geometry of self-assembled structures.

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Wed-AW1-03

### Controlling self-assembly in droplet laden colloidal systems using vapor mediation

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Drying of a functional sessile droplet containing colloids (ubiquitous in applications like biochemical assays, drug delivery systems, nanoreactors, spray painting, coating, pesticides/agriculture industries, washing, lubrication, etc.) forms self-assembled aggregates with unique morphological features. We first explain the fundamental forces acting on micro/nano colloids under the influence of evaporation-driven flow in droplets leading to striking self-assembled structures such as buckled precipitate morphology, coffee rings, uniform deposits, and lesser-known aggregates at the center of the drop. However, evaporation-driven flow inside naturally evaporating sessile droplets is meager (Velocity scale  $\sim O(10) \mu\text{m/s}$ ) and is uncontrolled. In low volatility droplets with high viscosity, the evaporation-driven flow is nearly absent. Most of the techniques to control flow inside droplets mentioned in the literature involve active methods (energy-requiring) and are bulky, require engineered surfaces that are expensive or interfere with physical and chemical processes, and thus not compatible with the practical systems. To overcome this limitation, we present a non-intrusive methodology to enhance and control flow inside the droplets without affecting their global evaporation

pattern. Sessile droplets of contrasting volatilities can communicate via long-range ( $\sim O(1)$  mm) vapor-mediated interactions, which allow the remote control of the flow-driven self-assembly of micro/nanoparticles in the drop of lower volatility. A high volatile droplet strategically positioned in the vicinity of the target droplet creates its vapor field around the target droplet. Asymmetrical vapor field leads to asymmetrical adsorption of the vapor on the target droplet. This induces Marangoni flow (Velocity scale  $\sim O(10)$  mm/s) internal to the droplet. The controlled Marangoni flow within the droplet segregates the particle population and causes preferential colloidal aggregation. Marangoni convection (Velocity scale  $\sim O(10^3)$  times higher than the evaporation-driven convection) can be vital to an efficient and on-demand manipulation of the suspended object of sizes ranging from micrometers to nanometers. The interplay of surface tension, inertial, buoyancy, and other molecular forces result in the transformation of flow inside the droplet lead to spatiotemporal control of agglomeration in droplet systems.

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Wed-AW1-04

Thermo-reversible solvent segregation driven gel (SeedGel) with well-controlled structures

**Yuyin Xi (xiyuyin@uw.edu)**<sup>1,2</sup>, **Juscelino Leão (juscelino.leao@nist.gov)**<sup>1</sup>, **Qiang Ye (qiang.ye@nist.gov)**<sup>1,3</sup>, **Ronald Lankone (rlankon1@alumni.jh.edu)**<sup>4</sup>, **Li-Piin Sung (li-piin.sung@nist.gov)**<sup>4</sup>, **Yun Liu (yunliu@udel.edu)**<sup>1,2,5</sup>

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Bicontinuous structures have been widely used in energy storage, membrane science, and biomedical devices. The interconnected channels and high specific surface areas are demonstrated to enhance the material performance in various applications. Moving forward, a simple, yet scalable synthesis method is of vital importance to further advance the development of materials. Here, we describe a new class of colloidal gel, solvent segregation driven gel (SeedGel), to stabilize bicontinuous channels during spinodal decomposition of a binary solvent. Silica nanoparticles in a binary solvent of water and 2,6-lutidine are used as a model system. In the gel state, the particles are jammed within one of the bicontinuous domains, i.e. particle domain, that percolate throughout the sample. The particle domain is enriched with one component of the binary solvent. The formation of such structures is thermally reversible, precisely reproducible, and highly tunable. In this talk, detailed results are presented to manipulate the bicontinuous structures. Ultra-small angle neutron scattering (USANS) and small angle neutron scattering (SANS) are used as the main techniques to quantitatively probe the structures of SeedGel across a wide range of length scales. The tunability of SeedGel structures are systematically investigated by varying solvent composition, particle concentration, temperature ramping rate, and final gelation temperature. A SeedGel phase diagram for this model system is also experimentally determined. This work provides a versatile method to prepare and customize bicontinuous structures that is potentially useful for various applications.

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Wed-AW1-05

Self-assembled nanoparticle superlattices with size-dependent reconfiguration

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We use liquid-phase transmission electron microscopy (TEM) to study the self-assembly of charged gold nanocubes, which showed a unique reconfigurable superlattice. The lattice can adopt two different states with same energy but different orientations, and our analysis showed the size-dependence of this reconfiguration process. Combining interaction modeling with simulation, we revealed the entropic nature of reconfiguration which dampens reconfiguration as the crystal size increases. We expect this tunable reconfiguration behavior to shed light on the design of responsive mechanical metamaterial.

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Wed-AW1-06

Phase separation of colloidal gels can promote and hinder liquid phase separation

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In this work, we investigate the role of competing phase separation in a ternary system comprising two immiscible liquids and colloidal particles with short-ranged attractions. We utilize particle-based simulations to probe microstructure and to understand the phase behavior of this system. Since the thermodynamic parameter space for such a system can be enormous, the net repulsion between the liquids that drives phase separation between them is held fixed, and a temperature is chosen such that liquid-vapor phase separation for the liquids is suppressed. Further, solvent-colloid interactions are chosen such that the colloids have equal affinity to either solvent. Even in this simple model system, a complex, non-monotonic phase behavior is observed. By varying colloidal attraction strength, range of attraction, and colloidal volume fraction, the microstructure of the colloidal particles changes significantly, which in turn influences the ability of the liquids to phase separate. We find that colloidal phase separation promotes formation of two liquid phases up to a certain degree, but that smaller solvent pores inhibits the formation of two liquid phases. Thus, controlling colloidal microstructure appears to be paramount in controlling the phase separation of immiscible liquids.

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Wed, 16 09:00 - 11:00

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Wed-BW1-01

In sheared highly polydisperse granular systems, large droplets affect smaller droplets significantly

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We study simulations of highly polydisperse emulsions under shear flow. By highly polydisperse, we mean with the largest droplet diameters being as much as ten times the smallest diameters. We quantify non-affine motion in these highly polydisperse samples -- motion where droplets move with displacements distinctly different from their neighbors, or different from the overall imposed shear flow. The largest droplets typically move affinely, as if they are in a simple effective fluid formed by the other droplets. In contrast, the smallest droplets are often forced to move non-affinely by the larger droplets. We quantify how the non-affine motion diminishes as a function of droplet size and distance from the larger particles. We further show how the behavior depends on the overall droplet size distribution; in general, the largest droplets are always the troublemakers. Our main conclusion is that highly polydisperse samples behave qualitatively differently than weakly polydisperse samples.

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Wed-BW1-02

Mixing dynamics of bilgewater emulsions in Taylor Couette flows



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Taylor-Couette flows between two concentric, rotating cylinders, is ideal for studying the mixing dynamics and stability of emulsions due to the availability of wide variation of hydrodynamic flow states. The need to control the concentration of oil discharge at sea from the marine vessels require a better understanding of the stability and formation of Navy standard bilge mix emulsions (50% marine diesel fuel, 25% steam lube oil, 25% Diesel lube oil) onboard these ships. In this study, a pre-prepared (IKA: T-25 digital Ultra-Turrax) concentrated oil-water emulsion is directly injected into the annulus of the Taylor-Couette cell containing surfactant-water solution at varied flow conditions to determine the intermixing rate or dispersion rate of the emulsion. The optical properties of the Taylor-couette cell enables us to visually study the mixing and spread of the emulsion in the solution. It was observed that the dispersion coefficient showed an approximately linear response to increasing inner cylinder speed of Taylor-couette cell. Samples were collected at different mixing stages from the TC cell and laser diffraction particle analyzer was used to characterize droplet size distribution for the mixing stages. The measurements indicate an initial droplet breakup followed by shear induced coalescence to form a larger median droplet size with time at lower mixing speed. Whereas as the mixing speed increases, the droplets continues to break under increased shear rate and a delay in droplet coalescence was observed.

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Wed-BW1-03

Remote Control of Aqueous Interfaces and Foam Stability with Photo-Switchable Polyelectrolyte-Surfactant Mixtures

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University Muenster Institute of Physical Chemistry

Using photo-switchable surfactants that can undergo E/Z photo-isomerization, we have expanded the properties of oppositely charged polyelectrolyte/surfactant (P/S) mixtures, which are ubiquitous in applications of foams and emulsions. We demonstrate that prevailing hydrophobic intermolecular interactions can be remotely modulated between poly(sodium styrene sulfonate) (PSS) and arylazopyrazole tetraethylammonium bromide (AAP-TB) surfactants and lead to unprecedented property changes of the P/S mixtures. In particular, we report on bulk and interfacial properties of PSS/AAP-TB mixtures as a function of mixing ratio and light irradiation. In the bulk, AAP-TB/PSS complexes are formed with varying electrophoretic mobility  $U_z$  and size. While green irradiation drives the AAP-TB surfactants in their predominant E conformation and leads to negligible  $U_z$  as well as large aggregates that precipitate with time at a P/S molar mixing ratio of 1/2, subsequent UV irradiation can reversibly disintegrate even large aggregates ( $>4 \mu\text{m}$ ) and P/S complexes. This is associated by a strong increase in the net charging state of PSS/AAP-TB complexes in the bulk, but also at air-water interfaces as confirmed by sum-frequency generation (SFG) spectroscopy. In fact, the P/S molar ratio where complexes with zero net charge at the polyelectrolyte chain are formed is about one order of magnitude smaller when the surfactants are in their Z compared to their E conformation. Clearly, E/Z photo-isomerization can be used to fine tune polymer-surfactant binding. In addition, through structure-property relation the molecular changes in bulk solution of PSS/AAP-TB mixtures and at the air-water interface can be used to control the stability of aqueous foam globally but also locally with light.

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Wed-BW1-04

Prediction and measurement of leaky dielectric drop interactions

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Weakly conducting, or 'leaky dielectric', drops suspended in another weakly conducting liquid undergo deformation and exhibit circulatory fluid flow under action of an externally applied electric field. These interfacially driven electrohydrodynamic (EHD) flows are useful in applications like electrocoalescence, microfluidics, electrorheology, and inkjet printing. The dynamics of a single leaky dielectric drop under weak fields is a well-studied problem, where a drop deforms to a steady prolate or oblate spheroid depending on the material properties of the drop and suspending phase. In these instances, the flow and electric field disturbances are fore-aft and axially symmetric, resulting in no net motion of the drop. In the case of more than one drop, as is common in many applications, that symmetry is broken, resulting in relative motion of the drops. Seeking to describe the dynamics of these systems, we present a pairwise theory via the asymptotic method of reflections for the relative velocity of arbitrarily located, widely separated leaky dielectric drops in a uniform DC electric field. From this result, we introduce a parameter  $\Phi$ , a function only of system material properties that can be used to predict a priori whether drops will come together to coalesce. We compare our theory to experimental measurements of drop trajectories, showing reasonable success in our ability to predict drop pair behavior over a variety of initial positions. Experiments of drops of varying drop size and 3 or more drops also show good agreement with predicted trajectories, underscoring the power of our asymptotic analysis to capture the physics governing leaky dielectric drop interactions.

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Wed-BW1-05

Influence of polarity change and photophysical effects on photosurfactant-driven wetting

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Photosurfactants show considerable promise for enabling stimuli-responsive control of the properties and motion of fluid interfaces. Although a number of photoswitch chemistries have emerged to tailor the photo-responsive properties of photosurfactants, systematic studies investigating how photo-responsive surfactant behavior depends on the photochemical and photophysical properties of the switch remain scarce. In this work, we develop synthetic schemes and surfactant designs to produce a well-controlled library of photosurfactants to comparatively assess the behavior of photoswitch chemistry on interfacial behavior. We employ photo-induced spreading of droplets at fluid interfaces as a model for such studies. We show that although photosurfactant response is largely guided by expected trends with changes in polarity of the photoswitch, interfacial behavior also depends non-trivially and sometimes counter-intuitively on the kinetics and mechanisms of photoswitching, particularly at the interface of two solvents, as well as on complex interactions with other surfactants. Understanding these complexities enables the design of new photosurfactant systems and their optimization toward responsive functions including triggered spreading, dewetting and destabilization of droplets on solid and fluid surfaces.

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Wed-BW1-06

Endoskeletal Drops for Photoacoustic Imaging

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**Introduction** We synthesized vaporizable endoskeletal droplets comprising a liquid fluorocarbon (FC) phase and a solid hydrocarbon (HC) endoskeleton with a Zinc-chelated naphthalocyanine dye mixed into the HC-phase. FC/HC endoskeletal droplets were previously synthesized by Shakya et al. to study how endoskeletal melting aids in the vaporization of the FC-phase. During our photoacoustic test, the FC/HC endoskeletal droplets are irradiated with a pulsed laser. The dye absorbs these photons, heats up the HC-phase and subsequently melts it. Interfacial melting of the HC endoskeleton and subsequent mixing with the liquid FC reduces the cohesion in the FC-phase and depresses its spinodal point. The FC-phase spontaneously vaporizes giving off a strong acoustic response. **Methods** The solid HC and dye were weighed in a glass vial and then heated in a water bath at 75°C to melt and mix. Lipid solution was added and the mixture was chilled in ice water before adding the liquid FC-phase. The vial was then sealed, heated and sonicated in water bath for a minute, and the mixture was emulsified in an amalgamator. The resulting emulsion was quenched in ice-water to form the final dye-loaded FC/HC endoskeletal droplets as shown in Figure 1(a). The photoacoustic experiment was carried out inside a water-tank with the droplets flowed through a tube. The tube was illuminated with a 760-nm pulsed laser, and a 20-MHz ultrasound transducer was used to record the acoustic response as in Figure 1(c). **Results** The peak-to-peak voltage amplitude received by the ultrasound transducer is plotted against the laser fluence in Figure 1(d). The plot shows the acoustic response from two kinds of droplets: sample droplets with dye and control droplets without dye. The plot indicates a very strong nonlinear photoacoustic response from the sample with dye compared to the control droplets. In addition, the plot demonstrates the acoustic response from an ink flowed through the same setup. The non-linear response received from the dye-loaded sample suggests that the droplets are vaporizing, which was confirmed with contrast-enhanced ultrasound imaging. **Conclusions** These novel dye-loaded FC/HC endoskeletal droplets have the potential to work as photoacoustic contrast agents given their highly nonlinear response at low fluences. Also, given their low phase-transition temperature, these droplets can be tuned to vaporize at physiologically relevant temperatures, which can make them applicable for contrast-enhanced ultrasound applications.

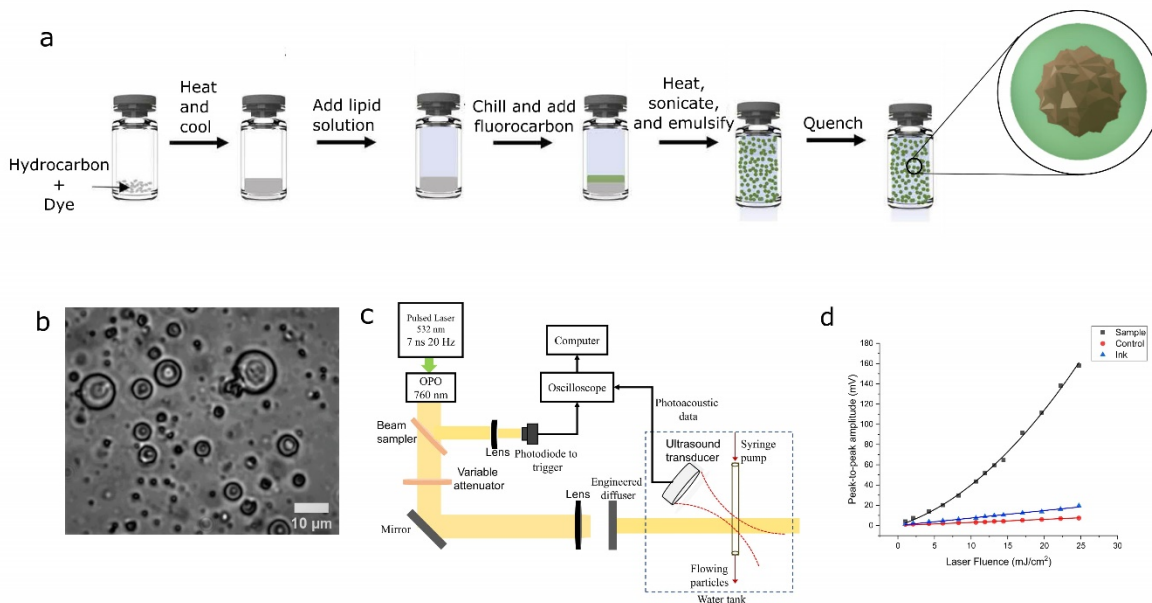


Figure 1 (a) General scheme for synthesizing FC/HC endoskeletal droplets. (b) Microscopic image of the droplets (c) The photoacoustic experimental setup (d) Photoacoustic response from the sample droplets with dye, control droplets without dye and ink.

Wed-DW1-01

## Polyelectrolytes Dynamics and Rheology, in a Pinch

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Stringiness, stickiness, and dispensing behavior of complex fluids are often assessed qualitatively by stretching a liquid bridge between two surfaces (say thumb and forefinger), and observing the capillarity-driven pinching of the fluid neck, and assessing filament lifespan. Dispensing and drop formation/deposition processes associated with printing, spraying, atomization, and coating flows involve similar filament pinching dynamics. Stream-wise velocity gradients that spontaneously arise within the pinching filament create an extensional flow field. However, the influence of macromolecular parameters and interactions on the response to extensional flows remains relatively less well-understood, partially due to the well-known challenges in the characterization of extensional rheology response. We show that dripping-onto-substrate (DoS) rheometry protocols that involve visualization and analysis of pinching of a columnar neck formed between a nozzle and a sessile drop can be used for measuring extensional viscosity and extensional relaxation time of polymeric complex fluids. The DoS rheometry protocols that we developed and popularized allow characterization of nonlinear viscoelasticity and extensional rheology of printing inks and polymer solutions that are beyond the measurable range of commercially-available capillary break-up extensional rheometer (CaBER). Biological macromolecules like proteins, DNA, polysaccharides, and many industrial polymers, are classified together as polyelectrolytes. In solution, the repeat units in their backbone are decorated with dissociated, charge-bearing ionic groups, surrounded by a cloud of counterions. Even though a large number of polyelectrolytes are processed or used as rheology modifiers in paints, pharmaceuticals, fertilizers, pesticides, and cosmetics, the shear and extensional rheology response of the charged macromolecular solutions is not as well understood as for their uncharged counterparts, and motivate this study. We characterize the pinching dynamics as well as shear and extensional rheology of solutions of three model polyelectrolytes poly(sodium 4-styrene sulfonate) (NaPSS), poly(acrylic acid) (PAA), and sodium carboxymethylcellulose (NaCMC) as a function of solvent and salt concentration. We identify universalities in the shear and extensional rheology response of salt-added unentangled semidilute solutions and examine the influence of solvent properties on polyelectrolyte dynamics. Unlike shear relaxation time that decreases with an increase in polymer concentration in the unentangled, semidilute salt-free solutions, the measured extensional relaxation time always shows an increase with polymer concentration for the unentangled systems. We elucidate the influence of both electrostatic and hydrodynamic interactions and stretching of macromolecules on stickiness, printability, jettability, and overall processability.

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Wed-DW1-02

## Differential dynamic microscopy enables high-throughput phase diagram mapping of polyelectrolyte complex coacervates

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Rapid formulation of complex fluids and biological materials demands accurate analysis and improved characterization methods for scarce and microscopically heterogeneous materials. Although microrheology holds promise to address this challenge, current analysis approaches involving multiple particle tracking

(MPT) limit throughput and place barriers on automation. Alternatively, differential dynamic microscopy (DDM) has recently emerged as a promising new tool to track how materials systems evolve in space and time. By representing image fluctuations in the Fourier domain, DDM connects real-space image data to dynamical properties accessed in light scattering, and was recently extended to the estimation of mean-squared displacements, without the need to track probes directly. However, in its current state, DDM analysis suffers from several drawbacks, including slow computation, lack of error quantification and limited robustness. We present a new strategy by using a statistical approach to estimate the contribution to the DDM signal from fluctuating noise, demonstrating improved computational efficiency through downsampling and improved robustness. This approach is applied to study polyelectrolyte complex coacervates involving two-component polyelectrolyte solutions that undergo liquid-liquid phase separation into polymer-dense (coacervate) and polymer-poor phases. In such systems, characterizing the properties of the dense phase conventionally requires carefully separating the dense phase from the dilute phase in order to use conventional bulk characterization methods to measure properties. Combining microscopy with microrheology analysis, we demonstrate that the dense phase can be characterized in situ, in which spatiotemporally resolved data can be used to track the evolution of the coacervate morphology over time. The morphology data are categorized and cross-correlated with the rheology to characterize the influence of viscoelasticity on phase separation (and vice versa). The resulting high-throughput measurements provide a simple and effective platform to explore driving factors for phase separation on micro and macro length scales, and potentially set the stage for mapping chemical design to physical material properties.

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Wed-DW1-03

## Nanoparticle Dynamics in Unentangled Polyelectrolyte Solutions

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Nanoparticles are very useful materials in a wide range of industries including oil and gas, materials, and medicine. Fundamental understanding of the transport properties of nanoparticles in complex media is required to effectively enhance their performance in applications. There are three size regimes of interest when studying the dynamics of nanoparticles in polymer solutions. When the nanoparticles radius  $R_{NP}$  is much smaller than the size or radius of gyration  $R_g$  of polymer chains, nanoparticle dynamics depend on the void geometry and solvent viscosity with polymer chains acting like barriers. Conversely, when  $R_{NP}$  is much larger than  $R_g$ , heterogeneities are averaged across nanoparticles surfaces and their dynamics couple to the bulk viscoelasticity of the solution. In the intermediate regime where  $R_{NP}$  and  $R_g$  are comparable, however, nanoparticles experience fluctuations in heterogeneities. The dynamics in this regime are not well understood. Recent experiments [Poling-Skutvik, et al.; ACS Macro Lett. (2015) 4, 1169 – 1173] and theories [Cai, et al.; Macromolecules (2011) 44, 7853 – 7863] proposed that nanoparticle dynamics in flexible (neutral) polymers couple to fluctuations of segmental relaxations of polymer chains in the intermediate regime. However, an understanding of the nanoparticle dynamics as polymer conformation changes is still lacking. Here, we study the dynamics polystyrene nanoparticles in sodium polystyrene sulfonate dissolved in deionized water using fluorescence microscopy. The polymer conformation is tuned by varying the solution ionic strength. We find that particle dynamics remain diffusive across all time scales. The diffusivities of large particles ( $R_{NP}/R_g > 1$ ) follow bulk predictions according to Stokes-Einstein (SE) at all ionic strengths. For smaller particles ( $R_{NP}/R_g < 1$ ), however, we find that their dynamics exhibit non-monotonic deviations from SE within the unentangled semidilute regime. The size-dependent dynamics do not collapse onto a master curve, suggesting that predictions for neutral polymers do not hold for charged polymers that have a non-Gaussian conformation. Moreover, we observe that the non-Gaussian parameter and the scaled particle diffusivity map onto the same concentration dependence, suggesting the rise of confinement effects despite the absence of entanglements. This improved understanding of the dynamics of nanoparticles will allow us to control their transport in complex media enabling application in enhanced oil recovery, composite processing, and drug delivery.

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Wed-DW1-04

## Spinnability and Centrifugal Force Spinning of Fibers of Poly(ethylene Oxide) Solutions

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Centrifugal force spinning has recently emerged as a highly promising alternative technique for the production of nonwoven, ultrafine fiber mats. Due to its high production rate, it could provide a more technologically relevant fiber spinning technique than electrospinning. In this contribution, we examine the influence of polymer concentration and solvent properties on the centrifugal spinning process and the fiber morphology. We find that increasing the polymer concentration transforms the process from a beaded-fiber regime to a continuous-fiber regime. Furthermore, we find that not only fiber diameter is strongly concentration-dependent, but the choice of solvent and nozzle properties also influence the fiber morphology and mechanical properties. A comprehensive investigation of shear and extensional rheology of the PEO solutions is carried out using torsional rheometry and dripping-onto-substrate (DoS) rheometry respectively to correlate spinnability to the processing conditions as well as to material properties.

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Wed-DW1-05

## Designing elastoplastic 3D printable edible materials using jammed emulsions stabilized with pea proteins

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3D printed materials are of great relevance for the production of therapeutic and specialized foods. An approach to forming 3D printable materials is to use jammed oil droplets. Jammed oil droplets are highly viscous and can be extruded through the nozzle of a 3D printer, while after chemical crosslinking they acquire a self-standing ability. However, the molecules currently used to stabilize and cross-link the oil droplets have questionable biocompatibility. Therefore, our research aims to produce 3D printable jammed emulsion using pea proteins. Pea protein stabilized emulsions were extremely stable with monomodal droplet size distribution. The jammed emulsions showed gel-like visco-elastic rheological properties. However, upon 3D printing, the material was not self-standing owing to the lack of plasticity. In order to induce plasticity, we used self-associating properties of pea proteins by pH trigger. Our previous work has shown that pea proteins self-associate into adhesive protein particles at pH 3. The adhesive nature of pea proteins could aid in creating additional droplet-droplet interaction to create plasticity in the jammed emulsions. Therefore, jammed emulsions in the presence of pea protein particles were formed by simple pH adjustment. These emulsions with protein particles formed a material with elastoplastic rheological properties. The emulsion flowed smoothly above a critical stress, and after extrusion exhibited the required self-standing properties for 3D printing. The adhesive protein particles act as physical cross-links between the jammed oil droplets, creating the plasticity necessary for 3D printing. In this research, we show that by understanding the associating properties of pea proteins and their behavior in bulk and on interfaces, pea protein-based 3D printable material was created for the first-time.

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Wed-DW1-06

## Polysaccharides As Food Thickeners

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<sup>2</sup> Motif FoodWorks, Inc., Boston, MA

Foods are multicomponent soft materials that often contain dispersed drops, bubbles, particles, or proteins. Often protein-based foams, emulsions, suspensions, and pastes contain polysaccharides that act as binders, thickeners, gelling agents or rheology modifiers, and influence shelf-life, rheology, processability as well as control over fiber, fat, salt, calorie count, texture, and mouth-feel. Stream-wise velocity gradients associated with extensional flows spontaneously arise during extrusion, calendaring, coating, dispensing, bubble growth or collapse as well as consumption including swallowing and suction via straws. Even though shear rheology response is fairly well characterized and utilized in food industry, elucidating, measuring and harnessing the extensional rheology response have remained longstanding challenges. The characterization challenges include the lack of robust, reliable and affordable methods for measuring extensional rheology response, whereas the product design challenges stem from the difficulties in assessing or predicting the influence of macromolecular properties on macroscopic rheological behavior. In this contribution, we address the characterization challenges for specific case of xanthan gum and cellulose gum thickeners by using dripping-onto-substrate (DoS) rheometry protocols that we developed that rely on analysis of capillary-driven thinning and break-up of liquid necks created by releasing a finite volume of fluid onto a substrate. The DoS rheometry protocols emulate the heuristic tests of thickening, stickiness or cohesiveness based on dripping a sauce from a ladle or dispensing from a nozzle onto a substrate. We investigate the concentration-dependent variation in shear and extensional rheology of polysaccharide thickeners. We show that adding glycerol or changing salt concentration can be used for tuning the pinch-off dynamics, extensional rheology response, and processability of unentangled solutions of cellulose gum, whereas entangled solutions are relatively insensitive to change in salt concentration.

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Wed, 16 09:00 - 11:00

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Wed-FW1-01

Using Atomic Force Microscopy to Quantitatively Study Tribochemical Reactions on 2D Materials  
**(Keynote Lecture)**

**Jonathan Felts (jonathan.felts@tamu.edu)**

Texas A&M Department of Mechanical Engineering

This talk will highlight recent advances in utilizing atomic force microscopy to quantitatively study mechanically driven reactions on surfaces. In particular, reactions on graphene provide a chemical system with relatively well defined chemical structure and bond orientation, making it possible to study reaction kinetics and thermodynamics with near atomic resolution at the sliding tip interface. By precisely controlling applied forces, sliding speed, temperature, and electric fields, it is possible to quantitatively determine critical reaction parameters, including the reaction rate, activation barrier of the reaction, and activation volumes. Further, it is possible to determine which component of the applied force (normal, shear, etc) drives particular reactions. The experimental framework developed here provides a rich suite of tools to understand tribochemical and mechanochemical reactivities at the atomic scale, by directly linking experimental measurements to fundamental theories used to describe reactivity.

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Wed-FW1-02

Dynamic measurement of ice growth by atomic force microscopy in aqueous solutions in the presence of ice-binding proteins

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Besides enabling organisms to thrive in cold environments, ice-binding proteins (IBPs) hold great promise in tissue preservation and food processing. These proteins lower the freezing point by binding to ice surfaces thus inhibiting crystal growth. Despite their importance, the microscopic action of these proteins is largely unknown due to until-now unresolved difficulties of achieving high-resolution, in-situ imaging. We present here a novel system design which enables dynamic atomic force microscopy (AFM) imaging of the ice-IBP system. Two different types of protein systems were studied, one exhibiting moderate ice-growth inhibition, and the other hyperactive inhibition. These proteins bind to different faces of the growing ice crystals, leading to characteristic structures which can be rationalized by the selective inhibition. AFM images reveal such structures at the tens of nm scale for the first time, and will be discussed in relation to previous, lower resolution optical images. Besides revealing the nascent crystal growth, the AFM was used to create mappings of local adhesion which gave insights on the location of protein binding. In order to achieve these results, several challenges had to be overcome including moderating and controlling heating from the AFM head and detection laser, preventing cantilever freezing, and isolating and monitoring the boundary between liquid and solid as observed at the growing ice front. Using the new set-up enabled control of growth in both slow and fast regimes, and even demonstrated the feasibility of measuring less-controlled ice growth in absence of the IBPs. Small pits were observed near the apex of growing tapered structures, which can be understood in light of the attachment of the IBP to specific planes. Although there exist several studies on crystals growing in thin films, this is the first demonstrated imaging of a growing bulk crystal immersed in its own melt with AFM

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Wed-FW1-03

Probing the mechanical and structural properties of inverse bicontinuous cubic phase membranes by Atomic Force Microscopy based Force Spectroscopy

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Non-lamellar lipid membranes are ubiquitous in nature; in particular, inverse bicontinuous cubic phase membranes occur spontaneously in stressed or virally infected cells and are involved in multiple biological processes like cell fusion and food digestion (Nature communications 6.1, 2015: 1-8). While numerous studies focused on the development of cubic phase nanoparticles ("cubosomes") for drug delivery purposes (Nanoscale, 2018, 10, 3480-3488; JCIS 541, 2019: 329-338), fewer efforts have been made for developing homogeneous solid supported cubic phase lipid films (Interface focus 7.4, 2017: 20160150). Analogously to Supported Lipid Bilayers (SLBs), these supported lipid films can be used as mimics of natural non-lamellar membranes for fundamental investigations, like the study of their mechanical properties. In this framework, we realize thin (~150 nm) solid supported cubic phase lipid films and characterize their structure by means of multiple surface-sensitive techniques. We then exploit Atomic Force Microscopy-based Force Spectroscopy (AFM-FS) to obtain the first nanomechanical characterization of cubic phase lipid



membranes (BioRxiv, DOI: <https://doi.org/10.1101/2021.03.29.437497>). Results from our AFM-FS analysis are strikingly similar to the ones obtained in mechanical compression tests on macroscopic inorganic 3D printed cubic structures, suggesting that the mechanics of these architectures can be regarded as length scale-independent and strictly related to their topology. Finally, by analyzing the indentation features along the AFM-FS curves, we demonstrate that our study can be used as a novel approach for characterizing the structure of non-lamellar mesophases. The herein presented results pave the way for future mechanical characterizations of non-lamellar membranes and highlight the role of AFM-FS as a valid alternative for studying the structural features of these mesophases, without relying on cryo-electron microscopy or large-scale facilities.

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Wed-FW1-04

Visualizing bimodal rotational dynamics of protein nanorods at solid-liquid interfaces by high-speed AFM

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Biomolecular assembly at solid-liquid interfaces is a classical and powerful approach to create bio-hybrid materials with promising applications in molecular recognition, (bio)mineralization, energy conversion, storage, and transportation of matter and information, etc. Especially, biomolecules can form hierarchical structures with epitaxial arrangements to inorganic substrates in response to various environmental stimuli. However, due to the lack of in-situ analysis at nanoscale, it is still unclear how their rotational dynamics define epitaxial assembly and how environmental stimuli, like cation ions, modulate the rotational dynamics accordingly. In the talk, I will present the most recent study on visualizing the rotational dynamics of de novo designed protein (DHR-micaN, where N refers to the number of repeat unit) [1] on muscovite mica in 10 mM KCl/NaCl by high-speed AFM. With the help of machine learning-based statistical analysis and the comparison to Monte Carlo simulation, we found that the rotations of DHR10-micaN between local angular energy minima follow two distinct mechanisms. Transitions between adjacent orientational states appear to follow in-plane Brownian motion, biased by the angle-dependent energy landscape, and the rates are exponential in the energy-barriers between local minima. In contrast, transitions between more distant angular states occur by non-classical quasi three-dimensional Levy-flight transitions, whose rates are decoupled from energy-barrier heights. [1] Pyles, H., Zhang, S., De Yoreo, J. J. & Baker, D. Nature 571 (2019), 251-256.

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Wed-FW1-05

Using Deep Learning for Classification and Correlation of Impact Copolymer AFM Images

**Ishita Chakraborty ([i.chak1983@gmail.com](mailto:i.chak1983@gmail.com))**

Stress Engineering Services

Deep learning models are used to classify AFM phase images as well as establish correlation between different structural properties of bulk materials and AFM phase images of polymer materials. Use of deep learning techniques are described in detail for classification and correlation of material properties. This study points out new ways establish relationship between bulk material properties and microstructural data.

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Wed, 16 09:00 - 11:00

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Wed-HW1-01

Force measurements of the interfacial properties of grafted zwitterionic polymer

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Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign  
Molecular surface properties of thin films of zwitterionic polymers are central to their ultra- low fouling properties. Interfacial forces of grafted poly(sulfobetaine) (pSBMA) chains were measured by Surface Force Apparatus (SFA), as a function of chain grafting density, molecular weight, and ionic strength. Forces were quantified between end-grafted zwitterionic pSBMA chains and mica, at low and high grafting densities and in the presence of different concentrations of monovalent salt. At high grafting densities where the polymers formed dense brushes, the equilibrium chain extension increased ~1.6 fold, as the NaNO<sub>3</sub> concentration increased from 10 mM to 1000 mM in buffer (pH= 7.0). Although the amplitude of the repulsive force did not change significantly between 10 and 100 mM salt, the brushes were much less compressible in 1000 mM NaNO<sub>3</sub>. At low grafting density, where the polymer formed mushroom-like coils, the repulsive force increased exponentially with decreasing separation distance. The exponential decay constant,  $R_{\text{eff}}$  was approximately 2, 4 and 6 times of Flory radius,  $R_F$  at 10, 100 and 1000 mM NaNO<sub>3</sub>, respectively. This behavior exhibits the characteristic anti-polyelectrolyte behavior and is distinct from that of both neutral, water soluble poly(ethylene glycol) and end-grafted polyelectrolytes. The findings reveal how polymer coverage and salt tune the range and magnitude of the repulsive barrier generated by grafted pSBMA thin films.

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Wed-HW1-02

Solvent Selection and Dilution Process to Distinguish Particle Size and Surface Treatment

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Process R&D, Dow Performance Silicones

Filler particles within a silicone matrix, such as fumed and precipitated silicas, are active ingredients that impart mechanical reinforcement to Liquid Silicone Rubber (LSR), and enable initial foam knockdown and subsequent control as the delivery system for the silicone foam control actives in antifoam control (AF) compounds. Filler incorporation and dispersion quality, thus, determines the product quality. As-manufactured silica is hydrophilic and agglomerated, and further processing is required to break down the agglomerates into finer aggregates and in some cases enable chemical or physical treatment to render the surface hydrophobic, which better compatibilizes silica within the silicone matrix. This work highlights the solvent selection and dilution process to enable distinction between particle size and surface treatment. Important considerations for solvent selection include the particle-solvent interaction, which affects the apparent particle size due to unfavorable interaction-induced agglomeration. The viscosity of the solvent and the shear stress during the dilution also affect the apparent particle size.

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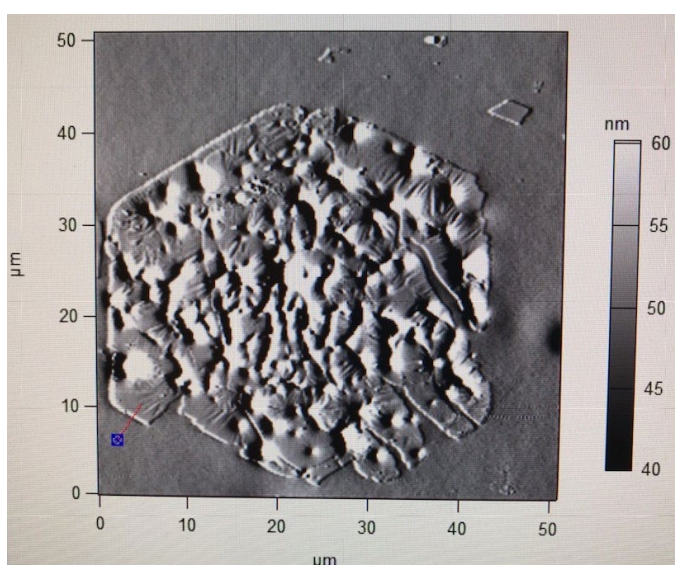
Wed-HW1-03

Investigation of capillary interactions between 2D particles at fluid-fluid interfaces

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Colorado School of Mines, Chemical and Biological Engineering

There is growing literature surrounding the scalable assembly and deposition of two-dimensional (2D) materials, including graphene, from fluid-fluid interfaces for uses in next-generation thin-film devices, but our lack of understanding of the lateral (in-plane) interactions between 2D particles at fluid-fluid interfaces is an impediment to rapid progress in this area. Since film properties depend on the assembled film morphology, which itself is a product of particle-particle interactions, it is desirable to understand the forces that drive self-assembly between 2D materials at fluid-fluid interfaces. There is evidence that weak capillary interactions play a significant role in such assembly behavior, but capillary interactions have not been directly observed or quantified in these systems. In this work we seek to use lithographic methods to fabricate size- and shape-controlled graphene, transfer it to an air-water interface, and observe both self-assembly behavior and evidence of capillary interactions with a combination of microscopy techniques and gel trapping (*Figure 1*). We will present the process for creating these particles and transferring them from the growth substrate, describe our observations of individual particles and particle assemblies, and discuss the consequences for our understanding of capillary interactions in these systems.



*Figure 1.* Monolayer graphene particle imaged with AFM on PDMS (via gel trapping).

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Wed-HW1-04

A colourful way to track the hindered diffusion of anisotropic nanoparticles

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Department of Chemical Engineering, University of Melbourne

Generating observations of anisotropic nanoparticles (e.g. Janus particles, nanotubes, rods) as they move and interact near an interface is critical to understanding and controlling their behaviour as building blocks for advanced materials or as synthetic vehicles for applications such as drug/vaccine delivery. Conventional microscopy tools are limited by particle anisotropy and the proximity of an interface, and further confounded by the diffraction limit for small particles. Here we discuss the use of Anisotropic Resonance Correlation (ARC) microscopy to measure the instantaneous position and orientation of any particle diffusing near an interface; working at millisecond time intervals, this new technique provides sufficient spatiotemporal resolution to elucidate mechanistic, diffusive and equilibrium behaviour. In order to demonstrate the physical insights enabled by ARC microscopy we describe results obtained for systems of ZnO nanorods diffusing under various salt concentrations. By tracking diffusion in each spatial mode to generate piecewise-ergodic sets of observations, we can determine hindered translational and rotational diffusion coefficients as a function of interfacial separation. Equivalently, we can measure separation-dependent rotational diffusion tensors and in each case demonstrate an asymptotic approach to the expected constant state in the bulk. These same data can also be used to measure orientation-dependent interaction potentials, completing a rich set of tools for probing anisotropic interactions relevant to the study of

assembly and transport phenomena. Aside from fundamental applications, this technique will be particularly useful for understanding and tuning the self-assembly of films and other systems incorporating anisotropic nanoparticles.

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Wed, 16 09:00 - 11:00

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Wed-JW1-01

Characterizing and engineering nanoscale flows in membranes (**Keynote Lecture**)

**Manish Kumar (manish.kumar@utexas.edu)**

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Membranes are rapidly becoming the fastest growing platform for water purification, wastewater reuse, and desalination. They are also emerging in importance for carbon capture, hydrocarbon separations, and are being considered for applications involving catalysis and sensing. All synthetic membranes have selectivity-permeability tradeoffs, i.e if a membrane has high permeability, it will have a lower selectivity between two solutes or between a dissolved solute and a solvent. This is due to the mechanism of solution-diffusion through a wide distribution of free volume elements in non-porous membranes such as reverse osmosis membranes used for desalination and reuse, and a wide pore size distribution in porous membranes. A simple solution, in concept, to such a challenge is to do what nature does – design precise angstrom to micron scale pores with no polydispersivity. However, so far such an ideal has not been realized in synthetic membranes and in particular for angstrom scale separations. We will discuss recent work on characterizing nanoscale flows in reverse osmosis membranes that illustrate this argument. We will then discuss bioinspired ideas, and its realization in our lab, and methods used to characterize nanoscale water and ion transport in such systems.

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Wed-JW1-02

Nanoscale shape-morphing in polyamide membranes enabled by 3D nanoscale imaging-analysis platform

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State-of-the-art reverse osmosis, nanofiltration, and desalination membranes are constructed as a thin film composite: they consist of crosslinked polyamide selective layer with an extremely thin thickness (i.e., layer thickness of about 10 nm and apparent thickness of >100 nm). These thin polyamide membranes are generally prepared via interfacial polymerization between aromatic or aliphatic diamine and aromatic acyl chloride. In general, their performance of polyamide membranes is governed by their morphology. However, the interfacial polymerization process leads to highly irregular and complex crumpled nanostructures that make the quantitative measurement of their physiochemical properties extremely difficult. Here, we demonstrate quantitative nanoscale shape-morphing in polyamide membranes and its relation to the membrane's mechanical heterogeneity by integrating 3D electron tomography, machine

learning-based shape classification, and liquid-phase AFM. From diverse nanoscale structures prepared by varying synthesis parameters, quantitative morphometry extracts large datasets of 3D geometry descriptors including interconnectivity, domain, void architecture, layer thickness, surface curvature, surface area, assembly structure (more than 50 descriptors). A data mining algorithm is employed to evaluate their categorical and numerical attributes and to rank descriptors from the most to least informative to composite functionality. This newly created knowledge on morphological properties at the nanometer resolution is related back to bridge synthesis and functionality. The elucidation of the molecular underpinning of the synthesis–morphology–property relationship would enable a new prediction-based design of polymeric materials, advancing beyond previous “trial-and-error” approaches. We anticipate that this imaging–morphometry platform can be applicable to other nanoscale soft materials and provides engineering strategies based directly on synthesis–morphology–function relationships.

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Wed-JW1-03

Electrochemically-active carbon nanotube coatings for biofouling mitigation: cleaning kinetics and energy consumption for cathodic and anodic regimes

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<sup>2</sup> Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, United States

<sup>3</sup> Department of Civil and Environmental Engineering, Rice University

<sup>4</sup> School for Engineering of Matter, Transport and Energy, Arizona State University

Biofouling is a major obstacle in engineered systems exposed to aqueous conditions. Many attempts have been made to engineer the surface properties of materials to render them resistant to biofouling. These modifications typically rely on passive antimicrobial or anti-adhesive surface coatings that prevent the deposition of bacteria or inactivate them once they reach the surface. However, no surface modification strategy completely prevents biofilm formation, and, over time, surfaces will be fouled and require cleaning. In this work, we demonstrate the capacity of electrochemical carbon nanotube coatings in dispersing biofilms formed on the surface. A systematic analysis of the biofilm removal kinetics in function of applied current density is made to identify the optimal current conditions needed for efficient surface cleaning. Operating the electrochemically active surface as a cathode produces superior results compared to when it is operated as an anode. Specifically, the 5.00 A m<sup>-2</sup> and 2.50 A m<sup>-2</sup> cathodic conditions produced rapid cleaning, with complete biofilm dispersal after 2 min of operation. Surface cleaning is attributed to the generation of microbubbles on the surface that scours the surface to remove the adhered biofilm. Energy consumption analyses indicate that the 2.50 A m<sup>-2</sup> cathodic condition offers the best combination of cleaning kinetics and energy consumption achieving 99% biofilm removal at an energy cost of ~\$ 0.0318 m<sup>-2</sup>. This approach can be competitive compared to the current chemical cleaning strategies, while offering an opportunity for a more sustainable and integrated approach for biofouling management in engineered systems.

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Wed-JW1-04

Mechanisms of silica scaling on organic foulant-coated surfaces

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The George Washington University

Silica scaling is one of the main problems in membrane-based brackish water desalination. The preconditioning of organic foulants on membrane surfaces was reported to facilitate silica scaling. However, the mechanism of silica scaling on organicfoulant-coated surfaces is still poorly understood. Recently, several studies have shown conflicting role of surface charge in silica scaling: while some studies found

that positively charged surfaces are more favorable for heterogeneous silica scaling, others reported increased heterogeneous nucleation in the presence of carboxyl groups. In addition, the possible existence of both bulk nucleation and heterogeneous nucleation complicates the understanding of silica scaling. The objective of this study is to elucidate the mechanisms of silica scaling on organic-foulant-covered surfaces. Lysozyme (LYZ), bovine serum albumin (BSA), humic acid (HA), and alginic acid (Alg) were used as model organic foulants for surface preconditioning. We investigated the kinetics of silica scaling on organic-foulant-covered surfaces by monitoring the mass of silica deposition using a quartz crystal microbalance with dissipation monitoring (QCM-D). The two conditions we employed, small oversaturation with negligible bulk nucleation and high oversaturation with fast bulk nucleation, allow us to investigate the kinetics of surface-induced heterogeneous nucleation and deposition of silica oligomers/colloids, respectively. Our results showed that deposited silica mass within 24 h on organic-foulant covered surfaces due to surface-induced heterogeneous nucleation increases in the order  $LYZ < BSA < HA < Alg$ . For the deposition of silica oligomers/colloids, the rate of silica scaling increases in the order  $LYZ < HA < Alg < BSA$ . To elucidate the mechanisms, we measured the interaction forces between foulants and silica using an atomic force microscope, and analyzed the interfacial free energy and hydration energy using contact angle measurement.

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Wed, 16 09:00 - 11:00

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Wed-KW1-01

Establishing the Potential role of Benzyl Isothiocyanate as an anticancer through novel green nanoformulations

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Assistant Prof. Department of Chemistry Panj University Chandigarh India

Benzyl isothiocyanate, an organic dietary compound, is allied with a major role in the potential chemopreventive effects. BITC has acknowledged rising attention as a therapeutic compound to be used in medicine because of its high potency and characteristic biopharmaceutical properties, like high permeability with marginal aqueous solubility. The highly volatile and hydrophobic nature brought a need to provide a suitable delivery-matrix to BITC to exploit its pharmacological potential to the fullest. Owing to the entrenched advantages of the nanostructured colloidal systems, the potent molecule has been formulated in nanoemulsions, nanoparticles, and supramolecular complexes and thoroughly characterized using UV-vis spectroscopy, FTIR, DSC, TEM, and SAXS. The nanoformulations helped in masking the acute odor, achieving a controlled release of BITC, and made its use viable by prolonging the retention time and thereby sustaining the biological effects. Different models like Higuchi, first-order kinetic decay, Korsmeyer-Peppas model were applied, suggesting a diffusion-controlled mechanism of release. Also, the bioaccessibility and stability of BITC in an in vitro digestion model were evaluated. The results promptly suggest the functional efficacy of the nanosystems in releasing BITC and attest to the ability of the complexes to provide an alternative to otherwise remedially sparse triple-negative breast cancer.

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Wed-KW1-02

Morphogenesis of silica microstructures in diatoms

**Maria Feofilova (maria.feofilova@mat.ethz.ch), Eric Dufresne (eric.dufresne@mat.ethz.ch)**

Department of Materials, ETH Zürich

Diatoms are single-celled organisms with a remarkable cell wall. The cell wall, called the frustule, is made of multi-scale nano- and micro- structured amorphous silica. The beautiful and intricate structures of the frustule have been and remain puzzling to scientists. While there is knowledge of the molecular components of the frustule, it is still not clear how the multi-scale arrangement of the structure is achieved. In this work, we used confocal fluorescence microscopy to obtain high-quality 3-D images of fluorescently-

labelled *C. Granii* diatom frustules, and precisely tracked the positions of their structural features. The associated 3-D point pattern, corresponding to micron-sized holes in the frustule, is projected into 2D and has strong short range order typical of a 2D crystal, while also exhibiting novel long-range order where bond-orientations preferentially point to the center of the diatom. We find that the degrees of short range and long-range 'radial' order are characteristic of different centric diatom species. Following a hypothesis first proposed, that phase-separated protein droplets template the structure (Sumper, 2002), we used molecular dynamics simulations to obtain diatom-like microscale patterns. By introducing a novel colloidal interaction term that favors radially orientted bonds, we capture the characteristic structure of *C. Granii*, as well as the full range of diverse point-patterns observed in other centric diatoms.

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Wed-KW1-03

### New Generation of Drug Delivery System based on Stimuli-Responsive Capsules

**Julie Oniszczyk (oniszczyk@icmpe.cnrs.fr), Malak Alaa Eddine (alaa.eddine@icmpe.cnrs.), Ones Mansour (mansour@icmpe.cnrs.fr), Laurent Michely (michelye@icmpe.cnrs.fr), Sabrina Belbekhouche (sabrina.belbekhouche@u-pec.fr)**

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Recent progress in supramolecular chemistry leads to unparalleled control over the composition and shape factor of colloidal systems. Among them, the design of capsules is a new expanding area of physical-chemical research.<sup>1,2</sup> Here, we report on the development of tailor made polymer capsules for potential applications in biomedical field. The primary focus is to enhance the loading/release of therapeutic agents. The implemented strategy is mainly based on colloidal templating and self-assembly.<sup>3</sup> Size, dispersity and concentration of the nanocapsules are easily fixed by the initial nanoparticle template, while wall thickness is dependent on the number of layers. The present strategy is advantageous in comparison with other synthetic routes because at all steps, only water is used as a solvent and not organic one. The possibility to control the mechanical property of the capsules brings new promising property which will be evidenced during the talk. The benefits of using these capsules will be presented in numerous biological applications. 1) Peyratout, C.S. et al., *Angewandte Chemie* 43, 2004, 3762. 2) Borges, J.O. et al., *Chemical reviews* 114, 2014, 8883. 3) a) Belbekhouche, S. et al., *Food Hydrocolloids*, 95, 2019, 219-227 / b) Belbekhouche, S. et al., *Colloids and Surfaces B: Biointerfaces*, 181, 2019, 158.

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Wed-KW1-04

### Lubrication performance of sustainable microgel particles for fat replacement applications

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With obesity being an increasing health concern, replacements of calorie-dense fat in diet is a necessity. To address this, creation of sensorially-appealing fat replacers has been a design challenge for colloid scientists. Proteinaceous microgels have recently been found to have ultra-lubricating properties<sup>1, 2</sup> and are hypothesised to act as fat replacers<sup>3</sup>. However, such microgels have not been applied to more sustainable plant protein<sup>3</sup>, the latter is often associated with generating high friction in between oral contact surfaces and consequently generate astringency issues<sup>4</sup>. The aim of this study was to design novel ultra-lubricating microgels using plant proteins and compare lubrication performance of various volume fractions (10-70 vol%) of the same to that of a fat emulsion. An array of characterization techniques combining oral tribology using 3D biomimetic tongue-like surface<sup>5</sup>, rheology, dynamic light scattering (DLS), atomic force microscopy (AFM), quartz crystal microbalance with dissipation monitoring (QCM-D) and adsorption techniques were used to characterize these newly designed microgels and their surface properties. Potato protein microgels at 5 and 10 wt% protein (PoPM5, PoPM10), pea protein microgel at 15 wt% protein (PePM15) and combined alternative protein microgel at 12.5 wt% (Po5:Pe7.5) were prepared at pH 7.0

by thermally crosslinking the proteins at 80 °C for 30 minutes to form gels, followed by shearing the protein gels. AFM and DLS revealed that microgels were sub-micron sized ranging in diameter from 85 to 232 nm with low polydispersity ( $\leq 0.25$ ). The microgels were relatively soft with storage modulus varying from 0.35 to 6.5 kPa. Irrespective of the type of proteins used, the microgel dispersions presented excellent lubrication performance especially at 40 vol% and 70 vol% owing to their adsorption properties as well as high effective viscosities. Strikingly, PePM15 microgels had similar friction coefficient values to that of the 20 wt% oil-in-water emulsion when introduced between 3D biomimetic tongue-like surface. Thus, we demonstrate for the first time that these sustainable protein microgels allow better incorporation of alternative protein in low calorie food without any negative mouthfeel consequences. References Sarkar, et al., *Langmuir* 33, 14699-14708 (2017). Andablo-Reyes, et al., *Soft Matter* 15, 9614-9624 (2019). Kew et al., *Trends Food Sci and Tech* 106, 457-468 (2020). Kew et al., *Food Hydrocolloid* 116, Art No. 106636 (2021). Andablo-Reyes, et al., *ACS Appl. Mater. Interfaces* 12, 49371–49385 (2020). Acknowledgement The European Research Council (ERC) is acknowledged for its financial support (757993).

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Wed-KW1-05

### Drainage of protein foams and foam films

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Many food, cosmetic and pharmaceutical foams contain proteins that influence both the interfacial and bulk properties of formulations. In this study, we characterize the drainage of protein-based foams as well as single foam films, and contrast their behavior with micellar foams formed with small molecular surfactants above the critical micelle concentration. Micellar foam films undergo drainage via stratification manifested as step-wise thinning in the plots of average film thickness over time. Stratification in micellar foam films is accompanied by formation of coexisting thick-thin regions visualized in reflected light microscopy as exhibiting distinct grey regions as intensity is correlated with thin film interference. We critically examine the drainage of protein foam films to determine how and when stratification can be observed, and evaluate the connection between drainage of single foam films and bulk foams.

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Wed-KW1-06

### Phase Instability in Pharmaceutical Surfactant/Preservative Formulations

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Formulation instability arising from incompatibility between surfactant and antimicrobial preservatives is a challenge for the pharmaceutical industry. This incompatibility usually results in increased solution turbidity caused by micelle aggregation. It is of particular interest to characterize the aggregation behavior in these surfactant/preservative solutions to reveal the fundamental cause of instability. Here, stability conditions are assessed for solutions containing a popular nonionic surfactant, polysorbate 80 (PS80), and a commonly used antimicrobial preservative, m-cresol. Small-angle neutron scattering (SANS) of these solutions reveals room temperature stability criteria, where PS80/m-cresol solutions are stable for at least 50 hours at m-cresol concentrations below 2 mg/mL or above 4.5 mg/mL. For m-cresol concentration between these two stability regimes (2 mg/mL to 4.5 mg/mL), solutions become unstable as large aggregates form and grow over the course of weeks. We propose a kinetic model capable of characterizing and predicting the multi-stage aggregation kinetics in PS80/m-cresol solutions. The SANS results also



provide insight into the critical influence of m-cresol concentration on stable micelle morphology, which will help reveal the cause of solution instability. This work identifies stable formulation criteria for PS80/m-cresol solutions and expands understanding of the effect of excipients on surfactant self-assembly.

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Wed, 16 09:00 - 11:00

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Wed-LW1-01

Enhanced colloidal stability and catalytic activity of gold nanoparticles in porous materials

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The assembled state of nanoparticles (NPs) within porous matrices plays a governing role in directing their biological, electronic, and catalytic properties. However, the effect of external stimuli such as temperature, salinity, and pH on NP assemblies within the pores is poorly understood. In this study, we use adsorption isotherms, spectrophotometry, and small angle neutron scattering to develop an understanding of the effect of spatial confinement on the assembled state and catalytic performance of gold (Au) NPs in the nanopores of amine-functionalized SBA-15 silica materials (mSiO<sub>2</sub>). We investigate the effect of pH and ionic strength on the packing and spatial distribution of Au NPs within mSiO<sub>2</sub>. We find that a combination of confinement and electrostatic attraction between Au NPs and pore wall increases the available surface area of Au NPs by restricting their aggregation in high ionic strength solution. We show that the ability of the adsorbed NPs to withstand the aggregation allows retaining their catalytic activity for a model reaction, here reduction of p-nitrophenol, which otherwise is significantly diminished due to bulk aggregation of the NPs. This fundamental study demonstrates the critical role of confinement on the adsorption and catalytic performance of nanoparticles, thus establishes a link between the structure-property relationship of such nanomaterials.

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Wed-LW1-02

The Effect of CeO<sub>2</sub> Aerogel Supports on Activity, Speciation, and Stability of Nickel for CO Oxidation

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Nickel-based heterogeneous catalysts offer an economic alternative to traditional Pt or Au based materials, but their specific activity and stability typically still fall short of these precious metals. Nanostructured materials with Ni affixed over oxide supports – such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, or CeO<sub>2</sub> – can improve performance by both exposing more active sites and promoting metal-support interactions. However, many questions remain regarding the nature of the active Ni phase, its stability under operating conditions, and the supporting oxide effect on this stability. In this work, we use CeO<sub>2</sub> aerogels as supports for photodeposited Ni nanoparticles and demonstrate that CeO<sub>2</sub> aerogels stabilize the active Ni phase for CO oxidation. The aerogel expression of CeO<sub>2</sub> provides an ideal support for Ni, with high surface area and a mesoporous structure that allow facile permeation of gas to the active sites. Activity for Ni nanoparticles on CeO<sub>2</sub> was found to be far greater than that of unsupported Ni or Ni supported by structurally similar TiO<sub>2</sub> aerogels, indicating a unique interaction between Ni and CeO<sub>2</sub>. CeO<sub>2</sub> aerogels with 2.5 wt.% Ni were shown to have both higher activity per mol of Ni and greater stability than higher weight loadings, with 95% CO conversion at 200 °C and no decline in activity after 12 hours of continuous reaction. Through *ex-situ* XPS analysis, it is revealed that intimate contact between Ni and CeO<sub>2</sub> stabilizes the highly active Ni(OH)<sub>2</sub> phase,

preventing the conversion to NiO that occurs in higher weight loading with aggregated Ni. These results reveal CeO<sub>2</sub> aerogels to be an ideal supporting oxide for Ni catalysts and provide important insights regarding the effect of Ni phase for CO oxidation.

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Wed-LW1-03

### Uncovering Mechanisms of Tunable Alcohol Oxidation over Cu/TiO<sub>2</sub> Aerogel Materials at the Gas-Surface Interface

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Virginia Tech Department of Chemistry

Oxidative reactions between alcohols and oxide-supported metal nanoparticles are of keen interest to both the commodity chemical industry and to the broader catalyst scientific community. Recently, high surface area Cu/TiO<sub>2</sub> aerogel materials have been shown to be active for CO oxidation, promoted by electronic metal-support interactions, and chemical warfare agent decomposition involving alkoxy loss. Here we provide insight into key steps in the oxidation of important alcohols, including methanol and 2-propanol, catalyzed by Cu/TiO<sub>2</sub> aerogels. Infrared spectroscopic measurements conducted in a high-vacuum cell were employed to isolate surface-bound reactants and intermediates, while a packed-bed flow reactor monitored evolved gaseous products *in situ*. Vacuum and flow cell studies compliment one another to reveal distinct mechanistic steps, highlighting the unique activity of the Cu/TiO<sub>2</sub> aerogels. Dehydrogenation of the bound methoxy species leads to a formate intermediate before completely decomposing to form H<sub>2</sub>O and CO<sub>2</sub>. C-C cleavage first occurs on alcohols with a higher carbon content, before following a similar dehydrogenation pathway in the combustion catalysis. Bridging O atoms immediately surrounding Cu nanoparticles are hypothesized to play a key role in the overall chemistry and are active sites for catalysis on the aerogels. These discoveries further the understanding of fundamental surface reaction mechanisms and the role that alcohol structure has on adsorption and oxidation at the gas-surface interface of metal oxide-supported metal nanoparticles.

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Wed-LW1-04

### Understanding the Role of SnO<sub>2</sub> Surface Structure on Alcohol Oxidations using Ambient-Pressure X-ray Photoelectron Spectroscopy

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The exposed crystal planes of tin dioxide (SnO<sub>2</sub>) play a critical role in the observed surface reduction properties and influence the resulting surface chemistries. SnO<sub>2</sub> has been extensively studied due to its use in many areas such as transparent oxide conductors, gas sensing, and oxidation catalysis. Recently SnO<sub>2</sub> has been demonstrated for the oxidation of volatile organic compounds (VOCs), where 2-propanol was used as a representative VOC. The dual valency of the Sn enables the reduction of the SnO<sub>2</sub> surface via a transition from Sn<sup>4+</sup> to Sn<sup>2+</sup> and the formation of oxygen vacancies. In UHV, the transition from stoichiometric to reduced SnO<sub>2</sub>(110) surface occurs between 440-520 K, while the transition for a SnO<sub>2</sub>(101) surface occurs between 560-660 K. A recent study indicated that the ratio of Sn<sup>2+</sup>/Sn<sup>4+</sup> on SnO<sub>2</sub> nanomaterials strongly impact the activity of the oxidation of carbon monoxide. For this study, we have utilized ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and low energy electron diffraction to characterize the surface chemistry of 2-propanol on well-defined SnO<sub>2</sub>(110) and SnO<sub>2</sub>(101) surfaces. AP-XPS was performed on the SnO<sub>2</sub> surfaces in the presence of 2-propanol up to 1 mbar, various 2-propanol/O<sub>2</sub> ratios, and over a range of temperatures. These studies allow us to directly compare the catalytic properties and the oxidation states of the two surface terminations under reaction conditions. The

oxidation selectivities will be compared for a range of reaction conditions for SnO<sub>2</sub>(101) and SnO<sub>2</sub>(110) surfaces and results will be related to the surface atomic structure.

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Wed-LW1-05

## Selective Deposition of Nanoarchitectures using Surface Functionalization for Designing Next-Generation Catalyst Materials

**Kathryn Perrine (kaperrin@mtu.edu)**

Michigan Technological University

Designing next-generation heterogeneous catalysts and semiconductors requires atomic level control for precise placement and growth of metal oxide nanostructures. It is desirable to grow catalysts of high surface area on a support with precise placement on the support, while with semiconductors, the ultra-thin films at the atomic level without edge placement errors is required. Area selective deposition (ASD) allows for the control over the metal oxide deposition, nucleation, and growth on a support by surface functionalization and surface limiting reactions. In this presentation, I will discuss our work on functionalization of HOPG (highly oriented pyrolytic graphite) surfaces for selective deposition of metal oxide nanostructures, as a proof-of-concept for designing heterogeneous catalysts. The effects of surface functional groups and defects on the growth of Al<sub>2</sub>O<sub>3</sub> using atomic layer deposition (ALD) and iron oxide architectures on HOPG surfaces was investigated using surface spectroscopy and microscopy analysis. Results show that ALD of Al<sub>2</sub>O<sub>3</sub> was grown selectively at OH functional group sites and tailored defects, which depend on the placement of the functional groups. At submonolayer coverages, the Al<sub>2</sub>O<sub>3</sub> nanostructures were found to grow at different locations of the surface after etching with two different acids. Etching the HOPG surface with nitric acid was found to functionalize defects, where nanoparticles were grown. When the HOPG surface was etched with hydrochloric acid, Al<sub>2</sub>O<sub>3</sub> was shown to grow on the terrace regions of the surface. The results of this lead to investigating how each acid at different concentrations affects the etching mechanism on the HOPG surface, where both acids produced hydroxy functional groups, but with different morphologies. These studies are in contrast to spontaneous deposition of iron oxide nanoparticles on tailored HOPG defects using an iron precursor solution. There it was found that FeO and FeOH species were identified on the surface of the nanoparticles. Further annealing was found to oxidize into primarily the hematite phase. These studies show that a combination of surface functionalization, defect engineering, and an understanding of surface chemistry can be utilized to selectively grow atomically precise metal oxide nanostructures for next-generation technologies.

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Wed-LW1-06

## Controlling Metal Deposition on Bimetallic Plasmonic-Catalytic Nanostructures Using Visible Light

**Michelle Personick (mpersonick@wesleyan.edu)**

Wesleyan University, Department of Chemistry

Controlling the localization of the component metals in bimetallic nanostructures is key to understanding the relationships between surface structure and catalyst performance. However, the synthesis of bimetallic nanoparticles with well-controlled surface architectures can be challenging because metals that have differing reactivity in their reduced states—which is often desirable for tuning catalyst selectivity—also have metal ion precursors with different redox chemistries. This difference in precursor chemistry can lead to undesired inhomogeneities during nanoparticle growth. For example, deposition of a catalytically active metal such as platinum at the surface of a plasmonically active silver nanoparticle can enable visible-light-tunable catalytic reactivity at the interface between the two metals. However, platinum has a higher reduction potential than silver does, which leads to the competitive process of galvanic replacement where each platinum ion oxidizes and displaces multiple silver atoms, generating surface defects. We have shown that visible light illumination can be used to overcome this undesired process of galvanic replacement by shifting the reaction to favor direct platinum ion reduction. This level of control is not achievable using purely chemical or thermal approaches and enables the selective generation of well-defined core-shell and core-

satellite nanostructures. The underlying mechanism involves the plasmon-assisted oxidation of a weak reducing agent, and therefore the approach has the potential to be generalizable to other catalytically relevant compositions.

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Wed, 16 09:00 - 11:00

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Wed-NW1-01

DNA-programmed Assembly of Nanoparticle Superlattices at Interfaces (**Keynote Lecture**)

**Robert Macfarlane (rmacfarl@mit.edu)**

Department of Materials Science, Massachusetts Institute of Technology

The programmability of DNA makes it an attractive structure-directing ligand for the assembly of nanoparticle superlattices with unique structure-dependent physical phenomena. While DNA base pairing has enabled the development of materials with nanometer-scale precision in nanoparticle placement and independent control over particle size, lattice parameters, and crystal symmetry, manipulating the macroscopic shape of the lattices remains challenging. By pairing this “bottom-up” assembly method with “top-down” lithographic techniques and assembling nanoparticle superlattices on a patterned substrate, complete control over crystal size, shape, orientation and unit cell structure can be realized. The key challenges in developing this technique are to first understand how different design factors affect the assembly process in this broken-symmetry system that is assembled at an interface, and subsequently develop structure-property relationships that correlate the above mentioned design parameters with the resulting overall material structure. Here, we examine both at-equilibrium deposition processes capable of generating single crystals with well-defined shapes, as well as post-deposition annealing to transform disordered particle arrangements into crystalline arrays. Using a combination of X-ray diffraction and electron microscopy techniques, both surface morphology and internal thin film structure are examined to provide an understanding of the mechanisms of particle crystallization under conditions where crystal growth is anisotropic due to a boundary condition. This novel method for controlling particle assembly draws several strong analogies to traditionally atomic epitaxy/heteroepitaxy, providing a useful tool for understanding thin film growth processes. As a result, we are able to realize 3D architectures of arbitrary domain geometry and size, thereby making materials with unprecedented precision across multiple length scales.

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Wed-NW1-02

Information storage via immobilization of encoded DNA on ultra-high surface-area magnetic soft dendritic colloids

**Cyrus Cao (ycao27@ncsu.edu), Kevin Lin (nlin4@ncsu.edu), Austin Williams (ahwilli5@ncsu.edu), Albert Keung (ajkeung@ncsu.edu), Orlin Velev (odvelev@ncsu.edu)**

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh

DNA could provide the needed technological leap for future digital data storage due to its high storage density, longevity, and energy efficiency. A generic DNA-based information storage system includes database synthesizing, information accessing, and reading. While previous research focused on improving the efficiency of database synthesis and information reading, a key challenge remained to address how to efficiently access specific information from a large complex system. One must find solutions to how file-encoded DNA strands are copied, separated, and purified in the batch processes. Here, we propose to immobilize the DNA database on a very high surface area, high accessibility 3-dimensional soft dendritic scaffold in a continuous packed-bed reactor. The new design would allow information to be copied and accessed by flowing reagents through the immobilized file-encoded strands. In this research, we aimed to understand the efficiency of binding the file-encode DNA to the soft dendritic colloids (SDCs). This can be achieved by 1) incorporating magnetic nanoparticles into SDCs, 2) separating colloidal particles using a

generic magnetic stand, and 3) dispersing the SDCs in aqueous solutions and activating their surface with chemicals to allow binding of fluorescently labeled DNA. Our present work investigated the degree of surface activation and the DNA binding efficiency. Future work will include gelling the soft dendritic colloids to form a packed-bed column for functionalizing with file-encoded DNA strands. This work lays the foundation of developing a colloidal DNA-based storage system that has the potential to provide a cost-effective, energy-efficient, and long-lasting alternative for the rising concerns in global digital information storage.

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Wed-NW1-03

Sum frequency generation (SFG) microscopy analysis of cellulose microfibrils in *Physcomitrium patens* and the effect of Cellulose Synthase (CESA) mutation

**Jongcheol Lee (jul1371@psu.edu)<sup>1</sup>, Alison Roberts (aroberts@uri.edu)<sup>2</sup>, Arielle Chave (ariellec@uri.edu)<sup>2</sup>**

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The moss *Physcomitrium patens* (*P. patens*) has potential as a model system to study protein structure-function relationships of cellulose synthases (CESAs) because of its ease of genetic mutation and culturing. However, analytical methods are limited due to mm-scale organs and low cellulose content of primary cell walls. Here, we analyze the cellulose content and the microfibril orientation in wildtype *P. patens* leaf tissues, one with only primary cell walls and one with primary and secondary cell walls. For cell type analysis, sum frequency generation (SFG) microscopy was applied with mm-scale spatial resolution. Additionally, we studied the effect of acidic region (DDED in *P. patens*), which lies adjacent to the FxVTxK motif within the region thought to act as a substrate gating loop by analogy to bacterial cellulose synthase. Gametophore development was restored in *cesa5* null mutants by expression of CESA5 with the DDED acidic region deleted, but cellulose content of the primary cell walls in the leaf lamina was only partially restored, in contrast to complementation with wild type CESA5, which fully restored cellulose content. The results suggest that the acidic region adjacent to the FxVTxK motif is required for normal cellulose synthesis.

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Wed-NW1-04

Sum frequency generation (SFG) microscopy analysis of cellulose microfibrils in *Physcomitrium patens* and the effect of Cellulose Synthase (CESA) mutation

**Jongcheol Lee (jul1371@psu.edu)<sup>1</sup>, Arielle Chave (ariellec@uri.edu)<sup>2</sup>, Alison Roberts (aroberts@uri.edu)<sup>2</sup>, Seong Kim (shk10@psu.edu)<sup>1</sup>**

<sup>1</sup> Department of Chemical Engineering, and Material Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, United States

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Cellulose is one of the most widely used natural resources we have been used for thousands of years. Thus, understanding its synthesis and structure is important. The moss *Physcomitrium patens* (*P. patens*) has potential as a model system to study protein structure-function relationships of cellulose synthases (CESAs) because of its ease of genetic mutation and culturing. However, analytical methods are limited due to mm-scale organs and low cellulose content of primary cell walls. Here, we analyze the cellulose content and the microfibril orientation in wildtype *P. patens* leaf tissues, one with only primary cell walls and one with primary and secondary cell walls. For cell-specific analysis, we applied sum frequency generation (SFG) microscopy system. SFG spectroscopy is known to detect crystalline cellulose selectively in plant cell walls. Micron-scale spatial resolution allowed to detect the low cellulose content in primary cell

wall in laminar tissue. Also, by comparing with reference samples where microfibrils are highly aligned, we found that the cellulose microfibrils in midrib tissue cell walls are highly aligned along the cell long axis. Additionally, we studied the effect of acidic region (DDED in *P. patens*) in CESAs, which lies adjacent to the FxVTxK motif within the region thought to act as a substrate gating loop by analogy to bacterial cellulose synthase. Gametophore development was restored in *cesa5* null mutants by expression of CESA5 with the DDED acidic region deleted, but cellulose content of the primary cell walls in the leaf lamina was only partially restored, in contrast to complementation with wild type CESA5, which fully restored cellulose content. The results suggest that the acidic region adjacent to the FxVTxK motif is required for normal cellulose synthesis.

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Wed-NW1-05

### Straining Membrane Vesicles and Cells in Aqueous Nematic Liquid Crystals

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Understanding how biological assemblies deform in response to mechanical interactions is central to understanding the functions of many biological systems. In this presentation, we will describe how aqueous liquid crystals (LCs) provide the basis of novel approaches to measuring the mechanical properties of membrane vesicles and cells. First, we will report how cycles of thermally induced phase transitions between nematic and isotropic phases can be used to exert cyclical elastic stresses on giant unilamellar vesicles (GUVs) and thereby evolve their shapes and properties. We observe GUVs to form a range of complex shapes, including stomatocyte, pear- and dumbbell-like shapes that depend on the extent of strain in the LC phase. Second, we will report on the use of LC elastic stresses to provide insight into the mechanical properties of cell membrane-derived vesicles. Specifically, we will describe experimental results in which LCs are used to strain giant plasma membrane vesicles (GPMVs) blebbed from cells expressing the mucin Muc1. We will show how the extent of straining of GPMVs changes with the level of expression of Muc1 on their membranes. Finally, recent results obtained with the straining of red blood cells in LCs will be shown to provide insight into the extent of variation of the mechanical properties of cells within a population. Overall, these examples will illustrate the utility of aqueous LC phases as elastic liquids for straining a range of soft biological assemblies.

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## Wed, 16 09:00 - 11:00

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Wed-OW1-01

### Atomically Precise Chemical, Physical, Electronic, and Spin Contacts (**Keynote Lecture**)

**Paul S. Weiss (psw@cnsi.ucla.edu)**

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Two seemingly conflicting trends in nanoscience and nanotechnology are our increasing ability to reach the limits of atomically precise structures and our growing understanding of the importance of heterogeneity in the structure and function of molecules and nanoscale assemblies. By having developed the “eyes” to see, to record spectra, and to measure function at the nanoscale, we have been able to fabricate structures with precision as well as to understand the important and intrinsic heterogeneity of function found in these assemblies. The physical, electronic, mechanical, and chemical connections that materials make to one another and to the outside world are critical and are intertwined in terms of their function. Just as the

properties and applications of conventional semiconductor devices depend on these contacts, so do nanomaterials, many nanoscale measurements, and devices of the future. We discuss the important roles that these contacts can play in preserving key transport and other properties. Initial nanoscale connections and measurements guide the path to future opportunities and challenges ahead. Band alignment and minimally disruptive connections are both targets and can be characterized in both experiment and theory. Chiral assemblies can control the spin properties and thus transport at interfaces. I discuss our initial forays into these areas in a number of materials systems.

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Wed-OW1-02

## Investigation of Ion Pairing Between Alkali Metal Cations and Anionic Surfactant Monolayers

**Kenneth Judd (kdj6@psu.edu)**<sup>1</sup>, **Paul Cremer (psc11@psu.edu)**<sup>1,2</sup>

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Ion pairing between alkali metal cations and packed and fully deprotonated anionic surfactant monolayers are examined with respect to the Law of Matching Water Affinities (LMWA), which predicts thermodynamic hydration properties determine the ability to form contact ion pairs between oppositely charged ions. Thermodynamic information obtained from Langmuir isotherms and interfacial water structure obtained from vibrational sum frequency spectroscopy (VSFS) produced a ranked order of preferential ion pairing between alkali metal cations with both carboxylate and alkyl sulfate, while specifically targetting the carboxylate and sulfate vibrational stretching modes separated water-mediated interactions from inner-sphere ion pairing. The results revealed the complexity of ion pairing at a soft matter interface, with pH, the chemical nature of the headgroup, and the interfacial charge density playing roles in determining the preferential nature of alkali metal interactions with carboxylate and alkyl sulfate as well as whether the ions are able to fully shed hydration shell water to form contact ion pairs.

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Wed-OW1-03

## Quantification of the Spatial Binding Preferences for Nanoparticle Surface Ligands through a Molecule Labeling Strategy

**Zhi Yang (zy28@rice.edu)**<sup>1</sup>, **Spoorthi Kamepalli (sk113@rice.edu)**<sup>1</sup>, **Sarah Rehn (smr14@rice.edu)**<sup>1</sup>, **Muhua Sun (ms166@rice.edu)**<sup>1</sup>, **Matthew Jones (mrj@rice.edu)**<sup>1,2</sup>

<sup>1</sup> Department of Chemistry, Rice University

<sup>2</sup> Department of Materials Science and Nanoengineering, Rice University

A precise description of the ligand shell on the nanoparticle surface will offer not only conclusive insight about crystal growth but also tailorable ways for selective functionalization of ligands. Yet the investigation of preferential binding is largely hindered due to lack of methods for quantifying spatial preference. In this study, 13 nm Au nanoparticle labeled thiol was designed as a tool for quantification of the binding preference on Au prisms under Transmission Electron Microscopy(TEM), statistical analysis of TEM images showed the thiol ligands binding preferentially to the edges and tips on the Au prism. In our method, triangular Au prisms were deposited in the Au labelled thiol ligand solution for observing binding events. A two-step washing protocol was developed for removing non-specific binding probes and allowing clear TEM imaging. The protocol has shown to be effective with testing the binding of control probes, which did not bind to the Au prisms through specific binding and were removed after stringent wash. The preference of binding on different crystallographic regions of the prisms was quantified by normalizing the probe positions relative to the triangular prisms. The ligand binding sites were obtained using non-parametric estimation, which showed that the tips and edges of the Au prisms are more active binding sites for thiol ligands.

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Wed-OW1-04

## Microgels at the air-water interface: compression and shear response probed by a novel quadrotrough

**Benjamin Thompson (bthompsn@udel.edu), Norman Wagner (wagnernj@udel.edu)**

Department of Chemical and Biomolecular Engineering, University of Delaware

Complex, fluid-fluid interfaces are all around us. We encounter them in consumer products, they structure our food, and they can be found in many biological systems such as the lining of alveoli. The main method for interrogating such systems is the Langmuir trough. An issue with this method is that upon compression, both the shape and area of the interface are changed and hence the response is due to both deviatoric and isotropic stresses and separation of the two contributions is a significant challenge.[1] Recently, a radial version of the Langmuir trough has been designed which, upon compression, keeps the shape of the interface the same while changing the area i.e., only compressional stress is applied.[2] Our work further expands on this by using a novel instrument which can independently control compression and shear. Poly(N-isopropylacrylamide) (PNIPAM) microgels are well studied and are a suitable model system to explore with our instrument. We have modified a reported synthesis of N,N'-methylenebisacrylamide cross-linked PNIPAM microgels, as well as ultra-low cross-linked PNIPAM microgels,[3] to significantly reduce the particle size (~90 nm) and investigated their response to pure compression/expansion, pure shear and combinations thereof. Furthermore, we have combined the Quadrotrough with other interfacial characterization techniques such as Brewster angle microscopy and particle image velocimetry to obtain new insights into how PNIPAM microgels behave at the air-water interface. [1] Jaensson, N.; Vermant, J. Tensiometry and Rheology of Complex Interfaces. *Curr. Opin. Colloid Interface Sci.* 2018, 37, 136–150. [2] Pepicelli, M.; Verwijlen, T.; Tervoort, T. A.; Vermant, J. Characterization and Modelling of Langmuir Interfaces with Finite Elasticity. *Soft Matter* 2017, 13 (35), 5977–5990. [3] Scotti, A.; Bochenek, S.; Brugnoli, M.; Fernandez-Rodriguez, M. A.; Schulte, M. F.; Houston, J. E.; Gelissen, A. P. H.; Potemkin, I. I.; Isa, L.; Richtering, W. Exploring the Colloid-to-Polymer Transition for Ultra-Low Crosslinked Microgels from Three to Two Dimensions. *Nat. Commun.* 2019, 10 (1), 1418.

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Wed-OW1-05

## Unraveling switch roles of lead ions in scheelite and fluorite flotation with AFM force mapping and first-principles calculations

**Jianyong He (hgy2016@csu.edu.cn)<sup>1</sup>, Wei Sun (sunmenghu@csu.edu.cn)<sup>1</sup>, Wenjihao Hu (huwenjihao@csu.edu.cn)<sup>2</sup>, Zhiyong Gao (zhiyong.gao@csu.edu.cn)<sup>1</sup>, Ruihua Fan (hgy2016@csu.edu.cn)<sup>1</sup>, Hongbo Zeng (Hongbo.Zeng@ualberta.ca)<sup>3</sup>, Zhiyong Gao (zhiyong.gao@csu.edu.cn)<sup>1</sup>**

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Metal ions play key roles in the selective modification of surface hydrophobicity, which has been utilized in the flotation separation of valuable complex ores such as scheelite and fluorite. We herein investigated batch flotation performance and  $\xi$  potential of scheelite and fluorite minerals with benzohydroxamic acid (BHA) as a collector in the absence and presence of lead ions [Pb(II)], respectively. It is found that lead ions play as a switch turning on the flotation of scheelite while turning off the flotation of fluorite. To unveil interaction mechanisms between BHA molecules and studied fluorite and scheelite surface, MBHA with a structure almost identical to BHA was self-assembled on atomic force microscope (AFM) tips via a typical thiol–Au bonding interaction. AFM force mapping results indicate that interactions between BHA and fluorite/scheelite surfaces are attractive/repulsive in the absence of lead ions, respectively. However, the



presence of lead ions has changed the force between BHA and fluorite/scheelite surfaces to be repulsive/attractive, respectively. These interface phenomena are further revealed by the FTIR, XPS, and systematic first-principles calculations. It is shown that BHA can adsorb on a positively charged fluorite surface due to the strong electrostatic attraction in the absence of lead ions. However, the BHA can not bind with the strong negatively charged scheelite and the hydroxylated Ca sites. In the presence of lead ions, lead ions taking on positive charges are left in solution to bind with the modified AFM-tip forming positively charged BHA-Pb complexes, which resulted in the repulsion between the AFM-tip and the fluorite surface. Very interestingly, the formation of both BHA-Pb complexes and the adsorption of lead ions has made the scheelite surface more attractive to BHA, which has resulted in more hydrophobic scheelite surfaces. Finally, we proposed a hybrid model to interpret the interaction of BHA and BHA-Pb complexes with the two minerals' surfaces. This work has shed some light on the development of selective modification methods of target surface by specific pre-depressing strategy.

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Wed, 16 09:00 - 11:00

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Wed-PW1-01

### Manufacturing Functional Materials from Polydisperse Anisotropic Nanomaterial Dispersions (Keynote Lecture)

**Virginia Davis (davisva@auburn.edu)**

Department of Chemical Engineering Auburn University

Dispersion processing is one of the most powerful methods for producing bulk materials including coatings, films, fibers, and molded or additive manufactured parts. Over the last ten years, the increased availability of an array of anisotropic nanomaterials has resulted in significant research into using fluid phase processing to transform these tiny building blocks into macroscale functional materials. Size polydispersity has significant impacts on the properties of anisotropic nanomaterial dispersions. Understanding the impacts of polydispersity on dispersions' rheological and microstructural is critical to manufacturing materials with desired properties. Such understanding can be achieved by extending the foundations provided by colloid and liquid crystal science. This talk will provide two examples from my recent research. First, the self-assembly of 1D cellulose nanocrystals into photonic films will be described. Second, the formulation and rheology of printable inks of MXenes, a 2D nanomaterial, will be described along with the electrochemical properties of printed devices. These results highlight the value of using the tools and principles of colloid science to manufacture novel functional materials.

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Wed-PW1-02

### Scalable synthesis of soft nanofiber forests using liquid crystals and emergent electro-optical properties

**Sangchul Roh (sr974@cornell.edu)**<sup>1</sup>, **John Kim (johnjk@umich.edu)**<sup>2</sup>, **Joerg Lahann (lahann@umich.edu)**<sup>2,3</sup>, **Nicholas Abbott (nla34@cornell.edu)**<sup>1</sup>

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<sup>3</sup> Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT)

We report that chemical vapor polymerization of [2.2]paracyclophane derivatives into films of a nematic liquid crystal (LC) formed from 4-(trans-4-pentylcyclohexyl) benzonitrile and 4-(trans-4-propylcyclohexyl) benzonitrile leads to the templated synthesis of shape-defined (bent), end-attached polymeric nanofibers with precise diameters and lengths. The polymer fibers form as dense arrays that extend into the LC template film. Upon application of an electric field across the LC-nanofiber film, we measure the reorientation of the LC to be coupled to the reshaping of the nanofiber (from bent to straight), thus defining a new class of nanostructures with electro-optical and mechanical properties that are determined by a

sharing of mechanical strain at the nano-scale. We construct an electromechanical model that captures the exchange of elastic energy between the LC and nanofibers. We also observe patterned orientations of LCs to template the formation of patterned arrays of nanofibers (e.g., defining mesoscale vortices), thus providing a new approach to generation of complex electro-optical responses that arise from the sharing of strain between the LC and nanofiber. Overall, these results reveal that LC-templated polymeric nanofiber arrays provide a scalable approach to the manufacturing of a new class of optical metamaterial films.

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Wed-PW1-03

## Highly Conductive Silicone Elastomers via Water-Induced Swelling and In Situ Synthesis of Silver Nanoparticles

**Hong Zhao (hzhao2@vcu.edu)**<sup>1</sup>, **Yuanhang Yang (yangy38@vcu.edu)**<sup>1</sup>, **Shun Duan (duanshun@mail.buct.edu.cn)**<sup>2</sup>

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<sup>2</sup> Beijing University of Chemical Technology, China

Flexible and stretchable conductors are crucial components for next generation flexible devices. Wrinkled structures often have been created on such conductors by depositing conductive materials on the pre-stretched or organic solvent swollen samples. In this work, water swelling is first proposed to generate the wrinkled structures on silicone elastomers. By immersing silicone/sugar hybrid in water, a significant amount of swelling occurs as a result of osmosis and capillary interactions with the sugar and silicone matrix. Considering the drastic swelling effect and controllable swelling ratio, water swelling is used to replace the conventional pre-stretching and organic solvent swelling to fabricate stretchable conductors. In situ growing of silver nanoparticles (AgNPs) was carried out on the swollen silicone elastomers. Wrinkled conductive silicone elastomers were successfully constructed after removing the residual water. The conductive elastomer has a sheet resistance of less than  $1 \Omega \text{ sq}^{-1}$  at zero strain and also shows high sensitivity when subjected to external deformation up to 100% strain. The silicone/sugar composite also possesses good 3D printability with the desired shear-thinning property, which is important in fabricating functional devices with designed shapes and patterns. Human motion detection has been demonstrated using the 3D printed sensors. This work provides a facile and environment-friendly strategy to fabricate superior flexible and stretchable sensing devices.

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Wed-PW1-04

## Chemical and Engineering Approaches for Soft Material Additive Manufacturing (**Keynote Lecture**)

**AJ Boydston (a Boydston@wisc.edu)**

Department of Chemistry University of Wisconsin Madison, WI 53706

Our research team focuses on discovering and developing new chemical approaches and engineering techniques for additive manufacturing. As representative examples, we will discuss two unique approaches for additive manufacturing with silicone resins. In each example, we aim for complete geometric freedom as one would enjoy from vat photopolymerization or material fusion techniques, yet neither of our approaches use any photochemical or powder bed technologies. In one discovery, we realized that heating at a patterned photothermal interface (HAPPI) additive manufacturing could be achieved using near-IR light sources in combination with photothermal vat materials. In this way, we were able to construct 3D objects using patterned light while relying on thermal curing of traditional silicone resins. The preliminary mechanical properties of printed parts after thermal post-treatment are on par with those of molded parts. Separately, we discovered that high-intensity focused ultrasound can be used as a method for converting liquid silicone resins into cured 3D object, even through optically opaque barriers.

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Wed, 16 09:00 - 11:00

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Wed-QW1-01

## Structural Investigations of LiCoO<sub>2</sub> (001) by UHV- Scanning Tunneling Microscopy and Low Energy Electron Diffraction

**Yuchen Niu ([niu@umd.edu](mailto:niu@umd.edu)), Janice Reutt-Robey ([rrobey@umd.edu](mailto:rrobey@umd.edu))**

Dept. of Chemistry & Biochemistry University of Maryland, College Park

Advances in energy technologies require deeper understanding and control of key structure- property relationships of battery materials. LiCoO<sub>2</sub>, though widely used in energy storage devices as cathode materials, such fundamental properties as surface atomic structure, and its impact on Li-ion insertion and surface reactivity, remain poorly understood. The lack of protocols to generate well-defined LiCoO<sub>2</sub> surfaces is hindering atomically precise characterizations. We report on two approaches to prepare high quality LiCoO<sub>2</sub> (001) surfaces. The first adapts surface chemical treatments commonly used to prepare singular metal oxide surfaces. A regimen of cycles of argon ion sputtering, ultra-high vacuum (UHV) annealing, and post oxygen treatment in the 10<sup>-6</sup> torr range is applied to singular LiCoO<sub>2</sub> platelets. Vapor-grown platelets<sup>1</sup> of 2-3 mm dimension display single crystallinity and [001] orientation, confirmed by XRD. As-grown surfaces exhibit 10- 20 nm topographic variations by ambient AFM imaging, and release considerable CO<sub>2</sub> gas upon heating under vacuum, indicating the presence of surface carbonates. UHV annealing at 600 °C yields a diffuse hexagonal low energy electron diffraction (LEED) pattern. LEED (001) features sharpen after several sputter-anneal cycles and corresponding UHV-STM images reveal a root mean square surface roughness of 1.6 nm, nearly an order of magnitude improvement from as-grown surfaces. Oxidative treatments introduce new diffraction features, suggestive of cobalt oxide formation, which disappear upon subsequent sputter-anneal cycles, yielding a smoother surface. The continued optimization of this regimen suggest atomically ordered (001) terraces may be realized. Our second approach involves LiCoO<sub>2</sub> (001) generation via *in situ* cleavage. We report the design and operation of a low-temperature cleavage device, integrated to our UHV-STM chamber, that allows UHV transferring of freshly cleaved crystals to STM. The defect density (esp. vacancies) of the LiCoO<sub>2</sub> (001) surface should be sensitive to cleavage temperature, due to high mobility of lithium ions and their response to mechanical stress. The effectiveness of this cleavage approach has been demonstrated on Sr<sub>2</sub>RuO<sub>4</sub> (001)<sup>2</sup> and adapted to the present work, preliminary results will be presented. (1) Lin, Q.; Li, Q.; Gray, K. E.; Mitchell, J. F. Vapor Growth and Chemical Delithiation of Stoichiometric LiCoO<sub>2</sub> Crystals. *Cryst. Growth Des.* **2012**, *12*, 1232–1238. (2) Pennec, Y.; Ingle, N. J. C.; Elfimov, I. S.; Varene, E.; Maeno, Y.; Damascelli, A.; Barth, J. V. Cleaving-Temperature Dependence of Layered-Oxide Surfaces. *Phys. Rev. Lett.* **2008**, *101*, 216103.

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Wed-QW1-02

## Polarizability of Metallodielectric Janus Particles in Electrolyte Solutions.

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Chemical and Biomolecular Engineering, Vanderbilt University

Metallodielectric Janus particles (JPs) and electric fields have been a useful combination for the development of innovative concepts on AC electrokinetics, directed transport and collective dynamics. The polarizability and its frequency dependence underlie the rich behavior exhibited by JPs. Nonetheless, direct measurements of polarizability are few and the interplay of different mechanisms remains unclear. This talk will discuss measurements and strategies to tailor the magnitude of the polarizability of JPs. Our approach uses electrorotation to measure the polarizability of particles with different thickness of metal in electrolyte solutions. On the other hand, we gain further insight into the basic polarization mechanisms through modeling based on the fundamental transport equations. JPs exhibit rich polarization spectra that depends strongly on the thickness of the metal layer, the conductivity of the medium and surface charge of the dielectric core. At intermediate frequencies—around 10 kHz—the results indicates that counterfield rotation stems from the charging of the double layer at the particle-electrolyte interface, while the transition to cofield rotation at high frequencies (above 100 kHz) stems from the Maxwell-Wagner relaxation. The latter

polarization mechanism is significantly affected by the conductivity within the electrical double layer. The insights from this study will provide helpful quantitative information for the design of colloidal machines with targeted propulsion, interparticle interactions and collective dynamics.

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Wed-QW1-03

Capillary force on an 'inert' colloid: a physical analogy to dielectrophoresis

**Joseph Barakat (josephbarakat@ucsb.edu), Todd Squires (squires@engineering.ucsb.edu)**

University of California, Santa Barbara

'Inert' colloids are  $\mu\text{m}$ -scale particles that create no distortion when trapped at a planar fluid-fluid interface. When placed in a curved interface, however, such colloids can create interfacial distortions of quadrupolar symmetry -- so-called 'induced capillary quadrupoles.' The present work explores the analogy between capillary quadrupoles and electric dipoles, and the forces exerted on them by a symmetry-breaking gradient. In doing so, we weigh in on an outstanding debate as to whether a curvature gradient can induce a capillary force on an inert colloid. We argue that this force exists, for the opposite would imply that all dielectrophoretic forces vanish in two dimensions (2D). We justify our claim by solving 2D Laplace problems of electrostatics and capillary statics involving a single particle placed within a large circular shell with an imposed gradient. We show that the static boundary condition on the outer shell must be considered when applying the principle of virtual work to compute the force on the particle, as verified by a direct calculation of this force through integration of the particle stresses. Our investigation highlights some of the subtleties that emerge in virtual work calculations of capillary statics and electrostatics, thereby clarifying and extending previous results in the field. The broader implication of our results is that inert particles -- including particles with planar, pinned contact lines and equilibrium contact angles -- interact through interparticle capillary forces that scale quadratically with the deviatoric curvature of the host interface, contrary to recent claims made in the literature.

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Wed-QW1-04

Liquid-Phase TEM Imaging of Oriented Attachment in Nanoparticle Superlattices Assisted by Machine Learning

**Chang Liu (changl5@illinois.edu), Lehan Yao (lehan2@illinois.edu), Qian Chen (qchen20@illinois.edu)**

University of Illinois at Urbana-Champaign

We utilize nanoparticle dispersion as a model system to study the fundamentals of order emergence and evolution at the nanoscale. Diverse superlattices with distinct Moire patterns are achieved under liquid-phase TEM which enables single-particle level imaging in real time and real space. To be specific, coalescence and oriented attachment of two dimensional/three dimensional (2D/3D) superlattices are observed, where both attach-rotate and prealign-attach behaviors occur. Machine learning is used for the first time to extract the structural information in 3D superlattices especially in the regions with Moire patterns, which further helps to identify single particle behaviors. Furthermore, the high spatiotemporal resolution enables us to identify single particles and to map out their trajectories sampling the energy landscape. The individual fast motion (e.g. surface and volume diffusion) along with collective motion (e.g. transient neck formation, translational and translational motion of the domains) drives the coarsening of the nanoparticle superlattice, which is attributed to the features of different interactions involved at the nanoscale. Our work proposes novel data acquisition protocol and offers new dynamic observations on the superlattice evolution with high spatial and temporal resolution, which can provide insight into material engineering at the nanoscale.

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Wed-QW1-05

## Synthesis of hybrid inorganic-organic microparticles with controlled composition

**Shreyas Joshi (ssjoshi@umass.edu), John Klier (klier@umass.edu), Peter Beltramo (pbeltramo@umass.edu)**

University of Massachusetts Amherst

The self-assembly of isotropic and anisotropic colloidal particles into higher-ordered structures has been of great interest recently due to the promise of creating metamaterials with novel macroscopic material properties. However, there are limitations in building such materials from monocomponent colloids, necessitating the development of Janus or multicomponent particles in order to more finely tailor microstructure and/or physicochemical properties. In this talk, we will present an emulsion polymerization approach to develop composite inorganic-organic microparticles with controlled size and inorganic nanoparticle loading. The resultant particles contain an inorganic constituent, TiO<sub>2</sub> nanoparticles, embedded within the organic constituent, diethyl methylene malonate (DEMM). A systematic study of the factors influencing the particle size and the microstructure is made by a design of experiments focusing on the effect of pH, surfactant concentration, and inorganic/organic ratio. The individual and interactive effects of these process variables are evaluated, identifying the importance of controlling the pH of the solution for modulating the overall particle size. The optimal synthetic procedure is then applied to different inorganic constituents (CdTe, ZnO) to form composite microparticles with tunable functionalities. Ongoing work is focused on quantifying the amount of inorganic nanoparticles in the organic matrix and developing strategies for tuning the inorganic/organic ratio in the final composite microparticles. This platform for synthesizing hybrid colloids may be extended in the future to anisotropic particles and will expand the possibilities of creating self-assembled metamaterials by controlling the functionality of the constituent microparticles.

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Wed-QW1-06

A smectic liquid crystal Langmuir film at the air/water interface: boundaries, thermodynamics and dynamics

**Huda Alwusaydi (halwusa1@kent.edu)<sup>1</sup>, Elizabeth Mann (emann@kent.edu)<sup>1</sup>, Jay Mann (jam12@case.edu)<sup>2</sup>**

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<sup>2</sup> Case Western Reserve University, Department of Chemical Engineering, Cleveland, OH, USA

Molecularly-thin smectic liquid crystal films at the air/water interface phase separate into regions with different numbers of layers, in analogy with free-standing smectic liquid crystalline films. We explore the boundary between two such regions, using a variety of experimental and numerical methods. We measure the line tension by stretching domains from their equilibrium circular shape and analyzing the free relaxation with a hydrodynamic model. We connect the line tension associated with the boundary to boundary structure and use the association to suggest effective line-active agents, to control the line tension and thus the domain size distribution, shape and dynamics. Such line-active agents, which are not well-understood and have proved difficult to design, are empirically important to dynamic functional domains within cell-membranes.

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## Wed, 16 11:20 - 12:10

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Wed-SW1-01

Redox-Active Electrochemical Interfaces for Molecularly-Selective Separations (**2020 LaMer Award Lecture**)

**Xiao Su (x2su@illinois.edu)**

Chemical and Biomolecular Engineering, University of Illinois Urbana-Champaign

Fundamental understanding and control of interfacial chemistry is critical for the development of new, more efficient separation processes. Molecular selectivity is key for many applications, such as small molecule purification in the chemical industry, or selective pollutant removal for environmental remediation. Thermal and pressure-based systems can often incur high energetic costs, while adsorption technologies require harmful solvents and regenerants. By combining interfacial design with electrochemical modulation, selective adsorption can be carried out without the need for any chemical eluents or physical processing, leading to sustainable separations. Redox-active interfaces offer an attractive platform for performing selective electrochemical separations. Electroactive polymers can offer a wealth of flexibility in terms of structural design, and control of electronic properties. First, we discuss the capabilities of redox-active metallopolymer electrodes to enable reversible capture and release of anions [1-2]. The underlying binding mechanisms are then unraveled by a combination of electronic structure calculations and spectroscopy. Second, the capabilities of redox-electrodes are leveraged towards not only selective capture, but tandem reactive transformation of emerging contaminants of concern [3], including metal oxyanions and even perfluoroalkyl substances (PFAS). Finally, we present new directions in the structural tuning of redox-polymers for multicomponent ion separations [4]. By synthetic control of the redox-units, we can tune the charge-transfer interactions at the interface, and enable precise molecular binding. The nanoscale effects are explored by in-situ electrochemical methodologies, to track the breathing behavior of the redox-films during ion binding. Our concepts point towards an emerging direction in electrochemical interface design – by superimposing properly tuned chemical interactions, we can reach beyond double-layer effects and achieve unprecedented molecular selectivity. On the long term, electro-responsive surfaces provide us with a promising platform for sustainable separations and process intensification. **References** [1] X. Su, H.J. Kulik, T. F. Jamison, T. A. Hatton, “Anion-selective redox electrodes: electrochemically-mediated separation with organometallic interfaces,” *Advanced Functional Materials*. 2016, 26(20), 3394-3404. [2] X. Su, T.A. Hatton, “Redox-electrodes for Selective Electrochemical Separations,” *Advances in Colloid and Interface Science*, 2017, 244, 6-20. [3] K. Kim, S. Cotty, J. Elbert, R. Chen, C.H. Hou, X. Su, “Asymmetric Redox-Polymer Interfaces for Electrochemical Reactive Separations: Synergistic Capture and Conversion of Arsenic”, *Advanced Materials*, 2020, 32(6), 1906877. [4] R. Chen, J. Y. Feng, J. Jeon, T. Sheehan, C. Ruttiger, M. Gallei, D. Shukla, X. Su, “Structure and Potential-Dependent Selectivity in Redox-Metallopolymers: Electrochemically Mediated Multicomponent Metal Separations.” *Advanced Functional Materials*, 2021, 31(15), 2009307

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Wed, 16 12:40 - 13:30

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Wed-SW2-01

Designing Nanoparticles for Self-Assembly of Novel Materials (**2021 LaMer Award Lecture**)

**Rose K. Cersonsky (rose.cersonsky@epfl.ch)**

Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan  
Laboratory of Computational Science and Modeling, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

The design of new materials has often relied on crystal structure as a primary source for design complexity and innovation, requiring new crystal structures and new manners of constructing and synthesizing these structures. Nanoparticle self-assembly, or the spontaneous emergence of order due to particle interactions, has been identified as a favorable synthesis route in the photonics community, among others, as photonic nanocrystals reflect wavelengths within the visible range due to the scale-covariance of photonic band structures. The effort to self-assemble photonic crystals has been fraught with obstacles — from difficulty in synthesizing the diamond structure (the holy-grail within the photonics community) to the degradation of photonic band gaps based upon thermal noise within the assembly. In this talk, I will provide historical context for the pursuit of photonic crystals in the colloidal community and discuss the unexpectedly diverse range of crystallographic structures that will support a photonic band gap, as determined by more than 150,000 photonic band structure calculations. These calculations identify nearly 300 previously unstudied targets for photonic crystals—including targets achievable via colloidal self-assembly [1]. I will demonstrate

avenues to predict the polyhedral nanoparticles that can cleanly self-assemble these targets and the implications, both good and bad, that small changes to nanoparticle shape have on the resulting crystal's behavior [2-4]. [1] R. K. Cersonsky, J. Antonaglia, B. D. Dice, S. C. Glotzer, "Unexpected Diversity of Three-Dimensional Photonic Crystals." Accepted for publication at Nature Communications. [2] R. K. Cersonsky, G. van Anders, P. M. Dodd, and S. C. Glotzer, "Relevance of Packing in Colloidal Self-Assembly," (2018). Proceedings of the National Academy of Sciences. <https://doi.org/10.1073/pnas.1720139115>. [3] R. K. Cersonsky, J. Dshemuchadse, J. Antonaglia, G. van Anders, S. C. Glotzer, "Pressure-Tunable Band Gap in an Entropic Crystal", (2018). Phys. Rev. Mat. <https://doi.org/10.1103/PhysRevMaterials.2.125201>. [4] Y. Zhou, R. K. Cersonsky, S. C. Glotzer, "A New Route to the Diamond Colloidal Crystal." In preparation. *Dr. Cersonsky is currently a postdoctoral researcher working with Prof. Michele Ceriotti at the Laboratory of Computational Science and Modeling at École Polytechnique Fédérale de Lausanne in Lausanne, Switzerland.*

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Wed, 16 13:40 - 15:00

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Wed-AW2-01

Surface charge heterogeneity directed particle migration and assembly

**Xiaoyu Tang (x.tang@northeastern.edu), Parth Shah (parthshah@ucsb.edu), Todd Squires (tsquires@ucsb.edu)**

Chemical Engineering, University of California, Santa Barbara

Detecting and delivering colloidal particles to a spot with surface charge heterogeneity is important in many applications, such as coating quality control, surface modification, and cargo delivery. Since the location of the spot with surface charge heterogeneity is not known, it is challenging to map variations in the surface charge density in a large area simultaneously in an inexpensive way. Here we demonstrate a system to automatically assemble particles in areas with surface charge heterogeneity thus detecting and delivering particles to the target location at the same time. We utilize colloidal particles that self-emit solutes that interact with the non-uniformly charged surface to drive them diffusiophoretically. The physical mechanism for the particle motion is unveiled and a theoretical framework is laid out to predict the particle migration behavior with different types of surface charge density patterns. We have demonstrated experimentally that initially uniformly distributed colloidal particles on surfaces assemble and form patterns that conform to the surface charge density pattern. This unique system opens new avenues to sense the surface heterogeneity and harness it for targeted cargo delivery.

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Wed-AW2-02

Probing interparticle interactions during formation of transient aggregates by chemical fuels

**Thilini U. Dissanayake (tumesha@terpmail.umd.edu), Justin Hughes (jchughes051@gmail.com), Taylor Woehl (tjwoehl@umd.edu)**

Department of Chemical and Biomolecular Engineering, University of Maryland, College Park

In recent years, several studies have used different chemistries to synthesize transient colloidal aggregates by tuning particle surface hydrophobicity. Here a chemical fuel is used to transform hydrophilic ligands on particles surfaces to hydrophobic semi-stable esters causing particle to assemble and then disassemble after some hours due to regeneration of original surface ligands by hydrolysis of ester groups. Despite the detailed investigation of the chemical reaction cycles of these assemblies, the interparticle interactions and aggregation kinetics intervening in formation of these transient assemblies are not explored. In this study we show that, strength of interparticle hydrophobic attraction forces combined with van der Waal's forces and electrostatic repulsion forces determines whether the particle assembly would be a transient aggregate or an irreversible aggregate using optical microscopy to image fuel driven assembly of sub-micron to micron sized polystyrene particles. Varying ligand to fuel ratio by changing fuel concentration for a particular

particle concentration demonstrated that these transient aggregates form inside a very narrow range, lower bound being no assembly and upper bound being irreversible aggregation. However decreasing particle concentration with a fixed fuel concentration showed that not only the extent of surface activation (ligand to fuel ratio), but there is a lower limit for particle concentration signifying the necessity of adequate number of active particle collisions in formation of these transient aggregates. Zeta potential data collected during the assembly at different fuel concentrations were used to model the pairwise interaction potentials considering van der Waal's forces and double layer forces and potential energy curve showed no secondary minima corresponding to transient aggregation formation. However, including hydrophobic attraction forces in the model showed that there is a shallow secondary minimum in the interaction potential corresponding to the fuel concentrations where transient aggregates were observed suggesting weak hydrophobic interactions whereas, there was no energy barrier in interaction potential for fuel concentrations showing irreversible aggregates suggesting strong hydrophobic interactions. This explains that weak bonding in transient aggregates allow interstitial water layers facilitating hydrolysis of hydrophobic ester groups on particles, which makes the individual particles more stable with time causing the aggregates to disassemble. Meanwhile in irreversible aggregates strong bonding cause closely packed aggregates preventing the hydrolysis of internal hydrophobic ester groups with time.

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Wed-AW2-03

### Inducing and Controlling Colloidal Stratification with a Binary Solvent Mixture

**Binghan Liu (bingl95@vt.edu)<sup>1</sup>, Gary Grest (gsgrest@sandia.gov)<sup>2</sup>, Shengfeng Cheng (chengsf@vt.edu)<sup>1</sup>**

<sup>1</sup> Virginia Tech

<sup>2</sup> Sandia National Laboratories

Drying a colloidal suspension is a process frequently used to fabricate materials. Recently, suspensions of polydisperse colloids are found to exhibit nontrivial stratification phenomena, which may lead to a new approach of quickly making layered materials. The ability to induce stratification on demand and to control the stratified structures will make this technique more appealing. Using molecular dynamics simulations, we demonstrate that stratification can be induced in a colloidal suspension with a mixed binary solvent consisting of two components with different volatilities. During evaporation, the two solvent components evaporate at different rates, which makes them to develop opposite concentration gradients in the direction of drying in the solution phase. Specifically, the more volatile component is depleted at the evaporating surface of the solution. This behavior of the mixed solvent can be used to induce a binary mixture of colloids initially suspended in the solution to stratify during evaporation, if the colloidal species have contrasting interaction strengths with the two solvent components. After drying, the two colloidal species form a stratified two-layer film with the group on top (i.e., closer to the evaporating front) preferring the less volatile solvent component. This process occurs even if the two colloidal species are identical other than their couplings to the solvent components. The simulations thus point to a relatively simple avenue to induce and control stratification of colloidal suspensions using mixed solvents, which can be implemented on a large scale. Supported by NSF (DMR-1944887) and a DOE ALCC award (computational hours).

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Wed-AW2-04

### Tunable assemblies of gold nanoparticles in smectic liquid crystals confined at curved interfaces

**Mackenzie O'Keefe (Mackenzie.OKeefe001@umb.edu)<sup>1</sup>, Jane Bernadette Denise M. Garcia (jgarcia546@ucmerced.edu)<sup>2</sup>, Daniel A. Beller (dbeller@ucmerced.edu)<sup>2</sup>, Mohamed Amine Gharbi (mohamed.gharbi@umb.edu)<sup>1</sup>**

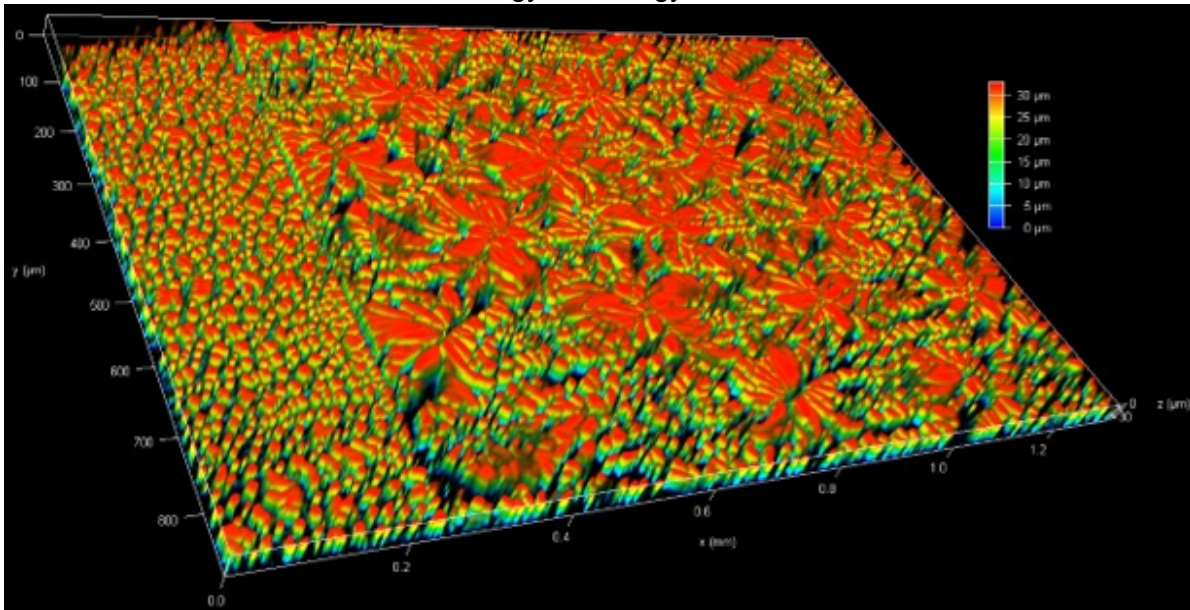
<sup>1</sup> Department of Physics, University of Massachusetts Boston

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Liquid crystals have drawn interest in the past decade due to their ability to trap colloidal objects in topological defects and direct their assembly into specific patterns. They have also brought about a high



impact in modern technologies, particularly in optics, e.g., microlens arrays, soft lithography templates, and optically selective masks. In this work, we study the formation of defects in smectic A liquid crystal with hybrid texture at undulated and double undulated surfaces fabricated using 3D printers. We investigate the role of surface morphology on the organization of focal conic domains (FCDs) and demonstrate new methods for assembling FCDs and disclinations into hierarchical structures. Then, we compare our experimental results to numerical studies of defects evolution in the phase transition from the smectic to the nematic phase. We examine how FCDs of nonzero eccentricity and spatially varying orientation transform into patterns of disclination lines using Landau-de Gennes free energy minimization. Finally, we expand our work to demonstrate the capabilities of these defects to spontaneously assemble gold nanoparticles into reconfigurable patterns and discuss the parameters affecting them. Our work paves the way for creating new procedures to control the assembly of functional nanomaterials into tunable structures that will find relevance in the field of energy technology.



**Figure 1:** 3D structure of defects in a smectic liquid crystal with hybrid texture confined at a double undulated surface.

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Wed, 16 13:40 - 15:00

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Wed-BW2-01

Preparation of carbon dioxide emulsions and foams using cellulose nanocrystals at high temperature and pressure

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Liquid carbon dioxide (CO<sub>2</sub>) emulsions and supercritical CO<sub>2</sub> foams were stabilized using cellulose nanocrystal (CNC) in American Petroleum Institute (API) brine at ambient and underground reservoir conditions (T = 343 K; P = 20.7 MPa). Ambient condition emulsions with heptane and perfluorooctane (PFO), as model compounds, showed that the less polar PFO could not be emulsified, while heptane formed stable emulsions at 298 and 343 K. The model compounds were used to optimize parameters such as CNC and surfactant concentration. The results suggest that polarity is a highly significant factor contributing to emulsion stability. CO<sub>2</sub> emulsions and foams prepared using CNC were resistant to creaming and foam drainage and macroscopic coalescence over 24 h. Emulsions prepared using a combination of CNC and dodecyl trimethylammonium bromide (DTAB), on the other hand, creamed at 298 K, and supercritical CO<sub>2</sub> foams made using CNC+DTAB showed macroscopic bubble coarsening at 343 K.

K. The interfacial tension ( $\gamma$ ) of CNC suspensions in CO<sub>2</sub> rich environment decreased with increased CO<sub>2</sub> pressure at both 298 K and 343 K. CO<sub>2</sub> foams and emulsions containing DTAB had larger initial viscosities but lower emulsion/foam stability over a period of 24 h. This finding suggests that reduced CO<sub>2</sub> mobility during injection may not always translate to long-term foam stability for geological carbon sequestration projects. This paper reports the first CNC-stabilized CO<sub>2</sub> foam in reservoir conditions, with the potential for geological greenhouse gas sequestration.

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Wed-BW2-02

Production and stabilization of foams by fatty acid crystals in high alcohol content solvents

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Foaming in liquids is ubiquitous in nature. Aqueous foams are encountered in many commonly products of our everyday lives and are widely studied. However, the formation and stabilization of foams using high alcohol content solvents such as ethanol is still a scientific challenge. Herein, we report for the first-time foams based on high ethanol content showing long-term stability by using natural fatty acid crystals. These platelet-shape crystals are adsorbed at the air-water surface protecting the bubbles against coalescence. The melting of crystals triggers the foam destabilization leading to thermoresponsive high ethanol content foams. These foams can be used as new formulations for alcohol-based hand sanitizers to better clean hands, protect the skin by the presence of fatty acids, and limit the transmission of virus and other pathogens.

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Wed-BW2-03

Liquid crystal emulsions stabilized by nanoparticles

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Past studies have reported that confinement of liquid crystals (LC) within micrometer-sized droplets dispersed in aqueous phases (e.g., LC-in-water emulsions) provides a versatile platform for designing droplet-based LC sensors that can respond sensitively to the presence of amphiphilic analytes in aqueous environments. In this talk, we present studies aimed at characterizing the adsorption and interaction of nanoparticles with LC emulsions as a potential approach to design responsive materials with (i) tunable sensitivity to aqueous analytes and (ii) improved colloidal stability. In one approach, we are using surfactant-nanoparticle complexes (CnTAB/SiO<sub>2</sub>) that adsorb to the LC droplet interface to stabilize LC emulsions for extended periods. The LC droplet size remains largely unchanged over time (e.g., droplet diameter  $\leq 4 \mu\text{m}$  over 3 months), and droplets that sediment over this time can be readily dispersed, demonstrating the remarkable colloidal stability of the system. Moreover, the addition of amphiphiles (e.g., SDS) to these CnTAB/SiO<sub>2</sub>-stabilized LC emulsions triggers bipolar-to-radial changes in LC droplet configurations similar to those observed in bare LC emulsions that can be readily observed using polarized light. We are also exploring the use of gold nanoparticles (AuNPs) chemically functionalized with binary mixtures of alkanethiols displaying polar (e.g., hydroxyl) and non-polar (e.g., methyl) groups that can adsorb onto LC droplets. Our results show that addition of surfactants such as SDS to aqueous dispersions of these AuNP-laden LC droplets also triggers bipolar-to-radial LC ordering transitions. Additional studies have focused on characterizing the extent to which the adsorption of AuNPs to LC droplet interfaces can confer colloidal stability to LC emulsions. Overall, our results suggest that LC emulsions stabilized by

nanoparticles provide a potential approach to design liquid-droplet sensors with improved colloidal stability for the detection of aqueous analytes.

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Wed-BW2-04

Superparamagnetic iron oxide ( $\text{Fe}_3\text{O}_4$ ) coated cellulose nanocrystals as a recyclable additive for the emulsification and demulsification of magnetically controlled castor oil/water emulsions

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Magnetic nanoparticles have potential applications in magnetically-controlled Pickering emulsions and liquid-liquid extractions. In this work, iron oxide-coated cellulose nanocrystals ( $\text{CNC}@Fe_3O_4$ ) were synthesized to prepare magnetically controlled castor oil/water emulsions. Shorter wood-pulp CNCs (WCNCs) and longer bacterial CNCs (BCNCs) were fabricated with superparamagnetic iron oxide NPs, separately, by a single one-step coprecipitation method. The colloidal, magnetic, and emulsifying properties of the composite nanocrystals are controlled by adjusting the cellulose to  $\text{Fe}_3\text{O}_4$  ratio. The highest ratio tested (1:4) resulted in the highest  $\text{Fe}_3\text{O}_4$  coverage of CNCs, according to TEM micrographs. FT-IR and Raman spectroscopy demonstrated that the CNCs and  $\text{Fe}_3\text{O}_4$  seemed to interact via hydrogen bonding between the surface hydroxyl groups of both particles. VSM study demonstrated that the hybrid NPs with magnetite loading of 1:4 had saturation magnetizations of 56 emu/g for  $\text{WCNC}@Fe_3O_4$  at a 1:4 ratio, and 60 emu/g for  $\text{BCNC}@Fe_3O_4$  at the same ratio, these were higher than the lower magnetite loadings of 1:1 and 1:2. However, UV-Vis spectroscopy and zeta potential measurement showed that the deposition of magnetite on CNCs lowered the colloidal stability of the hybrid NPs in aqueous media. The lower stability of the hybrid particles at a 1:4 ratio was beneficial to stabilize the Pickering emulsions. Moreover, increased magnetite loading provided superparamagnetic properties to the hybrid NPs which allowed demulsification induced by an external magnet. Herein, the castor oil/water emulsions were formulated with varied oil to water volume ratios. The emulsions formulated with the oil contents of 30% and 50% v/v and the addition of 1wt%  $\text{CNC}@Fe_3O_4$  (of aqueous phase) were oil-in-water (O/W) and could not be demulsified by the magnet, probably as a consequence of higher emulsion stability. However, the 70% and 90% v/v emulsions were water-in-oil (W/O) and were readily broken by an external permanent magnet, while the  $\text{CNC}@Fe_3O_4$  hybrid NPs were recovered and recycled. The demulsification capability of the fabricated magnetic cellulose nanocrystals has potential uses for magnetically-driven separations, oil recovery, and drug delivery.

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Wed, 16 13:40 - 15:00

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Wed-DW2-01

Spherically confined Brownian suspensions: influence of locally heterogenous structure on diffusion and rheology

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Spherically confined, hydrodynamically interacting colloids provide a framework for understanding biological cells over length and time scales where interparticle interactions and particle motion play central and nontrivial roles in whole-cell behavior. Under different biological conditions, a cell's overall size, crowding level, and the strength of electrostatic interactions of its constituent molecules can change. Therefore, it is important to understand how each of these changes alters the physics of biological processes that take place inside cells. In this work, we perform dynamic simulations with both Confined Stokesian Dynamics and Confined Brownian Dynamics algorithms. We disentangle the role of entropic and hydrodynamic effects on short- and long-time transport properties of particles under spherical confinement to better understand differences between real life systems under conditions of weak and strong hydrodynamics. Additionally, we find relationships between rheological properties, such as osmotic pressure and viscosity, and the variables volume fraction and particle size within the confinement.

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Wed-DW2-02

Diffusion of proteins throughout aqueous block polymer liquid crystals – the effect of polymer architecture, temperature, and concentration.

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Carnegie Mellon University

Protein therapeutics are prone to 1) aggregation and 2) thermal denaturation, which cause loss of functionality and detrimental side effects. Current technologies require refrigeration to stabilize proteins after spray/freeze drying or confinement in sugar glasses among other technologies. However, proteins are stable at temperatures higher than cold storage in the crowded intracellular environment, where concentrations of macromolecules can exceed 30-40 vol%.<sup>1</sup> Consequently, confinement<sup>1-3</sup> and macromolecular crowding<sup>4,5</sup> have been investigated as protein protection mechanisms.<sup>6</sup> A recent approach to confine, crowd, and stabilize proteins disperses proteins into the aqueous interstitial spaces in Pluronic [PEOm-PPOn-PEOm] liquid crystals.<sup>7,8</sup>

Proteins are first dissolved in an aqueous Pluronic dispersion that is liquid at low temperature. Upon heating above ~15°C, the polymer molecules self-assemble into micelles which then rapidly crystallize, trapping the proteins into the aqueous interstitial pockets. The properties and size of the aqueous pockets between micelles can be engineered by changing polymer architecture, concentration, additives, and temperature. In this work we use Fluorescence Recovery After Photobleaching (FRAP) to quantify the mobility of fluorescently labeled proteins (Bovine Serum Albumin – BSA) throughout Pluronic liquid crystals. Using an automated microscope, we test a range of concentrations ( $C_{gel} - 2x C_{gel}$ ) and temperatures (25-55°C) over time scales of ~24 hours. We find the diffusivity of BSA to decrease by up to 3 orders of magnitude as the polymer concentration is increased from the gel concentration,  $C_{gel}$ , to  $2x C_{gel}$ . Contrary to the expected increase in diffusivity with increasing temperature, we observe a decrease in diffusivity in some cases. Diffusion in these systems cannot be explained as transport through a bulk viscous media. The properties of the micellar corona impact the proteins' ability to move through micellar brushes as they diffuse between interstitial sites. Here, we use rheological studies to explain the observed trends in protein diffusivity. The influence of the polymer structure and crystalline phase behavior will be discussed as well.

**1** Eggers, D. K. *Protein Sci.* 10,250–261(2001) **2** Zhou, H. X. et al. *Biochemistry* 40,11289–11293(2001) **3** Menaa, B. et al. *Biomaterials* 29,2710–2718 (2008) **4** Ping, G. et al. *J. Mol. Recognit.* 17, 433–440(2004) **5** Ellis, R. J. *Trends in Biochemical Sciences* 26, 597–604(2001) **6** Zhou, H.-X. et al. *Annu. Rev. Biophys.* 37, 375–397(2008) **7** Domach, M. M. et al. *JALA - J. Assoc. Lab. Autom.* 15, 136–144(2010) **8** Pozzo, D. C. et al. *J. Rheol.* 49, 759–782(2005)

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Wed-DW2-03

Structural Investigation of Salt-Induced Local Ordering in Amorphous Protein Dense Phases

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Relatively little is known about biopolymer phase behavior, despite their presence both in vivo and during protein solution processing. The physical nature of a dense phase, whether crystal, dense liquid, or a nonequilibrium phase such as a gel, is strongly dependent on the solution conditions. Achieving desired phase behavior can require extensive empirical exploration, and unwanted phases may prove difficult to eliminate. Our goal is to provide a reliable knowledge base of biopolymer behavior under both ambient and high-pressure conditions<sup>1</sup>. We will optimize these studies with a novel high-pressure sample environment for simultaneous structural and rheological measurements. Greene et al showed for the first time that macroscopically amorphous salted-out protein dense phases contain nanocrystalline regimes<sup>2</sup>. The work presented here completes the structural investigation of salted-out ovalbumin under ambient conditions and provides a well-characterized protein dense phase for future validation of the novel sample environment. Small-angle neutron scattering (SANS), static light scattering (SLS), and small-angle x-ray scattering (SAXS) data are combined to provide a full structural profile. Attention is given to trends in microstructure development with aging time and how structural observations may serve as a predictor for macroscopic properties. The results provide insights into local crystallinity within amorphous protein dense phases and build the groundwork for an in-depth study of pressure effects on biopolymer material properties. References: 1. Teixeira, S. C. M., High-pressure small-angle neutron scattering for food studies. *Current Opinion in Colloid & Interface Science* 2019, 42, 99-109. 2. Greene, D. G. M., S.; Wagner, N.J.; Sandler, S.I.; Lenhoff, A.M., Local Crystalline Structure in an Amorphous Protein Dense Phase. *Biophysical Journal* 2015, 109, 1716-1723.

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Wed-DW2-04

## Rheology and Pinching Dynamics of Associative Polysaccharide Solutions

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Associative polysaccharides are cellulose derivative polymers with multiple short, side-chain (hydrophobic stickers) that associate in aqueous solution typically used as thickeners for an extensive range of aqueous-based formulations. Characterizing the influence of hydrophobically-associative stickers on the response to extensional flows that spontaneously arise in pinching necks formed during spraying, jetting or coating fluids have remained longstanding experimental and analytical challenges, due to relatively low viscosity and elasticity of industrially-relevant systems. In this study, we contrast the shear and extensional rheology as well as pinching dynamics of hydrophobically-modified hydroxyethyl cellulose (hmHEC) as sticky polymer with the bare chain (HEC) of a higher molecular weight using the recently developed dripping-onto-substrate (DoS) rheometry protocols. We show that the presence of stickers enhances zero shear viscosity as well as relaxation time (elasticity), and both properties display stronger concentration-dependent variation for sticky polymers. Striking differences are observed in neck shapes and neck radius evolution profiles, as well as the extensional viscosity as a function of both strain and strain rate. We present a comprehensive analysis of changes in pinching dynamics, concentration-dependent variation in steady, terminal viscosity as well as filament lifespan as a function of concentration for the sticky polymer, and describe the influence of multiple stickers on macromolecular strain, relaxation, and dynamics of associative polysaccharides. Finally, we discuss the influence of associative polysaccharides on the pinching dynamics and rheology of multicomponent formulations.

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Wed, 16 13:40 - 15:00

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Wed-FW2-01

Using high-speed, molecularly-resolved AFM and fast force mapping to investigate nucleation and solution structure at surfaces (**Keynote Lecture**)

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Investigating nucleation from solutions is challenging, because it arises from unstable density fluctuations, making the events that must be probed transient in nature and small in spatial extent. Moreover, when heterogeneous, nucleation is inherently linked to the structure and dynamics of the interfacial region near the substrate. Thus high-speed, molecularly resolved AFM combined with fast force mapping (FFM) provides a powerful combination to investigate nucleation from solution onto surfaces. Here I illustrate the fundamental insights into mechanisms of nucleation and the structure of the interfacial region made possible with these methods using results from investigations into nucleation of gibbsite ( $\text{Al}(\text{OH})_3$ ) on muscovite mica (001) and the structure of electrolyte solutions above mica and boemite ( $\text{AlOOH}$ ) surfaces. In the case of gibbsite nucleation, we combine AFM observations of individual molecular adsorbates, transient clusters, and stable islands with Monte Carlo simulations to put together a coherent picture of surface speciation and nucleation. The results reveal a surface population of ions that is dominated by hydrolyzed species ( $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_3$ ), even though  $\text{Al}^{3+}$  vastly dominates the bulk solution. These adsorbed ions evolve into subcritical clusters with increasing saturation state and temperature, constituting a population that decreases exponentially with size and exhibits dynamic fluctuations consistent with classical predictions. However, severe discrepancies with classical theory emerge when the values of key thermodynamic parameters are extracted from the data. These discrepancies are resolved when the impact of adsorbate charge on the capacitance of the mica-solution system is taken into account in calculating the work of cluster formation, but reveal a film formation process that occurs within a single phase region. Thus, the results imply that the gibbsite films constitute a nanostructured 2D mesophase. To define the solution structure above crystal surfaces at lattice resolution, we developed a self-consistent scheme to decouple long-range tip-sample interactions from short-range solvation forces. In the case of boemite, the results are benchmarked against molecular dynamics simulations that explicitly include the effects of the tip with different levels of approximation and systematically account for tip size, chemistry, and confinement effects. We find four laterally structured water layers within one nanometer of the surface, with the highest water densities at sites adjacent to hydroxyl groups. The findings reveal a complex relationship between site-specific chemistry, water density, and long-range particle interactions; and represent a major step forward towards quantitative data interpretation and widespread implementation of 3D FFM.

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Wed-FW2-02

*In Situ* Study of the Lubrication Mechanism of Phosphonium Phosphate Ionic Liquid in Nanoscale Single-Asperity Sliding Contacts

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Ionic liquids (ILs) have recently gained considerable attention owing to their unique and tunable physico-chemical properties (*e.g.*, low vapor pressure, high thermal stability), which have made them useful for a range of applications, including energy storage, catalysis, and lubrication. ILs are particularly attractive in lubrication, since their properties make them suitable for components working under extreme conditions, such as those found in engines and spacecraft. When ILs are used as lubricants, the interface between the IL and the sliding surfaces plays a pivotal role in controlling the friction and wear response. Despite the weight of published literature, remarkably little is still known about the lubrication mechanism of ILs. The development of a fundamental understanding of the mechanism by which ILs reduce friction and/or wear requires shedding light on the processes occurring at nanoscale asperities within macroscale contacts. This constitutes a significant challenge that requires the use of complementary surface-analytical techniques to understand the nanoscale mechanisms at play.

Here, we used atomic force microscopy (AFM) to visualize and quantify the processes occurring at sliding interfaces *in situ*, in single-asperity nanocontacts. The AFM tests, in which a diamond tip was slid on iron in phosphonium phosphate IL (PP-IL), indicated a significant friction reduction only after the removal of the native surface oxide from iron. Even though the AFM experiments allowed for the identification of changes in topography and friction, they could not provide any information about the composition of the regions scanned by AFM. The analysis of these regions is a challenging surface science problem owing to their limited dimensions and the small thickness of the surface material modified by the mechanical action of AFM tips. To address this challenge and elucidate the origin of the friction reduction observed by AFM, a multi-technique approach was employed. The results of laterally-resolved *ex situ* analyses of the surface chemistry of steel by synchrotron-based X-ray photoemission electron microscopy, low energy electron microscopy, and time-of-flight secondary ion mass spectrometry indicated that the mechanically-induced exposure of metallic iron during AFM tests carried out in PP-IL leads to an increase in surface coverage of adsorbed phosphate anions together with a change in surface potential. Based on these results and atomistic simulations of the configuration geometry of phosphate ions adsorbed on metallic and oxidized iron, a simple phenomenological model is proposed to account for the observed lubrication behavior.

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Wed-FW2-03

Manipulating colloids, measuring masses, and probing forces at the solid-liquid interface using atomic force microscopy

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The work presented here will focus on AFM-based methods and probes for measuring interaction forces in colloidal systems and detecting the position and mass of individual particles. The development of photothermal excitation and nanofluidic probes provides a diverse toolkit for measuring interfacial phenomena in liquids. Photothermal excitation eliminates instrumental artifacts observed in liquids and provides stable, quantitative measurements. Hollow, nanofluidic AFM probes enable manipulation of micron and sub-micron particles, making experiments flexible and removing tedious preparation steps. Combining both technologies has led to the development of a cantilever-based mass sensor that is capable of measuring masses with picogram resolution on millisecond timescales and particle position by combining measured resonant frequencies of several bending modes. We will discuss measuring individual colloid-

surface interactions, gentle imaging and spectroscopy of soft matter, and mass sensing of colloids and living mammalian cells.

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Wed, 16 13:40 - 15:00

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Wed-HW2-01

### Surface Forces and Stratification in Micellar Foam Films & Soap Bubbles (**Keynote Lecture**)

**Vivek Sharma (viveks@uic.edu)**

Chemical Engineering, University of Illinois at Chicago

Foam films and soap bubbles typically consist of fluid sandwiched between two surfactant-laden surfaces that are ~ 5 nm - 10 microns apart, and the drainage in films occurs under the influence of viscous, interfacial, and intermolecular forces, including disjoining pressure. Ultrathin foam films of soft matter containing supramolecular structures like micelles, nanoparticles, smectic liquid crystals, lipid bilayers, and polyelectrolytes undergo drainage via stratification, manifested as step-wise thinning in interferometry-based measurements of average thickness. In this study, we focus exclusively on stratification in micellar foam films formed with aqueous solutions of sodium dodecyl sulfate (SDS) above the critical micelle concentration (CMC). In reflected light microscopy, stratifying films (thickness < 100 nm) display regions with distinct shades of grey implying that domains and nanostructures with varied thickness coexist in the thinning film. Understanding and analyzing such nanoscopic thickness transitions and variations have been a long-standing experimental challenge due to the lack of technique with the requisite spatio-temporal resolution, and theoretical challenge due to the absence of models for describing hydrodynamics and thermodynamics in stratified thin films. Using IDIOM (interferometry digital imaging optical microscopy) protocols we developed recently, we show that the nanoscopic thickness variations in stratifying films can be visualized and analyzed with an unprecedented spatial (thickness ~ 1 nm, lateral ~500 nm) and temporal resolution (< 1 ms). Stratification proceeds by the formation of thinner domains that grow at the expense of surrounding films. Using the exquisite thickness maps created using IDIOM protocols, we provide the first visualization of nanoridges as well as mesas that form at the moving front around expanding domains. We contrast the step size measured in stratification studies with intermicellar distance obtained from scattering measurements, and explicitly measure the non-DLVO supramolecular oscillatory surface force contribution to disjoining pressure. Most significantly, we develop a self-consistent theoretical framework, a nonlinear thin film equation model that explicitly accounts for the influence of supramolecular oscillatory surface forces (using expressions we developed as a part of this study), as well as the physicochemical properties of surfactants. We show the complex spatio-temporal evolution of domains, nanoridges, nanoridge-to-mesa instability, and mesas in stratifying foam films can be modeled quantitatively, and we elucidate how surfactant type and concentration can be manipulated and controlled for molecular engineering of micellar foams.

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Wed-HW2-02

### Drainage via Stratification in Micellar Foam Films of Aqueous Sodium Naphthenate Solutions

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Sodium Naphthenate (NaN) found in crude oils can act as a surfactant and influence the stability, lifetime, and rheology of petroleum foams and emulsions. Here, we show that foam films formed by aqueous micellar solutions of NaN exhibit stepwise thinning or stratification, due to the influence of non-DLVO forces, including supramolecular oscillatory structural forces. We utilize Interferometry Digital Imaging Optical Microscopy protocols, previously developed by our group, to investigate the drainage and stratification in



micellar foam films ( $h < 100$  nm) with high spatial (thickness  $\sim 1$  nm, in-plane  $< 1$  micron) and temporal (time  $< 1$  ms) resolution. We determine how the NaN concentration influences the nanoscopic topography, stratification kinetics, and step-size of foam films, and contrast the results with behavior observed with stratifying foam films made with sodium dodecyl sulfate (SDS) solutions. We contrast the step-size obtained from foam film stratification experiments with the intermicellar distance obtained by small angle X-ray scattering and discuss the influence of surfactant concentration and type on foam stability.

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Wed-HW2-03

The effect of headgroup charge on the stiffness of symmetric and asymmetric phospholipid bilayers

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The presence of an electric transmembrane potential of around 100 mV in biological cells is due to a variety of factors, including the asymmetric distribution of charged phospholipids in each bilayer leaflet. Since charged phospholipids comprise a significant component of the overall phospholipid bilayer composition, understanding the effect of headgroup charge and resultant electrical stress on membrane material properties has important implications in a variety of physiological processes, such as cellular signaling, endocytosis, and membrane protein function. In this talk, we will discuss the impact of headgroup charge on the thickness, compressibility, and bending rigidity of artificial phospholipid membranes. We first create symmetric membranes with varying anionic DOPG and zwitterionic DOPC content which indicate that as the concentration of charged species increases, the membrane thickness and Young's modulus concurrently increase. Next, we describe the development of an experimental platform to create planar, free-standing, phospholipid bilayers with independent control of the phospholipid composition on either leaflet. Voltage-dependent capacitance measurements reveal a transmembrane potential that scales with the degree of membrane charge asymmetry, ranging from 0 to 80 mV, however the membrane Young's modulus is not merely a compositional weighting of the relative phospholipid components. Asymmetric membranes with the same overall phospholipid composition as their symmetric counterparts are thinner and less stiff, likely due to decreased headgroup electrostatic repulsion between leaflets. However, asymmetric bilayers with one leaflet composed of entirely zwitterionic phospholipids exhibit an increase in stiffness with increasing anionic lipid content in the opposing leaflet due to the development of a differential stress across the two leaflets. These results demonstrate quantitative biophysical insights into increasingly realistic artificial cell membrane mimics.

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Wed, 16 13:40 - 15:00

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Wed-JW2-01

Photoreactive Electrospun Filters for Controlling Airborne Transmission of SARS-CoV-2

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The COVID-19 pandemic has resulted in significant illnesses and deaths since late 2019. Airborne transmission of SARS-CoV-2 has been gradually recognized. SARS-CoV-2-laden aerosols ( $< 5$   $\mu\text{m}$ ) can suspend in the air and remain infectious for hours. Compared with conventional air filters, electrospun nanofibrous air filters always possess an increased filtration efficiency and a lower pressure drop amid aerosol challenging, which is attributed to their reduced pore sizes, increased surface areas and porosity,

and retained surface and volume charges. However, electrospun nanofibrous air filters only physically capture the viral aerosols rather than inactivating the viruses. Therefore, we developed photoreactive electrospun nanofibrous air filters that enable the capture-and-kill function for controlling coronavirus airborne transmission. Nanofibrous air filters were first electrospun from polyvinylidene fluoride (PVDF) with optimized conditions such as the flow rate of polymer solutions. For comparison, three commercially available masks were selected as the reference. Due to ultrafine fibers (~ 300 nm), a much smaller pore size (~ 2.7 μm) was observed in the electrospun air filters compared with the commercial masks. A customized aerosol filtration system was used to evaluate the aerosol filtration efficiency for all the samples. Murine hepatitis virus A59 (MHV-A59) was selected for aerosol generation and filtration. The results indicate that the electrospun air filters can capture 99.1-99.9% of MHV-A59 aerosols, which outperform commercial masks (44.9-98.2%). In addition, the filtration performance of all the commercial masks and electrospun air filters for NaCl aerosols was tested with the same system and compared with that for the MHV-A59 aerosols. Our result indicates that NaCl is a conservative surrogate for the coronavirus in aerosol filtration tests, since the removal efficiency for NaCl aerosols was always lower or equivalent to that for coronavirus aerosols. Moreover, a broad spectrum of visible-light-responsive photosensitizers such as rose Bengal were incorporated into the air filters, and the air filters all produced singlet oxygen under simulated indoor lighting. The photosensitized electrospun air filters were able to inactivate 1.5 log of MHV-A59 after 15 min of simulated indoor light exposure, and apparent genome damage and adverse impacts on viral lifecycle in host cells were observed. In summary, electrospun nanofibrous air filters hold promise for various air filtration applications by preventing coronavirus airborne transmission. Endowing the photoreactivity for the electrospun nanofibrous air filters not only physically capture the coronaviruses effectively but also chemically inactivate them to minimize the spread and infection of the pathogen.

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Wed-JW2-02

### Impact of NO/NO<sub>2</sub> Aging on the Capacity of Silver Mordenite for Iodine Adsorption

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The recovery of usable fuel resources from spent nuclear fuels through reprocessing represents a notable portion of the nuclear fuel cycle that, if properly utilized, would increase the efficiency of and reduce waste from nuclear energy. One area of concern, however, is the various radioisotopes off-gassed during reprocessing including iodine-129, krypton-85, xenon-135, and carbon-14. Of these gases, iodine, which is released in both organic and inorganic forms, has the longest half-life and greatest potential for environmental accumulation and it is, thus, the most consequential of the aforementioned radioisotopes. Over the last few decades, several silver based adsorbents have been considered for the capture of iodine in the reprocessing off-gas stream. Among the materials considered, reduced silver mordenite has been investigated and found to be quite promising on the basis of its high iodine adsorption capacity, thermodynamic stability, and regenerative capabilities. Nevertheless, the impact that other off-gas constituents, nitric oxide and nitrogen dioxide in particular, have on the mordenite's iodine capacity is not well understood. Overall, mordenites exposed to nitric oxide or nitrogen dioxide are known to have a diminished iodine capacity. This loss of capacity has been termed aging, though the underlying mechanisms governing aging have yet to receive a thorough exploration. The purpose of this work, therefore, is to investigate the mechanisms of aging in reduced silver mordenite and to develop reaction pathways that, as accurately as possible, describe these mechanisms. These mechanisms shall then be used to facilitate the development of models that can simulate the mordenite's performance.

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Wed-JW2-03

Aging mechanisms of silver-functionalized silica aerogel in NO<sub>2</sub>-containing gas streams

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Due to its high iodine selectivity and sorption capacity, silver-functionalized silica aerogel (Ag<sup>0</sup>-Aerogel) has considerable potential as a material for the capture of iodine radioisotopes released as byproducts of used nuclear fuel reprocessing. Ag<sup>0</sup>-Aerogel, nonetheless, experiences a steady capacity loss when exposed to other off-gas components. This sorption capacity reduction is known as aging though its underlying mechanisms remain unclear. To investigate aging, we exposed Ag<sup>0</sup>-Aerogel samples to 2% NO<sub>2</sub> in dry air (i.e. a relevant gas stream with a strong aging effect) at 150 °C for up to one month. The aged samples were then characterized using Scanning Electron Microscopy, X-ray Diffraction, Fourier-transform infrared spectroscopy, X-ray Photoelectron Spectroscopy and X-ray Absorption Spectroscopy. Our results coherently indicate that aging of Ag<sup>0</sup>-Aerogel in NO<sub>2</sub> involves three major processes: (i) propanethiolate, functional group connecting the silica aerogel backbone and metallic silver (Ag<sup>0</sup>) nanoparticles, is oxidized first to propanesulfonate and then to sulfate ion weakly binding to nanoparticle surfaces; (ii) Ag<sup>0</sup> on the nanoparticle is oxidized to Ag<sup>+</sup> and react with sulfate ions forming silver sulfate molecules; and (iii) silver sulfate molecules migrate off the nanoparticle surfaces and yields silver sulfate crystals. These silver sulfate crystals convert silver into a form that is unfavorable for iodine adsorption. Spectroscopic results reveal that silver oxidation or silver sulfate crystallization is the rate-limiting step. These findings elucidate the mechanisms of aging in Ag<sup>0</sup>-Aerogel, and may be used to guide the development of accurate predictive models.

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Wed-JW2-04

Pt catalyst on novel ceria-based support with fine CeO<sub>2</sub> particles for efficient emission control

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With the increasing environmental awareness and adoption of more stringent regulations for automotive emissions, designing highly efficient catalysts for vehicle exhaust emission control at low temperatures is a topical research area. Platinum group metals (PGMs) catalysts supported on ceria-based support have been widely studied and applied in industrial production. The strong interaction between PGMs and CeO<sub>2</sub> supports significantly determined the catalytic performance of PGMs catalysts. It has been reported that the state of CeO<sub>2</sub> supports such as particle size, crystallinity or exposed crystal facets might have a great impact on PGMs/CeO<sub>2</sub> catalysts. In this work, by using a commercial CeO<sub>2</sub> colloidal solution as the precursor of CeO<sub>2</sub>, a unique CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (CA-c) support with small CeO<sub>2</sub> particles of uniform size (~10 nm) was successfully synthesized by incipient impregnation method (IMI). Comparing with the

CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> support using Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O as precursor (CA-n), the CeO<sub>2</sub> particles in CA-c were much smaller, and more surface defects formed on CA-c. Moreover, higher CO oxidation activity, oxygen storage capacity (OSC) and thermal stability were achieved on CA-c. After the loading of Pt, it was found that Pt species were better dispersed on CA-c in a single-atom form, which was related to the smaller CeO<sub>2</sub> particles and richer surface defects on CA-c. Higher concentration of Pt-O-Ce structure was observed on Pt/CA-c than on Pt/CA-n, indicating the stronger interaction between Pt and CeO<sub>2</sub> on Pt/CA-c. After being activated by H<sub>2</sub>, Pt/CA-c-ACT ('ACT' meant activation by H<sub>2</sub>) showed a much better CO oxidation activity than that of Pt/CA-n-a. After the aging treatment (in air, 800 °C, 12 h), Pt/CA-c-800A-ACT still performed a better CO and C<sub>3</sub>H<sub>6</sub> elimination efficiency than Pt/CA-n-800A-ACT ('800A' meant aging treatment at 800 °C). Via a series of characterizations, it was found that more perimeter Pt sites at the interface of smaller Pt clusters and CeO<sub>2</sub> formed on Pt/CA-c-ACT, which contributed to the improved catalytic oxidation activity and OSC values. For Pd catalysts supported on CA-c (Pd/CA-n), it still exhibited higher CO oxidation activity than Pd/CA-n after activation treatment. This work provided a new strategy of using CeO<sub>2</sub> colloidal solution as CeO<sub>2</sub> precursor to prepare novel ceria-based supports with controlled CeO<sub>2</sub> particle size, which could be used as a superior support in PGMs catalysts (Pt, Pd, Rh...) to achieve better catalytic performance for emission control.

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Wed, 16 13:40 - 15:00

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Wed-KW2-01

From pointy fangs to polymer fibers: interfacial materials processing using a bloodworm multi-tasking polypeptide

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The jaw of the bloodworm *Glycera dibranchiata* is a hard, tough melanized structure that provides inspiration for biomimetic materials designs. Despite this, the molecular processes responsible for jaw formation have remained elusive. Detailed molecular biology experiments reveal that the protein content of the jaw contains high sequence homology consisting of more than 80% charged glycine and histidine residues. In this work, we show that one particular sequence, which we call *Glycera* multi-tasking protein (MTP), exhibits remarkable multi-functional behavior upon coordination-mediated binding of copper in solution. Specifically, we find that copper binding induces a combination of coacervation, interfacial assembly and catalytic activity toward oxidation of dopa, a key early step in the polymerization of melanin. This coordinated process can be kinetically monitored in vitro using interfacial rheology measurements at the air-water interface, which confirms the ability of interfacially adsorbed copper-bound MTP to produce solid melanized films when L-Dopa is added to the aqueous subphase. Inspired by the similarity of this interfacial polymerization to the production of nylon, we demonstrate that interfacial melanized films can be drawn into fibers with tensile properties similar to their synthetic counterparts. The results therefore not only provide insight into the processing mechanisms of the *Glycera* jaw, but also provide new processing routes for the synthesis of natural fibers as an alternative to synthetic analogues.

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Wed-KW2-02

Design and Use of a Thermogelling Methylcellulose Nanoemulsion to Formulate Nanocrystalline Oral Dosage Forms

**Liang-Hsun Chen (lhchen@mit.edu), Patrick Doyle (pdoyle@mit.edu)**

Department of Chemical Engineering, Massachusetts Institute of Technology

Oral drug products have become indispensable in modern medicine because of their exceptional patient compliance. However, poor bioavailability of ubiquitous low water-soluble active pharmaceutical ingredients (APIs) and lack of efficient oral drug formulations remain as significant challenges. Nanocrystalline formulations are an attractive route to increase API solubility, but typically require abrasive mechanical milling and several processing steps to create an oral dosage form. Utilizing the dual amphiphilic and thermoresponsive properties of methylcellulose (MC), a new thermogelling nanoemulsion and a facile thermal dripping method are developed for efficient formulation of composite particles with the MC matrix embedded with precisely controlled API nanocrystals. Moreover, a fast and tunable release performance is achieved with the combination of a fast-eroding MC matrix and fast-dissolving API nanocrystals. Using the versatile thermal processing approach, the thermogelling nanoemulsion is easily formulated into a wide variety of dosage forms (nanoparticle suspension, drug tablet, and oral thin film) in a manner that avoid nanomilling. Overall, the proposed thermogelling nanoemulsion platform not only broadens the applications of thermoresponsive nanoemulsions, but also shows great promise for more efficient formulation of oral drug products with high quality and tunable fast release.

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Wed-KW2-03

### In Vivo Quantitative Imaging of Nanoparticles and Cells Using Magnetic Particle Imaging (Keynote Lecture)

**Carlos M. Rinaldi-Ramos (carlos.rinaldi@ufl.edu)**

Department of Chemical Engineering, University of Florida, Gainesville, FL

J. Crayton Pruitt Family Department of Biomedical Engineering, University of Florida, Gainesville, FL 32611

Magnetic Particle Imaging (MPI) is a new molecular imaging technology capable of unambiguous and quantitative tomographic imaging of the distribution of superparamagnetic nanoparticle tracers in vivo. While the term MPI may be confused with that for Magnetic Resonance Imaging (MRI), the two rely on distinct physics. In MPI, a tomographic image of the distribution of superparamagnetic nanoparticles is constructed by scanning a so-called field free region (FFR) through the domain of interest. Outside the FFR there is a quasi-static bias field strong enough to saturate the magnetic moments of the nanoparticles. But inside the FFR the dipole moments of the nanoparticles are able to respond to a superimposed alternating excitation field. The signal used to construct an image in MPI arises due to the non-linear dynamic magnetization response of the nanoparticle dipole moments to the excitation field inside the FFR. At the field amplitudes and frequencies used in MPI there is no appreciable attenuation in field or signal strength in tissue. Further, while there are magnetic species in the body (e.g., ferritin), they do not contribute an appreciable signal for MPI, allowing for unambiguous imaging of the distribution of one of the superparamagnetic nanoparticle tracers. In this talk I will explain the physics of image generation in MPI, discuss work to understand how imaging performance relates to physical and magnetic properties of the nanoparticles, and discuss our work developing tracers and using MPI to quantify biodistribution of iron oxide nanoparticles in vivo, in the context of tracking nanoparticles and cell therapies.

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Wed, 16 13:40 - 15:00

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Wed-LW2-01

### Design and Characterization of a Bioinspired Molybdenum Catalyst for Aqueous Perchlorate Reduction

**Changxu Ren (cren005@ucr.edu)<sup>1</sup>, Peng Yang (pyang1@anl.gov)<sup>2</sup>, Eric Bi (ericbi384@gmail.com)<sup>1,3</sup>, Jinyu Gao (jgao034@ucr.edu)<sup>1</sup>, Mengqiang Zhu (mzhu6@uwyo.edu)<sup>2</sup>, Jinyong Liu (jinyongli@ucr.edu)<sup>1</sup>**

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Perchlorate ( $\text{ClO}_4^-$ ) is a pervasive, harmful, and inert anion on both Earth and Mars. Current technologies for  $\text{ClO}_4^-$  reduction entail either harsh conditions or multi-component enzymatic processes. This presentation describes our recent development of a molybdenum (Mo)-based catalyst for rapid  $\text{ClO}_4^-$  reduction. The topics include the design rationale, the comparison with the microbial  $\text{ClO}_4^-$  reduction system, the optimization of catalyst composition, catalyst characterization, and mechanistic insights. Specifically, the structure and redox cycling of Mo species in the catalyst were characterized by a series of X-ray spectroscopies and model probing reactions. At 20°C, the catalyst can fully reduce aqueous  $\text{ClO}_4^-$  in a wide range of initial concentrations (0.01 to 100 mM) into  $\text{Cl}^-$  with 1 atm  $\text{H}_2$ . For each Mo site, the initial turnover frequency (TOF<sub>0</sub>) for oxygen atom transfer from  $\text{ClO}_4^-$  and  $\text{ClO}_x^-$  intermediates reached 165 h<sup>-1</sup>. The turnover number (TON) reached 3,840 for a single batch reduction of 100 mM  $\text{ClO}_4^-$ . This study provides a water-compatible, efficient, and robust catalyst to degrade and utilize  $\text{ClO}_4^-$  for water purification and space exploration.

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Wed-LW2-02

Bioinspired Catalytic Reduction of Aqueous Perchlorate by One Single-Metal Site with High Stability against Oxidative Deactivation

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Reduction of perchlorate ( $\text{ClO}_4^-$ ) with an active and stable catalyst is of great importance for environmental, energy, and space technologies. However, after the rate-limiting oxygen atom transfer (OAT) from inert  $\text{ClO}_4^-$ , the much more reactive  $\text{ClO}_x^-$  ( $x \leq 3$ ) intermediates can cause catalyst deactivation. The previous Re-Pd/C catalyst contained a  $[\text{Re}^{\text{V}}(\text{O})(\text{hoz})_2]^+$  site (Hhoz = 2-(2'-hydroxyphenyl)-2-oxazoline) and readily reduced  $\text{ClO}_4^-$ , but  $\text{ClO}_x^-$  intermediates led to rapid formation and hydrolysis of  $[\text{Re}^{\text{VI}}(\text{O})_2(\text{hoz})_2]^+$ . While microbes use delicate enzymatic machinery to survive the oxidative stress during  $\text{ClO}_4^-$  reduction, a synthetic catalyst needs a straightforward self-protective design. This presentation includes our design rationale, validation, and mechanistic explanation for substantially improved catalyst stability. While the original catalyst severely deactivated after treating >1 mM of  $\text{ClO}_4^-$ , the new catalysts did not lose any activity after multiple spikes of 100 mM of  $\text{ClO}_4^-$  were fully reduced. Specifically, a suite of kinetics measurement, XPS characterization, reaction modeling, stopped-flow photospectrometry, and <sup>1</sup>H NMR monitoring revealed the mechanism for the surface-immobilized Re sites. This work showcases the power of coordination chemistry in improving catalyst stability for high-performance  $\text{ClO}_4^-$  reduction.

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Wed-LW2-03

Evaluation of a Molybdenum Catalyst for Perchlorate Reduction for Engineering Application

**Eric Bi (jinyongl@ucr.edu)<sup>1,2</sup>, Changxu Ren (cren005@ucr.edu)<sup>1</sup>, Jinyong Liu (jinyongl@ucr.edu)<sup>1</sup>**

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This presentation evaluates our new Mo-Pd/C catalyst to reduce aqueous perchlorate ( $\text{ClO}_4^-$ ) in a series of aspects directly relevant to water engineering applications. The aspects include the following: (1) the performance of  $\text{ClO}_4^-$  reduction in practical water matrices and extreme conditions, (2) potential poisoning processes and technical solutions, (3) long-term robustness under the hydrogenating and hydrolyzing

environment, and (4) catalyst regeneration. This study provides critical information regarding the application potential of the Mo-Pd/C catalyst and sets a new example of evaluating water purification technologies with reasonable considerations.

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Wed-LW2-04

Mapping cooperative ligand adsorption at the sub-particle level

**Rong (Rocky) Ye (ry279@cornell.edu), Ming Zhao (mz523@cornell.edu), Xianwen Mao (xm28@cornell.edu), Zhaohong Wang (zw632@cornell.edu), Diego Alejandro Garzon (da.garzon1@uniandes.edu.co), Heting Pu (hp443@cornell.edu), Peng Chen (pc252@cornell.edu)**

Department of Chemistry and Chemical Biology, Cornell University

Adsorption plays vital roles in many processes including catalysis, sensing, and nanomaterials design. However, quantifying molecular adsorption, especially at the nanoscale, is challenging, hindering the exploration of its utilization on nanomaterials that possess heterogeneity across different length scales. In this talk, I will introduce COMPEITS (i.e., competition-enabled imaging technique with super-resolution) that maps the adsorption of nonfluorescent small molecule/ion and polymer ligands on gold (Au) nanoparticles of various morphologies in situ under ambient solution conditions. The trends of adsorption affinity and cooperativity on different sub-particle regions, such as the corners, edges, and facets on the nanoplates, will be discussed and rationalized.

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Wed, 16 13:40 - 15:00

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Wed-NW2-01

Understanding the Transition from Non-living to Living: Characterization of Protocell Systems Based on Aqueous Phase Coexistence (**LaMer Keynote Lecture**)

**Fatma Pir Cakmak (fatmapir@mit.edu)**

MIT, Physics

Understanding how life might have started requires prebiotically relevant protocell models capable of concentrating genetic material that could be subject to Darwinian evolution. I have studied liquid-liquid phase separation as a way of compartmentalization for extant and prebiotic cells. Liquid-liquid phase separated systems could shed light on how to control physicochemical properties of formed compartments for protocell and artificial cells models. I have used a variety of materials including natural clay particles that could act as a catalyst in phase separated PEG/dextran systems. I investigated also prebiotically more relevant compartments than PEG/dextran formed through complex coacervation. These phase separated compartments formed with short peptides were quite resistant at different salt conditions. Besides, these compartments could provide rather different physicochemical properties than bulk water. Properties of the compartments depend on the type of the molecules used to form coacervate droplets. For instance, compartments formed with shorter length peptides were better at preserving double stranded RNA compared to coacervate compartments formed with longer peptides. This means that simpler compartments might provide an advantage to protecting secondary structure of genetic material. I further combined different compartmentalization methods. This study provides insights into how properties of coacervate and liposome affect assembly of both systems. I have established a guideline that is useful to understand governing interactions liposome assembly at the interface. Later a simple method to create lipid membrane templated with coacervates was investigated. Instead of complicated microfluidic devices, we can use simple vesicle hydration to create a membrane. All of my work focused on how to investigate physicochemical properties of different compartments and using gained knowledge to create innovative new models that could be used as a compartmentalization.

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Wed-NW2-02

## Manipulating Lipid Membrane Rigidity at the Nanoscale: Lessons for Drug Delivery

**Judith De Mel ([Idemel@olemiss.edu](mailto:Idemel@olemiss.edu))<sup>1</sup>, Sudipta Gupta ([g.sudipta26@gmail.com](mailto:g.sudipta26@gmail.com))<sup>2</sup>, Gerald Schneider ([gjschneider@lsu.edu](mailto:gjschneider@lsu.edu))<sup>3</sup>**

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Phospholipid vesicles have been a popular template for Nano drug delivery systems for decades. The compatibility of having a cell membrane-like structure allows these systems to not only function as a great template for targeted drug delivery but also as an excellent model system to mimic cell membrane properties especially membrane rigidity. Membrane rigidity is shown to be associated with a plethora of cellular functions spanning from molecular recognition, endocytosis, to critical conditions such as cell death and cancer metastasis. Therefore, understanding molecular-level phenomena that can cause changes in the self-assembly to manifest a membrane rigidity change is highly desirable. We have investigated changes in phospholipid vesicle structure and membrane rigidity using a combination of DLS, SAXS, SANS, Cryo-TEM, and neutron spin echo spectroscopy (NSE). NSE is an excellent way to quantify nanoscale changes in membrane rigidity as a response to molecular interactions. We have observed structural changes in the phospholipid vesicles by external ions, drug molecules as well as polymers which may increase or decrease membrane rigidity depending on the molecular-level interactions. Using these fundamental findings in re-thinking drug delivery strategies for Nanomedicine holds great potential for improved Nano drug delivery systems.

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## Wed, 16 13:40 - 15:00

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Wed-OW2-01

## The Role of Voids and Porosity On The Transport of Macromolecules through 3-D Printed Polymeric Materials

**Angela Zeigler ([angela.m.zeigler3.civ@mail.mil](mailto:angela.m.zeigler3.civ@mail.mil))<sup>1</sup>, Mark Varady ([mark.j.varady.civ@mail.mil](mailto:mark.j.varady.civ@mail.mil))<sup>1</sup>, Melissa Hulet ([melissa.s.hulet.ctr@mail.mil](mailto:melissa.s.hulet.ctr@mail.mil))<sup>2</sup>, Brian Ryu ([bryu@stanford.edu](mailto:bryu@stanford.edu))<sup>3</sup>, Roseanna Zia ([rzia@stanford.edu](mailto:rzia@stanford.edu))<sup>3</sup>**

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Additive manufactured materials are limited in field use as a result of inherent porosity and voids. A fundamental understanding of how the mesoscale structure affects the chemical transport diffusion through 3-D printed polymeric materials allows for full exploitation of the technology. Understanding of the efficacy of such materials includes detailed understanding of the migration rates through the material of solvent-suspended particles of various sizes and how the rate varies with the tortuosity of the void network. Studies of flow through porous media are well-established in the literature, but the geometry and connectivity of pore structures that arise from different additive manufacturing techniques have not been well studied, preventing the development of predictive models for mass transport. In this study, we seek a fundamental understanding of how porosity and voids affect migration of solvents and particles through materials. We present our results on experimental and computational measurements of permeability of solvents through a pore network inside solid materials with varying morphologies. Detailed characterization of solvent transport provides an understanding of the mechanism of how voids structure and connectivity affect the solvent flow traversing the network. Here we present the comparison between in situ and in silico permeability measurements and discuss the mechanisms of solvent transport in porous materials. Approved for public release: distribution unlimited.



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Wed-OW2-02

## Conformation Studies of Model Monodisperse Polystyrene Blends in Solution with Chain-End Interactions

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A comprehensive framework involving small-angle neutron scattering measurements, semi-empirical theories, and coarse-grained polymer reference interaction site model (PRISM) is developed to gain fundamental insights into the scattering of model monodisperse polystyrene (PS) blends in solution with chain end interactions. Our contribution pinpoints the origin of the nebulous excess scattering in thermodynamic equilibrium and isotropic semi-dilute PS solution in a marginally good solvent of xylene. A simultaneous occurrence of enhanced low- $q$  excess scattering and the augmented suppression of concentration normalized intensity at intermediate- $q$  was observed with an increasing concentration above the overlap concentration, which unequivocally pinpointed the chains reversible interaction and the equilibrium nature of interactions, respectively. The attraction between short-ranged chain ends of acidic methanol was modeled as a weak mean-field attraction between the polymer chains. Both the excess scattering and the global polymer conformation were modeled using PRISM by tuning the width of a weak enthalpy-driven ( $\epsilon=0.015/kT$ ) long-ranged attractive forces between the end-groups, which corresponded to the radius of gyration of the chain. Our robust yet rudimentary pair-potential approach was for the first time able to capture the chain-length dependent excess scattering in an isotropic solution with the structural assignment to chain end attraction. The chain-end interaction effects were investigated by labeling and contrast-matching a large fraction of partially deuterated PS chain to access single-chain statistics of a small fraction of labeled chains with essentially equal degree of polymerization. The end-group interactions manifest as an enhanced interchain correlation between the probed labeled chains invoked by the semi-dilute contrast-matched chains, thereby resolving the paradox of an apparent expansion of the probed chains upon crowding. This phenomenon steered the local packing of chain ends, discerned from pairwise intrachain correlation function  $g(r)$ , which increased their wavelength of local monomer density fluctuations. This end-group mediated concentration fluctuations in nearly overlapping crowded chains were screened when overlaid with the long-ranged attractive semi-dilute crowded chains that resulted in a decrease in the blob size. Notably, a competition between the two phenomena in the semi-dilute probed chains in the presence of semi-dilute contrast-matched chains resulted in a minimum of interchain correlations, which at lower  $q$  sharply increased due to the long-ranged end group mediated attractions. Our systematic investigation of the incommensurate phenomena determining single-chain conformation in the semi-dilute regime, i.e., short-ranged monomer-scale packing and long-ranged end-group mediated attraction will significantly help in a better understanding of the isotropic global polymer conformation with chain end interaction effects.

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Wed-OW2-03

## Deposit control in the engine: experiments and multi-scale molecular modeling

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Preventing deposit formation is a critical performance property for lubricant oils. In the current study, we investigate the complex mechanisms of deposit control by bringing experimental colloids science and multi-scale modeling to present a unified approach. We will describe the structure of colloidal insoluble particles at the molecular level with spectroscopy and at the macromolecular level with laser reflectance, light scattering and probe microscopy. For the modeling, highly accurate pairwise interaction energies between components including base oil, insoluble particles, detergents, and dispersants were calculated from many molecular configurations sampled via a statistical sampling method. These interactions were mapped on the all-atom molecular dynamics and mesoscale simulations to explain the role of detergents and dispersants on aggregation and deposit control. We discuss the mechanisms of controlling rate and extent of aggregation and deposition by electrosteric effects, thereby confirming the connection between colloidal stability and deposit control.

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## Wed, 16 13:40 - 15:00

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Wed-PW2-01

Controlled scalable nanofabrication of new classes of colloidal polymer morphologies in sheared liquids

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North Carolina State University, Chemical and Biomolecular Engineering

Soft nanomaterials are ubiquitous in modern society. As most materials' bulk properties arise from their nano- or microscopic features, it is crucial to develop nanofabrication methods that are versatile, tunable, and scalable. Here, we introduce a new method of fabricating a plethora of polymer colloidal morphologies. The basis of this liquid shear-based fabrication technique is formed by coupling the interfacial mass transfer of phase inversion with interfacial precipitation within sheared liquid. In this technique, a polymer solution is injected in a nonsolvent medium and is precipitated at the interface of the multiphase system under varying liquid shear and interdiffusion conditions. While the process is, operationally, quite simple, various combinations of its parameters lead to formation of a myriad of amazingly diverse colloidal morphologies out of almost any type of polymer. Our previous research on sheared liquid precipitation revealed the formation of microrod, fiber, and dendritic morphologies. Here, we demonstrate that these are just a few of the multitude of colloidal polymer structures that this liquid nanofabrication technique can produce. By developing a basic model which delineates the physical processes into three operational stages (hydrodynamic shear, mechanical response, and precipitation rate), we are able to show twelve distinctive parameter combinations which each results in a unique polymer morphology. The insights in the fundamental mechanisms underlying this method allows for tuning of material structure towards an "all-in-one" scalable nanofabrication platform.

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Wed-PW2-02

Fabricating Robust Nanostructured Constructs Using *In Situ* Self-assembly of Surfactants in *Liquid-in-Liquid* 3D printing

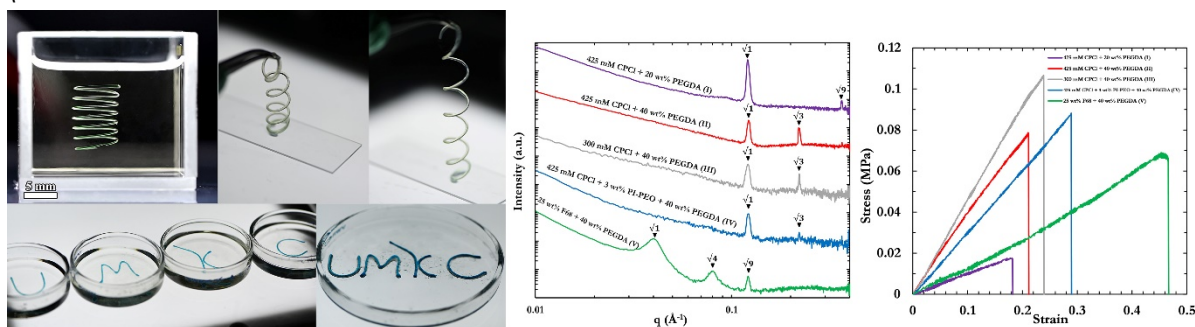
**Houman Honaryar** ([hh7bg@mail.umkc.edu](mailto:hh7bg@mail.umkc.edu))<sup>1</sup>, **Jacob LaNasa** ([lanasajake@gmail.com](mailto:lanasajake@gmail.com))<sup>2</sup>, **Elisabeth Lloyd** ([ecl5232@psu.edu](mailto:ecl5232@psu.edu))<sup>2</sup>, **Robert J Hickey** ([rjh64@psu.edu](mailto:rjh64@psu.edu))<sup>2,3</sup>, **Zahra Niroobakhsh** ([niroobakhshz@umkc.edu](mailto:niroobakhshz@umkc.edu))<sup>1</sup>

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The ability to print soft materials into predefined architectures with programmable nanostructures and mechanical properties is a necessary requirement for creating synthetic biomaterials that mimic living tissues. However, the low viscosity of common materials and lack of required mechanical properties in the final product present an obstacle to the use of traditional layer-by-layer additive manufacturing approaches. *Liquid-in-liquid* 3D printing as an emerging three-dimensional (3D) printing technique allows soft matters to be structured and solidified with high precision and complex structural features. Here, *in situ* surfactant self-assemblies at the water-oil interface have been used in the *liquid-in-liquid* 3D printing technique to fabricate aqueous constructs by injecting continuous threads of aqueous solutions within an oil phase. The photopolymerization of these printed liquid constructs renders them rigid and locks the shape of printed constructs. Small-angle X-ray scattering (SAXS) measurements confirm the presence of internal nanostructures (HEX and LAM morphology) for the cured prints. Tensile tests result reveals that printed constructs are mechanically robust and can be tuned by changing the composition of aqueous solutions (i.e. changing the type of the surfactant or concentration of components). SAXS measurements at the water-oil interface also confirm the formation of nanostructures induced by surfactant self-assembly during printing. Rheology measurements at the water-oil interface reveal the formation of interfacial gel-like materials which is attributed to self-assembly of surfactants and measured to have a wide range of mechanical moduli. The reported printing approach here allows for freeform fabrication of mechanically tunable and rigid constructs from aqueous soft materials that can be applied for the next generation of biomaterials such as amphiphilic systems containing biocompatible surfactants, peptides, or proteins. This freedom in using such soft materials for printing pushes different fields such as tissue engineering forward and opens new opportunities to recreate biological systems. Furthermore, this liquid-in-liquid 3D printing platform reported here permits for the first time patterning of soft materials into complex designs that exhibit structures in micro- or nanoscale which can be of use in applications such as optoelectronic devices or organic photovoltaics.



Wed-PW2-03

## PDMS/PMMA Interpenetrating Networks: Synthesis, Characterization, and Mechanical Properties

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Interpenetrating network (IPN) elastomers can effectively combine hard and soft materials into a tough, elastic network, where a rigid polymer reinforces a soft elastomer. This presentation discusses the combination of crosslinked Polydimethylsiloxane (PDMS) and linear Poly(methyl methacrylate) (PMMA), which are synthesized by two different UV polymerization approaches. The first of two different synthesis routes include a one-step cure of methacrylate terminated PDMS prepolymer mixed with MMA monomer and simultaneously polymerized to form a graft IPN, which can be viewed as a covalently crosslinked

copolymer network. The second synthesis involves a two-step cure where the PDMS matrix is first thermally cured by hydrosilylation, then MMA monomer is swelled in and polymerized. Both syntheses produce a well-dispersed PMMA phase inside a continuous PDMS phase. The addition of MMA drastically increased the elastic modulus and fracture toughness of the resulting network for both synthesis routes. In the two-step synthesis, as the weight fraction of PMMA increases, the material becomes more transparent, but the one-step synthesis shows the opposite trend. Results from small-angle x-ray scattering and atomic force microscopy show that the PMMA domain size decreases with increasing PMMA fraction in the two-step synthesis. However, in the one-step synthesis, the domain size is constant with the PMMA fraction. Therefore, we can conclude that the PMMA domain size controls transparency in the two-step synthesis, but transparency is controlled by the PMMA fraction in the one-step synthesis. This presentation will highlight work on understanding how the synthesis routes influence the morphology of the materials.

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Wed-PW2-04

### Au<sub>32</sub> Nanoclusters are a Seed for Gold Nanorod Synthesis

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A novel aqueous gold cluster is hereby identified in the seed solution for the well-established seed-mediated syntheses of gold nanorods (GNRs). Mass spectrometry allows for the assignment of the cluster as a 32 atom Au core with 8 halide ligands and 12 neutral ligands constituting a bound ion pair of a halide and the cationic surfactant: Au<sub>32</sub>X<sub>8</sub>[ATA<sup>+</sup>•X<sup>-</sup>]<sub>12</sub> (X = Cl, Br; ATA = alkyltrimethylammonium). Ligand exchange is dynamic and versatile, occurring on the order of minutes and allowing for the formation of numerous mixed-ligand clusters. GNRs seeded with optimized Au<sub>32</sub> cluster solution have higher shape purity and narrower size distribution than the ones seeded with traditional gold nanoparticle seeds, so we can claim with confidence that the Au<sub>32</sub>X<sub>8</sub>[ATA<sup>+</sup>•X<sup>-</sup>]<sub>12</sub> nanocluster is the actual seed for the GNR synthesis. This discovery provides numerous insights relevant to further understanding the mechanisms of nanoparticle synthesis.

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## Wed, 16 15:20 - 16:40

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Wed-AW3-01

Self assembled colloids and their aggregation in an anisotropic solvent.

**Devika Gireesan Sudha (dgireesansudha@ucmerced.edu)**, **Jocelyn Ochoa (jochoa36@ucmerced.edu)**, **Linda S Hirst (lhirst@ucmerced.edu)**

University of California Merced

The mutual attraction between colloidal particles in an anisotropic fluid, such as the nematic liquid crystal phase can lead to the formation of hierarchical aggregate morphologies distinct from those that tend to form in isotropic fluids. Previously it has been prohibitive to study the aggregation process for a large number of colloids due to the difficulty of achieving a well dispersed initial colloid distribution. I will be talking about our group's recently developed self-assembling colloidal system, and how we use it to investigate this process. Hollow, micron-scale colloids are formed in-situ in the nematic phase and subsequently aggregate to produce fractal structures and dense gels, the structure of which is determined by a quench through the isotropic to nematic phase transition. We use confocal fluorescence microscopy over a wide range of length scales to measure aggregate structure as a function of quench depth, observe ageing mechanisms in the gels and explore the driving mechanisms for aggregation in this unique system. Our analysis reveals that aggregate dynamics depend on a combination of Frank elasticity relaxation, spontaneous defect line annihilation and internal fracturing.

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Wed-AW3-02

Visualizing rapid assembly of platinum supraparticles during nanoparticle synthesis with liquid phase transmission electron microscopy

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Conventionally, nanocrystal self-assembly is carried out slowly over hours or days by modifying the solvent, temperature, or evaporating colloidal suspensions of nanoparticles coated in (bio)molecules. Recent research has demonstrated rapid formation of nanoparticle superlattices over minute time scales using electric fields, rapid solvent exchange, or temperature changes. The rapid assembly kinetics are at odds with the classical picture of self-assembly, which involves slow kinetics and weak interparticle interactions to allow nanoparticles to sample their local environment to find high coordination binding positions and correct misbonding. Here we utilize liquid phase transmission electron microscopy to demonstrate that self-assembly of ~3 nm platinum nanoparticles into 3D supraparticles during nanoparticle synthesis is enabled by rapid surface diffusion on the supraparticle. The electron beam was utilized to reduce an aqueous platinum salt into ~3 nm ligand free Pt nanocrystals (i.e. primary particles), which immediately assembled into 3D supraparticles over tens of seconds. Interestingly, the primary nanocrystals were nearly monodisperse despite the absence of capping ligand, which enabled them to assemble into supraparticles, some of which showed long ranged order. An interparticle interaction model demonstrates that weak van der Waals interparticle attraction is balanced by repulsive steric interactions from in situ generated capping ligands, creating net interparticle attraction forces on the order of thermal forces. Following particle attachment to a supraparticle, weak binding enabled nanocrystals to rapidly diffuse on the supraparticle to find high coordination binding sites. The primary nanocrystal attachment rate was measured to be orders of magnitude less than the estimated nanocrystal diffusion rate on the supraparticle surface, indicating that rapid surface diffusion enables formation of close packed supraparticles despite the perceived rapid formation kinetics.

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Wed-AW3-03

Oriental Control and Assembly of Shaped Nanoparticles at Interfaces

**Yilong Zhou (yz393@duke.edu)<sup>1</sup>, Tsung-Yeh Tang (ttsungye@eng.ucsd.edu)<sup>2</sup>, Brian Lee (brian.h.lee@duke.edu)<sup>1</sup>, Gaurav Arya (gaurav.arya@duke.edu)<sup>1</sup>**

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Self-assembly of shaped nanoparticles (NPs) into anisotropic structures, in which NPs are particularly oriented, offers an attractive approach for generating new functional materials. In this talk, we will demonstrate that the use of a fluid-fluid interface to trap shaped NPs can not only achieve control over their orientation but also assemble them into interesting higher-order structures. In particular, we carry out molecular dynamics simulations of polymer-grafted cubic NPs in a polymer bilayer to explore their orientational behavior and assembly. We show that the orientation of such nanocubes at the interface can be tuned into face-up, edge-up, or vertex-up orientations by grafting polymer chains onto their surfaces. The obtained orientations could be explained based on the amount of occluded interfacial area, interfacial deformation induced by shaped NPs, and the chain stretching at the interface. Furthermore, we show that such oriented nanocubes can self-assemble into unconventional structures, including rectilinear 1D strings, 2D porous monolayers, 2D close-packed monolayers, and quasi-linear bilayer structures. Next, by using two species of grafts, where one is hydrophilic and the other is hydrophobic, we are able to further manipulate the interactions between nanocubes by controlling the length and stoichiometry of the two

grafts. We find that the nanocubes at an air-water interface undergo multiple phase transitions as a result of Langmuir-Blodgett compression. Moreover, we demonstrate that the interplay between the interactions of the two polymers gives rise to a novel checker-board pattern of nanocubes. Overall, this work suggests that interfacial assembly of shaped NPs could be a promising approach for fabricating next-generation NP structures with possible applications in plasmonics, magnetics, optics, and catalysis where control over particle orientation and assembly is critical.

Wed-AW3-04

Structure and anisotropic dynamics of stimuli responsive colloidal ellipsoids at the nearest neighbour length scale

**Antara Pal (antara.pal@fkem1.lu.se), Mohammad Arif Kamal (mohammad\_arif.kamal@fkem1.lu.se), Peter Schurtenberger (peter.schurtenberger@fkem1.lu.se)**

Division of Physical Chemistry, Lund University, Lund, Sweden

Stimuli-responsive self-assembly of (an)isotropic colloids has resulted in a plethora of self-assembled structures with potential application towards the fabrication of smart materials. Although much effort has been invested for understanding the relationship between the shape of the building blocks and the self-assembled structures, knowledge regarding their dynamics is clearly lacking, which can act as an impediment in exploiting the full potential of the resulting smart materials. In the present article, using multispeckle ultra-small-angle X-ray photon correlation spectroscopy (USA-XPCS) and magnetic colloidal ellipsoids, we have carried out a systematic investigation to unveil the relation between the field-driven self-assembled structures and the corresponding collective dynamics at the nearest neighbor length scale. The USA-XPCS measurements have allowed us to probe the  $q$  dependence of the effective long time collective diffusion coefficient,  $D_{\text{eff}}(q)$ , over a wide range of volume fraction,  $\phi$ , and external magnetic field,  $B$ . Our results highlight that  $D_{\text{eff}}(q)$  scales with the inverse of the scattered intensity,  $I(q)$ , in different azimuthal directions for the various self-assembled phases that form at different  $\phi$  and  $B$ . At high  $\phi$ , the system approaches a kinetically arrested state both in the presence and absence of  $B$ . We find that the slowdown of  $D_{\text{eff}}(q)$ , at high  $\phi$  is anisotropic, which hints towards the formation of an oriented glass. Our approach opens up new avenues for exploring the stimuli-responsive dynamics of strongly interacting colloidal systems with diverse shapes and chemical compositions.

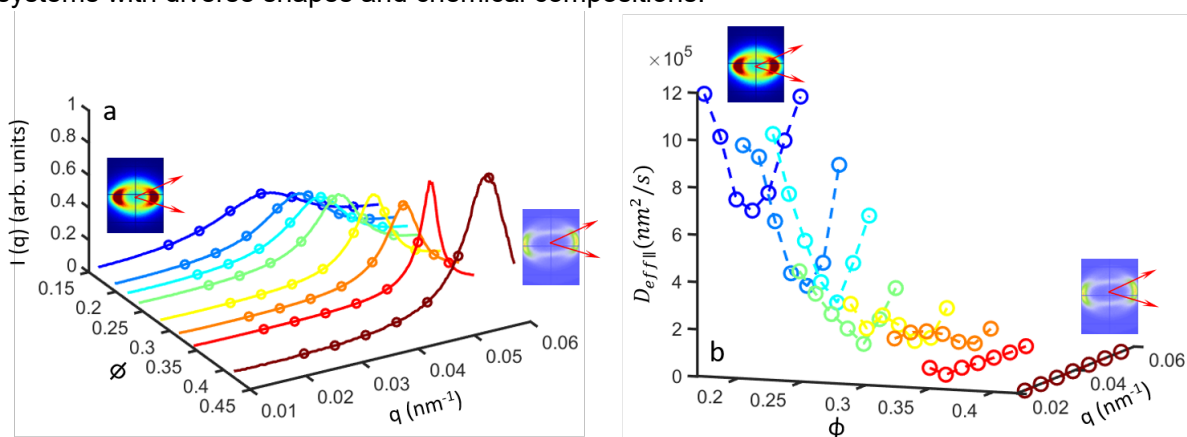


Fig1. (a) Scattering intensity ( $I$ ) as a function of  $q$  for different volume fractions of the particles; insets show the diffraction patterns for the lowest and highest concentrations. All the data correspond to 1000mT and along the direction of the field. (b) Effective diffusion coefficients ( $D_{\text{eff}}$ ) at particular values of  $q$  (indicated by the dots on the intensity profiles in (a)). Different colours correspond to different volume fractions of the particles.

Wed, 16 15:20 - 16:40

Wed-FW3-01

## Advanced Applications of Scanning Probe Nanolithography (**Keynote Lecture**)

**Gang-yu Liu (gyliu@ucdavis.edu)**

Department of Chemistry University of California Davis, CA 95616

This presentation discusses recent advanced in applications of scanning probe nanolithography. Combining a microfluidic probe with atomic force microscopy (AFM), sub-femtoliter aqueous droplets containing designated solutes, e.g., polymers, produce well-defined features with dimensions as small as tens of nanometers. The initial shape of the droplet and the concentration of solute within the droplets play a significant role in the final assembly of polymers due to the ultrafast evaporation rate and spatial confinement of the small droplets. These effects are used to control final molecular assembly in terms of feature geometry and distribution and packing of individual molecules within the features. Two applications will be discussed: 3-D nanoprinting and controlling the signaling processes and behavior of living cells. These new advances also enable controlling assembly of molecules at molecular level, bringing us closer to programmable synthesis for chemistry and materials science.

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Wed-FW3-02

## Closed-Loop Nanopatterning of Liquids with Dip-Pen Nanolithography

**Verda Saygin (saygin@bu.edu)**<sup>1</sup>, **Bowen Xu (bowenx@bu.edu)**<sup>1</sup>, **Sean Andersson (sanderss@bu.edu)**<sup>1,2</sup>, **Keith A. Brown (brownka@bu.edu)**<sup>1,3</sup>

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High-throughput screening technologies such as microtiter plates enable chemists and biologists to simultaneously perform thousands of experiments in an automated fashion. While transformatively smaller than the vials used by prior generations, the typical working volume for microtiter plates is in the range of microliters and there are still far too many compounds to study even with this degree of miniaturization. Dip-pen nanolithography (DPN) could provide a path to continuing this miniaturization in fluid handling as it encompasses approaches to pattern fluids with volumes at least 109times smaller than what is achievable in microtiter plates. While the patterning of such sub-fL volumes has been demonstrated with various different materials over the years, to achieve controlled and reliable experimentation with DPN, it is crucial to have precise and real time control over the size of features and amount of fluid that is transferred. Here, we enable closed-loop control over the fluid written using DPN by combining a novel process for quantifying the fluid on a probe, the utilization of a tipless probe architecture, and a control strategy for adjusting writing parameters *in situ*. Specifically, we employ a two-harmonic mode inertial sensing algorithm to reliably quantify the amount and location of fluid on the probe. Critically, sensing the mass of liquid on the probe before and after a fluid transfer event allows us to monitor the deposited amount with sub-fL precision. This capability allows us to investigate the fundamental mechanisms and characteristics of fluid transport at this scale. Taking inspiration from experiments of fluid transfer between macroscopic parallel plates, we find that the fraction of the liquid that is transferred from the probe to the substrate is only a function of the probe withdrawal speed and contact angles of both substrates. Based on this discovery, we show that the amount of fluid that will be transferred can be predicted based on the amount of ink on the probe, hence it is possible to control the transferred amount by selecting the writing parameters. With this insight in hand, we realize a closed-loop process for writing patterns with designed fL-scale feature sizes. Given the versatility of scanning probes to characterize fluids once they are written, this work lays the foundation for multifunctional research systems in which chemical experiments are set up, performed, and evaluated at the nanometer scale.

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## Wed, 16 -15:20 - 16:40

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Wed-HW3-01

Interaction forces and nanotribology of surfaces modified with bioinspired polyelectrolyte coatings

**Marina Ruths (marina\_ruths@uml.edu)**

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Structuring in polyelectrolyte films can be induced and controlled by modifying the solution conditions. These phenomena are of interest for controlling adhesion, friction, and lubrication of surfaces in biomedical applications. Changes in the solvent quality and the presence of multivalent ions in polyelectrolyte systems cause aggregation and strongly influence the normal and frictional forces between interacting layers. Some of these changes can be reversible upon changing the solution conditions and enable evaluation of the contributions to aggregation from solvent quality and electrostatic bridging of polyelectrolytes. To illustrate these phenomena, examples will be shown of structure formation observed with AFM and its effects on normal and friction forces as studied with the SFA.

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Wed-HW3-02

Investigation of Nanorehelogical Properties of Confined Geocolloids

**Thiranjeeva Lansakara (thiranjil@ucr.edu), Younjin Min (younjin.min@ucr.edu)**

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The investigation of geocolloidal interactions in the presence of contaminants has gained significant attention due to the ever-increasing release of pollutants into the environment. The confined geocolloids behave differently than their non-confined bulk phase. These behaviors can be further influenced with the adsorption of contaminant onto geocolloids. We investigated the nanorehelogical properties of highly monodisperse silica colloids of sizes ranging from 40 – 400 nm. Anisotropic silica geocolloids were prepared as a model system to the contaminant adsorbed geocolloids, using controlled chemical vapor deposition of silanes with different degrees of surface coverages. Viscosity and flow behavior of confined isotropic and anisotropic silica colloidal suspensions were evaluated with atomic force microscopy (AFM) and surface force apparatus (SFA) in micro and nano-length scales. During the confinement of nanoparticles with AFM force spectroscopy, oscillatory behavior was observed. These observed oscillatory wavelengths are in good agreements with the sizes of nanoparticles used in the current study. Viscosity of the geocolloids was significantly increased in the presence of salts under confinement carried out with SFA indicating the formation of aggregates. This was attributed to the screening of electrostatic repulsions between silica colloids in small, confined distances. We believe these findings would have significant impacts on the geophysics and environmental science communities providing a fundamental understanding on colloidal interactions.

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Wed-HW3-03

Polymer-surfactant complex and shear mediated non-equilibrium colloidal deposition trajectories

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This talk will present findings on colloidal deposition mechanisms in personal care products during rinsing processes involving formulation dilution and shear flow. We employ total internal reflection microscopy method to directly, sensitively, and simultaneously measure colloidal interactions, dynamics, and



deposition for a broad range of polymer-surfactant compositions. Measured colloid-substrate interactions and deposition behavior in quiescent conditions show non-monotonic trends vs. polymer-surfactant composition and are synergistic in that they are not easily explained as the simple combination of single component mediated interactions. We then employ a flow cell/microscopy assay that provides in situ characterization of colloidal deposition and detachment as a function of dilution and shear flow. Results show initial shear-mediated detachment of colloids in the presence of polymer-surfactant complexes that produce depletion attraction, which does not produce tangential forces that can resist shear detachment. Further rinsing produces preferential dilution of surfactants, which causes re-deposition of colloids due to the increasing number and strength of cationic polymer bridges between anionic colloids and substrates. By decreasing the initial surfactant to polymer ratio, preferential surfactant dilution yields enhanced cationic bridging to resist shear detachment, produce more re-deposition, and yield the highest deposited colloid amounts. Our measurements reveal how deposition is determined by formulation component dilution during rinsing and demonstrate a first principles approach to screen new formulation compositions, materials, and processing methods.

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Wed-HW3-04

Electrostatic Wetting Transition: Charge inversion and Like Charge attraction

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The study of the Electrical Double Layer is at the heart of interfacial sciences. In the so-called weak coupling limit, mean-field Poisson Boltzmann has enjoyed significant successes, but the absence of ionic correlations does not allow it to even qualitatively explain many fundamental moderate and strong coupling phenomena such as charge inversion and like-charge attraction. Here a self-consistent Gaussian fluctuation-based electrolyte solution theory that includes both ion-ion correlation and excluded volume effect will be presented in the context of these phenomena. Our theory predicts a surface charge induced phase transition leading to the formation of a three-dimensional condensed layer on the macroion surface. This correlation-induced layer leads to the renormalization of the surface charge, the value of which turns out to be a non-monotonic function of the bulk concentration, in agreement with experiments and simulations. We also show that the short-range attraction between two like charged bodies originates in the overlap of the condensed layers of ions on the two surfaces. At very high salt concentrations these condensed layers dissolve into the bulk thereby removing the attractive force component -- this is the reason behind the re-entrant condensation observed in charged colloidal suspensions. Our theory is the first of its kind to model both non-monotonicity in charge inversion and re-solubilization of charged colloids in a single self-consistent framework.

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Wed, 16 -15:20 - 16:40

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Wed-JW3-01

Interfacial tensions and film drainage times with surfactant stabilized emulsions: Towards improved liquid-liquid separation

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The dynamics at the liquid-liquid interface for surfactant-stabilized systems inform liquid separations and treatment strategies, such as coalescence. Effective separation and removal of the dispersed phase droplets require understanding of the effect of surfactant presence in these emulsions on their dynamics and stability. In this presentation, we highlight this effect using measurements performed across a range of droplet size, surfactant concentration, and viscosity ratios. The first factor studied here is the interfacial tension (IFT), as well as the characteristic timescale required for the IFT to reach equilibrium. Dynamic IFT measurements are performed here at two length scales: a millimeter scale using pendant drop experiments and a microscale using microfluidic tensiometry, with systems of light and heavy mineral oil containing varied concentrations of SPAN80 surfactant. It is found that the IFT decays faster in the case of micro-scale droplets due to a shift from diffusion-limit to adsorption-limited surfactant transport mechanism. In addition, as expected, the equilibrium IFT decreases with increasing SPAN80 concentration, and that the decay rate of the dynamic IFT is higher at greater surfactant concentrations. It was also found that the equilibrium IFT increases with increasing viscosity ratio of the outer to the inner phase, and that the rate of IFT decay is lower at a greater viscosity ratio. The surfactant diffusivity and interfacial adsorption and desorption rates are extracted by fitting a surfactant diffusion and equation of state equations to the dynamic IFT measurements. The second factor studied here is the time for the thin film to drain between two coalescing droplets. Similar to dynamic IFT, the film drainage time is closely tied to the stability of the droplet, with faster film drainage events indicative of less stable emulsions. In this work, the film drainage times are presented for varied surfactant concentrations, and results are related to the surfactant diffusivity and adsorption rates determined from the dynamic IFT measurements. The results of this study help understand the relation between the timescale for IFT equilibration and film drainage times, towards improved understanding of emulsion dynamics. Studying the factors that influence droplet coalescence will impact liquid separation processes by increasing the coalescence efficiency upon performing separation at conditions that will give lower film drainage times.

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Wed-JW3-02

## Heteroaggregation of Neutral and Charged Nanoparticles: Making Core-Shell Nanohybrids Through Self-Assembly

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Core-shell nanohybrids have many potential energy and environmental applications. Previous methods of synthesizing core-shell nanohybrids mostly involved extensive heating or stirring. In this study, core-shell nanohybrids were self-assembled through spontaneous heteroaggregation between model neutral nanoparticles (NPs) (i.e., hematite NPs or HemNPs) and model charged NPs (i.e., carboxylated polystyrene NPs or PSNPs). The heteroaggregation process does not require heating or stirring and thus can be much more energy efficient than previous methods if successfully applied. The pH of the dispersant solution at 1 mM NaCl was adjusted to 6.3 so that HemNPs were neutral and underwent favorable homoaggregation whereas PSNPs were negatively charged and underwent no homoaggregation. When the two types of particles were mixed, homoaggregation of HemNPs and heteroaggregation between HemNPs and PSNPs took place simultaneously, forming HemNPs-PSNPs heteroaggregates. The hydrodynamic diameter of heteroaggregates increased initially and became stable afterward. The transmission electron microscopy (TEM) images of heteroaggregates sampled in the stable stage show that HemNPs and PSNPs had self-assembled into core-shell structures in which HemNPs were the cores and PSNPs were the shells. The size of core-shell nanohybrids can be controlled by varying the concentration ratio of HemNPs to PSNPs. The elevated concentration of PSNPs reduced the size of nanohybrids because the abundant PSNPs could quickly surround HemNPs and form the shells, diminishing the chance for HemNPs to grow to larger cores through homoaggregation. The increase of the size of PSNPs resulted in the lower number concentration of PSNPs needed for forming stable nanohybrids and the larger size of nanohybrids.

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Wed-JW3-03

### All-Nanoparticle Surface Functionalization for Mid-Infrared On-Chip Sensing

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We report development of conformal nanoparticle (NP)-based coatings applied to the surface of mid-infrared (MIR) waveguides (WGs), to simultaneously achieve sensitivity and selectivity enhancement for gas sensing. The coatings were selected to be transparent in the MIR region of interest, facilitate penetration of gas through pores within the coating, and provide high surface area to volume ratio for gas adsorption. We investigated the effect of deposition conditions, such as withdrawal speed and solution pH, on the thickness, porosity and morphology of the coatings. Two types of LbL systems were explored: NP/NP and polymer/NP. The NP/NP system consisted of spherical solid ZnO<sub>2</sub> and SiO<sub>2</sub> NPs with diameters of 4.2 nm and 20 nm, respectively. The polymer/NP system was composed of branched polyethylenimine and mesoporous silica NPs of ~150 nm in diameter and was followed by calcination. Compared to the conventional layer-by-layer (LbL) deposition, with the controlled dipping technique the substrate withdrawal speed was a critical factor, where homogeneous and uniform coatings were only achieved in the convective regime ( $\leq 0.001$  cm/sec). Further, the submicron porous coatings enabled concentration of the gases within the vicinity of the WG through the adsorption of gas molecules at the nanoparticle surface providing enhanced detection sensitivity. In addition, the coatings improved the selectivity of the WGs due to the preferential interaction of polar gas molecules, such as acetone and ethanol, with the polar surfaces of metal oxide NP-based coatings. We discuss how silanization of such inorganic coatings can be used to further enhance the selectivity of gas molecules with different polarities. Using LbL-coated MIR WGs, we show selective and reversible sensing of mixtures of methane, acetone and ethanol using the C-H stretching vibrational bands of these analytes.

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Wed-JW3-04

### Fluorinated surfactant self-assembly in aqueous solution for sequestration applications

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Fluorinated surfactants find niche applications because of their unique ability to repel both water and oil, wet surfaces and render them non-stick, and high chemical and thermal stability. However, several widely used fluorinated surfactants are extremely resistant to degradation, accumulate in the environment, and have long half-lives in humans, consequently causing great concern. In the context of sequestering fluorinated surfactants from aqueous media and in designing new chemicals for potential replacements of fluorinated molecules, we research solution properties of fluorinated surfactants, with a focus on how such surfactants interact with (bind to) other molecules or particles/surfaces. We report here on ammonium perfluorooctanoate (PFOA) micelle formation and structure in aqueous solutions in the presence of various additives, probed with complementary experimental techniques (conductivity, surface tension, fluorescence, small-angle neutron scattering) and atomistic simulations. The results inform the fate and transport of per- and poly-fluoroalkyl substances (PFAS) in the environment.

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Wed-KW3-01

Osmotic-Capillary Principles for Microfluidic Pumping and Fluid Management for Sweat Sensing Devices

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Sweat is an essential biofluid for monitoring individuals' health as it contains several key biomarkers. However, sampling sweat for analysis is still challenging as most of the commercially available sweat sensing devices are either invasive in nature or work only during active perspiration. These devices may not function under low-sweating conditions and may be incapable of sensing in sweat from sedentary subjects. We demonstrate a new principle for the design of flexible and wearable patches, which are capable of extracting sweat under both resting and actively perspiring conditions using osmotic pressure difference for pumping, and evaporation for liquid disposal.<sup>1</sup> The patch is composed of silicone, hosting polyacrylamide hydrogel patch, and paper microfluidic conduit with a site of evaporation at the end (evaporation pad). The hydrogel is equilibrated with glycerin, glucose, or NaCl solution to build up the desired osmotic strength to extract fluid from the skin.<sup>2</sup> We investigate the performance of the patch using a model biomarker (dye) solution. In-vitro testing with gelatin-based model skin platform revealed that both glucose and glycerin-infused gels facilitate high analyte accumulation on the evaporation pad, with glucose as osmolyte having the highest driving pressure. The cumulative dye collection also depends on the dimensions of the paper channel, hydrogel area and paper pore size. Human trials show the potential to extract sweat and analyze it for lactate under both resting and non-resting conditions within a period of two hours. We used lactate as a concept demonstrator, as sweat appears to be more informative medium for lactate quantification than blood. The ability to measure lactate enables monitoring metabolism and oxidative stress levels in athletes and military personnel. Our group is currently investigating how this sweat sampling concept can be integrated in continuously operating wearable devices using enzymatic electrochemical sensors<sup>3</sup>, and with microneedle patches for long-term interstitial fluid (ISF) sampling. References: 1. Shay, T., Saha, T., Dickey, M.D., and Velev, O.D. (2020) Principles of long-term fluids handling in paper-based wearables with capillary–evaporative transport. *Biomicrofluidics*, 14 (3), 034112. 2. Saha, T., Fang, J., Mukherjee, S., Dickey, M.D., and Velev, O.D. (2021) Wearable Osmotic-Capillary Patch for Prolonged Sweat Harvesting and Sensing. *ACS Appl. Mater. Interfaces*, 13 (7), 8071–8081. 3. Yokus, M.A., Saha, T., Fang, J., Dickey, M.D., Velev, O.D., and Daniele, M.A. (2019) Towards Wearable Electrochemical Lactate Sensing using Osmotic-Capillary Microfluidic Pumping. 2019 IEEE SENSORS, 2019-Octob, 1–4.

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Wed-KW3-02

Quantitative, Label-Free Yeast Cell Viability Determination Using Total Holographic Characterization

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Assessment of cell viability is a challenge in many applications including biologics manufacturing. Traditional methods often include labeling with dyes and/or time consuming methods of counting cells. Total Holographic Characterization (THC) is presented as an efficient, automated, label-free method of accurately identifying cell viability. Results will be presented for experiments measuring yeast cell viability in a variety of different environments including alcohol concentrations of 0%-18%, temperatures from ambient to 60C and pH from 2-13. Control experiments were performed by manually counting living and

dead cells as distinguished with trypan blue dye. THC is a single-particle characterization technology that determines the size and index of refraction of individual particles. Results will demonstrate that THC can distinguish living and dead yeast cells by the index of refraction of individual yeast cells. All THC measurements are performed in the native environment of the sample with no need for dilution or addition of labels.

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Wed-KW3-03

Microfluidics for high throughput sorting and preservation of pancreatic islets

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Functioning of pancreatic islets which are group of cells that secrete insulin along with other hormones play a crucial role in management of Type 1 Diabetes Mellitus (T1DM). It has been widely clinically verified that islet transplantation to T1DM patients could possibly reverse the disease and reduce the burden on the healthcare system. Here we leverage microfluidic techniques to aid the transplantation process by processing islets to yield high purity transplant grafts and study islet osmotic response to design cryoprotection protocols. Islets vary greatly in size ranging from about 50µm to 350µm in humans. However, it has been reported that larger islets (> 150µm) do not thrive post transplantation and they do not contribute to the success of the transplantation. The elimination of larger islets from the graft would lead to a reduced immune response from the body post transplantation, consequently requiring lower dosage of immunosuppressants. Reducing the graft size also lowers the portal vein pressure during transplantation, thereby minimizing the chances of portal vein thrombosis. Acoustic microfluidic platform provides us with a unique opportunity to size separate large volume of islets at a high throughput. Also, long term preservation of islets is very crucial as it would help in creation of islet banks and buy more time for quality testing of islets before transplantation. Islets undergo volume changes on exposure to different cryoprotective chemicals during preservation processes as a result of osmotic pressure differences generated by such chemicals. We aim to characterize islet osmotic response to frequently used cryoprotective agents for development of preservation strategies that prevent volume excursions beyond the tolerable limits. Parameters governing membrane transport equations including hydraulic conductivity and solute permeability for commonly used cryoprotective agents were estimated.

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Wed-KW3-04

Engineering the nano-bio interface in paper immunoassays for infectious diseases

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The convergence of the fields of nanotechnology and medicine has resulted in innovative approaches for novel disease therapies, biomedical imaging and sensing, and numerous others. In particular, the use of gold nanoparticles in rapid diagnostics for infectious diseases has been emerging as an application with the potential to address some of the major challenges in global health. These assays are low-cost and can be used in rugged environments, so they are attractive for widespread deployment for disease surveillance, quarantining, and treatment. One of the biggest challenges for effectively using nanoparticles in biological

applications is the physical interface between the nanoparticles and its biological environment. Surface fouling and non-specific adsorption can lead to undesirable side effects such as diminished targeting specificity and cell uptake, unfavorable biodistribution, and toxicity. However, non-specific adsorption can actually be exploited for biological applications. We will discuss the unique interface issues in lateral flow immunoassays, and show how the unique properties of the nano-bio interface can be utilized for different medical applications including disease diagnostics for dengue, zika, chikungunya, Ebola, and other pathogens. One opportunity for extending the capabilities of paper immunoassays that are not possible with traditional paper immunoassays lies in exploiting the unique size and material dependent properties of the nanoparticles. We describe a route for leveraging the optical properties of gold nanostars to use paper immunoassays for multiplexed diagnostics for yellow fever, dengue, and zika viruses. By adapting immunoassays for selective sensing as opposed to specific sensing and using machine learning of the color test lines, we are able to construct a multicolor assay for yellow fever non structural protein 1(NS1) using cross-reactive antibodies raised for dengue and zika. In addition, we discuss routes to increase the sensitivity of paper-based immunoassays via surface enhanced Raman spectroscopy (SERS). By using gold nanostars as Raman nanotags with different Raman reporter molecules, we can construct multiplexed assays for zika and dengue.

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Wed-LW3-01

Towards New Tools for Heterogeneous Catalysis using Soft Materials: Hydrogenation of Nitrile-Containing Liquid Crystals on Palladium Surfaces

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Elementary surface reaction steps, including adsorption and dissociation, of a range of molecular adsorbates on transition metal surfaces have been elucidated to understand the chemical reactivity of surfaces (e.g., for heterogeneous catalysis). In this presentation, we will describe how it is possible to design molecular liquid crystals (LCs) supported on atomically thin (8 monolayers) palladium films (predominantly Pd(111)) that can be triggered to undergo orientational transitions by elementary surface reactions (e.g., dissociative adsorption of H<sub>2</sub> and hydrogenation of nitrile-containing LCs), thus amplifying atomic-scale surface processes in situ into macroscopic optical signals. Our approach integrates first-principles calculations, synthesis of new LCs and a range of experimental characterization approaches (polarization modulation infrared adsorption spectroscopy and polarized light microscopy). In particular, we find that LC orientational transitions triggered by hydrogenation of nitrile groups follow an Arrhenius-type expression, thus hinting that LCs offer the basis of fresh approaches to characterizing reaction barriers during heterogeneous catalysis. Overall, the results presented in this talk will illustrate how LCs can be used to amplify specific atomic-scale events into the macroscopic scale, thus providing fundamental insights into interfacial reactivity as well as offering the basis of programmable, stimuli-responsive materials.

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Wed-LW3-02

Changing the Shape of Water in Micropores and the Impact of Non-Covalent Interactions on Catalysis

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Catalytic reactions at solid-liquid interfaces involve complex networks of adsorption, surface reaction, and desorption processes, where each possesses a free energy of reaction and activation that contributes to measured rates and selectivities. The ways in which these free energies depend on the structure of solvating molecules and the topology of the surrounding voids is poorly understood. Here, we demonstrate how the numbers of hydrogen-bonds among intraporous H<sub>2</sub>O molecules and distributions of H<sub>2</sub>O oligomers depend upon zeolite topology (CDO, MFI, BEA, and FAU) and the density of SiOH nests. We show that the highly correlated motion of H<sub>2</sub>O within microporous environments leads to solvation effects that change turnover rates by several orders of magnitude. Turnover rates for 1-alkene (C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub>) epoxidation are up to 400-fold greater in hydrophilic Ti-zeolites (i.e., which contain large densities of SiOH defects) than within their hydrophobic (i.e., nearly defect-free) counterparts. These changes in rates with SiOH reflect differences in the structure of H<sub>2</sub>O molecules within the microporous voids of the Ti-zeolites. Infrared spectra of H<sub>2</sub>O within these porous environments (Fig. 1) reveal distinct populations of H<sub>2</sub>O in different hydrogen bonding configurations. These data, paired with MD simulations (Fig. 1), suggest that H<sub>2</sub>O molecules form bulk-like structures in FAU zeolites, but coalesce into oligomeric chains and clusters within BEA, MFI, and CDO zeolites. Changes in the excess enthalpies ( $\Delta H_{\text{excess}}^{\ddagger}$ ) and entropies ( $\Delta S_{\text{excess}}^{\ddagger}$ ) measured via catalysis strongly correlate with measures of the enthalpic cost and entropic gains of breaking hydrogen bonds within pure water obtained by in situ infrared spectroscopy. These relationships demonstrate that interactions among H<sub>2</sub>O molecules within the solvent couple short-range covalent interactions that drive adsorption and catalysis with longer range solvent restructuring. Here, H<sub>2</sub>O is responsible for these effects, which suggests judicious choices of zeolite framework and silanol density may be used to increase rates and selectivities for many other catalytic reactions or manipulate adsorption processes, provided that the solvent contains molecules with a proclivity to form hydrogen bonds.

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Wed-LW3-03

Surface chemistry control of the properties of aluminum nanocrystals for sustainable photocatalysis (**LaMer Keynote Lecture**)

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Controlled growth and surface chemistry modifications of colloidal plasmonic metallic nanoparticles have been a major and ever-increasing research focus because of their unique optical properties and enhanced chemical reactivity relative to larger mesoscale and bulk phase materials. In this regard, the recently emerged aluminum nanocrystals (AINCs) are particularly intriguing because of their potential as an earth-abundant substitute for more precious noble metals in plasmonic and photocatalytic applications. AINCs and nanostructures are air stable due to a self-passivating 2–4 nm amorphous native oxide layer that surrounds the metallic core with plasmon resonances that can be tuned from the ultraviolet to the infrared by varying nanostructure size and shape. The combination of the plasmonic Al core and the native oxide shell enables multifunctional plasmonic and catalytic functionalities. This talk will cover our recent efforts in tailoring the surface chemistry of AINCs for light-driven high-value chemical transformations via exploiting their surface oxide layer to growth metal catalysts species and metal-organic frameworks (MOFs) shell layers. The former relies on the native oxide for anchoring the active metal species, whereas the latter proceeds by the highly controlled oxide dissolution to supply Al<sup>3+</sup> ions for the MOFs backbone, which also provide a precise method for reducing NC size in a shape-preserving manner. Our studies further revealed that the Al native oxide layer exhibits unusual support environments and distinct surface chemistry compared to the typical  $\gamma$ -alumina, which could lead to unique metal-support interactions for controlling the nature of exposed metal active sites that were not previously observed in alumina-supported metal catalysts.

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Wed-NW3-01

Electroadhesion of Polyelectrolyte Hydrogels to Animal Tissues: A Simple Way to Reseal Cut or Damaged Tissues Without Sutures

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This work will present studies from our lab on the electrically induced adhesion of hydrogels made from polyelectrolytes to animal tissues. The basic phenomenon involves two non-sticky crosslinked acrylate hydrogels made with either anionic co-monomers (such as sodium acrylate) or cationic co-monomers (such as aminated acrylates). When a rectangular strip of a cationic gel (connected to an anode) is contacted for just a few seconds with a strip of anionic gel (connected to a cathode) under a voltage of ~ 10 V, the two gel strips form a strong adhesive bond. When the polarity of the electrodes is reversed, the phenomenon is reversed, i.e., the gels can be easily detached. While the above phenomenon of 'electro-adhesion' has been reported before for hydrogels, here we demonstrate electroadhesion in a new scenario – between cationic gels and certain animal (bovine) tissues, such as aorta, cornea, lung, cartilage, muscle, tendon and intestine tissues. When a cationic gel is contacted with a piece of tissue and an electric field (DC, 10 V) is applied for 20 s with a specific polarity, the gel becomes strongly adhered to the tissue. The adhesion persists indefinitely after the field is turned off. If the polarity is reversed, the adhesion is eliminated, and the two materials can be separated. Only cationic gels can be electroadhered to tissues, which suggests that the tissues have anionic character. In both cases of gel to gel adhesion and gel to tissue adhesion, an electroadhered gel patch provide a robust seal, allowing fluid to flow right through the lumen of a gel or tissue tube. These studies raise the possibility of using electroadhesion in surgery as either as a primary means of tissue repair or as an adjunct to suture repair. The advantages of this technique are the ability to achieve adhesion on command using an electric field, and moreover the ability to reverse the adhesion in case of an error.

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Wed-NW3-02

Chemically fueled assembly of protein hydrogels driven by a redox cycle

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Cellular transport along microtubules and the formation of the mitotic spindle are a few examples of chemical fuel driven out of equilibrium assembly in the living cells, i.e. dissipative assembly. These out of equilibrium kinetically controlled active structures are in a constant exchange of energy and mass with the environment. So far, a variety of artificial supramolecular assemblies, mainly hydrogels composed of small-molecule hydrogelators, have been developed that can mimic the properties of such biological out-of-equilibrium processes. However, the assembly of protein-based hydrogels has not yet been demonstrated but could exhibit new properties due to higher order biomolecular structure and specific binding interactions. Here we demonstrate assembly of bovine serum albumin (BSA) based transient hydrogels using a redox cycle, which exhibit protein structure dependent formation kinetics. The kinetics of this hydrogel system is controlled by a redox cycle involving fast oxidation of thiol groups to form the hydrogel over ~10 minutes and slow reduction of the disulfide bonds to dissolve the hydrogel over hours. High concentrations of BSA (~100 mg/mL) are dissolved in denaturing buffer where dithiothreitol (DTT, reducing agent) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, oxidizer) are used to form the redox cycle. Unlike small-molecule hydrogelators, we found that the formation/dissolution kinetics and lifetime of the hydrogel were regulated by the concentration and type of the chaotropic salt included, which modifies the concentration of solvent accessible thiol groups on



the BSA. These results indicated the lifetime of the hydrogel increased with increasing H<sub>2</sub>O<sub>2</sub> to free thiol ratio. Light scattering experiments revealed significant fluctuations in the viscosity and/or hydrogel domain size during gel formation and dissolution, suggesting nonhomogeneous reaction kinetics within the hydrogel.

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Wed-NW3-03

Multi-Compartment Capsules (MCCs) with Bacteria and Fungi in Distinct Compartments: A Platform for Studying Cross-Kingdom Signaling

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Recently, our labs have created 'artificial cells' in which subcellular compartments sequester certain components while at the same time enable intercompartmental molecular signaling. Our designs use common biopolymers like alginate and chitosan to create multi-compartment capsules (MCCs). Importantly, their assembly is simple, rapid, and scalable (using oil-free microfluidics). Moreover, they are comprised solely of biological components. MCCs (~ 500 µm in diameter) can be engineered with multiple inner compartments, each with a distinct payload. They are analogous to eukaryotic cells having distinct membrane-covered 'organelles' with separate functions. In the present study, we encapsulate microbial cells from two distinct kingdoms in the inner compartments of MCCs: i.e., *Pseudomonas aeruginosa* (bacteria) and *Candida albicans* (fungi). These two microbial species are often found in mixed infections, including in the lungs of cystic fibrosis patients. Interestingly, *Candida* exhibit a morphological plasticity in which their virulence is tied to their ability to create hyphae and form biofilms. Understanding the signaling events that enable this transition is of great interest; this morphological difference is induced by signaling molecules (specifically, autoinducer 1 or AI-1) secreted by the *Pseudomonas*. In our system, when the fungi and bacteria are cultured together within MCCs, we observe that the fungal cells mostly stay in a 'yeast-like' morphology, i.e., as spheroidal clusters. In contrast, in the absence of the bacteria, the fungi transition into a 'hyphal' form, i.e., into long multicellular filaments, which indicates that the cells are becoming more virulent. Thus, our MCC studies are able to detect cross-kingdom communication between the microbial cells. We anticipate that new fundamental insight will emerge, owing to the (i) simplicity in the assembly of the MCCs and (ii) the microenvironmental contexts by which they can be observed. In a similar manner, MCCs can also be used to probe other cell-cell interactions such as inter-species signaling between bacteria.

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Wed, 16 17:00 - 19:00

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Wed-RW-01

Organic matter is leaching from microplastics: Can they be removed from water by carbon adsorption?

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Microplastics (i.e., plastics fragments <5mm) in the aqueous system are among the many inevitable consequences of plastic pollution, which has cascading environmental and public health impacts. Our study aimed to analyze the 2-way surface interactions i.e., leaching and adsorption of common types of microplastics. First a background database was created for a total of six microplastics: polylactic,

polypropylene, polystyrene, polyethylene, polyethylene colored, and polyethylene recycled. Light (UV aging) and dark (hydrolysis) experiments were conducted to analyze the dissolved organic content (DOC), UV254, and excitation emission (EM) data to determine their leaching kinetics, propensities while unraveling the leaching mechanisms. The light and dark experiments were conducted using 50 grams of each microplastic type with 150 mL of nano pure water. For UV aging, the solution was placed in a quartz beaker in a UV aging chamber with 16, 350 nm UV bulbs for 24 hours of irradiation. The solutions for the dark experiment were placed in amber bottles and shaken in the dark for 1 hour. The results suggested there was a clear trend of organic matter being removed from the surface of the six microplastics with DOC, UV254, and EM data increasing from 1 hour to 24 hours of UV aging. Polystyrene had the largest and fastest increase in DOC concentrations (up to 6.8 mg/L), followed by polypropylene (up to 5.5 mg/L). These microplastics were chosen for adsorption analysis with the third microplastic being polyethylene due to the magnitude of production and environmental relevance. Our ongoing work will reveal the adsorptive removal of PE, PS, and PP leachates (vs. natural organic matter) by three generations of carbon-based adsorbents.

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Wed-RW-02

## Single-Particle Hyperspectral Imaging Reveals Kinetics of Silver Ion Leaching from Alloy Nanoparticles

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Gold-silver alloy nanoparticles have attracted attention for multiple applications, including heterogeneous catalysis, optical sensing, and antimicrobial properties. The inert element gold can act as a stabilizer for silver to prevent particle corrosion to slow down silver ion leaching and increase the durability of plasmonic alloy nanoparticles in sensing or catalytic applications. On the other hand, the intentional release of antimicrobial silver ions has been used to fight infections caused by bacteria. Understanding silver ion leaching from gold-silver alloy nanoparticles is, therefore, a prerequisite to designing alloy nanoparticles with either unintended or intended corrosion. However, little is known about the mechanism and kinetics of silver ion leaching from bimetallic gold-silver nanoparticles and how it is correlated with particle size and silver content, especially not on a single-particle level. To characterize the kinetics of silver ion release from gold-silver alloy nanoparticles, we employed a combination of electron microscopy and single-particle hyperspectral imaging with an acquisition speed fast enough to capture silver ion leaching for a statistically relevant number of individual nanoparticles. Our studies confirmed a reduction in corrosion rate due to the alloying with as little as 10-20 mole% gold. Single-particle leaching profiles revealed two leaching stages, with large heterogeneity in rate constants. We modeled the initial leaching stage with a shrinking-particle model with a rate constant that exponentially depends on the silver mole fraction. The second, slower leaching stage is controlled by the diffusion of silver atoms through a passivating gold-rich lattice and a change in electrochemical potential of the nanoparticle. Most nanoparticles released silver completely, but 25% of them appeared to arrest corrosion. High-resolution STEM-EDX mapping revealed that nanoparticles became slightly porous. Our findings suggest that alloy nanoparticles, produced by scalable laser ablation in liquid, together with kinetic studies of silver ion leaching, provide an approach to selectively design the durability or anti-microbial bioactivity of alloy nanoparticles.

Wed-RW-03

Patterning of thin polymer film from dynamics of contact line; guided by chemically patterned surface

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Due to a huge demand on microelectronics industry, the fabrication of micro-nano structures has become more significant when microelectronics industry began to fabricate the integrated chips using different Lithography techniques. Usually, there are three primary approaches to pattern surfaces like top-down approach, bottom-up approach and self-organization method. Compare to other two, self-organization method is not widespread. Many researchers have focused on this unconventional method to achieve ordered patterns for more than a decade. Many de-wetted micro-nano structures have been reported while casting a polymer solution. Many have reported reproducible ordered patterns also by controlling several factors. De-wetting is a spatio-temporal phenomenon which, shows the rupture of thin liquid film on a solid substrate into liquid droplets. Here, thin films play a significant role in ongoing de-wetting process. This, self-assembled colloidal lithography is very promising technique in order to fabricate micro-nano featured surface. Though, there are several difficulties but, this method is technically better in some areas and much cost-effective than conventional lithography process like photolithography or e-beam lithography. The flexibility of this printing process is remarkable in various fields, like surface modification, creating templates, sensors, data storage devices etc. This type of fabrication method is based on the so-called self-arrange of solute particle from an evaporating solution. A simple drop-cast is quite effective to re-arrange the solute particles to the edge of the contact line by capillary force and to deposit on the surface. This phenomenon is widely known as “coffee-stain” effect. Also, some others fabrication methods like mechanically or chemically induced contact line allows one to control over the deposited pattern to fabricate different ordered patterns of stripe or micro-nano drop of solute particle. Nevertheless being inexpensive, do not need complicated and expensive printing equipment to fabricate ordered patterns, opens a new area to print complex patterns with functional polymers for multifunctional application. Self-assemble, colloidal lithography, dewetting, chemically patterned surface. Acknowledgement: The authors thank DST SERB grant no. ECR/2015/000447, MeitY grant no. 5(9)/2012-NANO and Center for Nanotechnology, IIT Guwahati for financial aids.

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Wed-RW-04

A microneedle-based potentiometric sensing system for continuous monitoring of multiple electrolytes in skin ISF

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Electrolytes play a pivotal role in regulating cardiovascular functions, hydration, and muscle activation. The current standards for monitoring electrolytes involve periodic sampling of blood and measurement using laboratory techniques, which are often uncomfortable/inconvenient to the subjects and add considerable expense to the management of their conditions. The wide range of electrolytes in skin interstitial fluids (ISF) and their correlations with plasma create exciting opportunities for applications such as electrolyte and circadian metabolism monitoring. However, it has been challenging to measure these electrolytes in the skin ISF. In this study, we aim to develop a minimally invasive microneedle-based potentiometric sensor for multiplexed and continuous monitoring of Na<sup>+</sup> and K<sup>+</sup> in the skin ISF. The potentiometric sensor consists of a miniaturized stainless-steel hollow-microneedle to prevent sensor delamination and a set of modified microneedle electrodes for multiplex monitoring. We demonstrate the measurement of Na<sup>+</sup> and K<sup>+</sup> in artificial ISF with a fast response time, excellent reversibility and repeatability, and adequate selectivity. In addition, the sensor maintains the sensitivity after multiple insertions into the chicken skin model. Furthermore, the agarose gel model and chicken skin model experiments demonstrate the sensor's

potential for minimally invasive monitoring of electrolytes in skin ISF. The new sensor platform can be adapted for a wide range of other applications, including in situ analysis of nutrients, metabolites, and proteins.

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Wed-RW-05

## Nanoemulsion-Loaded Capsules for Controlled Delivery of Lipophilic Active Ingredients

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Nanoemulsions have become ideal candidates for loading hydrophobic active ingredients and enhancing their bioavailability in the pharmaceutical, food, and cosmetic industries. However, the lack of versatile carrier platforms for nanoemulsions hinders advanced control over their release behavior. In this work, a method is developed to encapsulate nanoemulsions in alginate capsules for the controlled delivery of lipophilic active ingredients. Functional nanoemulsions loaded with active ingredients and calcium ions are first prepared, followed by encapsulation inside alginate shells. The intrinsically high viscosity of the nanoemulsions ensures the formation of spherical capsules and high encapsulation efficiency during the synthesis. Moreover, a facile approach is developed to measure the nanoemulsion release profile from capsules through UV-Vis measurement without an additional extraction step. A quantitative analysis of the release profiles shows that the capsule systems possess a tunable, delayed-burst release. The encapsulation methodology is generalized to other active ingredients, oil phases, nanodroplet sizes, and chemically crosslinked inner hydrogel cores. Overall, the capsule systems provide promising platforms for various functional nanoemulsion formulations.

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Wed-RW-06

## Preparation of Cu-based Metal-Organic Structures Doped with Ag ion and Their Hydrogen Adsorption Behavior at Low temperature and Ambient Pressure

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From the viewpoint of transportation, materials that safely and efficiently store or adsorb hydrogen are important to realize a hydrogen-based society. However, there are still many problems that have not been overcome in hydrogen storage in metal-containing inorganic materials. For example, hydrogen can embrittle steel, so existing natural gas transport systems may not be suitable for transporting pure hydrogen gas. On the other hand, metal organic frameworks (MOFs), which consist of metal ions and organic ligands, can store a variety of gas molecules due to their high surface area and regular pore structure. This class is particularly lightweight compared to inorganic materials, and Cu-based MOFs (HKUST-1) in particular have been reported to exhibit excellent hydrogen adsorption properties, but have not been fully investigated despite the importance of their functional expression. In this study, we tuned the pore structure of Cu-based metal-organic structures by a simple method of doping with Ag ion and investigated their hydrogen adsorption properties at low temperatures. HKUST-1 prepared from trimesic acid and copper nitrate trihydrate was heated in EtOH containing silver (I) acetate to obtain the doped sample (Ag@HKUST-1), and its detailed structure was investigated. According to the X-ray photoelectron spectroscopy data, the oxidation numbers of Cu and Ag in Ag@HKUST-1 were +2 and +1. Its X-ray diffraction pattern was similar to that of pure HKUST-1, and the Ag doping did not cause any destruction of the crystal structure. Interestingly, Ag doping shifted the diffraction pattern of the (222) plane to the lower angle side, suggesting that the lattice parameter was expanded. The specific surface areas of HKUST-1 and Ag@HKUST-1 obtained by Brunauer–Emmett–Teller analysis of their respective N<sub>2</sub> adsorption isotherms were 1630 and

1925 m<sup>2</sup>/g, respectively. This means that the specific surface area of HKUST-1 was enlarged by the inclusion of Ag ions. The hydrogen adsorption isotherms (77 K) of HKUST-1 and Ag@HKUST-1 are shown in Figure 1. The atmospheric H<sub>2</sub> uptake of HKUST-1 and Ag@HKUST-1 was about 11.6 and 13.7 mmol/g, i.e., the doping of Ag ions increased the uptake value in the HKUST-1, and the H<sub>2</sub> adsorption at 77 K was improved by about 18% with the increase in specific surface area. In this study, we found that the hydrogen adsorption properties of HKUST-1 can be further enhanced by an easy approach to exchange the metal ions.

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Wed-RW-07

## Preparation of Pd-Rh Alloy Nanocatalyst Loading Porous Polymer and Decomposition Characteristics for Organic Dye Molecules

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Water shortage due to population growth is a future problem, and a rapid decomposition method for organic pollutants in factory wastewater is urgently needed, especially in developing countries. Photocatalytic degradation of organic dyes has attracted much attention, but this heterogeneous reaction system requires a light source and is only applicable to a limited number of substrates. Furthermore, when focusing on economically feasible methods, a simple strategy to degrade dye molecules in a highly efficient manner in a flow-reaction system rather than a batch system will become even more important in the future. Here, Pd-Rh alloy nanocatalysts with different composition ratios were prepared on porous coordination polymers (zeolitic imidazolate framework-67) with a high specific surface area that adsorbs dye molecules, to prepare heterogeneous catalysts for dye degradation suitable for flow-reactions. The activities of these heterogeneous catalysts towards azo dyes (methyl orange (MO), methylene blue (MB), congo red (CR)) was evaluated and their degradation characteristics in flow reactions in mixed solutions were investigated. Pd-Rh nanocatalysts loaded ZIF-67 (Pd<sub>x</sub>Rh<sub>1-x</sub>/ZIF-67, x is Pd amount percent) were prepared by dropping the reducing agent NaBH<sub>4</sub> solution into the ZIF-67 dispersion solution with the predetermined amount of Rh precursor reagent and Pd precursor reagent. The X-ray diffraction pattern of Pd<sub>x</sub>Rh<sub>1-x</sub>/ZIF-67 with different metal composition ratios was found to be similar to that of pure water ZIF-67. Also, the Brunauer–Emmett–Teller specific surface area obtained from its N<sub>2</sub> adsorption isotherm was ca 2000 m<sup>2</sup>/g. In other words, these catalysts were found to be almost similar to the specific surface area of pure ZIF-67 (2197 m<sup>2</sup>/g). This means that the metal nanocatalysts can be loaded without any noticeable damage to ZIF-67. The prepared Pd<sub>0.12</sub>Rh<sub>0.88</sub>/ZIF-67 showed catalytic properties for MO, and its TOF value was 7.7 h<sup>-1</sup>. This value was found to be about 2~3 times higher than that of pure Pd/ZIF-67 or Rh/ZIF-67 (Figure 1). Besides, Pd<sub>0.12</sub>Rh<sub>0.88</sub>/ZIF-67 was also effective against MB and CR. Furthermore, to evaluate the catalyst life of Pd<sub>0.12</sub>Rh<sub>0.88</sub>/ZIF-67, MO, MB, and CR mixture solutions were circulated through in a flow-reaction system, and the reaction solutions were measured by UV-Vis spectra every 10 min. The catalyst was an excellent dye decomposition catalyst for 1 hour, decomposing dye molecules with a conversion rate of more than 99 % without characteristic degradation.

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Wed-RW-08

## Use of an NIR-light-responsive W<sub>18</sub>O<sub>49</sub> to improve photocatalytic hydrogen evolution

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Significant progress has been reported in the design of components and structures of NIR reactive photocatalysts over the past few years. Since the NIR region covers a wide wavelength from 700 nm to 2500nm, which accounts for more than half of the solar energy emitted to the earth's surface, it is important to study photocatalysts using materials that are reactive to such NIR. Although  $W_{18}O_{49}$  is NIR reactive material, it hardly produces hydrogen through water splitting due to its positive conduction band compared to  $H_2$  reduction potential. This limitation of  $W_{18}O_{49}$  solved by making heterostructures with  $C_3N_4$ . Herein, we fabricated  $W_{18}O_{49}/C_3N_4$  heterostructures with simple solvothermal method and morphology was confirmed with SEM and TEM. The light absorption ability was evaluated by UV-vis spectroscopy. Single  $W_{18}O_{49}$  and  $W_{18}O_{49}/C_3N_4$  heterostructures exhibit absorption tail in the region of 600 nm to 1200nm. We finally demonstrated that the NIR active  $W_{18}O_{49}/C_3N_4$  has higher photocatalytic activity compared to the single  $W_{18}O_{49}$  and  $C_3N_4$  in water splitting.

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Wed-RW-09

Removal of Copper corrosion products from bronze artworks using PVA-based peelable systems

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In case of metallic objects, cleaning requires a deep knowledge of the alteration processes, especially in case of outdoor monuments, buried or underwater artefacts. The alteration products of Cu-based alloys cause the formation of overlapping structures, characterized by the presence of cuprite (a Cu(I) oxide) at the interface with the metal, and by an external layer of Cu(II) salts. Cuprite represents a protective layer against further corrosion; on the other hand, the presence of Cu(II) salts is usually considered as a symptom of the so called "bronze disease", a particularly dangerous phenomenon induced by the presence of copper oxychlorides (atacamite and paratacamite). For this reason, an adequate cleaning procedure should aim at the complete removal of the corrosion products while preserving the protective cuprite layer. Traditional cleaning procedures usually involve mechanical and/or chemical methods, which are scarcely selective and entail risks for the artefacts. To overcome this limitation, a system able to confine and gradually release a high selective complexing agent must be developed, so as to allow controlled and safe cleaning. Polyvinyl alcohol-based (PVA) hydrogels have proved to be optimal confining matrices for cleaning fluids and, thanks to their viscoelasticity, are able to adapt to modern and contemporary painted surfaces with a 3D texture. However, in the case of embossed surfaces and bas-reliefs with hard-to-reach cavities, commonly found in sculptures and metal artifacts, highly viscous polymer dispersions (HVPDs) of PVA, can be applied as pastes that are easily peeled off the surface with tweezers after solvent evaporation. Here, PVA-based HVPDs were loaded with tetraethylenepentamine (TEPA), whose copper(II) complex has a stability constant four orders of magnitude higher than that of EDTA tetrasodium salt, traditionally used by conservators for cleaning bronze. TEPA promotes alkaline hydrolysis of acetyl groups in PVA, leading to the association of the polymer chains into more ordered structures, reducing significantly the time needed for the formation of films as compared to HVPDs loaded with water. Besides, the solubility of TEPA in most polar solvents allows to upload higher quantities of chelating agent in the HVPD, as opposed to EDTA. The confinement of TEPA inside the PVA matrix allowed the effective and progressive removal of copper corrosion products from a 16th century Italian bronze masterpiece, preserving the natural cuprite patina of the historical bronze, in times drastically shorter than traditional cleaning methods.

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Wed-RW-10

Novel microcleaners for microplastic remediation using biodegradable dendricolloids

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The ever-increasing presence and accumulation of microplastics in the ecosystem has brought a surge of efforts in understanding microplastics' behaviors and their effects on organisms. Unfortunately, current removal methods of these highly undesirable dispersions may be resource-heavy, time-consuming, and cost-prohibitive. More importantly, these methods may not efficiently capture those on the smallest size scale which can have a more detrimental impact. While microplastic collection and separation is a large scientific challenge in itself, we must also consider the difficulties that arise when characterizing and degrading plastics on that size scale. To tackle this, our intercollegiate team proposes a massive microplastic remediation effort by novel microcleaners and microbiome processing which will be accelerated by artificial intelligence. Our group will focus specifically on developing biodegradable active microcleaners with soft dendritic microparticles, or dendricolloids, as a physical method of removing nano- and microplastics from aquatic environments. With their spread-out nanofibrils and large surface area to volume ratio, dendricolloids can physically capture enormous amounts of contaminants from polluted water. When fabricated from biodegradable polymers, they can further reduce the amount of post-processing pollution after waste collection as the dendricolloids themselves can degrade into more natural byproducts than non-biodegradable ones. Here, we investigate the interfacial properties of the dendricolloids to determine capture mechanisms of model microplastics within various conditions. Simultaneously, we will consider methods of rehydrating and dispersing the dendricolloids from a powdered state and environmentally benign propulsion mechanisms. Finally, our microcleaners will be tested with real microplastics samples from marine environments to test their applicability with less-pristine samples.

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Wed-RW-11

Template-assisted assembly of electrospun fibers: effect on collection efficiency

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Electrospinning is a simple method of producing nanostructured fibers [1, 2]. Controlling the spatial arrangement of nanofibers to achieve patterned morphologies has attracted attention for various textile, electronic and biomedical engineering applications [3, 4]. Metal templates such as grid electrode collectors create an “electric field lensing” effect that result in hierarchical self-assembly of the fibers [5, 6]. In this study, we investigate the effect of collector geometry on fiber collection efficiency (mass of fiber collected/mass expected). We systematically varied the grid size from 0.003 inch to 1.5 inches. We found that the patterned collector geometries can facilitate more efficient fiber collection. The efficiency of polyethylene oxide/soy protein isolate fibers collected (mass fiber collected/mass input) was 58% higher for a 0.25 inch square grid collector compared to a sample collected on the traditionally used aluminum foil. Furthermore, analysis using optical and scanning electron microscopy indicated formation of uniform fibers (i.e. no beading). A similar increase in collection efficiency was also observed with polyvinyl alcohol (PVA) and Nylon 6 electrospun fibers. Effect of mesh size on fiber collection area and basis weight (mass/area) will be included. Additionally, effect on the wettability of Nylon 6 fibers electrospun on the grid collector will be discussed and compared to those electrospun on aluminum foil. The results shown here serve as motivation for utilizing collector geometry to increase fiber mass throughput. This outcome can facilitate a more efficient approach towards the one step fabrication of non-construction garments. 1. Yıldız, A., A.A. Kara, and F. Acartürk, Peptide-protein based nanofibers in pharmaceutical and biomedical applications. *International Journal of Biological Macromolecules*, 2020. 148: p. 1084-1097. 2. Xue, J., et al., Electrospinning and Electrospun Nanofibers: Methods, Materials, and Applications. *Chemical Reviews*, 2019. 119(8): p. 5298-5415. 3. Wu, Y., et al., Template-assisted assembly of electrospun fibers. *Polymer*, 2010. 51(14): p. 3244-3248. 4. Pokorny, M., K. Niedoba, and V. Velebny, Transversal electrostatic strength of patterned collector affecting alignment of electrospun nanofibers. *Applied Physics Letters*, 2010. 96(19): p. 193111. 5. Vaquette, C. and J.J. Cooper-White, Increasing electrospun scaffold pore size with tailored collectors for improved cell penetration. *Acta Biomater*, 2011. 7(6): p. 2544-57. 6. Titov, K. and J.-C. Tan, Facile patterning of electrospun polymer fibers enabled by electrostatic lensing interactions. *APL Materials*, 2016. 4(8): p. 086107.

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Wed-RW-12

### Magnetically aligned PDMS beads for 3D printed architectures

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Magnetic interactions can be used to form smart gel systems. We present here a system based on soft micromagnets composed of polydimethylsiloxane (PDMS) beads with internally embedded magnetic nanoparticles (MNPs). The orientation of the internalized magnetic nanoparticles can be controlled via magnetic-field-directed assembly, allowing for the generation of anisotropic, chained nanoparticles in PDMS beads. We are currently using magnetic interaction templating to study and manipulate the magnetic response of our systems. The direct structure templating could potentially improve the precision of rheological measurements by anchoring the gels to 3D printed patterns. Another potential application of such a gel system could be water filtration. We will also report how the control of the capillary forces and magnetic interactions can be used to form new smart multiphasic gel systems. Our multiphasic gel system is composed of PDMS beads with randomly distributed and internally embedded magnetic nanoparticles. The beads are linked by capillary bridges, which are composed of a fatty acid that wets the PDMS beads. We present two types of gels that differ in the location of the magnetic nanoparticles (MNPs). The first magnetically responsive capillary gel, MRCG1, has the MNPs in the PDMS beads and the second one, MRCG2, has the MNPs in the capillary bridges. We will discuss the differences in rheological properties of these gels and will present a comparison of the gels' magnetic properties. We will also discuss their self-repairing properties. Overall, we have constructed and are developing further a rich toolbox of structures and interactions for making novel magneto-responsive gel networks.

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Wed-RW-13

### Measuring the Effect of Cations on Iron Surface Corrosion and Mineral Formation using Atomic Force Microscopy

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Iron interfaces play a significant role in the mineral cycle and in electrochemical processes. The mechanism that links corrosion, surface oxidation, and mineral formation is not fully understood. Corrosion involves both physical changes and redox reactions that occurs on metallic surfaces, which results from charge exchange and mass transfer of material. The three key reactants in corrosion are metallic iron, water, and oxygen, while ions catalyze the reaction. This study investigated the influence of cations from ionic electrolytes on iron surface corrosion and measured its influence on mineral formation. To investigate the role of cations in surface corrosion, atomic force microscopy (AFM) was used to measure surface corrosion as a function of time. Polished iron surfaces were exposed to two electrolyte solutions: magnesium chloride,  $MgCl_2(aq)$  and potassium chloride,  $KCl(aq)$ . *In situ* AFM at the liquid/solid interface and *ex situ* AFM after oxidation from atmospheric oxygen  $O_2(g)$  and carbon dioxide  $CO_2(g)$  was performed to observe physical changes of the surface of iron in real-time. This data is complemented with *ex situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy for chemical analysis at different regions of the surface. Resulting data suggests that mineral nucleation and growth are highly influenced from the cations in the electrolyte and the surface corrosion, which can elucidate mechanisms of environmental processes on earth and planetary surfaces.

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Wed-RW-14



## Inactivation of lung surfactant by phospholipase-catalyzed degradation

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The alveoli of human lungs are lined with a thin liquid film and a monolayer of lung surfactant (LS) at the air interface. LS reduces surface tension and stabilizes the lung against collapse and overdistension, and is thus necessary for respiration. Pulmonary diseases such as acute respiratory distress syndrome (ARDS), the most severe form of acute lung injury, inactivate LS (1). However, the inactivation mechanism remains unknown. The lungs of ARDS patients contain increased levels of a phospholipid-hydrolyzing enzyme (PLA<sub>2</sub>) that hydrolyzes lipids like DPPC into palmitic acid (PA) and lyso-PC (LPC) (2, 3). Since PA co-crystallizes with DPPC to form rigid, elastic domains (4), we hypothesize that PLA<sub>2</sub>-catalyzed degradation establishes a stiff, heterogeneous rheology in the monolayer, which will impair LS function. Here we study the evolution of a DPPC monolayer as it is degraded by PLA<sub>2</sub>. Using interfacial microbutton microrheometry coupled with fluorescence microscopy, we track the stiffness and morphology of the actively degrading monolayer. These results are compared to the stiffness and morphology of mixtures of DPPC and its degradation products, simulating the evolving monolayer composition. References: (1) Notter, R. H.; *Lung Surfactants: Basic Science and Clinical Applications*, 1; Lung Biology in Health and Disease; CRC Press, 2000. (2) Thompson, B. T.; Chambers, R. C.; Liu, K. D. Acute respiratory distress syndrome. *N. Engl. J. Med.* **2017**, *377*, 562-572. (3) Nakos, G.; Kitsioulis, E. I., Tsangaris, I.; Lekka, M. E. Bronchoalveolar lavage fluid characteristics of early intermediate and late phases of ARDS. *Intensive Care Med.* **1998**, *24*, 296-303. (4) Ding, J.; Warriner, H. E.; Zasadzinski, J. A. Viscosity of Two-Dimensional Suspensions. *Phys. Rev. Lett.* **2002**, *88*, 168102.

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Wed-RW-15

## Light Emission from Plasmonic Nanostructures

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The mechanism of light emission from metallic nanoparticles has been a subject of debate in recent years. Photoluminescence and electronic Raman scattering mechanisms have both been proposed to explain the observed emission from plasmonic nanostructures. Recent results from Stokes and anti-Stokes emission spectroscopy of single gold nanorods using continuous wave laser excitation carried out in our lab are show that varying excitation wavelength and power change the energy distribution of hot carriers and impact the emission spectral lineshape. We then examine the role of interband and intraband transitions in the emission lineshape by varying the particle size. We establish a relationship between the single particle emission quantum yield and its corresponding plasmonic resonance quality factor, which we also tune through nanorod crystallinity. Finally, based on anti-Stokes emission we extract electron temperatures that further suggest a hot carrier based mechanism. The central role of hot carriers in our systematic study on gold nanorods as a model system supports a Purcell effect enhanced hot carrier photoluminescence mechanism. These results provide vital insight into understanding the light emission mechanism and have an impact on fields utilizing hot carrier distributions such as photocatalysis and nanothermometry.

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Wed-RW-16

## Evanescent Wave Trochoidal Polarization Sensitivity is Modulated by Nanoparticle Symmetry

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Matter's sensitivity to light polarizations is classically characterized by linear and circular polarization effects, corresponding to the system's anisotropy and handedness, respectively. While polarized light-matter interactions are well understood on the macroscale, the polarization properties of light confined to nanoscale dimensions significantly diverge from their freely propagating counterparts. Polarized evanescent waves can support cycloid-like trochoidal field motion, generated by transverse oscillations that are out-of-phase with longitudinal oscillations, which are absent from free-space light. We have recently observed that trochoidal waves with opposite rotational directions preferentially excite hybridized plasmon modes in gold nanoparticle dimers. However, the symmetry properties responsible for this effect, named trochoidal dichroism, have not been investigated. Here, we lithographically fabricate nanoparticle assemblies with varying symmetry to uncover the geometric parameters driving sensitivity to trochoidal polarizations. We find that while symmetric structures, such as single nanorods, do not exhibit trochoidal dichroism, asymmetric nanoparticle arrangements facilitating a planar rotation of dipole orientations, with one or fewer planes of mirror symmetry, are trochoidal-active. In particular, fan-shaped nanorod assemblies tracing out the arch of the trochoidal field exhibit polarization-selective promotion of their bonding and antibonding hybridized plasmons. Further, we find that systems with high rotational symmetry exhibit signatures of trochoidal dichroism that are relatively invariant with respect to the light propagation direction. By characterizing trochoidal dichroism as a function of nanoparticle symmetry, we gain a deeper understanding of efficient nanoantenna design principles and molecular geometries that can be probed using this novel light-matter interaction.

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Wed-RW-17

## Plasmon Energy Transfer in AuNR-Polymeric Hybrid Nanoantennas

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Plasmonic nanomaterials have absorption cross-sections exceeding other classes of materials but dephase quickly into their dielectric environment. Harnessing the increased reactivity offered from plasmonically induced light absorption, scattering, and hot electron generation in parallel is challenging. To date, the competing processes found in plasmonic systems has limited large-scale applications. To understand plasmonic enhancement and increase photoconversion quantum yields, new composite materials and a deeper understanding of plasmonic energy conversion are needed. The work here seeks to understand the dominating transfer pathways in single particle plasmonic-polymeric hybrid systems. Single particle spectroelectrochemistry was used to characterize the energy transfer efficiencies of the hybrid structures by recording the surface plasmon resonance linewidth change during in situ polymerization. Non-radiative energy transfer efficiencies up to 50% are achieved for plasmonic-polymeric nano-antenna reactors. The understanding of interfacial transfer pathways between plasmonic-polymeric materials will lead to increased control and tunability in future design of hybrid nanomaterials.

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Wed-RW-18

## Machine-Learned Decision Trees for Predicting Gold Nanorod Dimensions from Spectra Alone

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Measuring the size of a single plasmonic nanoparticle is a critical step in correlating structure to optical properties but is often difficult to perform especially under irreversible conditions or non-immobilized nanostructures. Here, we demonstrate that gold nanorod dimensions can be accurately predicted over a wide range of aspect ratios using a simple machine learning model, decision tree. The model is trained using ~400 nanorod geometries and their corresponding scattering spectra obtained from finite-difference time-domain (FDTD) simulations. When validated on simulated FDTD spectra, 90 % of all predicted AuNR dimensions are within 10% relative error of the ground truth. Our results are tested using experimental spectra correlated with scanning electron microscopy images to obtain the sizes, estimating small and large nanorods dimensions with 8.5% relative error. Analysis of the decision tree structure reveals that a simple correlation with spectral peak position and linewidth of the localized surface plasmon resonance is adequate to predict nanorod dimensions, outperforming more complicated models. Our findings illustrate the advantages of using simple machine learning models to analyze single particle structural features from their optical spectra.

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Wed-RW-19

Enhanced optical asymmetry in supramolecular chiroplasmonic assemblies with long-range order

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Chiral assemblies of plasmonic nanoparticles are known for strong circular dichroism but not for high optical asymmetry g-factors, which differentiates them from liquid crystals (LCs) with a high g-factors between 0.01 and 1. The low g-factors of chiroplasmonic assemblies ( $10^{-4} < g < 10^{-2}$ ) are attributed to strong extinction and unfavorable combination of electrical and magnetic field components in hot spots between them. While such attribution is consistent with high g-factors observed for singular nanoparticles ( $5 \cdot 10^{-2} < g < 0.2$ ), it may also be associated with insufficient long-range order. In this presentation, we will show that these limitations can be overcome by the long-range organization of nanoparticles in a manner similar to the liquid crystals and found in helical assemblies of gold nanorods with human islet amyloid polypeptides. A strong, polarization-dependent spectral shift and the reduced scattering of energy states with antiparallel orientation of dipoles activated in assembled helices and increased optical asymmetry g-factors by a factor of more than 4600. The liquid crystal-like color variations and the nanorod-accelerated fibrillation enable drug screening in complex biological media. Improvement of long-range order can also provide structural guidance for the design of materials with high optical asymmetry.

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Wed-RW-20

Functional High Order Localized Surface Plasmon Modes in Au-Si-Au Nanodisk Stacking

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Conventionally, breaking the symmetry or arrangement of a system composed of subwavelength particles allows for the formation and control of higher-order localized surface plasmon (LSP) modes. An alternative approach to this morphological change is the use of active optical tuning via photo-induced semiconductor doping, which provides a mean to control higher-order LSP modes in symmetrical nanostructures [1]. Here, we used full-wave electromagnetic computational methods (finite-difference time-domain – FDTD) to investigate the excitation of higher-order LSP modes in a multilayer architecture composed of a stacking

of metallic and semiconducting nanodisks. We investigate the evolution of the high order LSP modes as a function of doping level in the semiconductor (Si) layer, sandwiched between two metallic (Au) disks. We demonstrate that higher-order modes can be efficiently excited by changing the thickness of the intermediate silicon-layer and then further controlled by optically doping of the Si layer. To accurately perceive the physics of the proposed hybrid nanoscale system, it is important to consider the nature and origin of the hybrid modes that result from the hybridization of the nanodisk primitive LSP modes. This allowed us to substantially improve the functionality of the nanodisk stacking structure as a practical platform to be employed in the integrated and coming generation ultradense nanophotonics circuits.

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Wed-RW-21

Probing incident light polarization dependent photothermal heating in plasmonic nanostructures via electronic Raman thermometry

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The Inverse faraday effect (IFE) is an optomagnetic phenomena in which circularly polarized electromagnetic excitation on a plasmonic nanostructure induces a static magnetic moment in the material. Circular drift current plays a key role during the IFE process. We aim to study the change in the photothermal properties of the plasmonic Au nanodisk array under circularly polarized laser excitation, possibly due to the presence of circular current, by utilizing electronic Raman thermometry technique. In this work, we observe that the temperature significantly increases under circularly polarized excitation compared to linearly polarized excitation with the same intensity. The temperature further increases when an external magnetic field parallel to the induced magnetic moment is applied. We suggest that the coherent motion of the electrons under circularly polarized excitation decreases the plasmon damping, and results in a better concentration of electric field inside the nanostructure, although the overall absorption cross-section decreases, and therefore leads to a higher photothermalization rate. This mechanism is supported by measuring the back-scattering of the nanostructure from the laser beam, as well as full wave simulations results. Our study helps understand the relationship between different intrinsic properties of plasmonic system and provides the evidence of possibly controlling the properties by changing the polarization state of the incident light.

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Wed-RW-22

Analyzing Plasmon Mediated Reactions through Raman Thermometry

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Hot electrons produced from plasmonic nanostructures have been used to facilitate photochemical reactions. However, because current methods for measuring hot electron temperature do not simultaneously consider the lattice temperature, some argue that the increasing lattice temperature is predominantly responsible for the procession of these reactions. Therefore, our lab has developed a two-temperature model which differentiates between the hot electron and lattice temperatures. This model can simultaneously measure their temperatures by use of continuous wave Raman Spectroscopy, and therefore identify correlations between the hot electron temperature and the rate of these reactions. This is important because we can now determine the role of hot electron temperature versus the role of lattice temperature within the same reaction. In addition, plasmon dephasing contributions can also be modelled to discern the broad background of the metal substrate from other signals such as vibrational peaks. The reaction I will present is the reduction of atmospheric carbon dioxide to amorphous carbon through hot electrons generated by lithographically prepared plasmonic substrates. Previously, it was believed that the

appearance of amorphous carbon in SERS and TERS experiments was the result of potential sample degradation or contamination. However, using our model and various flow-through experiments, I am able to demonstrate the link between the appearance of amorphous carbon to the hot electron temperature and the atmospheric composition. Moving forward, we intend to implement this link in other photochemical reactions as well.