96th ACS Colloid and Surface Science Symposium

List of Abstracts

Colorado School of Mines, Golden, Colorado, 10-13 July 2022

Monday, July 11th | 08:00 - 09:00 | Z1-Plenary Lecture 1

Mon-Z1-01

The Robotics Part of Micro and Nano Robots

Brad Nelson

ETH Zürich, Switzerland

The Robotics Part of Micro and Nano Robots Micro and nano robots have made great strides since becoming a focused research topic over two decades ago. Much of the progress has been in material selection, processing, and fabrication, and paths forward in developing clinically relevant biocompatible and biodegradable micro and nano robots are becoming clear. Our group, as well as others, maintain that using biocompatible magnetic composites with externally generated magnetic fields and field gradients is perhaps closest to clinical application. One of the most challenging aspects of the field is in the development of the magnetic navigation system (MNS) that generates the fields and field gradients needed for microrobot locomotion. In this talk, I will present an overview of MNSs and show how these systems are fundamentally robotic in the way they must be designed and controlled. Decades of work in robotic manipulation can be brought to bear on this problem as we move forward in bringing MNS technology to the clinic. I will also look at recent efforts in creating more intelligent micro and nano robots that exhibit increasingly complex behaviors, some of which can even be programmed in situ. The field appears to be on the cusp of realizing the fantastic voyage.

Monday, July 11th | 09:30 - 11:30 | A1-Active Matter

Mon-A1-01

The Mechanics of Active Matter

John Brady

Chemical Engineering California Institute of Technology

A distinguishing feature of many living systems is their ability to move – to be active. Through their motion living systems are able self-assemble: birds flock, fish school, bacteria swarm, etc. But such behavior is not limited to living systems. Recent advances in colloid chemistry have led to the development of synthetic, nonliving particles that are able to undergo autonomous motion by converting chemical energy into mechanical motion and work. This intrinsic activity imparts new behaviors to active matter that distinguish it from equilibrium systems. Active matter generates its own internal stress, which can drive it far from equilibrium, and by so doing active matter can control and direct its own behavior and that of its surroundings. In this talk I will discuss our work on active matter and on a new source of stress – the swim pressure – that is responsible for self-assembly and pattern formation in active matter systems. The role of confinement and flow on active systems will be discussed.

Mon-A1-02

Guiding Self-Assembly of Active Colloids by Temporal Modulation of Activity

Bo Zhang, Alexey Snezhko, Andrey Sokolov

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Self-organization phenomena in ensembles of self-propelled particles open pathways to the synthesis of new dynamic states not accessible by traditional equilibrium processes. The challenge is to develop a set of principles that facilitate the control and manipulation of emergent active states. Here, we report that dielectric rolling colloids energized by a pulsating electric field self-organize into alternating square lattices with a lattice constant controlled by the parameters of the field. We combine experiments and simulations to examine spatiotemporal properties of the emergent collective patterns and investigate the underlying dynamics of the self-organization.We reveal the resistance of the dynamic lattices to compression and expansion stresses leading to a hysteretic behavior of the lattice constant. The general mechanism of pattern synthesis and control in active ensembles via temporal modulation of activity can be applied to other active colloidal systems.

Mon-A1-03

Helical propulsion of patchy ellipsoids by induced-charge electrophoresis

Ahmed Al Harraq, Jin Lee, Bhuvnesh Bharti

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

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 alternating current (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 high-frequency AC electric field, ellipsoids dispersed in water 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, namely longitudinal and transverse. Our study reveals the role of patch shape on the trajectory of ellipsoidal particles propelled by induced charge electrophoresis. We develop heuristics based on patch asymmetries that can be used to design patchy particles with specified nonlinear trajectories.

Mon-A1-04

Autonomous colloidal crystals enabled by coupling electrokinetic flows to electrochemical reaction intermediates

Medha Rath [1], Eric Carmona [2], Sarangua Battumur [2], John Cumings [3], Paul Albertus [2], Taylor Woehl [2]

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Conventional external stimuli used for directed colloid assembly, such as electric or magnetic fields, produce a singular response at a given field condition and must be actively adjusted to effect a change in the colloid behavior. Conversely, biological systems execute complex, multistep processes in response to a single environmental stimulus by using complex reaction networks. Here we report assemblies of colloids that surpass the limitation of one response per applied stimulus and autonomously undergo multistep assembly and disassembly sequences in response to a single electrical signal. Application of an alternating current (AC) potential superimposed on an electrochemical potential to a solution of dielectric colloids containing the electroactive molecule para-benzoquinone formed transient colloidal crystals that disassembled after a few seconds and then autonomously assembled after tens of seconds. Disassembly of the colloidal crystals was temporally correlated with a transient pH spike several seconds after applying the electrical stimulus, which decayed over the time scale of particle assembly. Experiments and simulations showed the autonomous motion of the colloids was coupled to reaction intermediates formed by the electroreduction of parabenzoquinone, namely the quinone dianion, which is rapidly protonated and transiently increases the local pH near the colloids. A scaling analysis showed that the colloid behavior was consistent with competition between a time-invariant, attractive electrohydrodynamic (EHD) flow and a repulsive, transient electroosmotic flows (EOF) induced by a pH-dependent rectified DC electric field.

Mon-A1-05

Control of phoretic self-propulsion through particle geometry: Slender-body analysis for an asymmetric bent rod

Arkava Ganguly, Ankur Gupta

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Synthetic microswimmers have a wide range of applications such as non-invasive medicine, targeted drug delivery, and lab-on-chip devices. Over the last two decades, theoretical research has focused on predicting the motion of microswimmers, which are generally assumed to be spheroidal or cylindrical. The motion of these microswimmers is driven due to an asymmetry in the activity on the particle surface. However, in recent years, there has been an increasing interest in understanding the impact of geometric asymmetry of particles, and if the geometric design of the particle can provide an additional degree of freedom to tune the particle trajectory. A standard boundary element method could be used to resolve particle trajectories but soon become computationally expensive for particles with extremely high aspect ratios like active needles or filaments. Some asymptotic theories have been developed to describe the motion of slender phoretic rods. However, they are inadequate in describing the motion of bent particles with no axial symmetry. To this end, we theoretically investigate the motion of an active bent rod under the slender-body limit. Specifically, we vary the angle between the two rods, relative arm lengths, and the activity along the surface of the particle, and evaluate particle trajectories under different geometric and surface activity conditions. We find that under specific geometric and surface patterning conditions, particles move along a circular trajectory, which is in qualitative agreement with previous experimental data. Using particle trajectories, we evaluate the relative contribution of the geometric asymmetry in driving such active particles which would enable us to fine-tune the design of these active particles for specific use cases.

Monday, July 11th | 09:30 - 11:30 | C1-Colloids, Macromolecules, and Surfaces in Life Science

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Mon-C1-01

Bioelectronic building blocks -- micelles, pores, and granules

Bozhi Tian

Chemistry department, the University of Chicago

With the development of bioelectronic devices, personalized medicine and brain-machine interfaces are now possible. There has been significant progress in this area; however, there is still room for improvement in the chemical designs to improve the functionalities at the interfaces with cells and tissues. Specifically, biomimetic design principles enable the development of new devices that are more efficient at signal transduction and more biocompatible. During this presentation, I will give an overview of a few recent developments in our laboratory where we have identified new material building blocks for bioelectronics applications. I will discuss a micelle-enabled self-assembly process to prepare carbon-based and flexible micro-supercapacitor-like systems for applications in bioelectronic interfaces. The devices can conduct either a micro-supercapacitor-like operation or a conventional monopolar configuration under physiological conditions, resulting in modulation of cardiomyocytes in vitro, excitation of isolated heart and retinal tissues ex vivo, stimulation of the sciatic nerve in vivo, as well as bioelectronic cardiac recording. Furthermore, I will present a recently developed nanoporous/non-porous heterojunction for improved biointerfaces. By eliminating any interconnections or metal modifications, the heterojunction enables efficient non-genetic pulse stimulation of isolated rat hearts ex vivo and sciatic nerves in vivo, using radiant light exposure similar to that used in optogenetics. Finally, I will describe a class of granules-enabled hydrogel composites, based on several naturally occurring polymers and synthetic hydrogels. The composites possess many tissue-like properties, such as strain-strengthening properties. By enabling tissue-like materials with granules, pneumatically actuated bioelectronic devices, such as those used to record ex vivo heart electrocardiogram signals, can be developed. I will conclude my presentation by discussing future material developments in our laboratory.

Mon-C1-02

Imaging Disease with Colloids

Jesse Jokerst

UC San Diego

This presentation will describe my lab's work to improve medicine with colloids. In the first example, I will describe an activable gold/silver hybrid that responds the upregulated reactive oxygen species during infection: The particle produces a photoacoustic signal indicating infection and releases therapeutic silver ions. In the second example, I will discuss colorimetric sensing of the 3Cl protease critical to the viral life cycle of SARS viruses. Both examples will include physical characterization of the colloids and validation in animal models or human subjects.

Mon-C1-03

Covalently attached slippery surface coatings to reduce protein absorptions in bioelectronics

Yi Zhang, Yue Cao

Department of Biomedical Engineering and the institute of Material Science, University of Connecticut

Covalently attached slippery surface coatings to reduce protein adsorptions in bioelectronics

Yue Cao, Yi Zhang Department of Biomedical Engineering and the Institute of Materials Science, University of Connecticut, Storrs, CT 06269, USA. Abstract Bioelectronic interfaces have a wide range of applications in basic biomedical research and clinical medicine. The direct contact of electronic systems with the biological tissues enables the continuous monitoring and/or modulation of various physiological parameters. Nonetheless, the adsorption of various proteins in the biological environment represents a significant challenge for any implantable bioelectronics. Here, we present a covalently attached slippery surface coating to reduce protein adsorptions in bioelectronics. As a demonstration, we show that the adsorption of pro-inflammatory serum proteins, fibrinogen and albumin, can be significantly reduced by the slippery surface coatings. The preparation of slippery surface coatings relies on low-cost and simple preparation procedures. The whole process takes only a few minutes at room temperature. It also uses simple and scalable dip-coating methods. The low-cost operation and scalability enable the potential distribution to broad bioelectronics communities.

Mon-C1-04

Particle Surface Engineering for Structural Control in Injectable Polyethylene Glycol Granular Hydrogel Cell Scaffolds

Jing Liu, John Oakey

University of Wyoming

Injectable granular hydrogels have become intensely pursued for numerous biomedical applications, for example, as platforms for drug delivery and cell culture, scaffolds for accelerating tissue regeneration, and wound healing, due to their multifunctional properties, including injectability, heterogeneity, and controlled porosity. Granular hydrogels are comprised of micrometer-sized hydrogel particles (microgels), in this case monodisperse PEGDA hydrogel particles that are fabricated by using PDMS flow-focusing microfluidic device. However, PEG hydrogels alone cannot support cell adhesion because of their biologically inert nature. Therefore, the surfaces of PEGDA hydrogel particles were functionalized with an extracellular matrix protein, fibronectin via coupling to a network-anchored linker (Acrylate-PEG-Biotin) to promote cell adhesion and proliferation. Acrylate-based hydrogel photopolymerization in oxygen permeable PDMS microfluidic devices is subject to oxygen-inhibition, which dramatically affects acrylate conversion and therefore the physical and chemical properties of hydrogel microparticle interfaces. We demonstrate how photopolymerization parameters quantitatively define cell adhesion ligand density at hydrogel interfaces and thus cell adhesion behavior. We show that hydrogel particles formed with lower polymer mass fraction must be polymerized under higher UV intensity and particles with higher mass fraction need to be polymerized under lower UV intensity in order to promote cell adhesion and proliferation on these particles. These results support the hypothesis that the effective extent of hydrogel functionalization is dictated by a competition between linker incorporation into the network and cell adhesion ligand availability due to network density. Accordingly, macromer mass fraction must be matched to appropriate photopolymerization conditions in order to obtain a desirable linker density and the adhesion ligand density. Using this approach, adhesive ligand density can be decoupled from the hydrogel mass fraction in a quantifiable and predictive manner. To demonstrate the importance of this, granular gels with different mass fractions were assembled by gravitational settling, with low mass fraction granular gels possessing higher void fraction and cell proliferation while the gels with higher mass fraction showing lower void space fraction and cell proliferation. These findings illustrate how PEG hydrogel surfaces can be engineered to promote cell adhesion and proliferation and provide guidelines for designing complex PEG microgels and granular hydrogel cell scaffolds.

Mon-C1-05

Tailoring Nanoparticle Surface Chemistry for Chemically Selective Plasmonic Nanogaps

Chloe Groome, Regina Ragan

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Surface enhanced Raman scattering (SERS) is a promising label-free method for measuring ultra-low concentrations of analytes, offering single molecule limits of detection (LOD) when using carefully designed nanoarchitectures. Yet when approaching this LOD, SERS sensors typically lack signal reproducibility, limiting device applications such as biosensors. We have shown that chemically cross linking gold nanoparticles using electro-osmotic driving forces results in controlled 1 nm gaps that provide uniform enhancement factors of 10^9 over mm^2 areas, enabling single molecule detection limits. By combining SERS with machine learning, we have demonstrated the ability to detect trace concentrations of analytes necessary for applications such as rapid point-of-care medical diagnostic testing and environmental monitoring. Susceptibility of *Escherichia coli* and *Pseudomonas aeruginosa* to antibiotics was determined orders of magnitude faster than standard PCR tests with greater than 99% accuracy. While SERS with machine learning has successfully reached extremely low LOD for single analytes and been able to distinguish broad metabolic behavior of individual bacterial strains in far faster time frames than culturing, there are still challenges to overcome for biological samples. Many biomolecules yield overlapping Raman spectral features due to their structural and chemical complexity. In order to further expand capabilities to biological mixtures, extending nanogap chemistry will optimize chemical affinity with analytes of interest for multiplexing. I will show that by functionalizing gold nanoparticles with different ligands, gap chemistry can be designed to preferentially interact with select chemical groups. Nanogap chemistry is characterized via photo-induced force microscopy and the resulting force spectra is compared with density functional theory simulations of infrared spectra. These findings will inform the design of future integrated biosensing devices capable of multiplexed sensing of realistic biological samples.

Monday, July 11th | 09:30 - 11:30 | D1-Self and Directed Assembly

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Mon-D1-01

Electrostatic self-assembly of nanoparticles into static and out-of-equilibrium materials

Rafal Klajn

Weizmann Institute of Science

Self-assembly of inorganic nanoparticles into ordered structures (superlattices) has led to a wide range of nanomaterials with unique optical, magnetic, electronic, and catalytic properties. Various interactions have been employed to direct the crystallization of NPs, including van der Waals forces, hydrogen bonding, as well as electric and magnetic dipolar interactions. Among them, Coulombic interactions have remained largely underexplored, owing to the rapid charge exchange between nanoparticles bearing high densities of opposite charges (superionic nanoparticles). In this talk, I will describe a new method to assemble superionic nanoparticles under conditions (room temperature, concentrated salt solutions) that preserves their native surface charge density. Under these conditions, the Coulombic interactions between superionic nanoparticles are reminiscent of short-range intermolecular interactions. Our methodology was used to assemble oppositely charged NPs into high-quality superlattices exhibiting Catalan shapes. This methodology can be applied to a wide range of charged nanoparticles of various sizes, shapes, and compositions. I will also discuss how electrostatic interactions can be used to assemble nanoparticles into transient assemblies, whose lifetime depends on and can be controlled by the availability of a small-molecule ionic “fuel”.

Mon-D1-02

Chiral Assemblies of Pinwheel Superlattices on Substrates

Jiahui Li [1], Shan Zhou [1, 2], Jun Lu [3, 4], Haihua Liu [5], Ahyoung Kim [1], Lehan Yao [1], Nicholas Kotov [3, 4], Qian Chen [1, 2]

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Achieving self-assembly of chiral superlattices from nanoparticles has been a holy grail for metamaterials due to their unique properties. Here by utilizing highly uniform gold nanoparticles and harnessing the interparticle interactions, we demonstrate a new type of largescale and extended chiroptically active pinwheel superlattices due to phase transition from open lattices. The pinwheel lattices on substrate display optical asymmetry confirmed by electron microscopy and finite-difference time-domain simulation. Liquid-phase transmission electron microscopy and interparticle interaction calculation show that by controlling the interactions between nanoparticles, fine-tuning of pinwheel structures and versatile superstructures can be realized, which facilitates manufacturing metamaterials with unique optical and mechanical properties.

Mon-D1-03

1D and 2D Nanoparticle Assembly via Hybrid Manufacturing

Kenan Song

Engineering, Arizona State University

Nanoparticle preferential alignment and oriented structures improve functional and structural properties in composites compared to those with random counterparts. Traditionally used techniques such as drop-casting, chemically modified surfaces, and external fields have been used for nanoparticle self-assembly, but it has several disadvantages, including low scalability and slow assembly rates. Thus, there is a need to develop a new approach for generating hierarchical nanoparticle structures. This research combines advanced 3D printing and conventional nanoparticle processing methods to induce nanoparticles assembly for layer-by-layer deposition of 1D and 2D nanoparticles. These 1D and 2D nanoparticles were deposited onto the 3D printed substrate with well-controlled surface topologies (e.g., microchannels) via colloidal deposition techniques. The nanoparticles confined by microchannels experienced microfluidic forces (e.g., capillarity, secondary bonding, van der Waals), which led to site-specific deposition and preferential alignment of nanoparticles. These fabricated polymer/nanoparticle composites showed different deposition morphologies and dimensions, such as straight, wavy, and randomly oriented textures or bands. Furthermore, the influences of nanoparticle deposition morphology on mechanical and functional properties were investigated. Our novel protocal in using conventional/new manufacturing shows the potential to scale up microelectronics production by the additive manufacturing of electronic structures (e.g., interdigitated devices, FET, and circuits).

Mon-D1-04

Dynamics of protein nanorods at solid-liquid interfaces

Shuai Zhang

Materials Science and Engineering, University of WashingtonPhysical Sciences Division, Pacific Northwest National Laboratory

Inspired by nature, various approaches have been developed in the last few decades for building novel supramolecular nanomaterials, using proteins as versatile building blocks assembled into hierarchical structures. However, creating 2D protein architectures at solid-liquid interfaces in a pre-designed manner is still highly challenging. Both the dynamics and final organization of proteins at solid-liquid interfaces are determined by the energy landscape arising from the interplay between protein-protein and protein-surface interactions. Yet how that energy landscape responds to solution conditions and environmental stimuli remains unclear. To explore this mystery, in-situ characterization with high temporal and spatial resolution, combined with statistical analysis, is required. In this presentation, we will discuss the recent work of recording the in-plain dynamics of the protein nanorods, complementarily matching muscovite mica (001) surface, as a function of cation type and nanorod length by high-speed atomic force microscopy (HS-AFM). After statistically analyzing the data using an adapted deep learning approach, extract the free energy as a function of orientation and quantify the transition probabilities between distinct orientational states for a range of nanorod lengths and electrolytes. In addition, the comparison with kinetic Monte Carlo simulations shows the bimodal rotational dynamics of the protein nanorods. Transitions between minima occur through two distinct mechanisms: 1) simple in-plane Brownian motion between adjacent minima with rates exponential in barrier height, and 2) high-energy transitions, analogous to Levy-flights, between more distant minima with rates unrelated to the barrier height. In addition, we in-situ visualize the formation of protein-nanorod liquid crystals and describe the phase transitions between condensed liquid, orientationally disordered phase, and nematic phase, manipulated by balancing protein-substrate interaction protein-protein interaction, and entropic interaction.

Reference: 1 S. Zhang, et al., Proc. Natl. Acad. Sci, in press 2 J.L. Prelesnik, et al., Proc. Natl. Acad. Sci, 2021 3 S. Kalinin, et al., ACS NANO 2021 4 M. Ziatdinov, et al., NANO Letters 2021 5 H. Pyles, et al., Nature 2019

Mon-D1-05

Visualizing Dynamics of Polymerization Induced Assembly of Nanoparticles into Turing Patterns

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Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD, USA

Patterning of nanoparticles onto solid surfaces has a wide range of applications, such as quantum dot-based microelectronics to plasmonic nanoparticle biological sensors. Surface patterns are conventionally constructed by assembling nanoparticles onto topographical or chemical surface templates formed by lithography. Here we demonstrate and visualize formation dynamics of nanoparticle surface patterns, including cellular, striped, and labyrinth patterns, via simultaneous radical polymerization and chain scission of nanoscale polymer films coated with random initial arrangements of gold nanoparticles. Nanometers thick oligomeric aminosiloxane layers were grafted onto silicon nitride membranes and gold nanoparticles were covalently attached to the surface using amide coupling chemistry. The samples were imaged with liquid phase transmission electron microscopy (TEM) in the presence of a carbodiimide coupling agent in DI water and in situ movies were acquired over 5-10 minutes. The TEM electron beam caused surface diffusion of unbound oligosiloxanes and generated hydroxyl radicals that induced their polymerization and chain scission. Interestingly, polymerization initially occurred preferentially near regions containing more nanoparticles, but after several minutes polymer formation was hindered near larger nanoparticle assemblies leading to stable nanopattern formation. Depending on the electron beam intensity and imaging magnification, the nanoparticles and underlying polymer arranged into diverse nanopatterns resembling Turing patterns observed in nature, e.g., stripe patterns on Zebra and cellular patterns observed on fish. We propose a mechanism based on reaction-diffusion instability involving a positive feedback loop in the radical polymerization reaction due to the presence of gold nanoparticles, which act as radical generating hotspots. Systematic experiments and numerical reaction-diffusion simulations are presented to support the proposed mechanism.

Monday, July 11th | 09:30 - 11:50 | E1-Electrokinetics and Microfluidics

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Mon-E1-01

Microfluidics-generated Microgels for the Assembly of Biomedical Granular Hydrogels

Jason A. Burdick

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Hydrogels represent a class of biomaterials that have great promise for the repair of tissues, particularly due to our ability to engineer their biophysical and biochemical properties. Hydrogels can provide instructive signals through material properties alone (e.g., mechanics, degradation, structure) or through the delivery of therapeutics that can influence tissue morphogenesis and repair. In recent years, we have transitioned from traditional hydrogels to granular hydrogels that are comprised of smaller hydrogel units (i.e., microgels). Microgels can be readily fabricated through microfluidics, with variations in microgel size, shape, and throughput based on device design. Granular hydrogels are formed through the packing of microgels and can be designed to be injectable through shear-thinning behavior, heterogeneous through microgel mixing, and porous to support cell invasion. Here, I will give examples of the design and use of granular hydrogels based on hyaluronic acid for use as injectable therapeutics for endogenous tissue repair or in 3D printing to fabricate hydrogel constructs. For cardiac therapeutics, we injected heterogeneous granular hydrogels into the myocardium and showed selective microgel degradation to release factors and introduce porosity for cellular ingrowth. In 3D printing, we jammed microgels to form shear-thinning and self-healing hydrogels that could be printed either onto surfaces or within other hydrogels. These could be cell-laden or stabilized where necessary with secondary crosslinking. Additionally, we designed conductive granular hydrogels, through an in situ metal reduction process of silver onto microgels that resulted in high conductivity due to increased surface area when compared to traditional hydrogels. Most recently, we have developed anisotropic microgels and showed increased cellular invasion into formed granular hydrogels based on pore structure. Overall, the design of granular hydrogels opens up new opportunities in the design of functional hydrogels for biomedical applications.

Mon-E1-02

Gelation-controlled, fibrinogen solutions for continuous microfluidic droplet production

Alan Stenquist

University of Wyoming

Gelation-controlled, fibrinogen solutions for continuous microfluidic droplet production Alan Stenquist, John Oakey Department of Chemical Engineering, University of Wyoming, Laramie, WY, 82071, USA Cell-based therapies involving the co-delivery of cells and surrogate extracellular matrix scaffolds to damaged tissue hold tremendous promise as a regenerative medicine modality. Despite tremendous progress in cell-biomaterial delivery strategies, significant challenges remain in preventing acute cell death and promoting normal cell behavior post transplantation. Fibrin, the provisional protein matrix that forms rapidly at the site of injury, has evolved intrinsic properties that promote cell adhesion, migration, proliferation, and angiogenesis. Fibrin is formed when plasma soluble macromer fibrinogen is polymerized by the catalyzing enzyme thrombin to maintain hemostasis. Despite fibrin's extensive characterization and attractive properties for use in regenerative medicine, its rapid gelation presents a significant obstacle to miniaturization and control of material properties on cellular length scales. Additionally, fibrinogen's poor solubility restricts the range of soluble protein to near physiological levels thus limiting the ability to modulate mechanical properties or degradation profiles based on the mass fraction of fibrinogen present. Here, we describe a combination of solution modifications that both slow the rate of fibrin gelation and stabilize fibrinogen in solution, extending the pot life of fibrin-forming solutions while extending accessible compositions to cover a wide range of fibrin concentrations previously undescribed. These enhancements allow for the fabrication of fibrin gels with divergent mechanical properties as well as the continuous microfluidic processing of fibrin into homogenous microparticles. Key to this process is modulating the solubility of fibrinogen with an amino acid supplemented buffer. These highly charged amino acids interact with oppositely charged residues on the fibrinogen thus preventing protein aggregation by limiting intermolecular interaction of individual fibrinogen monomers. A small molecule inhibitor of thrombin, the catalyzing enzyme of fibrin delays the onset of gelation and allows for continuous microfluidic production of fibrinogen/thrombin solution emulsion droplets, which subsequently gel to form fibrin microspheres. Laminar flows are used to keep the fibrin and thrombin solutions separate, further preventing any unwanted in-device polymerization. Particles can be fashioned from a 2-10 w/w% fibrinogen content with mechanical properties dependent on the mass fraction present. The microfluidic process is capable of rapidly

generating large quantities of particles at room temperature, without the need for environmental control or harsh solvents, making the process cytocompatible.

Mon-E1-03

Collective dynamics and rheology of concentrated suspensions of conductive particles in an electric field: Implications for active rheology control

Siamak Mirfendereski, Jae Sung Park

University of Nebraska-Lincoln

The electric-driven suspension of small particles in a viscous fluid has been appreciated as a promising context for active control of rheological properties. A popular class of such suspensions is an electrorheological (ER) fluid, where non-conducting but electrically active particles are suspended in an electrically insulating fluid. ER fluids have been a subject of great interest in both academia and industries thanks to their intriguing rheological characteristics under the action of electric fields. However, other electrokinetic phenomena could arise when conductive particles are suspended in an electrolyte in an electric field, which may exhibit rheological responses that are not observed in typical ER fluids. Such suspension is expected to undergo two nonlinear electrokinetics, namely dielectrophoresis (DEP) and the so-called induced-charge electrophoresis (ICEP). The former is the underlying mechanism for ER fluids, while ICEP is the dominant mechanism for the suspension of interest. Recently, we observed interesting collective dynamics and rheology of such suspensions at the zero-shear-rate limit, where nontrivial behaviors are observed in concentrated regimes. In this study, we aim to investigate the dynamics and rheology of such suspension in a shear flow. We perform large-scale particle-level simulations using our recently developed computational model based on the Stokesian dynamics simulation. The simultaneous effects of the nonlinear electrokinetic phenomena and external shear flow are captured by the Mason number. The collective dynamics and stress response in a suspension are efficiently calculated as a function of the Mason number for a range of volume fractions. We have found that the shear viscosity starts to increase at a certain Mason number for a volume fraction of about 30%. More notably, the normal stress differences undergo significant changes with the Mason number. Such rheological changes also show to coincide with the transition in collective dynamics. We will further discuss these properties as a function of the Mason number. Lastly, we will present the active rheology control of such suspension using an electric field. Control parameters of interest are the direction, magnitude, and frequency of the electric field. By varying these control parameters, we have found dramatic viscosity changes in a wide range of volume fractions, indicating possible active control of shear-thinning or shear-thickening behaviors. We also will present significant variations in normal stress differences and microstructure due to these control parameters.

Mon-E1-04

Electrophoretically snagging mRNA in wormlike micelle networks

Jim Schneider, Kimberly Hui, Kyle Tynan

Carnegie Mellon University

The increased demand for mRNA vaccines requires new analytical methods to keep pace with manufacturing and quality control requirements. In multivalent vaccines, payloads of mRNA with similar but not identical lengths in the range of 2000-3000 bases must be independently dosed and checked carefully for purity. Because gel electrophoresis is slow and unable to discriminate mRNA in this length range, vaccine manufacturers rely on liquid chromatography for routine characterization, with attendant solvent and capital expense. Further, these methods are not practical for deployment in remote areas where vaccines may be subjected to intermittent lapses in proper storage. Faster, higher-resolution electrophoretic separations of kilobase DNA or RNA can be accomplished using weakly overlapping networks of wormlike micelles made of mixtures of nonionic surfactant. These networks present a temporary gel to the migrating ssRNA, where pores in the gel continually dissolve and re-form due to micelle breakup and lateral diffusion processes. Using these materials, rapid, length-based separations can be realized up to a critical length where resolution is lost. In this “biased reptation” limit, the migration of the ssRNA is controlled by time scale of pore breakup rather than that of chain electrophoresis. Here we demonstrate that attachment of 18-carbon hydrophobes and 10-100 base DNA oligomers gives large changes in the electrophoretic mobility of ssRNA in the biased reptation limit. These attachments locally hinder the transit of ssRNA through pores in the vicinity of the attachment, a process we refer to as “snagging.” In so doing, the migration of the entire kilobase chain is drastically altered by a seemingly small modification. In fact, attachments of oligomers longer than about 30 bases gives no additional mobility shift as they are longer than the transient pore size. We present results confirming this snagging mechanism and present a scaling theory to describe the migration of tagged ssRNA in these wormlike micelle networks. We will also discuss applications of the method for mRNA vaccine analysis and virus quantitation in complex systems.

Mon-E1-05

Ion transport in non-uniform (nano-cavity-doped) polyelectrolyte hydrogels

Reghan J. Hill

McGill University

The electrical conductivity of hydrogels is an important performance characteristic, and provides valuable insights on the microstructure and charge-transfer mechanisms. For an ideal, uniform polyelectrolyte hydrogel, the ionic conductivity reflects the fixed-charge density, added salt, and hydrodynamic permeability. However, when the microstructure is modified by phase-separation and/or templating strategies, the conductivity may also reflect micro-scale polarization and electroosmotic advection. In this talk, I will present a recently developed theoretical model for polyelectrolyte hydrogels bearing spherical nano-cavities (Hill, *J. Fluid Mech.*, 2022). Donnan equilibrium between the cavities and bulk imparts charge and ion-mobility contrast, leading to coupled ion-diffusion, electro-migration and electroosmotic-advection effects under a steady, uniform electric field (with open or closed electrodes). Results will be presented to elucidate conditions under which cavities may increase or decrease the conductivity with respect to a uniform hydrogel. Also addressed is a closed-form solution for the hydrodynamic permeability. These theories provide new physical insights to guide the design and optimization of hydrogel nanocomposites for energy-related materials, membranes, and bio-medical applications.

Monday, July 11th | 09:30 - 11:30 | F1-Emulsions, Bubbles & Foams

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Mon-F1-01

Engineering fluid-fluid interfaces through processing and multicomponent adsorption

Lynn Walker

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 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.

Mon-F1-02

Debye Length and Surface Charge Determines Lipid Film Draining Characteristics

Oscar Zabala, Peter Beltramo

University of Massachusetts, Amherst

Membrane fusion is a critical biological process required for proper functioning of cells and involves the interaction between opposing lipid headgroups as two membrane bilayers approach. The chemistry of the lipids present in each bilayer determine their membrane physicochemical characteristics (stiffness, charge), and therefore plays an important role as the membrane deforms during the fusion process. For example, headgroups such as phosphatidylethanolamine (PE) make fusion more likely through induced negative curvature. Additionally, the ionic environment surrounding opposing monolayers impact interactions between headgroups. Ions are ubiquitous in a biological setting, where Zn^{2+}, Mg^{2+} help control bone formation while Na^{+}, Ca^{2+}, act as signaling molecules. While PE induces a negative membrane curvature, fusion does not proceed unless in the presence of calcium. To gain further understanding of the compositional and ionic effects on the interactions between opposing phospholipid leaflets, in this work we use a thin film balance to create aqueous lipid films and study their dynamic thinning behavior. Experiments are designed such that two monolayer headgroups face towards each other with an aqueous buffer in between, creating a thin film analogous to the first step in membrane fusion. We finely control the disjoining pressure to carry out both dynamic and equilibrium film thinning experiments. We introduce NaCl and $CaCl_2$ to understand the effects of mono/divalent cations on zwitterionic non-fusogenic (DOPC) and fusogenic (DOPE) lipids. We find final film thickness decreases with increasing Debye length, while capillary numbers increase. Additionally, we explore the behavior of anionic headgroups DOPG and DOPS to provide insight into the headgroup charge-dependent coalescence times and drainage characteristics.

Mon-F1-03

Characterization of the Solubilization Capacity of Sophorolipid Micelles

Daniel Miller [1], Janet McMillan [2], Caroline Nimako-Boateng [1], Michael Cherry [1], Ying O'Connor [3], Timothy Young [4], Aslin Izmitli [3], Beth Johnson [4], Chris Tucker [2], Tom Kalantar [2]

[1] Core Research and Development, Dow Inc., Collegeville, Pennsylvania 19426, United States[2] Core Research and Development, Dow Inc., Midland, Michigan 48667, United States[3] Dow Home & Personal Care, Dow Inc., Collegeville, Pennsylvania 19426, United States[4] Dow Home & Personal Care Dow Inc., Midland, Michigan 48667, United States

Characterization of the Solubilization Capacity of Sophorolipid Micelles Daniel S. Miller, 1 Janet McMillan,2 Caroline Nimako-Boateng,1 Michael Cherry,1 Ying O’Connor,3 Tim Young,4 Aslin Izmitli,3 Beth Johnson,4 Chris Tucker,2 Tom Kalantar,2 Ben Reiner,1 and Isabelle Van Reeth5 1Core Research and Development, Dow Inc., Collegeville, Pennsylvania 19426, United States 2Core Research and Development, Dow Inc., Midland, Michigan 48667, United States 3Dow Home & Personal Care, Dow Inc., Collegeville, Pennsylvania 19426, United States 4Dow Home & Personal Care Dow Inc., Midland, Michigan 48667, United States 5Dow Home & Personal Care Dow Inc., Seneffe, Belgium Market trends are moving towards biosurfactants as more sustainable, greener alternatives to petrochemical surfactants. Sophorolipids (SLs) are a class of biosurfactants produced by non-pathogenic strains of yeast.1 These so-called glycolipids are comprised of a hydrophobic hydroxylated fatty acid tail attached to a hydrophilic sophorose head group via a β-glycosidic linkage. SLs exist in two forms: (i) an acid form where the carboxylic acid of the SL is free, or (ii) a lactone form where the carboxylic acid is connected to sophorose via an ester linkage. The diversity of SL structures leads to a rich array of self-assembled microstructures that are sensitive to solution conditions such as salinity and pH.2,3 In this presentation, we reveal the impact of these microstructures on the capacity of SL micelles to solubilize oils. The solubilization capacity is compared to alkyl polyglucosides and petrochemically-derived alcohol ethoxylates. Overall, we provide fundamental structure-property insights that will enable design of formulated products for use in home and personal care markets. 1. Hayes, Douglas G., Daniel K. Solaiman, and Richard D. Ashby. Biobased surfactants: synthesis, properties, and applications. Elsevier, 2019. 2. Baccile, Niki, et al. "Unusual, pH-induced, self-assembly of sophorolipid biosurfactants." ACS Nano 6.6 (2012): 4763-4776. 3. Penfold, Jeff, et al. "Solution self-assembly of the sophorolipid biosurfactant and its mixture with anionic surfactant sodium dodecyl benzene sulfonate." Langmuir 27.14 (2011): 8867-8877.

Mon-F1-04

Pressure Dependence of Highly Efficient Microemulsions with Short-Chain Alkanes

Maximilian Krappel [1], Jessica Hippele [1], Christian Bittner [2], Thomas Sottmann [1]

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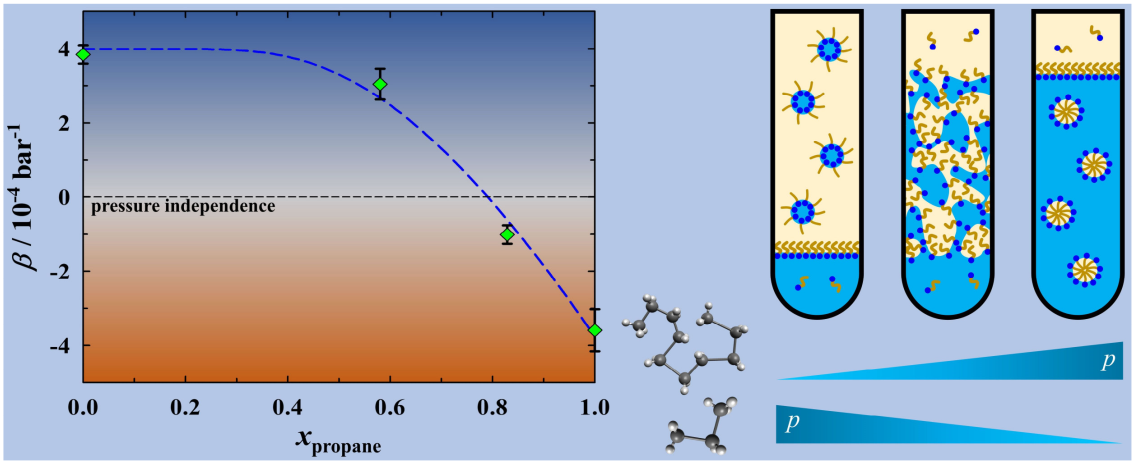
The influence of pressure on the properties of emulsions and microemulsions is generally weak due to the very low compressibility of the components. However, this is no longer true if the formulations contain components that are gaseous at ambient conditions. Examples and applications of such formulations are CO_2 microemulsions for the production of nanofoams [1] or crude oil microemulsions containing short-chain alkanes as found in enhanced oil recovery [2]. To deepen the knowledge on such systems, we studied the pressure dependence of microemulsions consisting of brine/butyldiglycol, *n*-alkanes, and a mixture of anionic surfactants between 1 and 350 bar. Using the highly efficient mixture of an alkyl alkoxy sulfate and alkyl sulfonate surfactant, we were able to formulate one-phase microemulsions containing equal amounts of brine/butyldiglycol and *n*-alkanes with only a few wt% of this surfactant mixture. By increasing the fraction of propane in an *n*-decane/propane oil mixture systematically, an inversion of the pressure-dependent phase sequence was found. In *n*-decane-rich microemulsions, a pressure increase leads to an inversion of the membrane curvature from water-in-oil (w/o) to oil-in-water (o/w), resulting from a stronger headgroup hydration. By contrast, increasing the pressure in the propane-rich microemulsions leads to a curvature change from o/w to w/o, caused by the better interaction between the compressible propane and the hydrophobic surfactant tails at elevated pressures. For the selected system, we found that with roughly equal masses of *n*-decane and propane in the oil mixture, corresponding to a propane molar fraction of almost 80 %, the pressure effects on headgroup hydration and surfactant tail-alkyl chain interactions compensate each other, leading to a microemulsion that does not exhibit a pressure dependence, i.e., an HLD pressure coefficient of $\beta \approx 0$ [3]. Due to their even higher compressibility, the shorter-chain homologs methane and ethane are expected to increase the magnitude of pressure effects even more drastically.



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Mon-F1-05

Spindle-like vesicle shapes in external fields.

Rodrigo Reboucas, Michael Miksis, Petia Vlahovska

ESAM - Northwestern University

A phospholipid bilayer is the main structural component of cells and internal cellular organelles. For the past two decades, researchers have used giant unilamellar vesicles (GUVs) as a popular biomimetic model to study membrane biophysics. This work focuses on the mechanical properties and deformation of GUVs which qualitatively resemble the rich dynamics of living cells in external fields (e.g., under electric potential difference across the plasma membrane). Here, the classical Helfrich bending energy model is minimized under constraints of constant area and volume and the corresponding Euler-Lagrange equations are solved numerically to yield equilibrium shapes. We investigate the parameter space of vesicle geometric properties and environmental stimuli (e.g., osmotic pressure), and report regimes where vesicle morphologies resemble spindle-like structures observed in recent experimental results of vesicles embedded in nematic liquid crystals and vesicles suspended in electrolyte solutions under strong AC electric fields. Results show that under conditions of constant bending rigidity and low excess-area, spindle-like vesicle shapes are accessible. Allowing for a spatially varying bending rigidity to simulate the effect of an external field yields similar spindle-like configurations with lower bending energy; the origin of this local variation is the subject of ongoing research.

Monday, July 11th | 09:30 - 11:10 | G1-Energy Systems

Mon-G1-01

Engineering Physico-Chemical Interactions at Interfaces for Performance Enhancements in Energy Systems

Kripa Varanasi

Massachusetts Institute of Technology

Physico-chemical interactions at interfaces are ubiquitous in energy systems. In this talk, we show how interfacial properties can be engineered across multiple length scales for significant performance enhancements in a wide range of energy processes including thermal-fluid and electrochemical processes. First, we will describe how surface chemistry/morphology can be engineered to enhance thermal transport in heating & cooling systems, reduce friction, enhance flow assurance in the energy industry, and provide self-healing barriers for protection against scaling and corrosion. Next, we will describe our approaches to solve important problems at the Energy-Water Nexus. These include water capture from power plant cooling towers and water-less cleaning of solar panels using space-charge driven non-Laplacian electric fields. The third part of the talk will focus on our efforts on enhancing electrochemical processes ranging from CO2 capture and conversion and hydrogen electrolysers by addressing bottlenecks at the electrochemical-fluid dynamic interfaces. We will finally discuss our efforts in improving photobioreactors and enhancing biological routes for CO2 capture and utilization. We will also discuss entrepreneurial efforts to translate some of these technologies into useful products and markets.

Mon-G1-02

Dual Effects of a Low Dosage Model Kinetic Hydrate Inhibitor on Hydrate Particle Morphology and Interparticle Force

Joshua Worley, Carolyn Koh, Jose Delgado

Chemical and Biological Engineering, Colorado School of Mines

The formation of gas hydrate plugs represents a major safety and environmental concern in subsea pipelines. Kinetic hydrate inhibitors (KHIs) are cleaner, cheaper, and greener low dosage hydrate management chemicals which can prevent catastrophic hydrate plug formation in both gas and oil-dominated flow lines. Polyvinylpyrrolidone (PVP), a model KHI, was investigated across a range of concentrations, to discover its effects on hydrate interparticle force, morphology, and growth. PVP reduces interparticle force at short contact times by 40-54%, but, in higher concentrations, can cause unconverted water to remain at the particle surface, increasing capillary bridging. PVP also reduces interparticle force by 20-40% for up to an hour, well after the onset of particle sintering, and it can reduce the sintering rate by 15-17%. PVP also reduces film growth rates by 30-50% depending on the concentration of the chemical in the aqueous phase. Nucleation and growth effects were visually observed to occur at 0.01wt% PVP in low pressure studies, which is two orders of magnitude below the 1-3wt% KHI traditionally employed in hydrate management. Low concentration PVP causes major morphological changes to the hydrate particles in both short and long-term observations. As particle morphology influences interparticle force and agglomeration, it was vital to document and explain the morphological changes caused by the PVP. Images and videos of the drastic particle morphology changes in both the short term (during the 30-minute annealing period) and the long term (up to 2 hours after the annealing period) were displayed. A mechanism by which the PVP causes the morphology changes was presented, explaining how the stochastic adsorption of chemicals at the particle surface leads directly to the observed particle morphology. Pressure and temperature are also important factors in hydrate formation and hydrate management. As such, film growth and short-term contact force experiments were performed at higher temperature to determine its effect on the functionality of the KHI. Further, high pressure studies were performed to determine the effect of the pressure and driving force on the KHI and to see if low pressure results carried over to high pressure experiments. Higher pressures could also require higher PVP concentrations to elicit the same effects seen at lower concentrations in the atmospheric pressure apparatus, so high pressure scoping studies were performed to see how the pressure affects the required concentration. Morphology was also observed during the higher pressure and temperature experiments to explore whether the morphology effects are a function of temperature or pressure. The results presented in this research show that ultralow concentrations

of KHIs (0.0005wt%) can have combined effects on the interfacial activity and crystal growth and morphology of hydrates, showing KHIs to be a dual function inhibitor of both interparticle interactions and hydrate growth. Scoping studies at higher pressures and temperatures also showed how results depend on the system conditions. These results will inform KHI applications from industrial flow assurance to carbon dioxide transport for unimpeded carbon capture and sequestration, and they could provide a potential morphological screening tool for KHIs. Funded by NSF Award #2015201

Mon-G1-03

Bridging Database Analysis with Microrheology to Reveal Super-Hydrodynamic Conductivity Scaling Regimes in Ionic Liquids

Ryan Cashen, Megan Donoghue, Abigail Schmeiser, Matthew Gebbie

University of Wisconsin - Madison

Ion transport through electrolytes critically impacts the performance of energy storage devices. Many frameworks used to model ion transport assume hydrodynamic mechanisms, focusing on maximizing conductivity by reducing viscosity. However, solid-state electrolytes illustrate that non-hydrodynamic ion transport can define device performance. Increasingly, structural transport mechanisms, such as hopping, are proposed for concentrated electrolytes. Yet viscosity-conductivity scaling relationships in ionic liquids are often analyzed with hydrodynamic models. In this talk, we discuss our analysis of hydrodynamic transport models of viscosity-conductivity scaling in ionic liquids, made possible by bridging databases of physical and computational features. Further, I will highlight how many ionic liquids exhibit positive deviations from the Nernst-Einstein model, implying ions move faster than hydrodynamic limits. We verify these findings using microrheology and conductivity experiments. I will discuss how our results reveal super-hydrodynamic regimes in ionic liquids, suggesting mechanisms of correlated ion motion. I will conclude with a brief overview of how machine learning tools can improve predictions of conductivity from molecular properties, including predictions from solely computational features. Our findings reveal that many ionic liquids exhibit super-hydrodynamic viscosity-conductivity scaling, which could be harnessed to enhance electrochemical device performance.

Mon-G1-04

Synthesis of lithium doped silicon clathrate through thermal diffusion

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Si clathrates are cage-like, crystalline Si inclusion compounds. Room temperature and atmospheric pressure metastable clathrates are synthesized as either type I (M8Si46) or type II (MxSi136, 0<x<24, M=alkali-metal) phases in the presence of alkali atoms which sit inside the cage acting as interstitial guests. Si clathrates have many potentially interesting electronic properties. Type II Si clathrates have been proposed as anodes for lithium-ion batteries. The cage-like clathrate structure may facilitate the lithium diffusion and make the lithiation less sensitive to volume expansion compared with diamond silicon. In support of this, theoretical calculations suggest that lattice constants of lithiated clathrates increased very slightly. Moreover, lithiated clathrates are expected to exhibit excellent electrical conductivity due to the metallic behavior of clathrates. These properties make Si-Li clathrates potentially promising for electrochemical applications. Realizing this potential requires the synthesis of type-II Si clathrates with Li in the cages and understanding of lithium-ion diffusion in the structure. The major barrier to the direct formation of Li-guest clathrates is that unlike Si-Na clathrates which have been formed through the decomposition of a Zintl precusor NaSi phase, the Li-Si phase diagram is more complex and an equivalent Li-Si phase which can decompose into LixSi136 clathrate has not been demonstrated. An alternative approach to synthesizing clathrates with Li guests begins with low-x NaxSi136 and diffuses Li guests into the structure. Electrochemical insertion of lithium into NaxSi136 clathrate cages has been reported. This approach, however, led to amorphous phases after several intercalation cycles probably due to the large amount of Li inserted and associated bond breaking within the structure. In our work we explored thermal diffusion of Li into the guest sites of a nearly empty clathrate framework to synthesize LixSi136. This is made possible by our ability to synthesize extremely low Na type II NaxSi136 (x~0.016). Low-x NaxSi136 is sealed into a quartz ampoule with Li metal under vacuum and annealed at temperatures between 250oC to 400oC. XRD shows that the clathrate structure with Li is unstable converting to polycrystalline or amorphous phases for anneals above 375oC (or at slightly lower temperatures with more lithium). At lower temperature (<350oC), XRD shows that guest content in the material increases after diffusion. Raman shows a frequency reduction due to diffusion especially for higher frequency modes. Li guests are expected to be donors and this frequency reduction is consistent with previous reports that donating electrons to the anti-bonding conduction band of Si clathrate causes a reduction of vibrational frequency. Time-of-flight SIMS confirmed the presence of Li and was used to obtain the ion profiles to extract diffusion constants. EPR was applied to detect low-concentration guests and study the interaction of lithium guests with clathrate cages. Results in this work provide a new method for filling the clathrate cages potentially allowing many alternative guest atoms to be explored. They also provide useful insights into the potential use of Si clathrate as an anode material in Li-ion batteries. This work was supported by National Science Foundation (Award number 1810463 and 2114569).

Monday, July 11th | 09:30 - 11:10 | I1-General aspects of Colloids and Interface

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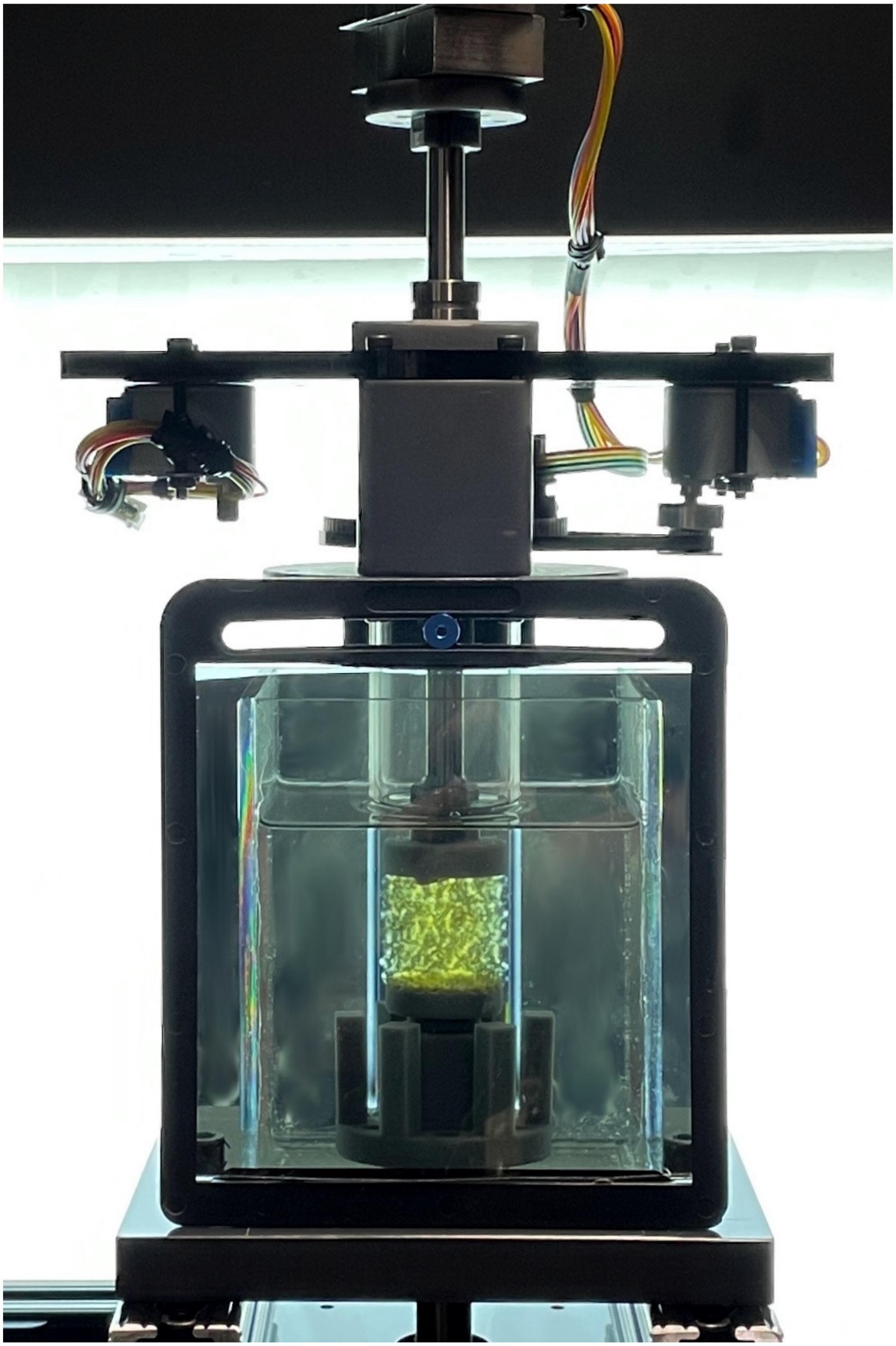
Mon-I1-01

Photoporomechanics

Wei Li, Yue Meng, Ruben Juanes

Massachusetts Institute of Technology

Effective stress—the fraction of the total stress that is transmitted through the solid skeleton—controls the mechanical behavior of porous media [1]. However, effective stress has until now been a physical quantity that could only be calculated by subtracting pore pressure from the normal component of the stress tensor, or inferred from its "effect", typically the solid skeleton deformation. Here, we use photoelasticimetry to visualize the evolving effective stress field in fluid-filled granular media in processes that couple fluid flow and mechanical deformation, an experimental technique we refer to as photoporomechanics [2]. We provide an application of photoporomechanics to illustrate the evolution of effective stress during one-dimensional consolidation: a process by which the stresses caused by a sudden load are gradually transmitted through a fluid-filled granular pack as the fluid drains and excess pore pressures dissipate. We also apply photoporomechanics to uncover the underpinning grain-scale mechanics during fluid-induced deformation and fracture of granular media [3]. We inject air into a liquid-filled photoelastic monolayer granular pack in a circular Hele-Shaw cell, and find two different modes of fluid invasion: fracturing in fluid-filled elastic media (with strong photoelastic response), and viscous fingering in frictional fluids (with weak or negligible photoelastic response). We directly visualize the evolving effective stress field and conceptualize the system's behavior by means of a mechanistic model, revealing that a jamming transition determines the distinct rheological behavior of the wet granular pack, from a friction-dominated to an elasticity-dominated response. We then extend photoporomechanics into tomography and visualize, for the first time, force chains in fully 3D granular media [4]. Our experimental study unveils the astonishing 3D nested, parallel and helical force-chain patterns under isotropic, triaxial shear and rotary shear conditions, respectively—thus opening the door to improved understanding of the grain-scale underpinning of coupled solid-fluid processes in granular media.



References: [1] Juanes, R., Meng, Y., & Primkulov, B. K. (2020). Multiphase flow and granular mechanics. Physical Review Fluids, 5(11), 110516. [2] Li, W., Meng, Y., Primkulov, B. K., & Juanes, R. (2021). Photoporomechanics: An Experimental Method to Visualize the Effective Stress Field in Fluid-Filled Granular Media. Physical Review Applied, 16(2), 024043. [3] Meng, Y., Li, W., &

Juanes, R. (2022). Fracturing in wet granular media illuminated by photoporomechanics. Submitted for publication. [4] Li, W., & Juanes, R. (2022). 3D Force Chain Tomographic Scanner, US Application No. 63/296,426.

Mon-I1-02

Surface modification of prepared Graphene oxide (GO) using synthesized SPION particles

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Magnetically responsive GO has wide application in rheology, medicine and in composite materials in tuning their physical and chemical properties. This work is concerned with the preparation, surface modification and characterization of Graphene oxide particles. The objective is to modify Graphene oxide (GO) particles using superparamagnetic iron oxide nanoparticles (SPION) to make it responsive to magnetic field. Modification of GO particles is done via adsorption of iron oxide nanoparticles on GO surface by directly mixing the two samples at pH=2. Comparison of the properties of modified GO was done with that of pure GO and SPION particles. GO preparation was done via Hummer's process using graphite particles, while the pure SPION particles were prepared using co-precipitation technique. The adsorption of SPION on GO surface is tunes using electrostatic interaction between the two having oppositely charged surfaces at low pH. The surface charge of the GO and SPION particles are found to be -2 and +40(unites) respectively, as determined by the zeta analysis at pH=2. Alternating gradient magnetometry (AGM) analysis confirmed the superparamagnetic behaviour of the iron oxide nanoparticles whose size was determined via DLS and TEM analysis. XRD analysis showed the crystalline behaviour of SPION along with the presence of both phases (magnetite/maghemite) in the sample. Size distribution and surface modification of GO-SPION was further analyzed using master-sizer, microscopic and SEM analysis. The modified GO particles showed magnetic response when kept in magnetic field as compared to the non-magnetic pure GO particles. The modified GO particles is then aligned in composite membrane using magnetic field to tune the optical properties of composite media.

Mon-I1-03

Uphill granular heaping flow via magnetically-driven particle rotation

Samuel Wilson-Whitford [1, 2], Jinghui Gao [1], Maria Chiara Roffin [1], William Buckley [1], James Gilchrist [1, 2]

[1] Department of Chemical and Biomolecular Engineering, Lehigh University, PA, USA[2] Polymer Science and Engineering, Lehigh University, PA, USA

Gravity-driven granular flows are ubiquitous in nature and contribute to such natural phenomenon as avalanches and landslides, but also have significant impact on industrial processing and man-made systems. The juxtaposed simplicity of the system components and their subsequent response complexity have fascinated scientists in the soft matter and complex systems communities. One typical behavior of a granular system is heap formation. When a granular material, such as sand, is continually poured onto a flat surface, a heap is formed. At the surface of this heap, we observe a continuous gravity driven boundary flow in which grains are transported from an uphill to a down hill position. As grains are transferred from the boundary layer to the underlying static bed, the heap itself will grow but the dissipation of potential energy through frictional particle-particle and hydrodynamic particle-fluid interactions within the boundary layer shear flow leads to a fundamental slope angle, known as the angle of repose. Although a wealth of studies exist focusing on systems of passive particles, what has not been explored thoroughly is the behavior of granular systems of responsive particles. For example, what would happen if the shear force applied to the system comes in the form of direct rotational torque applied individually to each particle in the granular bed. In this work, a bed consisting of responsive 50 micron ferromagnetic Janus particles is prepared. These responsive Janus particles are rotated through the application of magnetic torque by an external rotating magnetic field resulting in uphill granular heaping which for all purposes demonstrates quintessential granular behavior, such as boundary layer flow, but against gravity, giving rise to a negative angle of repose (downhill to uphill). It is proposed that the behavior is governed by frictional control as a direct result of the magnetic field strength. These observations elucidate a whole new way to observe granular systems and have a significant impact on the way in which granular systems could be applied.

Mon-I1-04

Avalanches in Strong Imbibition

Bauyrzhan Primkulov [1], Benzhong Zhao [2], Christopher MacMinn [3], Ruben Juanes [1]

[1] Massachusetts Institute of Technology[2] McMaster University[3] University of Oxford

Earthquakes, landslides, avalanches, solar flares, and financial markets are examples of self-organized criticality (SOC), a near-equilibrium process where small perturbations lead to scale-free (and thereby essentially unpredictable) consequences. A classic example of SOC is the drainage of a wetting fluid from a porous medium (Furuberg et al., PRL 1988). In drainage, the wetting fluid retreats preferentially from pore bodies as the non-wetting fluid invades. Reversing the flow direction leads instead to imbibition, where the wetting fluid invades by preferentially coating the solid surfaces. Here, we show with experiments and simulations that strong imbibition shares all of the scale-free features of drainage—avalanches, intermittency, and spatiotemporal correlation scaling—a striking finding, given that these two processes occur through radically different displacement mechanisms at the pore scale.

Monday, July 11th | 09:30 - 11:30 | J1-Molecules and Particles at Fluid Interfaces

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Mon-J1-01

Microrheology of Airway Mucus

Gerald Fuller, Maggie Braunreuther

Chemical Engineering, Stanford University

Mucus that lines the lungs acts as the primary defense against inhaled foreign particles and infectious agents by trapping these invaders and preventing them from penetrating the cell layer below. Effective mucus clearance, and thus removal of the trapped invaders, is vital for healthy airway function. Cystic Fibrosis (CF) is a genetic disease that is characterized by hindered ion transport in airway epithelial cells. As a result, the mucus secreted by these cells becomes dehydrated, forming thick stratified layers. This change in mucus material properties can severely impair mucus clearance, leading to airway obstruction, chronic infection, and inflammatory lung damage. It is well established that CF mucus exhibits viscosities orders of magnitude greater than those of healthy mucus. However, thus far it has not been feasible to measure mucus properties on live cells as it is produced by the epithelial cell layer, neglecting the relationship between the physiological environment and mucus rheology. A new instrument, the “Magnetic Live Cell Rheometer”, recently developed by the Fuller group has been adapted to examine mucus rheology in situ via magnetic microrheology. Human airway epithelial cells (HAECs) are grown in 2D air-liquid interface (ALI) cultures, mimicking the airway surface environment. During rheological experiments, we maintain cells at ALI and use micron scale magnetic wires (microwires) to probe the properties of the mucus as a function of distance from the cell layer. We apply and remove a magnetic force and track microwire displacement to determine the compliance and viscosity of healthy and diseased mucus on the respective HAEC cultures. We then test existing mucoactive drugs designed to reduce the elasticity and viscosity of the mucus layer to establish correlation with clinical response and assess the impact of genetic variants. With this method, we demonstrate the ability to study mucus rheology in a physiologically relevant environment, examine phenotypic differences in mucus rheology, and rapidly test drugs on mucociliary mechanics.

Mon-J1-02

Interfacial rheology of lipid and polymer bilayer membranes

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[1] Northwestern University, USA[2] Max-Planck Institute of Colloids and Interfaces, Germany

Living cells maintain electric potential difference across the plasma membrane as well as the membranes of various organelles. Using giant vesicles as an in-vitro membrane model system, we explore the effects of electric field on the interfacial shear rheology of biomimetic bilayer membrane made of lipids and block-copolymers. We utilize a probe-free and high-throughput method to measure surface shear viscosity that was a recently developed by our group (Faizi et al, Biophys. J, 2022). In this talk, I will present experimental results suggesting that bilayers do not behave as simple two-dimensional fluids as commonly assumed but their viscosity may be modulated by electric fields. We find that membrane viscosity may decrease with increasing electric field magnitude, while membrane electric polarization has the opposite effect. The mechanisms underlying the electrorheological responses of the bilayer systems will be discussed.

Mon-J1-03

Dynamic Crowding Effects of Colloids on Planar Biomembranes

Paige Liu, Peter J. Beltramo

University of Massachusetts, Amherst Chemical Engineering

Lateral diffusion in cell membranes is critical to biological processes such as the formation of protein complexes and intercell communication. This diffusion is complicated by extreme crowding to the extent that 30-50% of the area fraction in a cell membrane is occupied by membrane proteins. However, the impact of this crowding on membrane properties and the resulting mobility of these inclusions are poorly understood. In this vein, we seek to elucidate the changes in diffusivity and fluidity of lipid bilayers with respect to increasing the area fraction of model crowders. We use 1 µm fluorescent polystyrene particles functionalized with neutravidin as our model crowders. The particles are then loaded onto a planar, freestanding, phospholipid bilayer doped with biotinylated lipids, creating a covalent linkage between avidin and biotin groups. The particle area fraction, or degree of crowding, is controlled between the dilute limit and upwards of 15%. The particle motion in the plane of the bilayer is imaged at 20 FPS using fluorescence microscopy. Multiple particle tracking is then used to generate particle trajectories, which are used to calculate mean squared displacement (MSD) curves. The slope of these curves can then be used to calculate a translational diffusion coefficient (D_A) as well as an exponential factor (n) that can be used to characterize the diffusion. From D_A and n, it is clear when any deviations from the Brownian motion arise to indicate crowding effects. We have measured these values for particle crowding at up to 15% area fraction. The diffusion coefficient of the particles has been found to decrease with increasing crowding, and above 10% area fraction, n is found to be lower than 1, indicating some degree of subdiffusion. Using the Saffman-Delbrück (SD) and Hughes-Pailthorpe-White (HPW) hydrodynamic models, we are able to calculate an apparent membrane viscosity as a function of particle crowding. For dilute particle concentrations, we find these viscosities to be within the range of measured membrane viscosities reported in literature. We have found the apparent viscosity of the membrane to increase with crowding that scales with the measured area fraction of the particles in a power-law relationship with a slope of around 0.2 for both the SD and HPW viscosities, with a slightly higher dependence on particle crowding for the SD model. This is in contrast to the scaling factor of 2 found for bulk colloidal suspensions and with recent results using monolayer phospholipid systems. In summary, we have found increasing crowding at the model membrane interface to decrease the diffusivity of the particles as well as increase the apparent viscosity of the membrane-particle system. This may be due to steric hindrance of the particles and/ or the immobilization of the membrane lipids as the membrane adsorbs to the particles. Ongoing work entails pushing the crowding towards

physiological conditions as well as varying the particle sizes used as tracers to span different hydrodynamic regimes.

Mon-J1-04

Interfacial Rheology of the Tear Film

Xiaojie Xu, Yi Zuo

Department of Mechanical Engineering, University of Hawaii at Manoa

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 the dry eye disease (DED), affecting 10-30% of the world population. There is an urgent need to better understand the biophysical and rheological properties of the TFLL with the long-term goal to develop translational solutions in effectively managing the DED. We have studied the surface tension and interfacial dilational rheology of a model TFLL using a novel experimental methodology called the constrained drop surfactometry (CDS), recently developed in our laboratory.[1] Specifically, we focused on a novel lipid class newly discovered in meibomian lipids, i.e., the fatty acid esters of hydroxy fatty acids (FAHFAs), which consist of two acyl chains connected through a single ester bond. FAHFAs exist in an extremely low abundance in natural sources and show potent antidiabetic and anti-inflammatory activities. Biophysical function and contribution of FAHFAs to the tear film is still poorly understood. We used palmitic-acid-9-hydroxy-stearic-acid (PAHSA) as a model FAHFA in a recombinant TFLL. With combined biophysical experiments,[2] atomic force microscopy observations,[3] and all-atom molecular dynamics simulations,[3] it was found that the major biophysical function of phospholipids in the TFLL is to reduce the surface tension; while the primary function of FAHFAs is to regulate interfacial rheology of the TFLL, thus optimizing the viscoelastic properties of the tear film 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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Mon-J1-05

Surface-enhanced Raman Spectroscopy (SERS) Hotspots: Optoelectronic Mapping for Sensor Optimization

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Surface Enhanced Raman Spectroscopy or SERS is a highly sensitive technique for detecting target analytes adsorbed on a SERS active substrate. Production of these substrates requires much consideration ranging from surface morphology to optical and electronic properties. Proper consideration of these parameters will lead to the generation of SERS hotspots, the junctions between plasmonic nanostructures that lead to SERS enhancement. Further understanding and characterization of a SERS active substrate's hotspots can help lead to a further refined and robust sensor. Our model substrate to study hotspot generation consists of a film of gold coated silica spheres in a range of sizes, 490 nm – 2 µm in diameter. Langmuir-Blodgett deposition allows for quick and consistent substrate preparation by depositing particles from an air-water interface. Langmuir-Blodgett deposition allows for easily controllable deposition pressures which varies the inter-particles spacing and hence the hotspot formation. Beyond a function test of SERS activity using Raman spectroscopy, we also use a range of characterization and analysis techniques to understand the film properties and SERS hotspot generation and how those link to SERS activity. Atomic Force Microscopy (AFM) and scanning electron microscopy (SEM) are used to characterize the morphology of the substrates, with this data also providing more general information about the range of film structures attainable under different compression and relaxation regimes. Photo-Kelvin probe force microscopy (photo-KPFM) maps work function data, indicating how the electronic activity of the film changes under laser irradiation used to excite the plasmonic hotspots, simulating the electronic activity experienced during Raman spectroscopy. The combination of the morphological, electronic, and spectroscopic data yields a more complete understanding of hotspot formation in these interesting systems.

Monday, July 11th | 09:30 - 11:30 | L1-Surface science and catalysis

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Mon-L1-01

Understanding and Engineering Catalytic Materials Using Nanocrystal Precursors

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Catalytic processes are central to the goal of a sustainable future. A promising approach in developing catalytic materials is represented by the design of catalytic sites based on the knowledge of structure-property relationships, and in the precise synthesis of these sites at the atomic level. Colloidal nanocrystals, with tunable active sites and compositions, can help in this mission. This approach can provide not only fundamental understanding of catalytic reactions, but also a way to precisely engineer reaction sites to produce efficient catalysts that are active, stable and selective for several important transformations. Advances in the synthesis of these materials will be presented. Examples of the use of these building blocks as supported systems or in combination with hybrid organic materials will be shown, both to understand trends in methane and CO2 activation, and in the preparation of optimized catalytic systems combining multiple active phases. In all these examples, important efforts to obtain precious structure-property relationships will be highlighted, with this knowledge used to prepare more efficient and stable catalysts for reducing the emission of greenhouse gases and for the sustainable production of fuels and chemicals.

Mon-L1-02

Synthesis of ternary molybdenum carbide nanoparticles *via* a mild solution-based route for the catalytic conversion of renewable carbon sources

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The unique physicochemical properties of transition metal carbides (TMCs) have led to their widespread evaluation for catalytic applications such as the conversion of biomass or environmental chemical pollutants (e.g., CO_2, CH_4) to commodity chemicals and/or fuels. These materials are traditionally synthesized *via* carburization pathways where a transition metal salt or metal oxide and a carbon source (*e.g.*, graphite, hydrocarbons, CH_4/H_2) are heated to high temperatures (600-800 °C). However, these methods offer minimal control over the physical properties of the resultant particles, such as size and morphology, which influences their catalytic performance. Regardless of these limitations, recent investigations into improving catalytic activity of TMCs have revealed that modifying the chemical composition, through doping with transition metals, is a promising method toward enhancing the activity, stability, and/or selectivity of these materials. For example, the addition of ionic metal precursors to TMC surfaces to form alloys has led to improved reactivity for a range of noteworthy transformations including methane decomposition, CO hydrogenation, and CO_2 reduction. Herein, we expand upon recent synthetic developments from our group that enabled the preparation of phase-pure molybdenum carbide (a-MoC_{1-x}) nanoparticles (NPs) at relatively mild temperatures (*i.e.*, 300 °C) *via* a solution-phase synthesis route. Decomposition of late first-row transition metal precursors in the presence of *in situ* generated a-MoC_{1-x} has resulted in the formation of a series of ternary carbides, $Mo_{2-x}M_xC$ (M = Fe, Co, Ni, Zn). This presentation will focus on the synthesis, structural and spectroscopic characterization, and catalytic performance of NP-$Mo_{2-x}M_xC$ catalysts. Comparison of the reactivity of NP-$Mo_{2-x}M_xC$ to that of the parent a-MoC_{1-x} particles provides insight into the effects of alloying metal carbides on reductive transformations.

Mon-L1-03

Ligand exchange on colloidal α-MoC_{1-x} nanoparticles

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Transition metal carbides (TMCs) are promising low-cost catalysts for various transformations, including CO_2 reduction, ammonia synthesis, and hydrodeoxygenation reactions due to their multifunctionality and noble metal-like behavior. Moreover, nanostructuring of TMCs offer additional advantages for catalysis from the large surface-area-to-volume ratios and kinetic control over composition and morphology inherent in nanoparticle catalysts. Recently, small, colloidally prepared α-MoC_{1-x} nanoparticles demonstrated superior performance for thermocatalytic CO_2 hydrogenation compared to their bulk analogue. While these nanoparticles offer promising catalytic performance, a barrier for their practical utilization is the removal of the large organic ligand content on their surface, which must be removed to access their catalytic ability. Typical high-temperature annealing to remove these ligands often results in coking, which can reduce their catalytic performance. One way to circumvent this issue is by replacing the long-chain aliphatic ligands with smaller, short-chain ligands that can be easily removed through volatilization or decomposition. Here, we present the facile exchange of native oleylamine ligands on the surface of colloidal α-MoC_{1-x} nanoparticles for shorter *tert*-butylamine ligands. Analysis of the ligand exchange reactions with solution ^1H NMR spectroscopy reveals the equilibrium of ligand exchange of native oleylamine ligands for shorter chain amine ligands. FT-IR spectroscopy and thermogravimetric analysis-mass spectrometry confirm the displacement of the native oleylamine ligands for *tert*-butylamine, indicating successful ligand exchange. Additionally, catalytic site densities were determined by carbon monoxide (CO) chemisorption, demonstrating that a mild pretreatment at 250 °C resulted in generating ca. 25% of the total binding sites, while the native oleylamine-terminated material showed no available surface binding sites after this low temperature pretreatment.

Mon-L1-04

Assessing the Role of Surface Carbon on the Surface Stability and Reactivity of β-Mo2C Catalysts

Sean Tacey, Matthew Jankousky, Carrie Farberow

National Renewable Energy Laboratory

Transition metal carbides, such as molybdenum carbide (Mo2C), show promising performance in many catalytic applications, including conversion of methane to syngas, CO2 capture and conversion, hydrogenation, water-gas shift, Fischer-Tropsch synthesis, and hydrodeoxygenation for conversion of biomass to hydrocarbons by catalytic fast pyrolysis. However, the ability to rationally design metal carbide formulations for targeted catalytic applications is limited because the atomic-scale structure and composition of the catalytically active sites on metal carbides, and their evolution under varying reaction environments, are not well-understood. Herein, ab initio thermodynamics are utilized to study the relative stability of low-Miller index facets of β-Mo2C at varying carbon chemical potential (μC). By systematically constructing the unique Mo-terminated surfaces for each facet and optimizing surface-carbon overlayers at varying carbon coverage, stable surface structures are identified beyond those generated by cleaving the bulk orthorhombic structure. When reconstruction of the surface carbon is considered, the (111) and (101) surfaces are predicted to be most stable, dominating the β-Mo2C Wulff particle surface area across a broad range of μC. The surface-carbon coverage is predicted to steadily increase for all low-index facets under more carburizing reaction conditions. The structural characteristics of the facet and the accumulation of surface carbon result in distinct changes to the predicted adsorption energy of atomic H and O, common catalyst reactivity descriptors. Whereas H binding is only slightly affected by surface carbon, O is systematically destabilized. The findings reported indicate that consideration of only bulk-terminated surfaces of metal carbide catalysts, and the common focus of theoretical studies on the bulk-truncated, close-packed β-Mo2C(100) surface, is likely insufficient to capture the reactivity of the working β-Mo2C catalyst.

Mon-L1-05

Towards the development of intracellular catalysis supported on mesoporous silica nanomaterials

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As we think about advanced medicine and new biomolecule synthesis, we need to turn to cells and biological systems where drugs and precursors to new consumer goods can be synthesized. We are investigating mesoporous silica nanomaterials (MSN), functionalized with a series of catalytic active sites (inorganic and biological) that are physisorbed and covalently tethered to the pore surface and external surface of the MSN. Because catalytic active sites can be cytotoxic to viable cells, we are investigating pore properties that can be tuned and modified so single site, nanoparticle, and enzymatic catalytic sites can be active in the pores and not interfere with the health of the cell. Our initial effort into this grand plan has been a tandem system initially using two independent metal nanoparticles to catalyze the oxidative esterification of allyl alcohol. Using separate gold nanoparticle (Au NP) and palladium nanoparticle (Pd NP) catalysts we studied the initial oxidation of the alcohol followed by ester formation to allyl acrylate. Our next generation tandem system finds us replacing the first step of the reaction (Pd NP catalyzed oxidation of allyl alcohol) with an enzyme, alcohol dehydrogenase and conducting the tandem reaction in aqueous buffer at ambient conditions. Future directions of including tethered organometallic catalysts in syntheses conducted in biological and biological simulated environments will be shared.

Mon-M1-01

“Particles with gecko legs”: Hierarchically branched soft dendritic colloids for novel types of gels and superhydrophobic/superhydrophilic coatings

Orlin Velev

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC

We will discuss the unique capabilities enabled by a new class of soft dendritic colloids (“dendricolloids”) with hierarchical morphology and nanofibrillar corona. These colloids with branched and fractal morphology are fabricated by a simple and scalable process of multiphasic polymer or biopolymer precipitation in turbulently sheared liquid media. The ultralow interfacial tension, combined with concurrent polymer phase separation, results in the formation of hierarchical fibrillar polymer microgels. The branched, dendritic particles are surrounded by a corona of polymer nanofibers, which endows them with extraordinary strong adhesive properties, and enables unique structure-forming abilities (Nature Materials, 18:1315, 2019). We will first analyze the origin of the adhesive effects, which are closely associated with the omnipresent van der Waals forces and the phenomenon of “contact splitting” analogous to the one that allows the legs of the gecko lizards to stick to any surface. We will discuss how the fractal branching and contact splitting phenomena enable a range of highly unusual properties – gelation at very low volume fractions, strong adhesion to surfaces and to each other, and ability to bind strongly and form new types of gels, nonwoven sheets and ultrasoft membranes. We will then show how alginate soft dendritic colloids can be used in hierarchical hydrogel networks with mechanical properties resulting from synergistic combination of the colloidal and molecular networks (Nature Comm., 12:2834, 2021). These alginate “homocomposite” hydrogels have remarkable mechanical properties due to the dendricolloid microgel network, allowing to 3D print and inject them into architectures with increased toughness. The morphological similarity of the dendricolloids to the gecko lizards’ setae endows them with excellent dry adhesion and cohesion abilities. We will discuss the perspectives of using the dendricolloids in new superhydrophobic, superhydrophilic and icephobic coatings, microplastics-capturing water cleaners and other types of functional materials being developed in our group.

Mon-M1-02

Mechanistic Insight into Electric-Field Induced Adhesion of Polyelectrolyte Hydrogels

Leah Borden, Srinivasa Raghavan

Department of Chemical and Biomolecular Engineering, University of Maryland College Park

This work will present studies from our lab on the electrically induced adhesion of oppositely charged hydrogels 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 ~ 10 V DC, the two gel strips form a strong adhesive bond. When the polarity of the electrodes is reversed, the phenomenon is reversed, and the gels can be easily detached. While the above phenomenon of 'electro-adhesion' has been reported before between two hydrogels, the mechanism governing this adhesion has remained elusive. Speculative mechanisms have been proposed however these have not been tested experimentally. Following a recent discovery by our lab that the phenomena of electroadhesion is much more widespread; different types of soft materials can be electroadhered to polyelectrolyte hydrogels such as tissues and fruit, the mechanism becomes important to understand. The fundamentals governing electroadhesion may have a significant impact in medical applications of electroadhesion such as in tissue repair by hydrogel patches. Therefore, in this talk we will explore various aspects of electro-adhesion's mechanism, using gel to gel adhesion as a model.

Mon-M1-03

Interfacial strength dominates microscale fold formation in adhesive, soft static friction

Justin Glover [1], Xingwei Yang [2], Rong Long [2], Jonathan Pham [1]

[1] Chemical and Materials Engineering, University of Kentucky[2] Mechanical Engineering, University of Colorado Boulder

Studies on friction started centuries ago, yet an understanding of small-scale static friction on soft materials remains incomplete. This is partially due to the diversity in material properties that exist in soft materials, as well as with challenges in experimentally visualizing and probing the mechanics. We employ a unique approach that includes lateral force microscopy combined with confocal microscopy to investigate the mechanism of static friction for a microscopic contact on a soft, adhesive surface. In our specific experiments, a microscopic glass particle is placed into contact with a soft, adhesive polydimethylsiloxane (PDMS) surface, which is then pulled laterally. Confocal microscopy imaging reveals the emergence of seemingly similar folding at the leading edge when samples are light-aged or exposed to UV-ozone. In both sample treatment cases, a high peak lateral force is recorded using lateral force microscopy, leading to the expectation that the work of adhesion increases. However, the light-aged samples are found to have a low pull-off adhesion distance in the normal direction, while the UV-ozone samples display a large pull-off adhesion distance. Unexpectedly, this means that the cause of folding is not solely defined by the pull-off adhesion since folding occurs on samples with high and low pull-off distances. To investigate how adhesion relates to the lateral resistance and the formation of folds, we employ simulations through finite element analysis. Often, adhesive interactions are bucketed into an adhesive energy; however, our simulations show that adhesion energy alone is not sufficient to predict the nucleation of folds or to predict the lateral resistance. Rather, the specific parameters of interfacial strength and separation must be considered. In this case, the adhesion energy is defined as the traction stress integrated over the distance at the interface upon applying lateral motion. Together, our experimental and numerical results demonstrate that the maximum interfacial stress, not the adhesion energy, plays a dominating role in the emergence of self-contacting folds.

Mon-M1-04

Polydimethylsiloxane brushes and their exciting properties in the fields of adhesion and wettability

Kevin Golovin

University of Toronto

The difference between liquids and solids is intuitive and learned from a young age. Liquids can flow, exhibit limited cohesion, and cannot support shear stress. Solids take on three-dimensional, rigid shapes and exhibit strength, stiffness, and toughness. By challenging these definitions, hybrid materials with fascinating material properties may be engineered. In this talk I will discuss the ongoing work in my group investigating nanometer-thick polydimethylsiloxane (PDMS) ‘brushes’, i.e. linear polymer chains covalently grafted to a substrate at only one end. As engineers, we explore these interesting interfaces from both an applied and fundamental perspective. As PDMS is well above its glass transition temperature, the chains exhibit ‘liquid-like’ behaviour that leads to anomalous properties including (1) the repellency of solvents that absorb into and swell bulk PDMS, including liquids with lower surface tension than the surface energy of PDMS, (2) adhesion to various solid foulants orders of magnitude below bulk PDMS, and (3) quasi-rheological properties akin to liquid PDMS but while remaining covalently tethered. Applications of such functional surfaces including oil-repellency without the use of perfluorinated compounds, anti-icing materials, materials lacking contact angle hysteresis, and grease resistant food packaging.

Mon-M1-05

Cooperative Hydrogen Bonding - Towards Robust Underwater Adhesion

Zach Lamberty, Joelle Frechette

Department of Chemical and Biomolecular Engineering, University of California, Berkeley

Developing resilient underwater adhesives can be challenging, especially if contact between interacting surfaces needs to be made in water. For example, epoxy polymeric adhesives have found a variety of uses due to their exceptional adhesive strength, toughness, and applicability to many types of substrates.1 However, they suffer from a great reduction in adhesion when applied in wet environments, severely limiting their applications.2 Previous work has compared the effect of various surface treatments on the adhesive strength of DGEBA epoxy adhesives to aluminum panels in dry and hot/wet conditions. Surfaces treated with the tris buffer (tris(hydroxymethyl)aminomethane) outperformed untreated and silane/DOPA treated surfaces in both dry and wet lap shear tests. Cooperative hydrogen bonding was hypothesized as the possible mechanism for enhanced adhesion.3 In this presentation we report on our experiments characterizing the contribution of cooperative hydrogen bonding on underwater adhesion. We characterized adhesion between oligomers modified with a trivalent hydrogen bond group (tris, or tris(hydroxymethyl)aminomethane) in their backbones. We found that underwater adhesion of these oligomer was comparable to adhesion in air. We hypothesize that the strong underwater adhesion is due to the presence of the tris group and that the underlying mechanism for the strong adhesion is cooperative hydrogen-bonding. To validate this hypothesis, we varied the detachment rate during the detachment of 100 nm oligomer from mica (or aluminum). Beyond adhesion measurements we also monitored the contact radius and crack velocity. By varying the rate of crack propagation during detachment the lifetime of interfacial bonds can be determined, allowing us to characterize the kinetics of adhesive bonds in situ. We then relate rate-dependent adhesion to a model4 for cooperative hydrogen bonding suggesting that through cooperation, polymer hydrogen bonds can compete with interfacial water to maintain adhesive interactions under water. Beyond demonstrating strong underwater adhesion, these results also provide a methodology to connect intermolecular interactions to macroscale surface forces measurements that can be extended to adhesives with different chemistry.

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Mon-P1-01

Surface-Enhanced Raman Scattering (SERS) Taster: A Machine Learning-Driven Multireceptor Platform for Multiplex Profiling of Wine Flavors

Yong Xiang Leong, Yih Hong Lee, Charlynn Sher Lin Koh, Gia Chuong Phan-Quang, Xuemei Han, In Yee Phang, Xing Yi Ling

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Integrating machine learning with surface-enhanced Raman scattering (SERS) accelerates the development of practical sensing devices. Such integration, in combination with direct detection or indirect analyte capturing strategies, is key to achieving high predictive accuracies even in complex matrices. However, in-depth understanding of spectral variations arising from specific chemical interactions is essential to prevent model overfit. Herein, we design a machine-learning-driven "SERS taster" to simultaneously harness useful vibrational information from multiple receptors for enhanced multiplex profiling of five wine flavor molecules at parts-per-million levels. Our receptors employ numerous noncovalent interactions to capture chemical functionalities within flavor molecules. By strategically combining all receptor–flavor SERS spectra, we construct comprehensive "SERS superprofiles" for predictive analytics using chemometrics. We elucidate crucial molecular-level interactions in flavor identification and further demonstrate the differentiation of primary, secondary, and tertiary alcohol functionalities. Our SERS taster also achieves perfect accuracies in multiplex flavor quantification in an artificial wine matrix.

Mon-P1-02

Drop Wetting and Sliding on Soft, Swollen Elastomers

Zhuoyun Cai [1], Jonathan Pham [1], Artem Skabeev [2], Svetlana Morozova [3]

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Soft, slippery surfaces have gained increasing attention due to their wide range of potential applications, for example in self-cleaning, anti-fouling, liquid collection, and more. A design approach in creating slippery surfaces is using swollen elastomers, which are polymer networks swollen with a fluid lubricant. Understanding the physics of soft surface interaction is important for fundamental soft matter physics, biomaterials, and adhesives. Our research experimentally investigates the wetting behavior on soft infused networks, with the aim of providing insight towards a physical description, and with a particular focus on low modulus elastomers (~100 kPa and less). By using silicone oil–swollen polydimethylsiloxane (PDMS) elastomers, we investigate both static and dynamic wetting situations on these swollen elastomers. In the static wetting case, we develop a new approach to visualize the crosslinked polymer and swelling lubricant separately by employing fluorescent molecules and confocal microscopy. By controlling the degree of crosslinking and the swelling ratio, we show that the swelling fluid separates from the polymer network near the water-elastomer contact line, which depends on details of the material properties. The fluid separation height increases with swelling, while the network deformation height decreases, demonstrating a synergy between network deformation and fluid separation at the three-phase contact line. In the dynamic wetting state, we study how the polymer network density and degree of swelling relate to the pinning force of a water drop. Specifically, we study when a water drop sticks or slides on a vertical, silicone oil–swollen elastomer; gravity drives the drop to slide while surface interactions promote drop adhesion. At a particular drop volume, gravity overcomes drop pinning and the drop slides. We find that the critical drop volume for sliding decreases when increasing the degree of swelling. This is likely associated with oil separating from the bulk substrate when it encounters a water drop, lubricating the surface and decreasing the pinning force. Our results demonstrate the importance of considering the fluid inside of gels when investigating both the static and dynamic wetting of soft, lubricant-infused elastomeric surfaces.

Mon-P1-03

Transport of a Binary Electrolyte in a Cylindrical Pore: Effects of Overlapping Double Layers and Asymmetry in Ion Valences and Diffusivities

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Transport of electrolytes near charged surfaces is important in many physical applications, such as electrokinetic remediation, electrochemical carbon capture and energy storage, among others. Many of these applications employ porous geometries to maximize charged surface area. In porous geometries, the formation of electric double layers adjacent to the surfaces produces electric field screening, which in turn impacts transport. Nevertheless, most studies in this context represent electrodes as flat plates and consider valence- and diffusivity-symmetric electrolytes. Extending these findings to incorporate the simultaneous effects of arbitrary Debye lengths and asymmetric electrolytes is crucial to understanding and optimizing supercapacitor charging. In this talk, we will present a new theoretical approach to model ion transport in a pore for a binary electrolyte with arbitrary Debye length, ionic valences, and ionic diffusivities [1, 2]. This framework is built upon a perturbation expansion of the Poisson-Nernst-Planck equations for low applied potentials. A fundamental consequence of asymmetric diffusivities is the emergence of nontrivial salt dynamics even at low potentials – which could be exploited for desalination applications – coupling the charge and salt density dynamics. We are able to obtain an analytic solution for the charge, salt, and potential profiles when the resistance of the static diffusion layer adjacent to the pore may be neglected. A key takeaway of our analysis is the identification of two timescales governing the charging dynamics of asymmetric electrolytes, dependent on the valences, diffusivities, and the Debye length. This dependence governs the transition of a timescale set by ambipolar diffusivity at thin double layers to one determined by cation and anion diffusivities at overlapping double layers and is controlled by valences and diffusivities at intermediate Debye lengths. This parameter dependence sets a disconnect between the charging timescale and the capacitance of the pore which is overlooked in widely used transmission line representations.

[1] Henrique, F., Zuk, P. J., & Gupta, A. (2022). Charging Dynamics of Electrical Double Layers Inside a Cylindrical Pore: Predicting the Effects of Arbitrary Pore Size. Soft Matter, 18(1), 198-213
[2] Henrique, F., Zuk, P. J., & Gupta, A. (2022), submitted

Mon-P1-04

Unravelling the Mysterious Behaviour of Tetrahedral Liquids: The Topological Nature of the Liquid-Liquid Phase Transition

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The origin of the anomalous thermodynamic properties of liquid water has been a topic of fierce debate over the last four decades, with a consensus yet to be established. One hypothesis, which has received strong support from both numerical and experimental studies, is that there is a first-order liquid-liquid phase transition (LLPT) line for water in the supercooled region of its pressure-temperature phase diagram, terminating at a liquid-liquid critical point (LLCP). However, direct observation of the LLPT in experiments has proved elusive due to rapid crystallization into ice from the deeply supercooled liquid. In order to develop a model system that is amenable to experimental investigation and displays a LLPT, here we design a colloidal analog of liquid water. Using Monte Carlo simulations, we show that this colloidal water model -- a tetrahedral network liquid self-assembled from triblock patchy colloidal particles via tetrahedral clusters -- captures the anomalous thermodynamic behavior of supercooled water and displays a LLCP. By introducing a topological order-parameter, we remarkably reveal that the LLPT in colloidal water is between two topologically distinct liquid networks, thus addressing a long-standing puzzle in the tale of two liquids: what fundamentally distinguishes the two liquids? Finally, we show that this order-parameter is not only able to describe the LLPT for colloidal water, but also for two widely used molecular models of water, thereby establishing the generality of the topological description of LLPT in tetrahedral liquids, which should have far-reaching implications in understanding LLPTs.

Mon-P1-05

Porous microellipsoids cloak interparticle capillary interactions

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Colloidal assembly at immiscible fluid interfaces is an effective “bottom-up” method of creating interesting two-dimensional (2D) micro/nano-structures because large pinning energies force the constituent pieces into alignment along the plane of the interface. However, the capillary forces between physically-anisotropic micron-scale particles pinned to fluid interfaces overwhelm all other naturally-present forces and lead to strong, orientationally-specific, interparticle attractions. Reducing the magnitude of the interparticle capillary energy as well as its dependence on in-plane particle orientation is key to the controlling the resultant assemblies and creating more complicated 2D structures. The work presented here studies the how the introduction of nanoscopic chemical and physical heterogeneity to the surface of polymer microellipsoids alters the interparticle interactions when they are pinned at an aqueous-air interface. We use a combination of Mirau interferometry and video microscopy to show that porous micron-sized ellipsoids at an aqueous-air interface behave in fundamentally different ways than their smooth counterparts. Specifically, the capillary interaction energy is reduced by over an order of magnitude, making porous ellipsoids ideal building blocks for interfacial assembly. Mirau interferometry is used to measure the interfacial deformation surrounding a single interfacially pinned particle with ±1 nm resolution along the axis perpendicular to the fluid interface. Particles with a nanoscale porous network show no quadrupolar deformation of the fluid interface, a trademark of smooth, homogeneous, colloidal ellipsoids due to Young’s law. Eliminating the quadrupolar deformation via surface engineering is direct evidence of decreasing interparticle attraction, since the magnitude of the capillary interaction energy is directly proportional to the magnitude of the quadrupolar deformation squared. This observation is confirmed using video microscopy monitoring of the trajectories of two particles as they approach towards one another. This method indirectly quantifies the capillary attraction by equivalence with viscous drag opposing particle motion. In agreement with the interferometry measurements, deducing the capillary interaction energy via this method supports over an order of magnitude decrease in the capillary attraction for porous ellipsoids relative to homogeneous, smooth, ellipsoids of similar size and aspect ratio. Moreover, these measurements provide direct evidence of a shorter-range attraction between porous ellipsoids relative to homogeneous, smooth ellipsoids. The interactions of particles with a nanoscale porous network also appear to have no orientational specificity, in stark contrast to the homogeneous particles which have increasingly constrained

rotational degrees of freedom upon approach as well as specific final arrangements. Taken together, these results indicate that incorporating nanoscale surface topography into anisotropic particles is an effective avenue to control interparticle interactions, resulting in particles with similar overall size and aspect ratio behaving in stark contrast depending on their surface topography. As a result, such particles are promising candidates as building blocks for assemblies of anisotropic particles with long-range orientational and translational order.

Mon-P1-06

Introducing Patchy MOF Particles for Precise, Hierarchical, and Reconfigurable Colloidal Self-Assembly

Dengping Lyu, Wei Xu, Yufeng Wang

Department of Chemistry, The University of Hong Kong

Colloids with surface patches (or patchy particles) can bind and assemble with directionality. However, the bonding between the usually high-symmetry, dome-shaped patches is not precise, as it cannot lock the exact position and orientation of the relevant particles. In this talk, I will introduce a distinct class of patchy particles, in this case, patchy MOF particles, that exploit the morphological and chemical information of metal-organic frameworks (MOFs). Synthesized by a facet-selective heteroepitaxial growth strategy, the patchy MOF particles feature reduced symmetry and possess a polyhedral matrix, flat hexagonal patches, as well as anisotropic surfaces chemistry. Guided by these shape/chemical information and mediated by a site-selective liquid-bridging interaction, the patchy particles self-assemble into hybrid supra-colloidal (or supra-framework) structures (for example chains) with unprecedented precision. The position and orientation of the particles within assemblies are fully coordinated and precisely aligned. Moreover, I will show that, by utilizing a thermal responsive swelling agent, the assembled hybrid pMOF superstructures can be thermally actuated to undergo reversible shape changes. Our strategy not only defines new modes of colloidal bonding, but also provides a powerful means toward creating hierarchical and multicomponent MOF materials with advanced properties.

Monday, July 11th | 13:00 - 14:40 | A2-Active Matter

Mon-A2-01

Active fluids of colloidal rollers

Petia Vlahovska

Northwestern University

Birds and fish often form flocks and schools that move around like fluid when viewed on a scale much larger than the individuals. Similar large-scale coherent motions have been observed with self-propelled micro-particles such as bacteria and motile colloids. Recently, the Quincke instability (spontaneous spinning of a dielectric particle in an applied uniform DC field) has attracted great interest as a means of propelling colloids, by simply letting the particles roll on a surface. Quincke rollers swarm and exhibit directed motion in microfluidic channels or form a vortex in a circular confinement (Bricard et al, Nature 2013, Nature Comm. 2015). In this talk, I will present our experiments showing how Quincke rollers can be designed to perform Run-and-Tumble-like locomotion mimicking bacteria such as E. coli (Karani et al, Phys. Rev. Lett. 2019). Populations of these Quincke random walkers self-organize and exhibit behaviors reminiscent of bacterial suspensions such as dynamic clustering and mesoscale turbulent-like flows, and new collective dynamics such as emergent multi-vortex states (Zhang et al. Soft Matter, 2021). When enclosed in a drop, the Quincke rollers drive strong shape fluctuations and drop motility resembling amoeba crawling (Kokot et al., Comm. Phys, 2022). This research has been supported by National Science Foundation award DMR-2004926.

Mon-A2-02

Rolling of Janus particles in magnetic fluids

Mustapha Bello, Ahmed Al Harraq, Bharti Bhuvnesh

Cain Department of Chemical Engineering, Louisiana State University

Using uniform time-periodic magnetic fields, we demonstrate the coherent dynamic surface rolling of Janus particles with chain(s) of nanoparticles in magnetic fluid. We show the rolling and tumbling of a single Janus particle with translational motion at a relatively low magnetic field. As the magnetic field increases, Janus particles motion changes to a translating vortex motion with the formation of a chain of nanoparticles at the apex of the Janus side. The nanoparticles chain translates in tandem with the Janus particle as it rolls on the surface of the substrate. By tuning the number density of Janus particles, we further demonstrated the dynamic assembly of multiple Janus particles and their chains. Our study provides a fundamental link between the structure and dynamics of colloids subjected to external magnetic field, which both acts as an external energy source and structure directing force.

Mon-A2-03

Arrested motility states in populations of shape anisotropic active Janus particles

Jaideep Katuri [1], Ruben Poehnl [2], Andrey Sokolov [1], William Uspal [2], Alexey Snezhko [1]

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The emergence of large-scale collective phenomena from simple interactions between individual units is a hallmark of active matter systems.[1] Active colloids with alignment-dominated inter-particle interactions tend to develop orientational order and form motile coherent states, such as flocks and swarms.[2] Alternatively, a combination of self-propulsion and excluded-volume interactions results in self-trapping and active phase separation into dense clusters.[3] In this work, we reveal an unconventional collective phenomenon of arrested motility states in ensembles of shape-anisotropic active colloidal particles. Metallo-dielectric Janus particles self-propel in liquid solution when exposed to AC electric fields via induced charge electrophoresis (ICEP).[4] We find that systems of discoidal active ICEP particles spontaneously form aggregates of reduced motility – an arrested motility phase – at high particle densities. We demonstrate that the shape asymmetry of the particles promotes hydrodynamically-assisted formation of active particles' bound states in a certain range of excitation parameters, ultimately leading to a spontaneous collective state with arrested motility. Unlike the jammed clusters obtained through self-trapping, the arrested motility phase remains sparse, dynamic, and reconfigurable. The demonstrated mechanism of phase separation seeded by bound states formation in ensembles of oblate active particles is generic and should be applicable to other active colloidal systems.

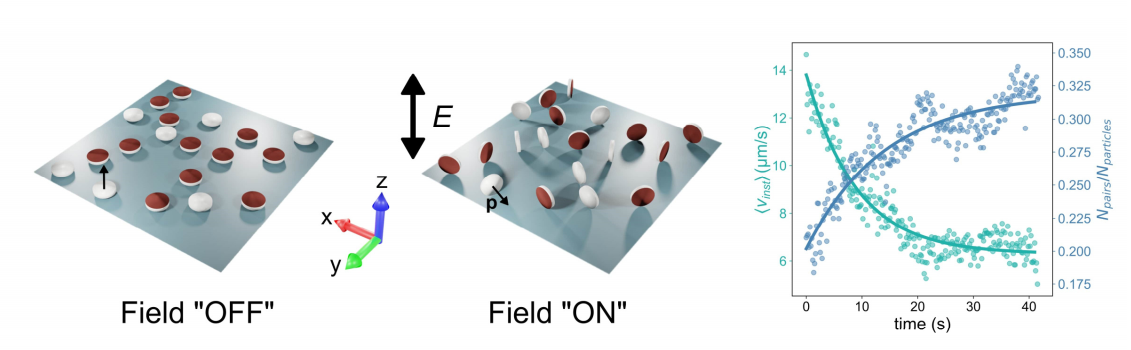

Figure 1: **Arrested motility of shape anisotropic active Janus particles.** *Left* Schematic of disk shaped particles made of SU-8 (white) with axisymmetric coverage by a metal layer (brown) placed between two conductive ITO glass slides (grey, only bottom glass shown). In the absence

of an AC field, the particles settle face down on the glass slide. When an AC field in applied, the Janus particles orientation (normal to the disk) becomes perpendicular to the direction of the applied field (*Middle*). *Right* Time evolution of average ensemble velocity (cyan) and number of bound pairs (blue) in the system

(1) Ramaswamy, S. The Mechanics and Statistics of Active Matter. Annu. Rev. Condens. Matter Phys. 2010, 1 (1), 323–345. (2) Vicsek, T.; Czirók, A.; Ben-Jacob, E.; Cohen, I.; Shochet, O. Novel Type of Phase Transition in a System of Self-Driven Particles. Phys. Rev. Lett. 1995, 75 (6), 1226–1229. (3) Cates, M. E.; Tailleur, J. Motility-Induced Phase Separation. Annu. Rev. Condens. Matter Phys. 2015, 6 (1), 219–244. (4) Gangwal, S.; Cayre, O. J.; Bazant, M. Z.; Velev, O. D. Induced-Charge Electrophoresis of Metallodielectric Particles. Phys. Rev. Lett. 2008, 100 (5), 058302.

Mon-A2-04

Multimodal microwheel swarms for targeting in three-dimensional networks

Coy Zimmermann [1], Paco Herson [2], Keith Neeves [3, 4], David Marr [1]

[1] Department of Chemical and Biological Engineering, Colorado School of Mines[2] Department of Anesthesiology, University of Colorado Denver | Anschutz Medical Campus[3] Department of Bioengineering, University of Colorado Denver | Anschutz Medical Campus[4] Department of Pediatrics, University of Colorado Denver | Anschutz Medical Campus

Traditional drug delivery requires drug to be administered throughout the body which limits therapeutic benefit due to harmful side effects at high concentrations. A promising alternative is using drug-laden microscale bots that directly target the diseased area. We have previously demonstrated that magnetically actuated colloidal microwheels (µwheels) assembled in situ from superparamagnetic 4.5 µm beads can translate rapidly and be well directed. Here we show that, at high concentrations, µwheels assemble into swarms that, depending on applied magnetic field actuation patterns, can be designed to transport cargo, climb steep inclines, spread over large areas, or provide mechanical action. Characteristic velocity and radius distributions for these µwheel swarms are obtained using particle tracking image analysis and a custom rotating microscope/magnetic actuation system. In addition, we demonstrate the ability of swarms to navigate complex three-dimensional branching microenvironments. Taking inspiration from cerebrovascular stroke models, swarms are actively driven through 3D printed branching vascular networks. A targeting efficiency, defined as the number of beads captured in a target vascular branch divided by the total number of beads injected, of ~38% was achieved in branching arterial networks with multiple turns. This demonstrates reliable targeting of colloidal payloads with weak magnetic fields (5 mT) over macroscale length scales (40 mm). Lastly, targeting efficiency is predicted by simulating swarm translation in the network, allowing application to arbitrary vascular networks and paving the way to µwheel targeting in vivo.

Monday, July 11th | 13:00 - 14:40 | C2-Colloids, Macromolecules, and Surfaces in Life Science

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Mon-C2-01

Capillary-osmotic wearable patch assays for sweat analysis of K+, lactate and cortisol

Sneha Mukherjee, Sabrina Pietrosemoli Salazar, Tamoghna Saha, Michael D. Dickey, Orlin D. Velev

Department of Chemical and Biomolecular Engineering, North Carolina State University

Our group has introduced a simple and efficient platform for sweat sampling and handling based on osmotic-capillary principles and paper microfluidics. It can harvest sweat noninvasively without the necessity of active perspiration. The patches use three robust physical effects: osmosis, capillary wicking, and evaporation. Osmotic sweat withdrawal is achieved by interfacing the skin with a hydrogel disk containing concentrated solute. The extracted sweat is transported on a paper strip via capillary wicking and disposed on an evaporation pad. We will discuss how these principles were applied in the development of a class of simple and inexpensive wearable skin patches for analysis of K^+, lactate and cortisol, based on lateral flow assays (LFAs). Our LFA platform is composed of silicone, a paper microfluidic conduit attached to a commercial K^+ strip, and a polyacrylamide hydrogel with a higher osmotic strength than sweat. The polyacrylamide hydrogel patch is equilibrated with glucose and glycerin solutions to build up the desired osmotic strength. Glucose as an osmolyte has the highest driving pressure. In-vitro testing on gelatin-based model skin (pre-infused with a known quantity of K^+ ions) allowed calibrating the platform with model sweat. Human trials revealed that it can function with very low sweat volumes (~2-3 µL) and can detect K^+ levels from human skin under moderate-intensity exercise and rest. We also observed that sweat potassium levels are independent of the sweat rate and proportional to blood. We are also developing wearable skin LFAs for detection of cortisol (in sweat) as a key stress biomarker. The patch could also efficiently sample sweat lactate directly from the surface of the skin. The results show that lactate in sweat increases with exercise as a direct result of muscle activity. We are also working on interfacing the paper platform with electrochemical sweat lactate sensors, which will allow long-term continuous electronic readout of the results from the wearable interface. Thus, the platform can find a broad range of applications in both self-contained patch assays and electronically monitored long-term health trackers.

Mon-C2-02

The Determination of Metal Ions using a Nanoparticle-Based Liquid–Liquid Extraction Method

Tyler Sodia [1], Kevin Cash [1, 2]

[1] Quantitative Biosciences and Engineering[2] Chemical and Biological Engineering

Liquid phase extraction methods that use optically responsive ligands enable cost-efficient and user-friendly techniques for measuring analytes. However, these approaches are limited by the excessive use of organic solvents and multi-step procedures. In this work, we developed an alternative extraction approach by replacing the macroscopic organic phase with hydrophobic polymeric nanoparticles that are soluble in an aqueous feed. The concentration of analytes in our polymeric nanoparticle suspensions are governed by similar partition principles as liquid–liquid phase extraction techniques done with bulk solvents. By encasing optically responsive metal ligands inside the nanoparticles, we introduce a one-step metal quantification assay based on traditional two-phase extraction methodologies. As a proof of concept, we encapsulated bathophenanthroline inside the particles to extract and then quantify Fe^{2+} in a dissolved supplement tablet and creek water with colorimetry. These Fe^{2+} nanosensors are sensitive, selective and can adopt a fluorescent readout by adding a fluorophore into the particle core. To show that this new rapid extraction assay is not exclusive to measuring Fe^{2+}, we replaced bathophenanthroline for either 8-hydroxyquinoline or bathocuproine to measure Al^{3+} or Cu^{+}, respectively, in water samples. Utilizing this simple nano-extraction approach will allow users to rapidly quantify metals of interest without the drawbacks of large-scale phase extraction approaches while allowing for the expansion of phase extraction methodologies into a larger variety of research areas.

Mon-C2-03

A Prussian Blue Enhanced Carbon Nanotube Composite for Disease Biomarker Detection

Charles Chusuei, Raja Pandey

Middle Tennessee State University

A Prussian Blue (PB) zinc oxide (ZnO) nanoparticle carboxylic acid-functionalized multiwalled carbon nanotube (PB/ZnO/COOH-MWNT) composite was fabricated for the detection of dopamine (DA) and hydrogen peroxide. ZnO nanoparticles were tethered to COOH-MWNTs using sonication. Upon attachment of the PB to the ZnO/COOH-MWNTs, which consisted of ZnO nanoparticles 13 nm in diameter, the ZnO coalesced into larger clusters with an average diameter of 573 ± 4 nm. Current response versus various concentrations of DA was measured using chronoamperometry. The optimum conditions for DA measurements were at pH 7.0 using the oxidation current. The sensor has a linear dynamic range from 10 to 900 μM with a limit of detection of 0.378 ± 0.015 μM, suitable for practical neuroblastoma screening at the lower concentration range and process controls for polydopamine synthesis at the upper concentration range, important for modifying polymeric membranes for water purification. The standard addition method (SAM) was coupled with chronoamperometric sensing (CA) to overcome these obstacles. CA SAM showed the ability to accurately measure hydrogen peroxide within the 1-21 μM range, suitable for monitoring cancer cell apoptosis and offering analytical advantages over standard enzyme-linked immunosorbent assays (ELISA) for rapid, matrix-effect-free analysis.

Mon-C2-04

Detecting label-free SARS CoV-2 using high throughput analysis of colloidal suspensions

Valeria Milam, Mary Catherine Adams

School of Materials Science and Engineering, Georgia Institute of Technology

Double-stranded probes typically enable superior target specificity over single-stranded probes; however, care must be exercised to ensure the right balance of stability and responsiveness of the double-stranded probe to the target of interest. Studies involving double-stranded probes typically involve fluorescence spectroscopy of oligonucleotide duplexes initially in a quenched or signal-off state in a solution. Ideally, conversion to a signal-on state only occurs in the presence of specific, unlabeled target sequences. Here, we explore the overall stability and selective responsiveness of a family of 20 candidate locked nucleic acid (LNA) and DNA double-stranded probes immobilized on microspheres. Using flow cytometry as our quantitative tool, each microsphere suspension is rapidly (~1 minute per suspension) interrogated to measure the overall stability as well as responsiveness to unlabeled SARS-CoV-2 RNA and ~243 similar, yet imperfectly-matched RNA sequences serving as model variants. While clear and surprising trends in stability and RNA target responsiveness are evident across the sequence parameter space explored here, one double-stranded probe system emerged as highly stable, yet specifically responsive to SARS-CoV-2 RNA.

Mon-C2-05

It’s a trap!: acoustically trappable microparticles for immunoassays in a pipette

Cooper Thome, John Fowle, C. Wyatt Shields IV

Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, 80303, USA

Biosensing is an essential part of patient diagnosis, pandemic response, and disease management; however, many biosensing techniques require complex preparation and processing steps. For example, enzyme-linked immunosorbent assay (ELISA) is considered the gold standard for quantitative biomarker detection due to its high sensitivity and specificity, but the assay includes numerous blocking, labeling, and washing steps that require significant user engagement for large portions of the assay (up to several hours). Here, we present a simple microparticle-based assay to rapidly isolate and purify biomarkers from whole blood in a handheld pipette for sensitive and streamlined biomarker detection in under an hour and fifteen minutes. A key aspect of this technology is the preparation and use of functional negative acoustic contrast particles (fNACPs), a unique set of acoustically responsive and modularly functionalized microparticles. fNACPs can be decorated with a range of biorecognition motifs (e.g., antigens, antibodies, aptamers) for the specific capture of target biomarkers from whole blood. Owing to their modular functionalization, fNACPs can capture a variety of biomarker targets. After capture, targets can be labeled in situ by fluorescent secondary antibodies and analyzed by flow cytometry. Also, due to the poly(ethylene glycol) linkers between the particle surfaces and capture antigen, nonspecific adsorption of biomarkers and secondary antibodies is extremely low at physiological concentrations. We demonstrate decoration of fNACPs with ovalbumin (OVA) for the capture and detection of anti-OVA immunoglobulin G (IgG) antibodies at picomolar levels when analyzed by flow cytometry, a sensitivity competitive with commercial ELISAs. The second major innovation of the presented technology is the handheld pipette, which contains an acoustofluidic trapping channel. The trapping channel establishes a half-wavelength acoustic standing wave across channel, which yields a pressure node along the center of the channel and antinodes along the walls of the channel. Red blood cells and white blood cells have positive acoustic contrast factors and thus experience primary acoustic radiation forces that guide their displacement toward the node of the standing wave. However, fNACPs are forced toward the antinodes of the standing wave due to their negative acoustic contrast, where they are trapped by secondary acoustic radiation forces. We show that the discriminant forces acting on fNACPs and blood cells enables their efficient (over 99%) separation in short timescales (under 40 seconds). By integrating the acoustofluidic trapping channel and multiple assay buffer chambers into the handheld pipette, all fNACP-based assay

steps can be carried out in the pipette with minimal user engagement. Subsequent analysis of fNACP fluorescence via flow cytometry enables rapid assay results, which provides a quantitative measure of target biomarker concentration in samples. Using the acoustofluidic pipette, we demonstrate a rapid and sensitive fNACP-based assay for detection of anti-OVA IgG from whole blood, with minimal sample preparation, all in under an hour and 15 minutes. Because of their versatile functionalization and efficient biomarker capture, fNACPs are a promising platform for multiplexing the specific capture and sensitive quantification of numerous biomarkers in a single assay.

Monday, July 11th | 13:00 - 14:40 | D2-Self and Directed Assembly

Mon-D2-01

Harnessing Coulombic Forces to Guide Colloidal Self-Assembly

Stefano Sacanna [1], Theodore Hueckel [1], Jeremie Palacci [2], Glen Hocky [1]

[1] New York University[2] UCSD

From snowflakes to nanoparticle superlattices, a menagerie of complex structures emerge from simple building blocks attracting each other with Coulombic forces. On the colloidal scale, however, this self-assembly feat is not easily accomplished. Although many colloids bear an innate surface charge, their strong electrostatic attraction is not directly suitable for crystallization. Instead, particles must be finely crafted to serve as self-assembling units. In this talk, I'll show the robust assembly of crystalline materials from common suspensions of oppositely charged colloids through a generic approach which we refer to as polymer-attenuated Coulombic self-assembly. I will demonstrate that, when particles are held separated at specific distances by a neutral polymer spacer, the attractive overlap between oppositely charged electrical double layers can be systematically tuned, directing particles to disperse, crystallize, or become permanently fixed on demand.

Mon-D2-02

Isomerization in colloidal clusters

Hashir Gauri, Ahmed Al Harraq, Bhuvnesh Bharti

Cain Department of Chemical Engineering, LSU

Assembly of simple two-dimensional colloidal clusters of six particles in thermal equilibrium favors the least symmetric shapes which is dictated by the free energy minima and higher entropy. However, we test this observation further by examining the assembly of clusters in magnetic nanoparticle dispersions to modulate competing attractive and repulsive interactions between the colloidal particles. The long-range dipolar repulsions can be tuned by the strength of external magnetic field and gives extended control over the assembly of the clusters. In contrast, it is observed that the particles with acquired dipoles surrounding the two-dimensional clusters effect the assembly of cluster and favors the formation of highly symmetric triangle clusters instead. We further investigate the effect of the long-range repulsions induced in the system with varying ferrofluid concentration and magnitude of external magnetic field.

Mon-D2-03

New classes of soft magnetic microbeads by hierarchical assembly of nanoparticles confined in droplets

Abhirup Basu, Sarah Costello, Orlin D. Velev

Department of Chemical and Biomolecular Engineering, North Carolina State University

Magnetic field driven colloidal assembly is a facile method for creating hierarchical structures. Paramagnetic particles acquire magnetic dipoles upon application of the magnetic field and interact to form varied structures, ranging from linear to higher-dimensional arrangements depending on the intensity and direction of the magnetic field. While the assembly of magnetic nanoparticles (MNPs) assisted by magnetic field in infinite geometries has long been established, little is yet known about how these particles interact in confined geometries. In the current study, directed assembly of iron oxide nanoparticles inside microdroplets of sizes ranging from 2 to 25 µm by using a static magnetic field was investigated. Liquid polydimethylsiloxane (PDMS) precursor embedded with MNPs was dispersed in a shear-thinning fluid to synthesize the microdroplets with randomly distributed nanoparticles. The controlled assembly of the MNPs was achieved by applying an external magnetic field, and then the microdroplets were crosslinked to form soft PDMS microbeads with embedded aligned nanoparticle structures. By changing the MNP concentrations from 1.25 wt% to 10 wt%, we discovered structural phase transitions inside the PDMS beads ranging from disconnected short chains to 2D linear chains to 3D networked bundles. It was found that below a critical microbead size, the MNPs did not align to form chains, and then the number of chains increased with the increase in the size of the PDMS microbeads. We established correlations between the number of chains formed inside the beads with the cross-sectional area of the beads. The number of chains increased linearly with the microbead size; interestingly, the number of chains decreased with increase in MNP concentration. Instead, the average cross-sectional area per unit chain was found to increase from 0.83 µm^2 to 8.39 µm^2 as the MNP concentration was increased from 1.25% to 5%, which supported the increase in the hierarchy of the assemblies from disconnected chains to 3D bundles. Our experimental results will be further validated by COMSOL simulations to provide a toolbox for modeling induced dipolar interactions in confined spaces. The soft magnetic microbeads that will be synthesized in large amounts could find applications in new responsive gels, 3D printed soft actuators, biomedical formulations, and novel drug delivery techniques.

Mon-D2-04

Directing the self-assembly of spherical block copolymer micelle solutions with low intensity magnetic fields

Michelle A. Calabrese, Grace Kresge

Chemical Engineering and Materials Science, University of Minnesota

Block copolymers (BCPs) are attractive for use in developing advanced materials due to their tunable properties and self-assembly via block chemistry, composition, and length. However, practical methods for processing BCPs into advanced materials with long-range order remain difficult, where techniques like magnetic field alignment are typically infeasible because of large required field strengths and the limited range of responsive chemistries. We recently discovered magnetic field-induced phase formation in weakly diamagnetic, coiled BCPs that cannot be attributed to traditional mechanisms of phase alignment. Here, stable ordered phases are created by temporarily applying weak magnetic fields (0.05-0.5 T) to low viscosity solutions of spherical BCP micelles, causing up to a six order of magnitude increase in the modulus that is stable upon field removal. Prior work on field-directed assembly of BCPs has required large field strengths ($B > 5$ T), use of rod-like blocks, substantial chain anisotropy, or combinations thereof to achieve field-induced responses, and has focused on alignment of a structure or phase with inherent anisotropy, which causes anisotropy in the magnetic susceptibility. However here, a thermally-reversible three-to-six order of magnitude increase in the suspension modulus is observed when low intensity fields ($0.05 \leq B \leq 0.5$ T) are applied to a number of aqueous polymers and oligomers, across a range of concentrations (5-60% wt). This anomalous behavior is reproducible across sample preparations, polymer batch, and supplier. Magnetic susceptibility and inductively coupled plasma measurements illustrate that the behavior is not due to impurities; in situ small angle x-ray and neutron scattering (SAXS/SANS) confirm that the response is not an artifact of the measuring device, confinement, or sample drying. While this technique produces both cubic and aligned phases, the absence of structural anisotropy in the micelle building blocks eliminates phase alignment as the primary driver of magnetic this fieldinduced phase creation. The anomalous rheological response results from field-induced microstructure changes, which occur at field strengths far below that expected based on the polymer magnetic susceptibility anisotropy, $\Delta\chi$. Using a combination of magnetorheology (MR), small angle x-ray/neutron scattering, and Fourier transform infrared spectroscopy (FTIR) we show that in low intensity magnetic fields, the amphiphile chain conformation and polymer-solvent interactions are altered, facilitating structural transitions. While MR is performed at temperatures far below zero-field thermal phase transitions, the induced elastic modulus, G'_B, is up to 3 orders of magnitude larger than results from temperature ramps at 0 T. Distinct time- and field intensity-

dependent rheological features during magnetization suggest that phase selection and access to metastable states can be controlled by altering field strength and magnetization time. This new assembly strategy enables discovery of structures and dspacings inaccessible via traditional self-assembly, thus providing a platform for developing materials with preciselycontrolled dimensions and grain size at mild conditions and with minimal input from external fields.

Monday, July 11th | 13:00 - 14:40 | F2-Emulsions, Bubbles & Foams

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Mon-F2-01

Manipulating dynamic partitioning of surfactants into droplets to influence droplet phase behaviors

Wangyang Xue [1], Rebecca Balaj [1], Lauren Zarzar [1, 2, 3]

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Emulsions, which are mixtures of immiscible fluids, are widely used in cosmetics, pharmaceutical formulation, and oil recovery. Surfactants are used to stabilize emulsion droplets, and typically, surfactants are expected to be preferentially soluble and dispersed in the continuous phase. However, if the surfactant is also soluble in the dispersed phase, then surfactant partitioning can occur. It has been shown previously with bulk-scale equilibrium partitioning studies that some water-soluble non-ionic surfactants can reach higher concentrations in the oil phase than in the aqueous phase, even though such surfactants preferentially stabilize oil-in-water emulsions. In this work, we report on the partitioning of surfactants into microscale oil droplets of varying size and oil composition in non-equilibrium conditions, wherein the droplet itself is solubilizing and has a finite lifetime. Through the single-droplet chemical analysis based on quantitative mass spectrometry, we analyze the partitioning of surfactant into droplets over time and find that, for many cases, concentrations in the droplet phase reach higher concentrations than in bulk conditions. We discuss the effect of surfactant chemical structure and concentration, droplet size, and oil chemistry on the kinetics and degree of surfactant partitioning. As a result of surfactant partitioning, we find the accumulation of surfactant in oil droplets can significantly change the drop interfacial tension and droplet density. We show that the surfactant partitioning can be exploited to induce phase separation inside droplets to create complex emulsions and how that phase separation can be reversibly controlled with external stimuli such as light and pH change.

Mon-F2-02

Interaction of recently formed droplets with a micron-scale interface during spontaneous emulsification

Olivia M. Haider, Michael L. Davidson, Lynn M. Walker

Department of Chemical Engineering, Carnegie Mellon University

Spontaneous emulsification is the phenomenon where emulsion droplets form between two immiscible phases without any additional mechanical energy input or application of a thermal gradient. Previous work in our group showed the formation of droplets with siloxane-based surfactants at the dodecane-water interface. Several system parameters impacting emulsification rate and droplet type were determined. Droplets were shown to be interfacially active and remain at the oil-water interface with limited coalescence. The goal of this work is to measure the impact of spontaneously formed droplets on interfacial mechanics with siloxane-based surfactants. Using a microtensiometer platform, the dilatational modulus and interfacial tension are measured during the early stages of interfacial development as droplets form at the interface.

Mon-F2-03

Electroconvection and Electrohydrodynamic Induced via Corona Discharge for Contactless Emulsion Formation

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[1] Department of Mechanical, Industrial, and Manufacturing Engineering, The University of Toledo[2] Department of Electrical Engineering and Computer Science, The University of Toledo

Commercially available emulsion formation methods are not scalable and typically require significant power for operation. Here, a contactless method of emulsification via corona discharge is presented. Using a pin-to-plate electrode configuration, the corona discharge forms, creating an ionic wind and a non-uniform electric field. The ionic wind carries water droplets (formed by a humidifier) towards a ground electrode that is submerged inside a silicone oil medium, so-called electroconvection. The non-uniform electric field induces motion and circulates the silicone oil via electrohydrodynamic pumping. By these two effects, this contactless method enables the immersion of the water droplets into the moving oil medium, continuously forming a water-in-oil (W/O) emulsion. Impact of corona voltage, pin-to-plate distance, and oil thickness on the size and stability of the formed emulsions are studied, leading to an optimum emulsion formation condition. It is found that a corona voltage of 10 kV, oil thickness of 8 mm, and horizontal and vertical pin-to-plate distances of 20 mm and 15 mm, respectively results in more uniform emulsions with water droplet sizes of 8 – 12 μm.

Mon-F2-04

Continuous Emulsification in 3DP Fixed Beds: Drop Size Distribution and Emulsification Efficiency

Kaitlin Kay, Andres Hyer, Robert McMillin, James Ferri

Chemical and Life Science Engineering, Virginia Commonwealth University

Multiphase processes are important in a wide range of industries, including cosmetics and consumer products, automotive and petrochemicals, and fine chemicals and pharmaceuticals. Process intensification, PI, is a framework of improving the efficiency and reducing waste of processes, ranging in scope from a single unit operation to entire processes. A key principle in PI is to provide molecules with the same process experience. Multiphase processes present numerous challenges in accomplishing a uniform process experience; continuous processing is one approach used to address these challenges. Nearly all approaches that leverage continuous processing encounter issues that arise from the hydrodynamics associated with a unit operation. Therefore, it is advantageous to consider strategies that seek to optimize the hydrodynamics. Different applications in multiphase processing require customization. One approach to customizing device hydrodynamics is the use of additive manufacturing (AM). A distinct advantage to AM is that it affords nearly independent variation of the geometric parameters of a design. Therefore, using AM, it should be straightforward to customize the hydrodynamics of a unit operation. We built and tested fixed bed reactors capable of dispersing two immiscible phases using three dimensional printing (3dP). We characterized the hydrodynamics of these reactors in emulsification operations using pressure drop, drop size distribution, residence time distribution, and computed properties such as tortuosity and dispersion efficiency. We establish key relationships among fixed bed design variables and process performance metrics. In emulsification operations, other factors such as the concentration of emulsifying agent, oil to water volume ratio, and total volumetric flow rate also play a role. In this study, we report the effect of bed internal geometry and void fraction on emulsification efficiency and dispersion drop size distribution. We discuss a balance of heuristic design principles and a quantitative modeling frameworks to guide the design of fixed beds for dispersing one liquid into another.

Mon-F2-05

Stable Membraneless Complex Coacervate Emulsions

Shang Gao, Advait Holkar, Samanvaya Srivastava

Department of Chemical and Biomolecular Engineering, University of California, Los Angeles

In this presentation, we will discuss our progress in creating stable membraneless water-water emulsions comprising complex coacervate microdroplets. Complex coacervation is a liquid-liquid phase separation phenomenon driven by the electrostatic association of oppositely charged multivalent macromolecules in water, creating coacervate microdroplets enriched with charged moieties. These aqueous membraneless microdroplets possess numerous attributes desired in colloidal reactors and protocell models. However, the membraneless coacervate-water interface that facilitates many of the bio(techno)logical functions of the coacervate microdroplets also promotes their coalescence, resulting in their rapid coarsening and sedimentation. We will discuss our recently discovered strategy to stabilize complex coacervate microdroplets without introducing membranous sheaths around the droplets by utilizing the assembly of anionic comb polyelectrolytes at the water(coacervate)-water interface. We will demonstrate the tunability of microdroplet size, their months-long stability, and their ability to withstand high ionic strength environments. Selective sequestration of charged (bio)molecules (proteins and enzymes) into the crowded environments of stabilized coacervate microdroplets will be argued to affect a significant (up to 10-fold) and sustained acceleration of enzyme-mediated bioreactions. Aided by the low cost of the constituent polymers and the simplicity of the formulations, we will argue that the stabilized coacervate emulsions serve as efficient enzyme-encapsulants in economical, large-scale flow bioreactors.

Monday, July 11th | 13:00 - 14:40 | G2-Energy Systems

Mon-G2-01

Automated high-throughput synthesis of colloidal inorganic nanoparticles through sonochemical methods

Fabio Baum [1], Maria Politi [1], Cameron Tavakoli [2], Josiah S. Mace [2], Joshua Vasquez [3], Nadya Peek [3], Lilo D. Pozzo [1]

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In the current shift from fossil fuels toward clean energy sources, it is crucial to develop new materials for energy harvesting and storage. However, the time from initial studies to deployment of materials for use in society is typically very long (>10 years). Materials Acceleration Platforms (MAPs) are a research initiative to combine artificial intelligence with high-throughput robotic platforms to accelerate this process. Currently, MAPs still present limitations, such as inflexible design oriented towards specific reactions and a high initial cost of implementation. To overcome these issues, we combined an open-source liquid handling robot, OT-2 from Opentrons, and a custom-built motion platform with an ultrasonication tool, called 'sonication station' to accelerate the discovery and development of colloidal dispersions and nanomaterials. Our approach can achieve high-throughput formulation of such dispersions with a fraction of the typical cost. Additionally, this combination is highly flexible and handles many chemical reactions as long as they can be performed by sonochemical methods. Our platform proves to be very versatile, allowing us to synthesize four different classes of colloidal nanomaterials: cadmium selenide quantum dots, lead-free cesium bismuth bromide ($Cs_3Bi_2Br_9$) perovskite nanoparticles, upconverting nanoparticles (rare earth-doped $NaYF_4$), and exfoliated metal boride nanostructures (TiB_2 and AlB_2). We studied how the presence of dopants affected the optical properties of the materials, and how the use of different ligands and surfactants affects their colloidal stability and particle size. To characterize the large number of samples we generated, we also used high-throughput characterization techniques, such as the commercially available microplate readers for UV-Vis spectroscopy and the photoluminescence (PL) spectroscopy, the robot-assisted high-throughput small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS), and coating of sample arrays onto silicon wafers for x-ray diffraction (XRD).

Mon-G2-02

A Theoretical Framework to Couple Dynamics of Electrical Double Layers and Redox Reactions for an Arbitrary Number of Ions

Nathan Jarvey, Filipe Henrique, Ankur Gupta

University of Colorado-Boulder

Electrochemical capacitors are energy storage devices which are distinguished by their high power density. Hybrid supercapacitors use both interfacial reduction/oxidation reactions and the electrostatic movement of ions into electrical double layers to store energy. Electrode materials often consist of activated carbons, which promote physical energy storage due to their large surface area to volume ratio, and metallic oxides which promote electrochemical reactions. While significant advancements in material optimization have been made recently, the transport processes which govern the dynamics of coupled double layers and reduction/oxidation reactions remains unclear. In this talk, we present a physics-based theoretical framework [1] to capture the dynamics of a model electrochemical cell while accounting for the simultaneous effects of double layers and reduction/oxidation reactions. We employ a perturbation analysis to solve the Poisson-Nernst-Planck equations, which enables us to predict spatial variations in ion concentration and potential based at two distinct timescales: electrical double layer charging and bulk diffusion. Our framework is generalized to account for any number of ions and reactions as well as arbitrary ion valences and diffusivities in the limit of thin electrical double layers. From our analysis, we discover that the electrochemical reaction rate directly affects electrical double layer formation and the two processes cannot be treated independently. Furthermore, our model reveals that thickness of the electrical double layer is dependent on the reduction/reaction rates, which implies that reactions can be used to control the capacitance of the overall system.

[1] Jarvey N., Herique F., Gupta A., Charging of an Electrochemical Cell: Theoretical Framework to Couple Dynamics of Double Layers and Redox Reactions for an Arbitrary Number of Ions, submitted

Mon-G2-03

Examining sorption kinetics of CO2 uptake in pristine and degraded aminopolymer sorbents through fluorescent monitoring

Glory A. Russell-Parks [1, 2], Noemi Leick [2], Gerard M. Carroll [2], Brian G. Trewyn [1, 2], Wade A. Braunecker [1, 2]

[1] Colorado School of Mines- Chemistry Department[2] National Renewable Energy Laboratory

Mitigating climate change involves the incorporation of renewable energy to reduce CO2 emissions as well as actively capturing the already present CO2 from the atmosphere. The latter is the motivation behind efforts in direct air capture (DAC). Amine-based DAC systems often utilize derivatives of poly(ethylenimine) (PEI) loaded onto a mesoporous oxide support as an efficient capture medium. Gas diffusion in these systems is tightly coupled with polymer mobility, which in turn is affected by interactions with the pore wall of the support, by confinement, by the presence of co-adsorbates (moisture), and by electrostatic crosslinks that develop as a function of CO2 chemisorption. While a better understanding of polymer mobility will be crucial for optimizing DAC systems, there is a need for the development of sensitive benchtop techniques that can provide additional and complementary information regarding the factors affecting polymer mobility. Recently, we developed a fluorescent probe molecule based on tetraphenylethylene (TPE) to study PEI mobility in confinement in mesoporous silica, and we benchmarked the probe response across a wide range of temperatures and conditions. The intramolecular rotations within the probe molecule, and hence its fluorescence intensity and the shape of the emission spectra, are strongly dependent on the viscosity of the supporting medium. Here, we expand on that initial work by demonstrating we can use fluorescence to monitor the kinetics of CO2 sorption in a PEI-mesoporous oxide composite using both simulated flue gas (10% CO2 in N2) and 400 ppm CO2 in N2. Furthermore, we have begun studying the functionality and properties of oxidatively degraded PEI, and are examining CO2 sorption within PEI samples of different amounts of degradation. The latter results will be influential in designing more efficient DAC systems for real-world operating conditions.

Mon-G2-04

Modeling and experimental analysis of pH swing-based approaches to electrochemical CO_2 capture

David Kwabi

Mechanical Engineering, University of Michigan

The use of renewable electricity to drive large-scale electrochemical CO_2 removal and concentration from point sources, air, and seawater is receiving considerable interest as one strategy for mitigating climate change.[1] The low concentration of CO2 in air however makes rapid and energy-efficient CO_2 capture challenging. Understanding and optimizing the energetic cost of CO_2 separation at practically reasonable throughputs is a prerequisite for engineering devices that can be widely deployed. I will review our past and current efforts at developing electrochemical pH-swing-based CO_2 separation (EPCS) using a combination of modeling and experiments. In EPCS, CO_2 is captured from a mixture of gases into an aqueous electrolyte in the form of (bi)carbonate ions when its pH is increased from acidic to strongly alkaline conditions, and then released as a pure gas when the pH is reversed. We have shown that CO_2 separation is experimentally possible for less than 100 kJ/molCO_2 using such a pH swing cycle that is driven by proton-coupled electron transfer (PCET).[2] Thermodynamic modeling shows that the minimum work input for electrochemical CO_2 separation is the sum of exergy losses incurred from differences in CO_2 partial pressure between the CO_2 source/exit streams and the electrolyte. This framework rationalizes minimum work inputs for pH-swing and redox-mediator-based CO_2 separation cycles, and motivates the measurement or estimation of the aforementioned CO_2 partial pressures in future experimental studies. More recently, we have begun to consider a new design for EPCS in which PCET-active species are conformally attached to the internal surface area of a highly porous electrode, and effect a reversible pH swing in an adjacent layer of aqueous electrolyte upon redox cycling. We have formulated a continuum reaction-transport model that simulates reactive CO_2 capture into and release from the electrolyte layer, as well as transport of (bi)carbonate species, and protons, in response to an applied current or voltage. Possible pathways toward achieving an energetic cost of direct air capture of CO_2 less than 100 kJ/molCO_2 will be discussed, as well as our efforts toward experimental demonstration of this concept.

References 1. Renfrew, S. E.; Starr, D. E.; Strasser, P., Electrochemical Approaches toward CO2 Capture and Concentration. ACS Catalysis 2020, 10 (21), 13058-13074. 2. Jin, S.; Wu, M.; Gordon, R. G.; Aziz, M. J.; Kwabi, D. G., pH swing cycle for CO2 capture electrochemically driven through proton-coupled electron transfer. Energy & Environmental Science 2020.

Monday, July 11th | 13:00 - 14:20 | I2-General aspects of Colloids and Interface

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Mon-I2-01

Spatiotemporal cluster heterogeneities in 3D printed colloidal gels

Lilian Hsiao, Kristine Smith

Chemical & Biomolecular Engineering, North Carolina State University

In liquid-based manufacturing applications such as 3D printing, the interplay between pressure-driven flow and attractive interactions between colloids results in complex particle trajectories and velocity gradients that are not evident from bulk rheological measurements. This may cause microstructural gradients to develop which result in unpredictable product performance. To study flow-induced gradients in gels, we use a colloidal system of thermoresponsive nanoemulsion droplets of poly(dimethylsiloxane) suspended in a continuous phase, comprised of a liquid precursor that contains poly(ethylene glycol diacrylate). The nanoemulsions undergo self-assembly at elevated temperatures to form gel networks with different length scales. We use high-speed confocal microscopy to investigate its spatiotemporal evolution as it flows through a cylindrical channel at various temperatures and shear rates. The trajectories of fluorescent tracer beads in the oil-rich domains are tracked using 2D image processing. Comparison of the bead velocity profiles to those obtained from a Herschel-Bulkley fit to bulk rheometry data shows agreement at low temperature but not above the gel point. These data suggest that time-dependent variations in cluster properties are responsible for statistically significant deviations from theoretical predictions, especially when attractive interactions are strongest at elevated temperatures.

Mon-I2-02

Microfluidic Platform for Characterizing the Convective Heat Transfer Properties of Nanoemulsions

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High power electronics such as electric vehicle batteries and server farms are approaching a thermal management engineering challenge due to increasing rates of Joule heating in applications; conventional thermal management fluids do not possess the heat sink rates to match or exceed the heat source rates. Adding various additives is a promising approach to engineering the properties of thermal management fluids for intended applications. The thermal conductivity of mixtures and suspensions has been extensively studied; however, there are few reports that study their convective heat transfer properties. Additionally, observation of these fluids in-situ is rarely undertaken creating a degree of separation between experimentation and characterization. Beyond nanoparticles, Pickering nanoemulsions may allow for greater rates of heat transfer via extended heat transfer pathways and thermophoresis of the nanoemulsions. This work aims to test Pickering nanoemulsions for their convective thermal properties using a microfluidic platform comprising a microheater and a PDMS microchannel. An infrared camera is used to measure temperatures of the fluid in-situ under laminar flow conditions. The thermal conductivity can be qualitatively assessed by examining the axial temperature profile, while the convective heat transfer coefficient (and by extension the Nusselt number) can be quantitatively assessed via a macroscopic energy balance between Joule heating of the microheater and convective cooling of the fluid.

Mon-I2-03

Using the Hydrophilic-Lipophilic Deviation Concept and Microemulsion Phase Behavior to Predict Lecithin-Tween 80 Marine Oil Dispersant Effectiveness

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In general, marine oil dispersants are composed of blends of surfactants dissolved in solvent and they work by reducing the crude oil-seawater interfacial tension (IFT). The reduction of the IFT, coupled with interfacial turbulence via wave action, promotes the breakup of the crude oil slick into oil droplets that are dispersed into the water column and eventually broken down by oil degrading bacteria. In the wake of the Deepwater Horizon oil spill, there was a desire to develop 'green' dispersant formulations due to concerns about the environmental persistence and toxicity of current commercial formulations -- this led to the use of the food grade surfactants L-α-phosphatidylcholine (lecithin) and polyoxyethylenated sorbitan monooleate (Tween 80) in lab scale dispersant effectiveness testing. When blended at specific lecithin (L) and Tween 80 (T) weight ratios these surfactants proved to be effective at dispersing crude oil in lab scale tests. However, these effective LT blends did not generally exhibit key characteristics that were thought to explain a given dispersant's effectiveness. As a result, the ability to *predict* whether a specific LT blend would act as an effective dispersant remained challenging. In this work, we investigate whether LT dispersant effectiveness can be correlated with thermodynamic phase behavior in model dispersant-oil-water ternary systems and compare these results with theoretical hydrophilic-lipophilic deviation (HLD) calculations. Specifically, we studied 6 different ternary systems comprised of various LT dispersant formulations (D) + hexadecane (O) + synthetic seawater (W) (D ranging from 0:100 – 100:0 L:T w/w). We hypothesized that the thermodynamic phase equilibria in DOW systems of a given LT dispersant correlated with that blend's effectiveness as a dispersant, and we tested this by mapping the phase behavior of each ternary system over the course of multiple weeks. From this, we determined that there is an empirical correlation between LT dispersant effectiveness and the microemulsion phase behavior of that LT blend and expect that the observed fundamental thermodynamic principles can be used to predict the effectiveness of any general dispersant blend. Further, we developed a protocol that allows the phase behavior to be observed on much

shorter/industrially relevant timescales (ca. hours) with the use of a few general guidelines that can be used to interpret test results. These findings expand on the fundamental understanding of dispersant interfacial chemistry and provide a useful tool to guide the efficient development of new marine oil dispersants.

Monday, July 11th | 13:00 - 14:40 | J2-Molecules and Particles at Fluid Interfaces

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Mon-J2-01

Active behaviors of oil droplets stabilized by surfactants and particles

Lauren Zarzar

Penn State University

Chemotactic interactions are ubiquitous in nature and can lead to complex emergent behavior in multibody systems and living organisms. However, developing synthetic embodiments of chemomechanical frameworks for generating behaviors like self-propulsion or non-reciprocal interactions of tunable strength and directionality has been challenging. Emulsions, which are mixtures of immiscible liquids characterized by chemical inhomogeneity and non-equilibrium states, are unique materials in which to study how spatially controlled chemical gradients affect inter-droplet "communication", leading to organized assembly and motion. We present a framework for rationalizing and predicting micelle-mediated interactions between droplets of different chemistries and explore the ramifications for chemically programmable active fluids. We show how chemotactic signaling between "source" and "sink" microscale oil droplets of different chemistries in micellar surfactant solutions can result in predator-prey-like nonreciprocal chasing interactions. We further explore the self-propulsion of complex droplets, such as Janus oil droplets, where the structure of the droplet (combining both source and sink) has significant implications on activity. The introduction of particles at droplet interfaces further provides a route to tune to chemical asymmetry and induce active behavior into otherwise inactive emulsions. Our findings demonstrate how chemically-minimal systems can be designed with controllable, chemotactic interactions to generate self-propulsion, emergent self-organization, and collective behaviors.

Mon-J2-02

Interfacial rheology of passive colloidal 2D crystals with active particles

Jacob John, Giovanniantonio Natale

Department of Chemical and Petroleum Engineering, Schulich school of engineering, University of Calgary, Alberta, Canada

Understanding the deformation behavior of structured interfaces is important due to its significance in biological processes and industrial applications. Interfaces containing motile particles can be used as model systems to study various events in nature such as, the yielding of disordered solids, motion of microorganisms, human crowd behavior and the motion of molecular motors at cell membranes. In this work, the behavior of platinum coated active Janus polystyrene particles in a two-dimensional crystalline assembly of spherical polystyrene particles is studied. The rheological behavior at the oil-water interface is investigated using interfacial shear rheology and micro rheology. At high surface coverage of the particles and low ionic strength, the passive particles form a two-dimensional crystal with a hexagonal lattice structure due to dipole-dipole interactions. These interfaces exhibit a viscoelastic solid-like behavior in the linear regimes and undergoes strain-stiffening and reversible structural rearrangements at large strains. However, in the presence of motile particles, interesting microstructural features are observed in the absence of external flow. This ranges from the dislocation of particles from the crystal lattice to the complete irreversible yielding of the crystal, with increase in the ratio of active particles. We characterize the changes in particle configuration and micromechanics induced due to the motility of active particles using video microscopy and particle tracking. The effect of activity on the yielding kinetics and the strain-stiffening characteristics is studied using interfacial shear rheology. The presence of activity results in liquid-like characteristics of the interface and also diminishes the strain-stiffening behavior.

Mon-J2-03

Going with the flow: colloidal dynamics at moving immiscible fluid interfaces

Joanna Schneider, Sujit Datta

Princeton University

A wide array of processes, from membrane defouling to contaminant transport and groundwater remediation, involve interactions between surface-deposited colloidal particles and a moving immiscible fluid interface. Previous works studying the interactions between individual particles and a moving interface have shown that the interplay between colloidal interactions, hydrodynamics, and capillarity plays a critical role in determining the transport of both colloids and fluid. However, in many cases, particle deposits form dense aggregates, giving rise to new complexities that cannot be described by single-particle models. To address this fundamental gap in knowledge, here, we directly visualize the interactions between multilayer colloidal particle deposits and moving immiscible fluid droplets in microchannels. As the immiscible fluid interface passes over particles, we observe that they strongly adsorb to it, despite their lack of surface activity under quiescent conditions. We show that this surprising behavior arises due to the influence of capillary forces exerted by the fluid interface as it impinges on the particles, forcing them to overcome the electrostatic energy barrier to adsorption. Thus, the surface coverage of the interface by particles increases with time as the fluid droplet traverses the channel. Eventually, the interface becomes saturated with adsorbed particles—triggering an abrupt fluid-solid transition in its rheology that alters subsequent flow. As a consequence, the interface has a finite “carrying capacity”, continually sloughing off particles when it is sufficiently jammed. While injection of immiscible fluid interfaces has been explored for its potential to remove deposited particles from solid surfaces, our study reveals the limitation that fluid interfaces can rapidly become saturated by particles. Our results show that this limitation can be overcome by increasing fluid interfacial area, suggesting a new approach to anti-fouling using dispersed droplets.

Mon-J2-04

Salt-Induced Diffusiophoresis of a Nonionic Micelle: Roles of Salting Out and Proximity to Surfactant Cloud Point

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Diffusiophoresis is the migration of colloidal particles in a fluid due to concentration gradients of other solutes such as salts. This transport mechanism has attracted much attention because of its many potential applications in the fields of microfluidics, dynamic self-assembly, separation and purification techniques, enhanced oil recovery, and drug delivery. Most diffusiophoresis studies have focused on the case of charged colloidal particles in the presence of salts. However, an important class of water-soluble colloidal particles is represented by neutral particles whose interfacial properties are governed by polyethylene glycol (PEG) motifs. Hence, it is important to understand salt-induced diffusiophoresis of neutral PEG-based colloidal particles. In this work, diffusiophoresis of nonionic micelles of tyloxapol, a Polyoxyethylene surfactant, was characterized in the presence of Na_2SO_4. Multicomponent-diffusion coefficients were measured at 25 °C for the ternary tyloxapol-Na_2SO_4-water system using Rayleigh interferometry. These data together with measurements of cloud points and dynamic-light-scattering diffusion coefficients were used to characterize salt-induced micelle diffusiophoresis as a function of salt concentration. Salt osmotic diffusion, which describes Na2SO4 diffusion induced by micelle concentration gradient was also determined and allowed us to characterize the salting-out effect responsible for micelle diffusiophoresis from high to low salt concentration. A hydration model was employed to theoretical describe the observed behavior of diffusiophoresis. Our results show that diffusiophoresis becomes the dominant mechanism responsible for micelle transport near the surfactant cloud point. This work provides guidance for the development of strategies for manipulating the motion of PEG-based colloidal particles with host-guest properties by exploiting salt concentration gradients and proximity to the surfactant cloud point.

Monday, July 11th | 13:00 - 14:40 | M2-Wetting & Adhesion

Mon-M2-01

Spontaneous charging affects the motion of sliding drops

Hans-Juergen Butt

Max Planck Institute for Polymer Research, Mainz, Germany

Water drops moving on surfaces are an everyday phenomenon seen on windows and they form an essential part of many industrial processes. Previous understanding is that drop motion is dictated by viscous dissipation and activated dynamics at the contact line. Here we demonstrate that these two effects cannot fully explain the complex paths of sliding or impacting drops. To accurately determine the forces experienced by moving drops, we imaged their trajectory when sliding down a tilted surface, and apply the relevant equations of motion. We found that drop motion on low-permittivity substrates is substantially influenced by electrostatic forces. Our findings confirm that electrostatics must be taken into consideration for the description of the motion of water, aqueous electrolytes and ethylene glycol on hydrophobic surfaces. The results may be relevant for improving the control of drop motion in many applications, including printing, microfluidics, water management and triboelectric nanogenerators.

X. Li, P. Bista, A. Stetten, H. Bonart, M.T. Schür, S. Hardt, F. Bodziony, H. Marschall, A. Saal, Xu Deng, R. Berger, S. Weber, H.-J. Butt: Spontaneous charging affects the motion of sliding drops. Nature Physics 2022, DOI 10.1038/s41567-022-01563-6.

Mon-M2-02

Low power, electro-active control of cell bio-adhesion

Victor Leon, Baptiste Blanc, Sophia Sonnert, Kripa Varanasi

MIT Mechanical Engineering

Biological systems are notoriously difficult to control. A major technical issue is controlling where and when bio-adhesion occurs on surfaces in engineered systems. Promoting bio-adhesion may be useful to pattern cells for tissue engineering. Preventing bio-adhesion is useful in micro-algal photobioreactors, where cleaning operations are costly and time consuming. Current methods to promote or inhibit bio-adhesion depend on directly modifying the surface chemistry (e.g. hydrophobicity, molecular end groups). Here, we study the interaction between micro-algae (i.e. freshwater Chlorella vulgaris and saltwater Nannochloropsis oculata), and an engineered surface that can actively change its zeta potential based on the magnitude and polarity of applied voltage without changing its chemistry. Since the studied algae have negative zeta potentials, colloidal DLVO theory suggests that a surface with negative zeta potential should repel algae and a surface with positive zeta potential should attract algae. We observe that algae adhesion is inhibited at negative zeta potentials and enhanced at positive zeta potentials with a power draw of ~nW by applying -/+ 1V. Using microfluidic experiments, we report the effect of varying voltage magnitude, voltage polarity, wall shear, algae species, and solution salinity on bio-adhesion. We also conduct longer term (2 week) bio-adhesion experiments to observe the effect on practical performance.

Mon-M2-03

Control of Droplet Wetting and Adhesion via All-Aqueous and pH-Sensitive Polyelectrolyte Multilayer Coatings

Jordan Brito [1], Kaustubh Asawa [2], Alexander Andrianov [3], Chang-Hwan Choi [2], Svetlana Sukhishvili [1]

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Techniques for surface modification that allow precise droplet manipulation are desired for applications in microfluidics, microreactors, and water harvesting. Although commonly inspired by nature, the existing techniques are often not environmentally friendly, widely applicable, or precisely tunable. Here, we pursued an all-aqueous strategy to achieve hierarchically structured surfaces, inspired by rose petals, with high hydrophobicity and controlled contact angle hysteresis. A layer-by-layer (LbL) technique using water-soluble fluorinated polyelectrolytes produced unique parahydrophobic nanocoatings with pH-responsive adhesion. The high hydrophobicity of these coatings (reaching a contact angle >120° on flat surfaces) is controlled by the strength of ionic binding, and further enhanced through the spontaneous formation of hydrophobic domains. When depositing as few as five bilayers (~25 nm) on structured surfaces, these versatile coatings reach a contact angle >150° with attenuated contact angle hysteresis, enabling the highly controlled transfer of aqueous droplets. The pH-selective droplet transfer was demonstrated between surfaces with the same microstructure and coating components but assembled at different pH levels. The capability of these LbL films to endow surfaces with controlled hydrophobicity through adsorption from aqueous solutions and control the adhesion and transfer of droplets between surfaces can be used in droplet-based microfluidics applications and water harvesting.

Mon-M2-04

Temperature-dependent soft wetting on polymer melts

Krishnaroop Chaudhuri, Jonathan Pham

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Wetting studies on soft surfaces have been mostly limited to equilibrium cases at room temperature, most often on crosslinked elastomers or gels. In this work, we investigate the transient wetting characteristics of a polymer melt surface (poly n-butyl methacrylate) at temperatures much higher than its glass transition temperature (T_g). When a glycerol drop is placed on the polymer melt surface, an out-of-plane wetting ridge forms at the three-phase contact line. We use stylus profilometry to measure the height and the profile of the wetting ridge for different temperatures over different times of contact between the drop and the melt. We show that the wetting ridge growth rate is dependent on the system temperature as well as the time of the experiment (i.e., the duration of drop deposition). Using oscillatory shear rheology, scaling laws are developed to predict the time-dependent growth of the wetting ridge based on polymer chain dynamics. We demonstrate that for a range of temperatures, both Rouse and reptation kinetics can be related to the rate of ridge growth over different timescales. Moreover, the shape profile of the wetting ridge is predicted using modified analytical model by including the time-dependent storage modulus, which is a departure from the constant shear modulus values often used for soft elastomers. This illustrates that the shape of the wetting profile can be predicted by a simple consideration of the storage modulus, at the appropriate rheological time scale, within the context of current soft wetting models.

Monday, July 11th | 13:00 - 14:40 | P2-Langmuir Student Awards Session

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Mon-P2-01

Control of colloidal interaction landscapes in magnetic nanoparticle dispersions

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Colloidal materials with reconfigurable structure and properties require dynamic energy landscapes. Self-assembly should be driven by interactions that depend not only on the initial composition of the suspension, but also by parameters that are transient and programmable. To achieve this, we exploit the dual discrete-continuous nature of magnetic nanoparticle dispersions. These fluids are composed of discrete nanoparticles that trigger short-range depletion attractions. Concurrently, they can be seen as continuous solvents with bulk magnetic properties that render any suspended non-magnetic microparticle effectively diamagnetic. Through the continuous nature of these dispersions, we showcase the magnetic field-driven assembly of anisotropic clusters. These form because of an interaction energy landscape comprising two minima originating from the multipolarity of patchy particles. Programming such interactions controls directional binding of isotropic particles on patchy microspheres. Through the discrete nature of magnetic nanoparticle dispersions, we develop a dynamic version of traditional short-range attraction vs long-range repulsion (SALR) colloids. Fine-tuning the balance of attraction and repulsion among isotropic microspheres, we access an energy dissipative cluster phase. Our findings highlight the potential to dynamically modulate the structure of colloidal materials both at a single cluster level and in its phase behavior.

Mon-P2-02

Catalytic descriptors for CO_2 methanation reactivity on transition metals

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[1] Colorado School of Mines, Chemical and Biological Engineering[2] National Renewable Energy Laboratory (NREL)

CO_2 methanation on transition metals (e.g., Co, Ni, Pd, Pt, Rh, Ru) occurs at relatively mild reaction conditions (473-673 K, 1-10 bar), rendering this process an attractive CO_2 utilization route. This reaction often occurs in parallel with the reverse-water-gas shift reaction, prompting questions about catalytic structure-function relationships that drive CO/CH_4 selectivity at methanation conditions.[1] Both CO and CH_4 are valuable C_1 feedstocks, capable of being upgraded to higher hydrocarbons via well-established processes.[1,2] This work uses density functional theory (DFT) calculations to identify the distinguishing properties of transition-metal active sites during elementary steps of CO_2 hydrogenation at methanation conditions. Such insights will help explicate different reactivities across metals, better informing design strategies for carbon utilization materials. The results of this analysis indicate that Co, Ni, Rh, and Ru surfaces activate CO_2 via direct dissociation (forming CO* + O*; * indicates bound species), which is kinetically and thermodynamically favored over hydrogen-assisted activation through COOH* or HCOO* intermediates (Fig. 1a). Hydrogen-assisted CO_2 activation preferentially occurs via the COOH* (HCOO*) intermediate on Pd and Pt (Cu) surfaces. The ability of a metal to activate CO_2 by direct dissociation correlates with the O-affinity of the metal surface (Fig. 1b); strong O* adsorption energies facilitate direct dissociation, whereas metals that weakly adsorb O* require hydrogen assistance. Resulting surface intermediates are removed by stepwise hydrogenation to C_1 products and water. On surfaces that directly dissociate CO_2 (Co, Ni, Rh, Ru), the rate-limiting step for CO_2 hydrogenation and water formation is the first hydrogenation of CO* and O*, respectively. Temperature-corrected activation barriers for the first CO* hydrogenation increase in the order of Ru, Co < Rh < Ni, and barriers for O* hydrogenation increase in the order of Ni < Co < Rh < Ru. Barriers for O* hydrogenation are lower than those for CO* hydrogenation, with the exception of Ru, where they are isoenergetic. Although these results are applicable to kinetically relevant steps at the clean-surface limit, a more rigorous macroscopic study is necessary to draw conclusions about relative reactivities; therefore, ongoing work includes microkinetic modelling of CO_2 hydrogenation pathways. Future work will apply this methodology among all seven metals (Co, Cu, Pd, Pt, Ni, Rh, Ru) to explicate C_1 product selectivities (e.g., CO, CH_4, CH_3OH). Furthermore, at CO_2 methanation conditions on Co, Ni, Rh, and Ru, CO* formation is at an energetic minimum on the reaction pathway, with binding energies ranging from -206 kJ/mol on Ru to -180 kJ/mol on Co.

Therefore, CO* is expected to saturate these metal surfaces at working conditions, and future work will also address surface coverage effects during CO_2 hydrogenation. Ultimately, insights from this study will elucidate transition-metal properties controlling key elementary steps that drive CO/CH_4 selectivities during CO_2 hydrogenation, helping to advance catalyst development for carbon-neutral C_1 feedstock production.

[1] Garbarino, G., Bellotti, D.; Riani, P.; Magistri, L.; Busca, G. Int. J. Hydrogen Energy 2015, 40 (30), 9171–9182. [2] Winter Mortensen, A., Henrik, W.; Dalgas Rasmussen, K.; Sandermann Justesen, S.; Wormslev, E.; Porsgaard, M., Nordic Initiative for Sustainable Aviation 2019.

Mon-P2-03

Electrostatic dust removal from solar panels via adsorbed moisture-assisted charge induction

Sreedath Panat, Kripa Varanasi

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Photovoltaics have found nearly exponential growth in the past decade owing to global push for renewable energy. Even though the installed photovoltaic capacity is increasing rapidly, the shortage of land area and capital expenditure could limit the number of new installations in future. Therefore, it is crucial to ensure highest operational efficiency for the existing solar plants. Current photovoltaic systems operate below their peak capacity due to a big challenge that affects all of the large-scale solar farms: dust accumulation. Since most of the big solar farms are located in dust-laden desert regions due to availability of flat land and sunlight, this is a global problem. It has been shown that under moderate soiling conditions, the efficiency of power production can drop by ~30% per month. For a 150 MW solar power plant alone, a mere 1% drop in solar panel efficiency amounts to ~$250,000 loss in annual revenue. It is estimated that globally, a 3-4% efficiency drop amounts to ~$5 billion loss. Therefore, to minimize losses solar panels are cleaned regularly, conventionally by using fresh water, resulting in global consumption of more than 30 billion gallons of water per year. This much water can otherwise satisfy the annual water needs of up to 2 million people in developing and underdeveloped regions. The amount of water consumed is only expected to rapidly increase as the installed solar base grows. Therefore, there is a pressing need for waterless solar panel cleaning method to make photovoltaics efficient and sustainable. We propose a waterless, contactless electrostatic solar panel cleaning system. Previous attempts using interdigitated microelectrodes for electrostatic dust removal have shown some potential but are proven to be not viable for practical application. In this work, we develop an effective electrostatic dust removal system using charge induction and repulsion. We find that dust particles, despite primarily consisting of insulating silica material, can be electrostatically repelled from electrode surfaces due to charge induction assisted by adsorbed moisture from the ambient. We experimentally determine the charge on dust particles by conducting Stokes experiments under an electrostatic field. By comparing electrostatic force of repulsion with Van der Waals force of adhesion and gravitational force, we define the threshold electric potential for particle removal. We also show that electrostatic dust removal works over a broad range of relative humidity, making our approach widely applicable to various geographic regions. Last, we develop a lab-scale prototype and demonstrate 95% recovery of lost power output using our electrostatic dust removal approach, without consuming a single drop of water. Our proposed system has negligible operational cost compared to water-based

methods. The dust removal mechanism can be operated for an entire solar farm with just a couple of dedicated panels, drawing virtually zero power from the solar panel installation. The electrostatic cleaning system is also modular and can be easily retrofit on existing panel arrays. With upcoming projects such as the record breaking $13.6 billion Dubai desert solar park, our proposed water free, sustainable, dust removal system will have large scale impact.

Mon-P2-04

Acoustic Fields for the Propulsion and Self-Organization of Active Colloids

Jeffrey McNeill [1], Yun Choi [1], Yi-yu Cai [2], Francois Nadal [3], Cherie Kagan [2], Thomas Mallouk [1]

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The design of self-propelling and self-organizing colloids has become popular in recent years because of prospects in the realization of artificial living and adaptive materials and systems. A promising but underexplored mode of actuation in active colloids is ultrasound, which is tunable, simple, and biologically relevant. Here, we explore various modes of propulsion and assembly by standing and travelling acoustic waves. First, we will discuss the mechanism of density driven nanorod propulsion at acoustic standing waves, which is revealed to be a type of Purcell motor. Acoustic standing waves can also be used to trap and actuate acoustically powered spinners that rotate at high speeds and phase separate from each other. Through complex mixtures of flat and chiral spinners, we can generate up to six distinct phases in practice, and observe evidence of physically interesting phenomena such as chiral vortex states. Lastly, we will present work on bubble swimmers propelled by simple travelling waves. These swimmers can be propelled at low powers and are attracted to surfaces and particles, allowing for complex maneuverability and tweezing capabilities. Additionally, we present their non-equilibrium self-assembly with each other and passive particles to make complex colloidal molecules. These results provide convincing evidence that acoustics could play a significant role in the design of future active systems with advanced functionality.

Mon-P2-05

A self-consistent theory for complex electrostatic phenomena at interfaces

Nikhil Agrawal, Rui Wang

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One outstanding challenge in the physical chemistry of electrolyte solutions is to quantitatively describe double-layer structure and properties in systems with spatially varying dielectric permittivity, large concentration gradients, high interfacial charge, or strong ion-ion correlations. A solution to this problem is critical to understanding many complex interfacial phenomena such as like-charge attraction, charge inversion, and polyelectrolyte swelling and relaxation, among many others. The standard mean-field Poisson Boltzmann (PB) theory fails to even qualitatively explain these as it does not take electrostatic correlations into account. Going beyond PB to accurately quantify ionic correlations and dielectric contrast is a numerically implausible task. The reason is the need to resolve the correlation function at two very different length scales, one associated with ion scale (short-range) correlations and the other associated with interface level (long-range) inhomogeneities. Contemporary ways to solve this dual length scale problem are using a phenomenological approach, a non-local density functional-based approach, or a liquid-state theory-based approach. While phenomenological models and density functional-based approaches need unphysical parameters and ad hoc approximations, the liquid state method, although rigorous, suffers from numerical convergence issues at high ion valencies. Overcoming these drawbacks and finding a self-consistent and numerically soluble approach to model complex electrical double layers is crucial to developing novel technologies for gene therapy, stable colloidal dispersions, stimuli-responsive brushes, polyelectrolytes for batteries, etc. The aim of this work is to capture the aforementioned interfacial electrostatic effects by accurately resolving the two-point correlation function derived from the Gaussian Renormalized Fluctuation theory. Our equations not only self consistently solve for ionic fluctuations and dielectric variations via a self-energy term but also include the effect of excluded volume of ions and solvent through incompressibility constraint. We have developed a hybrid numerical method to solve these equations by decomposing the total correlation function into short-range and long-range correlation contributions. To test the approach, we modeled the vapor-liquid interface in ionic fluids. Analogous to two-phase coexistence in real gases, ionic salts dissolved in a solvent also phase separate into a high ion density `liquid' and a low density `vapor' phase because of coulombic interactions. Unlike existing methods, our equations smoothly converge for this vapor-liquid interface for both symmetric and asymmetric electrolytes. For symmetric salts, the surface tension predicted by our theory is in quantitative agreement with the simulation data. Furthermore, our work provides the first calculations for the concentration distribution and electrostatic potential profiles between vapor and liquid phases for asymmetric salts without any approximations. Our results highlight the importance of carefully accounting for the asymmetries between cations and anions as they lead to local charge separation and electric potential profiles.

Monday, July 11th | 15:10 - 16:30 | A3-Active Matter

Mon-A3-01

Interaction between electrically powered self-propelling particles and biological cells

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Towards lab-on-a-particle platforms we suggest using mobile active (self-propelling) particles (also known as "micro-motors") to further advance diagnostic testing and sample analysis; with advantages of the traditional lab-on-a-chip (e.g. portability, efficiency) but overcoming current challenges (e.g. complexity, predetermined design, fluid control). Our recent work [1] demonstrated that using dielectrophoresis (DEP), a frequency-dependent mechanism can selectively load and release the transported cargo. This offers a label-free method to generically, selectively and dynamically manipulate (load and release) a broad range of organic/inorganic matter [2]. Adding directed motion via magnetic stirring enables to develop these active particles into in-vitro assays with single cell precision. Such micromotors were recently used for biosensing [3] as well as purification of targeted organelles of interest from a mixed biological sample [4]. Besides the local electric field gradient intensification essential for DEP, an important novelty of our mobile microelectrodes is also the strong local electric field intensification induced by the active particle. This property was recently exploited by us to demonstrate a novel method of local and targeted (i.e. only those cells that are in contact with the active particle) electroporation of bacteria [5], mammalian cells [6] as well as in-situ electro-deformation of a selectively trapped nucleus [4] acting as a promising label-free biomechanical marker. These all demonstrate the potential of active particles as a ground-breaking and critical tool for a wide range of applications in life sciences that require single-cell resolution.

[1] A. Boymelgreen, T. Balli, T. Miloh and G. Yossifon, Nature Communications 9:760 (2018). [2] X. Huo, Y. Wu, A. Boymelgreen and G. Yossifon, Langmuir 36, 6963–6970 (2020). [3] S. Park and G. Yossifon, ACS Sensors 5, 4, 936–942 (2020). [4] Y. Wu, A. Fu and G. Yossifon, Small 1906682, 1-12 (2020). [5] Y. Wu, A. Fu, and G. Yossifon, Science Advances 6, 1-11 (2020). [6] Y. Wu, A. Fu, and G. Yossifon, Proc. Natl. Acad. Sci. 118:38 e2106353118 (2021).

Mon-A3-02

The Hydrodynamics of Cargo Transport By a Diffusiophoretically Driven Locomotor

Subramaniam Chembai Ganesh [1], Jeffrey Morris [1], Joel Koplik [2], Charles Maldarelli [1]

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Self-propelled “active” colloids, driven by chemo-mechanical transduction mechanisms, are envisioned as microbots, able to conjugate to cargo, and transport the freight along landscapes in liquid continua in applications including targeted drug delivery in cellular and tissue environments, scavenging of contaminants in the environment, and the directed movement of materials in microfluidic networks. In this study we examine theoretically the hydrodynamics of the model problem of the active maneuvering of a spherical particle as cargo by a self-propelling locomotor. The locomotor is a spherical Janus particle which is diffusiophoretically driven by a surface chemical reaction on one face of the colloid (the active side). The reaction consumes a solute fuel from the environment and produces a product which interacts with the colloid to drive a slip velocity proportional to the surface gradient of the product concentration along the colloid surface. The solute/colloid interaction is repulsive so that the interfacial slip propels the particle forward with the active face at the back. In our model, the colloid particle is placed behind the cargo particle, and the active side of the Janus particle is positioned away from the cargo so that the cargo in pushed by the locomotor. We examine the simplest case in which the active side is a cap which is symmetrically positioned along the line of centers between the cargo and particle so that the active colloid and the cargo move in-tandem with relative velocities along their line of centers. The concentration field of the reaction product, which drives the motion, is solved in the limit in which diffusion is dominant (low Peclet number), and the axisymmetric hydrodynamic flow is obtained from the resultant slip velocity by solving for the stream function assuming inertia is negligible (Stokes flow). The Laplace equation for the concentration field, and the stream function equation for the flow are solved using a novel twin multipole expansion approach which can obtain solutions up to and including contact between the cargo and the locomotor. The validity and accuracy of this solution technique is verified by comparison with existing bispherical and tangent sphere solutions for the hydrodynamic motion of pairs of particles. We examine different regimes for this axisymmetric pushing of the cargo by the locomotor. These regimes result from different sizes of the active face of the locomotor, and the size of the cargo relative to the Janus particle. We estimate the interparticle repulsion forces required to produce a configuration wherein the locomotor and the

cargo move together with the same velocity but with an intervening film of liquid between them ('contactless towing')

Mon-A3-03

Aerosolized colloidal microbots uncouple size from function

Coy Zimmermann [1], Tyler Schraeder [1], Brandon Reynolds [1], Emily DeBoer [2], Keith Neeves [2, 3], David Marr [1]

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Pulmonary drug delivery is commonly performed using inhalers which disperse µm-scale droplets throughout the lungs. However, once delivered, drug transport can be diffusion-limited and impeded by mucous build-up, especially in cystic fibrosis patients. In addition, inhalation-based therapies cannot selectively target within the lungs to treat localized diseases, such as cancer. Microbots show good promise for overcoming these issues; however, microbots are typically fabricated in sizes greater than the optimal droplet size for inhalation-based deposition in the lung. Here, we present a novel microbot delivery system that uncouples size from structure and function by delivering colloidal paramagnetic building blocks into the lungs for assembly in situ to form microwheels capable of translation, selective delivery, and mechanical work deep within lung mimics. To verify beads are successfully loaded, aerosolized bead-laden droplets are captured in oil to determine loading and size distributions. Aerosolized microwheel velocity distributions are measured and are not significantly different after delivery. Clear 3D-printed lung mimics are fabricated to demonstrate two targeting methods; one which generally drives microwheels deeper, and one which selectively targets specific areas. Together, this work opens the previously inaccessible pulmonary system for inhalation-based microbot therapies.

Mon-A3-04

Rheotaxis of active droplets

Prateek Dwivedi, Atishay Shrivastav, Dipin S. Pillai, Rahul Mangal

Indian Institute of Technology Kanpur

Rheotaxis is a well-known phenomenon among microbial organisms and artificial active colloids, wherein the swimmers respond to an imposed flow. We report the first experimental evidence of upstream rheotaxis by spherical active droplets. It is shown that the presence of a nearby wall and the resulting strong flow-gradient at the droplet level is at the root of this phenomenon. Experiments with optical cells of different heights reveal that rheotaxis is observed only for a finite range of shear rates, independent of the bulk flow rate. We conjecture that the flow induced distortion of an otherwise isotropic distribution of filled/empty micelles around the droplet propels it against the flow. We also show that nematic droplets exhibit elastic stress-induced oscillations during their rheotactic flight. A promising potential of manipulating the rheotactic behavior to trap as well as shuttle droplets between target locations is demonstrated, paving way to potentially significant advancement in bio-medical applications.

Monday, July 11th | 15:10 - 16:30 | C3-Colloids, Macromolecules, and Surfaces in Life Science

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Mon-C3-01

Development of a Physiologically-Relevant In Vitro Angiogenesis Platform

Laura A.E. Brunmaier [1], Timothy M. Brenza [1, 2], Tugba Ozdemir [1], Travis W. Walker [1, 2, 3]

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The current standard for investigating fundamental biological mechanisms and performing biomedical testing is cell culture and animal models. Two-dimensional cell culture has been pivotal in advancing our understanding of biological processes; however, cellular response in a 2D environment often differs from an in vivo response. The purpose of the animal model is to serve as a medium for investigating the interactions between a complex system with a device, drug, or biological modification, which may overcome the challenges discussed in 2D cell culture. However, evidence indicates that the results from animal models cannot confidently predict human outcomes either. The challenge behind this extrapolation is attributed to genetic, immunologic, and cellular differences between animals and humans. These hurdles incentivize the development of standardized, physiologically-relevant, in vitro models using human cells cultured in three-dimensional hydrogel systems that may provide a reservoir for data collection surrounding human cell responses. Here, we present a human cell culturing platform that models the human vascular system that is adaptable to various assay types including drug delivery, angiogenesis, and materials characterization.

Mon-C3-02

Measurements of the mechanical response of live neurospheres to oxidative stress

Roza Vaez Ghaemi, Yun-Han Huang, Chike Okwara, Vikramaditya Yadav, John Frostad

University of British Columbia

Stem-cell-derived 3D tissues such as spheroids are excellent models for investigating mechanisms of tissue formation and responses to physiological and mechanical cues. Neuronal spheroids, also known as neurospheres, have attracted particular interest. While much is known about the differentiation and maturation of neurospheres and their responses to biochemical cues, understanding about their mechanical properties pales in comparison. This is a significant shortcoming given the recent findings about how mechanical stimuli trigger the onset of neurodegenerative conditions. In this talk, novel methods to characterize the mechanical properties of neurospheres are presented. These methods are then used to determine the impact of oxidative stress by exposure to hydrogen peroxide on the mechanical properties of the neurospheres.

Mon-C3-03

Rheological characterization of covalent adaptable thioester networks for delivery of human mesenchymal stem cells (hMSCs)

Shivani Desai [1], Benjamin Carberry [2], Kristi S. Anseth [2], Kelly M. Schultz [1]

[1] Lehigh University[2] University of Colorado at Boulder

Human mesenchymal stem cells (hMSCs) are recruited at different stages of wound healing and are responsible for calling appropriate cells to the wound to enable healing and, ultimately, tissue regeneration. Researchers have been developing injectable synthetic scaffolds which can be used to deliver additional hMSCs to the wound to enhance these natural repair processes. For effective delivery, these scaffolds should recover their rheological properties once delivered by a syringe and provide a microenvironment in the wound that enables basic cellular processes. Covalent adaptable networks (CANs) have cross-links that can break and reform in response to external stimuli, including shear, making them potential candidates as injectable cell delivery scaffolds. This bond rearrangement also enables these hydrogels to more closely mimic aspects of the native extracellular matrix (ECM). Cells rearrange the native ECM to undergo basic functions including migration, spreading and proliferation. Adaptable cross-links in CANs allow these cellular functions. To tune properties of CANs to make them effective cell delivery vehicles, rearrangement of the network when subjected to shear applied by a syringe and hMSC-mediated remodeling are characterized. In this study, bulk rheology and microrheology characterize covalent adaptable thioester networks that are formed by photopolymerizing 8-arm poly (ethylene glycol) (PEG)-thiol and PEG thioester norbornene. To measure the injectability of these scaffolds, we measure network recovery by applying low and high strain in a cyclic manner at physiological conditions. We then characterize network degradation with multiple particle tracking microrheology (MPT). MPT measures the Brownian motion of fluorescent probe particles embedded in a sample which is used to calculate the ensemble-averaged mean-squared displacement (MSD) and rheological properties using the Generalized Stokes-Einstein Relation. MPT measurements taken during network degradation characterize the evolving microstructure of the material. Using time-cure superposition we calculate the critical relaxation exponent, n, which is 0.53±12 for these networks. This value of n indicates that the network is equally viscous and elastic and is similar to a percolated network. The value of n also quantitatively defines the state of the material when cell-mediated remodeling and network rearrangement in the pericellular region is measured. Using MPT we also characterize network rearrangement in the presence of hMSCs. Experiments with hMSCs indicate that cell-mediated rearrangement causes phase transitions in the pericellular region. This work quantifies

dynamic structural properties of thioester networks with and without hMSCs which informs the design of these scaffolds for tissue regeneration and cell delivery.

Mon-C3-04

Investigation Temporal and Spatial Mechanical Properties of Sulfate Reducing Bacteria Biofilm by Microrheology

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Sulfate-reducing bacteria (SRB) is regarded as one of the most troublesome groups of bacteria that influence the mechanism of microbially-induced corrosion (MIC). In the past two decades, considerable efforts have been devoted to comprehending the corrosion process that is associated with SRB, while the interactions between the development of the biological system and the environment are still not fully understood. We will describe a protocol for determining the growth of SRB in different available and developed setups. This work aims to generate a frugal, cost-effective enumeration procedure that is based on simple spectrophotometric measurements of SRB growth. Rheological properties of SRB biofilm were analyzed with multiple particle tracking (MPT). This technique was used to examine the viscoelastic characteristics in various parts of the biofilm during development. MPT relies on tracking the Brownian motion of particles that are embedded in a medium to calculate the mechanical properties of the medium in the vicinity of the particles. In addition, MPT resolves the local mechanical properties of the biofilm hydrogel spatially and temporally. To investigate the mechanical properties of SRB, we have developed a set of protocols that utilize MPT to characterize the mechanical properties of anaerobic bacteria in situ. To avoid biofilm disruption and eradication, fluorescent tracer particles are integrated into the media of the biofilms prior to inoculation. In this study, the primary contributors to biofilm mechanical properties, contributing to the overall viscoelastic character, have been investigated. The biofilm has been examined at different times after cultivation and under alternate environmental conditions. our preliminary data confirms the establishment of biofilm growth and also the data from microrheology shows different levels of heterogeneity in the biofilm.

Monday, July 11th | 15:10 - 16:30 | D3-Self and Directed Assembly

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Mon-D3-01

Novel principles of fabricating high-performance sustainable biopolymer films hierarchically reinforced with dendricolloids

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The excessive production and consumption of petroleum-based plastics have created ominous environmental and ecological impacts which is driving increased interest in developing biodegradable, renewable alternatives. We will report a new class of naturally derived-polymer based films, which are envisioned as multi-functional biodegradable material. These films are based on nano and micro-scale reinforcement using the recently discovered soft dendritic colloids (SDCs). The SDCs are characterized by being highly branched polymeric particles surrounded by a nanofibrillar corona produced from polymer precipitation in a turbulently sheared non solvent medium. The developed films are based on an agarose (AG) polysaccharide matrix reinforced with chitosan (CS) SDCs, which are both biopolymers derived from marine waste. Owing to the hierarchically branched SDCs fiber entanglement network, the films acquire superior properties such as mechanical robustness and hydrophobicity. The outstanding mechanical performance is attributed to a strong interlayer adhesion as well as an effective load transfer between the two networks. Due to a dense network formation and intermolecular interactions between the positively charged SDCs and the negatively charged matrix, the films become hydrophobic, which may overcome the most challenging limitation to bio-derived functional materials. Due to the abundance of polar functional groups along both AG and CS molecules, intra- and intermolecular hydrogen bonding interactions between the SDCs and the matrix were characterized using infrared spectroscopy. Morphological analysis showed that SDCs are well incorporated in the films indicating good spatial distribution within the matrix with no obvious signs of agglomeration. The swelling of the films and their oxygen and water vapor permeabilities showed synergistic effects due to the SDCs inclusion. These films can find applications as next-generation functional biodegradable materials with comparable or superior properties to the current petroleum-based systems.

Mon-D3-02

Improved Nanoformulation and Bio-functionalization of Linear-Dendritic Block Copolymers with Biocompatible Ionic Liquids

Christine Hamadani [1], Indika Chandrasiri [1], Mahesh Loku Yaddehige [1], Gaya Dasanayake [1], Iyanuoluwani Owolabi [2], Alex Flynt [2], Timothy Lodge [5], Thomas Werfel [3, 4], Davita Watkins [1], Eden Tanner [1]

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While many recent advances have been made in nanomedicine, intravenous therapies are still limited by biological barriers such as protein corona-based opsonization and targeted/selective organ accumulation. New modular nanomaterials, such as cationic polyamidoamine (PAMAM)-Linear Dendritic Block Copolymers (LDBCs) have emerged with high encapsulation efficiencies that can be tuned and functionalized for more efficient cancer-cell targeted delivery. However, depending on structural composition and surface properties, LDBCs also exhibit high polydispersity (PDI), poor shelf-life, and potentially high cytotoxicity to non-target interfacing blood cells for purposes of intravenous drug delivery. We have previously shown that room-temperature Ionic Liquids (ILs) composed of choline carboxylic acids can form a serum protein-phobic surface coating to resist corona formation, improve PDI, and increase stability of 50 kD Poly-lactic-glycolic Acid (PLGA) linear block co-polymer nanoparticles (NPs). Additionally, this coating induced red blood cell (RBC) hitchhiking and drove selective biodistribution to the lung in-vivo. Here, we show that choline carboxylic-acid based ILs electrostatically solvate LDBCs by direct dissolution, and form stable and biocompatible IL-integrated LDBC nanoassemblies, with comparative RBC-hitchhiking ability and altered cellular uptake behavior ex-vivo. When modified with choline and trans-2-hexenoic acid, IL-LDBCs evidenced half the PDI of LDBCs, and suggested anionic surface integration via Dynamic Light Scattering (DLS) by shifting the cationic surface charge towards neutrality (n=5). NMR evidenced twice the total amount of IL on the LDBCs relative to our IL-PLGA platform. TEM suggested formation of a nanoparticle surface coating, which acted as a protective agent against RBC hemolysis, from 73% (LDBC) to 25% (IL-LDBC) (n=4). However, drastically different uptake behavior of IL-LDBCs vs. IL-PLGA NPs in RAW macrophage cells suggested a different conformational IL-NP surface assembly. By controlling the physical chemistry of polymer-

IL interactions and assembly on the nanoscale, we can drive biological function for more effective and targeted intravenous nanotherapies for cancer drug delivery.

Mon-D3-03

Enabling 3D Printing of Constructs with Internal Nanostructured Features Guided by Self-assembly

Zahra Niroobakhsh

Civil and Mechanical Engineering, University of Missouri-Kansas City

Fabrication of constructs with small nanofeature is a daunting task, especially for soft materials, due to the weak mechanical strength and the low structural stability of constructs. In the present work, the printing of robust 3D constructs with tunable mechanical properties and internal nanostructures is achieved, which has previously not been possible neither with traditional 3D printing techniques or the liquid-in-liquid printing methods. In this technique, extruding an aqueous solution (containing surfactants and photocurable polymers) into a stabilizing lipid bath followed by photopolymerization can generate robust constructs with internal nanostructures and tunable mechanical properties. We present the structure-properties relationship using shear rheometry, tensile measurements, and small-angle X-ray scattering (SAXS). We will further explain the underlying stabilization phenomena and morphological phase transitions using experiments and dissipative particle dynamics (DPD) simulation.

Mon-D3-04

Time-Alcohol Superposition of Chitosan/Hyaluronic Acid Complex Coacervates

Sarah Perry, Juanfeng Sun, Jessica Schiffman

Department of Chemical Engineering, University of Massachusetts Amherst

Complex coacervation is an associative liquid-liquid phase separation phenomenon resulting from the complexation of oppositely-charged macro-ions. As our understanding of how parameters such as polymer chain length, polymer chemistry, salt concentration, and pH affects the phase behavior and rheology of complex coacervates matures, we looked to understand the effect of solvent quality. In particular, we examined the effect of adding small amounts of either methanol or ethanol to complex coacervates of the natural polymers chitosan and hyaluronic acid. Characterization of the resulting linear viscoelastic response suggests the possibility for using not only traditional strategies such time-salt superposition to understand trends in the rheological response, but also time-alcohol and time-salt alcohol superposition.

Mon-F3-01

The impact of viscous stress and Marangoni stress on the micro-scale droplet film drainage

Yun Chen, Cari Dutcher

Department of Mechanical Engineering, University of Minnesota

Liquid-liquid droplet emulsions are ubiquitous in systems such as bilgewater, food processing, and water-entrained diesel fuels. The dispersed droplets are usually stabilized by the surfactant molecules at the interface that can reduce the interfacial tension (IFT) force, which inhibits the droplet coalescence. In addition to reduced IFT, other factors can also impact droplet stability. When two droplets approach each other, a thin film forms between the droplets and must drain before they can coalesce. Thus, the emulsion stability is determined by the time scale for the film drainage. Studies have shown that viscous stress and Marangoni stress at the droplet interface can influence the film drainage time. Based on different liquid-liquid systems, both viscous stress and Marangoni stress will inhibit the film drainage to a certain extent. In this work, systematic droplet coalescence experiments will be presented. Systems with different viscosity ratios are investigated to understand the impact of viscous stress. In addition, the film drainage time is also measured for surfactants with different concentrations inside the droplets. The Marangoni number has been calculated based on different physics to understand the impact of the Marangoni stress on the film drainage between the droplets.

Mon-F3-02

Effect of temperature and salinity on the stability and coalescence of water in oil emulsions

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The dynamics at the liquid-liquid interface for surfactant-stabilized systems is important for different applications, such as liquid-liquid separations and treatment strategies. The interfacial properties are affected by several factors, such as the temperature of the system and the salinity of the emulsion. The first factor studied here is the temperature. In industrial applications, oil-water emulsions are subject to a wide range of temperatures, depending on their processing conditions. This is known to affect the interfacial tension, as well as the bulk and inner phase viscosity. In this work, the effect of temperature on interfacial tension is studied by means of a microfluidic device mounted on a cold stage. The cold stage used is capable of accessing sub-ambient temperatures, and the microfluidic device used is capable of measuring interfacial tension by using a contraction-expansion mechanism. Measurements are done for water emulsions in model light mineral oil, with different SPAN 80 surfactant concentrations added to the oil phase. The results of interfacial tension measured are validated using pendant drop experiments. It was found that the interfacial tension increases at sub-ambient temperatures, compared to ambient temperatures. In addition to that, the dynamics of surfactant transport is studied by fitting an equation of state based on Langmuir isotherm to the dynamic IFT measurements to extract the adsorption and desorption rates of surfactant. It was shown that at sub-ambient temperature, early time variation in interfacial tension can be resolved, contrary to ambient temperature at which only late time results were resolved, suggesting slower transport at sub-ambient temperature. The second factor studied is the salinity of water droplets in oil. The interfacial tension of salt water in model oil systems in the presence of different surfactant concentrations is measured using pendant drop experiments. Preliminary results suggest that the presence of salt decreases the interfacial tension, suggesting a more stable droplet. In addition to that, the stability of those droplets is studied by measuring their ability to coalesce. The coalescence of salty water droplets in oil mixtures, in the presence of surfactants, is studied using a microfluidic device, and compared to the no-salt mixtures. The device allows the measurement of the film drainage time, which is the time taken for the droplets to coalesce. It is posited that due to the lower interfacial tension value, the salt may increase the film drainage times of water droplets in oil.

Mon-F3-03

A pairwise hydrodynamic theory for polydisperse margination in wall-bounded suspension flows.

Rodrigo Reboucas [1], Michael Loewenberg [2]

[1] ESAM - Northwestern University[2] Yale University

A pairwise hydrodynamic theory is developed for margination and demixing phenomena in dilute polydisperse suspensions of drops under small-capillary-number conditions. Stationary distributions of each particle type are determined by coupled hydrodynamic diffusion driven by gradients of all species concentrations and a wall-migration drift velocity due to drop deformation. Cross-flow displacements resulting from pair interactions between drops generate the diffusive fluxes. Pair trajectories are reduced to quadratures of the standard mobility functions for spherical drops. Small deformation in the near-contact region between interacting pairs of drops is assumed to prevent coalescence but otherwise has little effect on their trajectories; previous simulations support this model. The efficiency of this formulation enables a quantitative exploration of the parameter space of the problem. Particle distributions show demixing in bidisperse mixtures with smaller drops disproportionately populating the region near a solid boundary, even in excess of their bulk concentration under some circumstances. Equal-size drops with different internal viscosities or different surface tension also undergo segregation. A simplified analytical solution governs the distribution of particles in strongly bidispersed systems.

Mon-F3-04

No silver bullet: compositional ripening in water-in-oil systems

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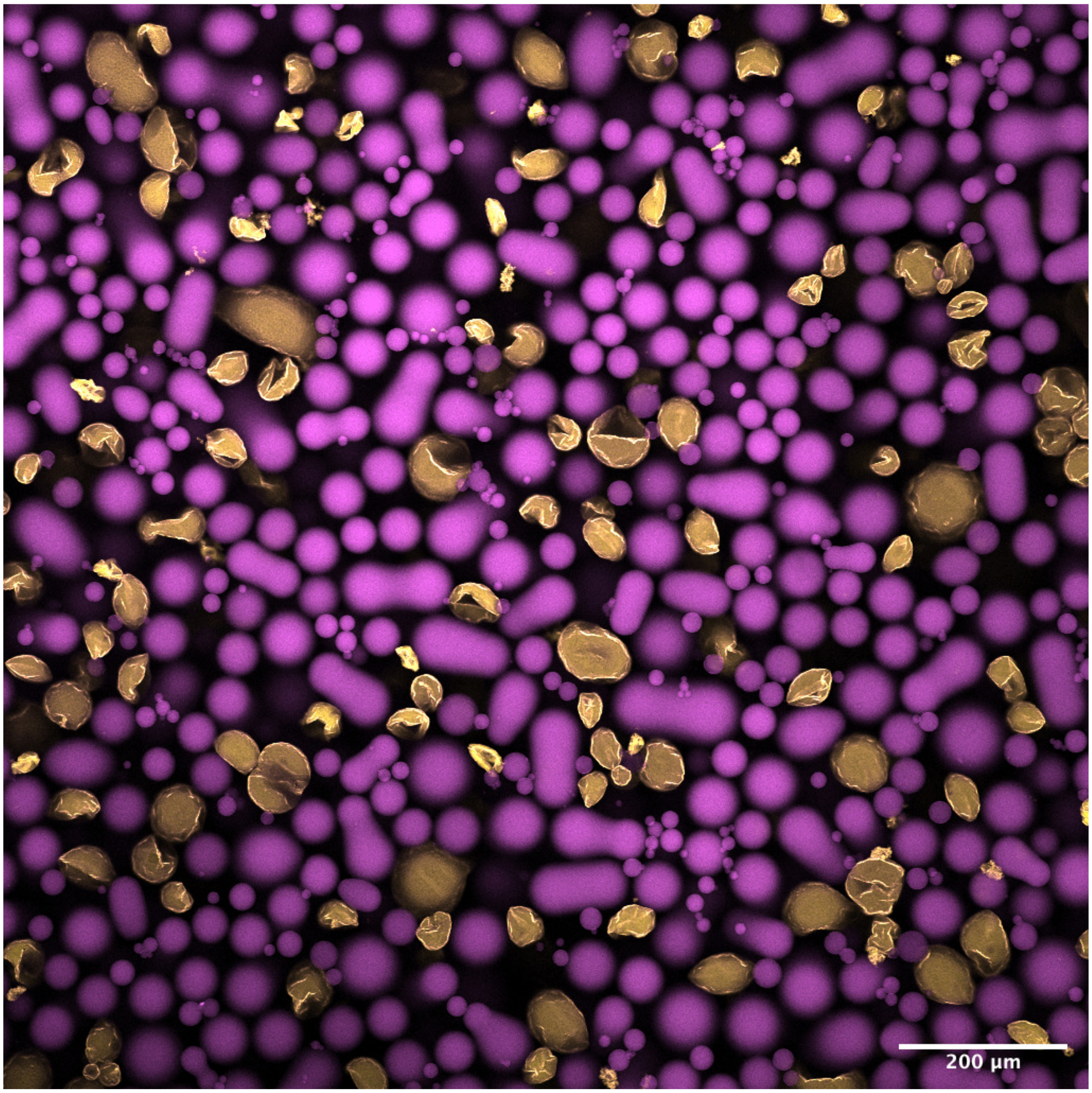
One approach to achieve low calorie foods is to substitute regions of high calorie content with water droplets. Such water-in-oil emulsion systems are naturally unstable due to coalescence and Ostwald ripening. These effects can be reduced, for example, via an interfacial layer of solid particles. In complex food systems consisting of multiple species of dispersed phases, compositional ripening may also occur in which the water undergoes mass transfer to regions filled with other less soluble species. Here we present a model system to study compositional ripening for water-in-oil particle stabilised (Pickering) emulsions. Water-in-dodecane emulsions stabilised by PMMA particles were prepared and combined with similar emulsions that included sugar in the water. Overtime, the pure water droplets appear to crumple (Figure 1. yellow droplets) due to the loss of water; in extreme cases they eventually 'explode'. Simultaneously, the sugar-filled droplets (Figure 1. purple droplets) slowly coalesce. We associate this behaviour with the water droplets undergoing mass transfer to the sugar droplets, driven by the composition differences. Evidently, our interfacial coating of particles is unable to suppress this effect. Using particle tracking, quantitative analysis of the individual droplets shows a decrease in the concentration of the sugar solution results in a reduction in the rate of change of water droplet size. This is in agreement with the theory that a decrease in chemical potential difference between the two droplet species reduces the driving force of compositional ripening. Observations of droplet 'explosions' indicate that the driving force is vastly stronger than that of Ostwald ripening. Forthcoming experiments will show further explorations to the system including modifying the continuous phase and the liquid-liquid interface.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Mon-I3-01

LaMer Keynote: Training and memory in electrochemical jamming dense suspensions

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Shear-induced jamming of dense suspensions and resulting rapid solidification are important behaviors that allow access to stress mitigating functional response. We have designed particles whose crosslink density can be varied in response to an external electric field. Upon exposure, a dense suspension exhibits a drastic change in mechanical properties, namely jamming and solidification. The degree of jamming can be tuned by repeatedly switching the electric field on and off. In addition, we found that the suspension can form a structural memory under oscillatory shear (“training”) that incorporates a yield strain. The structural memory persists even after the external stimulus is removed, and the yield strain depends strongly on the applied training strain. The trained suspension can unjam and lose its memory when the applied strain exceeds the yield strain. In addition to the electrochemical jamming, the crosslinker exhibits photo-responsiveness which enables control of jamming and structural training upon ultraviolet light exposure. Trainability of the suspension may enhance the impact-resisting functionality as various structural rigidities can be achieved by embedding different amounts of yield strain.

Mon-I3-02

Surfactant-induced Marangoni Spreading over Structured Substrates

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Localized deposition of surfactant on the surface of a thin liquid film on a solid surface induces a surface tension gradient, inducing Marangoni flow from regions of low surface tension to high surface tension. The spreading of surfactant on the film, and the fluid flow within the film are influenced by the depth of the film. Therefore, Marangoni spreading over a structured solid surface where structures has length scales on the order of the capillary length of the liquid is expected to be altered by the surface structure. Such effects are of importance in coating flows on structured surfaces where impurities landing on the film could create Marangoni flow. Numerical simulations are used to examine the Marangoni spreading caused by a localized deposition of an insoluble surfactant monolayer on a thin film on flat and grooved substrates. The spreading dynamics are characterized by measuring the surface distortion or ridge seen in Marangoni spreading, and the expanding edge of the surfactant monolayer. Results on flat substrates show that the ridge dynamics are sensitive to the film thickness. The grooved surfaces further enhance the ridge peak dynamics. Neither the film thickness nor the substrate topography affect the evolution of the surfactant front. To investigate further we simulate the spreading over a single bump where we probe the spatial and temporal relaxation of the movement of the Marangoni ridge and the surfactant front.

Mon-I3-03

Investigation of the Propulsion of Metallodielectric Janus particles in AC Electric Fields

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Inspired by swarming motion of living organisms in nature, active particles use the stored energy in the environment to initiate self-propulsion. Successful use of active particles in different applications, including cargo transport and drug delivery, depends on the ability of these particles to travel in predefined directions. Janus particles (JPs) under AC electric fields constitute a good model system for the study of active motion and collective dynamics. In a recent study, we detailed the frequency dependence of the polarizability of JPs. In this study, our goal is to link the motion of JPs to their polarizability. This work aims to understand the mechanisms behind the reversal of motion at high frequencies and the effect of electrolyte concentration via experiments and modeling. The experimental investigation focuses on the effect of the structural properties of JPs (e.g. thickness of metal patch) and the properties of the medium (e.g. conductivity) on the propulsion of particles. On the other hand, we gain mechanistic understanding of propulsion under AC fields by solving the coupled Poisson-Nernst-Planck and Stokes equations. Preliminary results show that general trends in the propulsion of particles at different frequencies, such as the reversal of direction of motion, begin to emerge once details in the transport of ions are accounted. Thus, such observations suggest an important correlation between the propulsion and polarizability of particles that can be exploited in the design of polarizable colloids for cargo transport.

Mon-I3-04

Interfacial Characterization of Silicone Polyethers at a Polyol/Air Interface

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The Dow Chemical Company

Silicone polyethers (SPE) are often used as surfactants in various polyurethane foam formulations. They are hypothesized to assist in foam formation by stabilizing newly formed bubble interfaces. Since the SPEs directly impact the formation of bubbles during foaming, they are known to impact the physical properties of the final foam, such as the cell size distribution, foam density, and open cell content. A simplified, non-reactive blend of a polyol, water, and triethylphosphate was used as the continuous phase to study the equilibrium and dynamic surface tension of SPE surfactants. Traditional surfactant characterization techniques such as Wilhelmy plate tensiometry, pendant drop tensiometry, and dilatational interfacial rheology, were then used to measure the equilibrium surface tension, dynamic surface tension, and interfacial elasticity, respectively, of the SPE surfactants at the air/polyol interface. The SPEs all achieve similar minimum surface tensions, but they show different dynamic surface tension behavior. The interfacial rheology results were found to be highly impacted by the viscosity of the continuous phase, such that it was not possible to measure the interfacial elasticity with an SPE at the interface.

Monday, July 11th | 15:10 - 16:30 | J3-Molecules and Particles at Fluid Interfaces

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Mon-J3-01

3D printing of conductive bicontinuous ink for wearable EMI shielding

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Manufacturing of porous conductive materials has garnered increasing attention for producing lightweight electromagnetic interference (EMI) shielding materials with enhanced efficiency. In this study, we harnessed direct ink writing to produce a bicontinuous structure to fabricate lightweight, wearable, conductive foams with high shielding efficiency. The 3D printable inks are composed of water/resin bicontinuous structure stabilized solely by graphene oxide (GO) nanosheets, where the nanosheets can be reduced to impart conductivity. A pseudo-ternary phase diagram of water, resin, and GO was constructed to optimize the domain feature of the bicontinuous printed objects. We found that by tuning the nanoparticle loading wt% and water/resin mass ratio, the rheology of the thixotropic bicontinuous inks, and mechanical properties and conductivity of the foams can be adjusted. Confocal fluorescent microscopy and scanning electron microscopy were employed to characterize the domain features and porosity. After curing the printed structure with UV light and reducing the GO nanosheets with ascorbic acid, conductive porous microstructures were realized by simply removing water under reduced pressure without any further post-processing. This overcomes limitations of other porous material-producing techniques including metal coating, template removal, particle washing and so on. Additionally, the ink can be printed onto different fabric materials and show excellent adhesion, which is significant for wearable applications. The printed bicontinuous structure was characterized for its EMI shielding capabilities, where 0.3 mm thick structures with only 4.0 wt% GO showed great shielding effectiveness. This work provides a template for identifying different phase behaviors for fluid-fluid systems stabilized by nanomaterials, as well as producing tunable 3D-printable wearable porous EMI shielding material through direct ink writing without complicated post-processing or requiring a high loading of conductive filler.

Mon-J3-02

Particle-Templated Conductive $Ti_3C_2T_z$ MXene Polymer Films via Pickering Emulsion Polymerization

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MXene/polymer composites have gained attention in recent years due to their excellent electrical properties and wide use in applications such as electromagnetic interference (EMI) shielding, energy storage, and catalysis. However, the difficulty of dispersing MXenes in commodity polymers limits the fabrication of highly conductive MXene/polymer composites with satisfactory EMI shielding properties, especially those with low MXene loadings. Here, we report the production of MXene/polymer films by hot pressing of MXene-armored polymer particles. This feedstock was prepared via dispersion polymerization in Pickering emulsions stabilized by $Ti_3C_2T_z$ nanosheets. The composition of the $Ti_3C_2T_z$ armored polymer particles was confirmed by scanning electron microscopy and X-ray photoelectron spectroscopy. The $Ti_3C_2T_z$/polymer films were produced by hot pressing the armored particles above the T_g of the polymer and are electrically conductive due to the network of nanosheets templated by the particle feedstocks. For example, the particle-templated $Ti_3C_2T_z$/polystyrene film had an electrical conductivity of 0.011 S/cm with only 1.2 wt % of $Ti_3C_2T_z$, which resulted in a high radio frequency heating rate of 13–15 °C/s in the range of 135–150 MHz and an EMI shielding effectiveness of ~21 dB within the X band. This work provides a new approach to fabricating MXene/polymer composite films with a templated electrical network at low MXene loadings.

Mon-J3-03

Engineering Catalyst Interactions with the Liquid-Liquid Interface in Biphasic Reaction Systems

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A critical step in lignocellulosic biofuel production is upgrading of biomass-derived pyrolysis oils, in which reduction of oxygenated and unsaturated functionalities produces fuels suitable for direct substitution or mixing with conventional petroleum-based fuels. Most current efforts to upgrade pyrolysis oils utilize molecular hydrogen as the reducing agent, however, the high costs and petrochemical sourcing of hydrogen have spurred interest in the use of a transfer hydrogenation reagent, such as formic acid, as a hydrogen source. Formic acid is a liquid at room temperature with high hydrogen storage capacity, sustainable production chemistries via CO_2 reduction, and desirable properties as a liquid phase hydrogen carrier. However, it is poorly soluble in nonpolar solvents. As a result, the transfer hydrogenation of hydrophobic bio-oil species with formic acid takes place in a biphasic mixture, which makes the hydrogenation of hydrophobic reagents more challenging, with a preferred catalytic cycle in which the catalyst must access both water and oil phase reagents. Furthermore, many common catalyst supports are metal oxides, such as silica, with innately hydrophilic surfaces that demonstrate partitioning to the water phase in biphasic reaction mixtures of oil and water. We investigate the effects of covalent attachment of organic ligands onto the metal oxide support on biphasic reaction activity. Support modification by attachment of silanes, e.g., butyltriethoxysilane, is performed via a facile liquid phase deposition which results in covalent binding of organic functional groups to surface hydroxyl groups. Modification of the catalyst support with organically functionalized silanes changes the support wettability, which affects the partitioning of the catalyst between the oil (hydrophobic surface) and water (hydrophilic surface) phases as well as moderates interaction of the catalyst with the liquid-liquid interface itself. A “neutrally wetting” particle will favorably bind to the liquid-liquid interface to reduce system free energy, resulting in interesting reaction environments, such as particle stabilized (Pickering) emulsions. Furthermore, the location of an interfacially active catalyst provides beneficial mass transport conditions for reagents in both the oil and water phase. The control of the catalyst surface wettability with organic monolayers allows for exploration of mass transport and stabilization of emulsions using the catalyst itself. The transfer hydrogenation of unsaturated compounds with formic acid was performed at low temperature and the results correlated to catalyst surface wettability. The experimental results present strategies for optimization of biphasic catalytic reaction systems by increasing reagent mass transport, as well as

provide evidence of the significance of catalyst surface wettability on catalyst performance in a biphasic system. The results indicate that catalyst wettability must be accounted for when designing catalysts for optimized multiphasic reaction systems. We address the significance of catalyst location in a biphasic mixture and report on preliminary investigations of the stabilization of complex reaction environments with catalytic interfacial particles.

Mon-J3-04

Porous all-in-liquid 3D printed structures: Arresting oil-water interfacial layers with emulsions

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All-in-liquid devices have broad potential applicability in processes ranging from energy storage to drug delivery and tissue engineering. Conventionally, they are produced by the jamming of nanoparticle-polymer at the oil-water interface, where one liquid is arrested in a desired non-equilibrium shape in the second liquid phase. Such structures lack the multiscale porosity that exits in equivalent solid hierarchies. Remarkably, we report on printing spongy all-in-liquid materials utilizing the direct ink writing technique. Stable liquid columns of nanoparticle dispersions are produced inside micellar solutions due to the rapid formation of a highly viscoelastic emulsion phase at the interface. The diffusion time of the generated emulsified zone into the micellar solution is longer than the convection time scale. Thus, emulsions remain at the interface during the injection period. The printed aqueous phase becomes an emulsion zone, creating a porous texture in the oil phase. Consequently, a 3D structure with flexible walls consisting of layered emulsions is achieved, which is counterintuitive to the current liquid-based printed structures. We show the applications of emulsion-based 3D printed all-in-liquid materials in liquid lab-on-chip devices and natural gas/hydrogen storage.

Mon-M3-01

Designing Non-textured, All-Solid, Slippery Hydrophilic Surfaces

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Slippery surfaces are sought after due to their wide range of applications in self-cleaning, drag reduction, fouling-resistance, enhanced condensation, biomedical implants etc. Recently, non-textured, all-solid, slippery surfaces have gained significant attention because of their advantages over super-repellent surfaces and lubricant-infused surfaces. Currently, almost all non-textured, all-solid, slippery surfaces are hydrophobic. In this work, we elucidate the systematic design of non-textured, all-solid, slippery hydrophilic (SLIC) surfaces by covalently grafting polyethylene glycol (PEG) brushes to smooth substrates. We demonstrate two distinct regimes of slipperiness based on critical grafting density (σ^*, which occurs when the tethered brush size is equal to the inter-tether distance): $\sigma^* < 1$, where slipperiness increases with increasing grafting density, and $\sigma^* \geq 1$, where slipperiness is maximum and constant. Furthermore, we demonstrate the exceptional performance of SLIC surfaces in relevant thermofluidic (i.e., dropwise condensation) and biofluidic (i.e., fouling-resistance) applications compared to non-slippery hydrophilic surfaces and slippery hydrophobic surfaces. Based on our results, SLIC surfaces constitute an emerging class of surfaces with the potential to benefit multiple technological landscapes ranging from thermofluidics to biofluidics.

Mon-M3-02

Wetting properties of quench-stressed mixed monolayers on gold.

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Recent studies have shown that the conduction of heat from a solid surface to an adjacent fluid can be improved by increasing the strength of the solid-fluid interaction. Tuning of surfaces and geometries for efficient heat conduction, as well as enhanced droplet evaporation and tailored condensation, should then be possible by tuning the hydrophilicity and morphology of the surface in question. To this end, thermal quenching was performed on mixed composition self-assembled monolayers (SAMs) during initial monolayer formation. Two types of alkanethiol, differing in functional group, are assembled on initially atomically-flat Au(111) surfaces. Samples were cooled from ~60C to room temperature to augment surface morphology and possibly to promote phase separation in the mixed monolayers. A control set was fabricated at room temperature for comparison. Atomic force microscope (AFM) images were taken of the surface of the SAMs to characterize the morphology and composition at the surface. Mixed composition thermally annealed SAMs have a complex morphology influenced by the types of functional head groups. The head group interactions may influence phase separation in the mixed thiol SAMs as well as changes in substrate morphology. Contact angle measurements were performed to characterize the surface wettability using the sessile drop method. The morphological differences between mixed SAMs on thermally treated substrates as compared to room-temperature controls were shown to have a pronounced effect on the measured static contact angles.

Mon-M3-03

Surface Tension Measurements of Solar Salt at High Temperatures

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For energy storage for solar thermal and many nuclear engineering practices, molten salts are used as a heat storage medium or heat transfer fluids due to their unique properties such as low vapor pressure and high heat capacity. However, their properties are not very well measured since experiments should be done at high temperatures and, sometimes, high pressure. In addition, many kinds of molten salts are expensive, yet many different methods require a large amount (> 30 g) to measure properties. In this report, we present a method that uses only small amounts (~ 50 mg) of molten salt in measuring surface tension with ADSA (Axisymmetric Drop Shape Analysis) method. Though ADSA method is very well known and used for many years, the implementation of the method inside an oven at high temperature limits the maneuver that is required for aligning the liquid droplets to a camera. Since the droplets cannot be placed as a liquid, but as solid, the formation of an axisymmetric droplet is not guaranteed. Therefore, this report presents the challenges of using the ADSA method at high temperatures with molten salt inside a closed oven. The goal was to measure the surface tension of solar salt (eutectic mixture of 60 wt. % sodium nitrate and 40 wt. % potassium nitrate) from 250 to 450°C. First, the method and the computer code written for the method were verified by capturing and analyzing water droplet images inside an oven at room temperature. This yielded the water surface tension value within a reasonable error (< 2.8 %). Subsequently, solar salt was used to measure its surface tension. Small discs of frozen solar salt were placed on boron-nitride-coated microscope slides at room temperature. These slides were placed inside an oven and the temperature was increased to the desired temperature which melted the frozen solar salt. The droplets were images with a long-range microscope installed outside the oven. The analysis with the ADSA method yielded the surface tension of solar salt from 109.9 to 115.6 mN/m (depending on temperature) which is in good accordance with the literature.

Mon-M3-04

Dynamics of Forced Wetting in Square Capillaries

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Dynamics of capillary flows in confined spaces depend strongly on wettability and the geometry of the confinement. Under certain conditions, the capillary flows are enhanced in the corners, resulting in the formation of thin films known as rivulets, which propagate along the corner continuously. Since these rivulets can influence the overall fluid movement in these applications, understanding their propagation dynamics is of crucial importance for applications related to microfluidics and porous media. In this study, we investigate the dynamics of forced wetting in a square capillary using a combination of theory, simulations and experiments. The forced wetting is accomplished in two ways: immersion and pumping. In immersion, we force the square capillary into a liquid pool at a constant speed. In pumping, the fluid is fed into the capillary from its bottom at a constant volumetric flow rate. In both cases, we characterize the wetting by measuring the evolution of liquid heights at two locations: center (main meniscus) and in the corner (rivulet) of the square capillary. Under immersion, the main meniscus relaxes to a steady regime, where it descends at a constant speed which is always smaller than the immersion speed. The rivulet starts descending immediately with a constant speed, which later attains a constant height measured relative to the main meniscus. Using first principles, we predict the evolution of main meniscus height and its speed. The predictions match the experimental observations very well. Numerical simulations of pumping show that the main meniscus ascends without any delay at speeds determined by the volumetric flow rate. Like the main meniscus, the rivulet also rises upwards, but at speeds smaller than the main meniscus. Similar to immersion, the rivulets eventually attain a constant height relative to the main meniscus.

Mon-Q1-01

Kinetics of aggregation of amyloid-β under different shearing conditions

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Amyloidogenic proteins like the Aβ-40 are known to aggregate into fibrillar networks. The rate of aggregation and fibril yield is sensitive to external energy input, such as shear. We performed experiments on Aβ-40 solution under two different flow conditions - simple shear using a Couette cell and non uniform shear using an orbital shaker. These experiments show that, under uniform shear, both the mass of fibrils and aggregation rate increase with the shear rate. In the case of orbital shaking, the lag time decreases with the rotational speed of the shaker, but the final fibril mass is the same for all agitation speeds. To explain this contrasting behavior of aggregation kinetics, a population balance model is developed to account for the effect of shear on the aggregation of Aβ. A competition between elongation and depolymerization rates yields different equilibrium masses of fibril at different shear rates. The model results agree quantitatively well with experimental data on the rate of aggregation and mass of fibrils as a function of shear rate.

Mon-Q1-02

Surface modification of two-dimensional MXenes with conjugated phosphonic acids for tunable electronic properties

jacob levin

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$Ti_3C_2T_x$, a member of the MXene family, is a promising two-dimensional transition metal carbide with highly desirable electrical and physical properties. Having surface terminations of hydroxyl, oxygen, and fluorine groups makes MXenes appealing for simple surface functionalization. One of the long-standing challenges of MXenes is their poor stability in ambient environments, leading to rapid degradation. This work reports functionalization of the $Ti_3C_2T_x$ MXene surface with vinyl aromatic phosphonic acids ligands (VArPAs) of varying molecular dipole moments. It is hypothesized that the ligand dipoles will strongly affect the MXene workfunction and electrical properties, while the strongly bonded ligands will “cap” the surface leading to increased stability and improved physical properties. The effect of the VArPA ligands on MXene work function, conductivity, size, thickness, and roughness was studied by Atomic and Kelvin Probe Force Microscopy (AFM & KPFM). Elemental and diffraction analysis was performed using a 4-dimensional scanning transmission electron microscopy in a scanning electron microscope (4D STEM-in-SEM).

Mon-Q1-03

Nanoparticle tracking to probe transport in porous media

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Harvard University

Porous media are used extensively in processes including water treatment, pharmaceutical sterilization, and heterogeneous catalysis, where hindered mass transport is either essential to the process or a necessary but undesirable limitation. Unfortunately, there are currently no universal models capable of predicting mass transport based on a description of the porous material because real porous materials are complex and because many coupled dynamic mechanisms (e.g., adsorption, steric effects, hydrodynamic effects, electrostatic interactions, etc.) give rise to the observed macroscopic transport phenomena. While classical techniques, like dynamic light scattering, provide useful information about mass transport in porous media at the ensemble level, they provide limited insight into the microscopic mechanisms that give rise to complex phenomena such as anomalous diffusion, hindered pore-space accessibility, and unexpected retention under flow, among many others. To address this issue, we have developed refractive index matching imaging systems, combined with single-particle tracking methods, allowing the direct visualization of single-particle motion within a variety of porous materials. Here, we provide concrete examples of understanding nanoparticle transport in porous materials using single-particle tracking from two perspectives: (1) understanding fundamental elementary particle transport processes in porous media, including pore accessibility and cavity escape, which limit transport in porous media, and (2) facilitating applications in industrial processes, e.g., by understanding the mechanisms of particle fouling and remobilization in filtration membranes.

Mon-Q1-04

Correlating the surface energetics, molecular adhesion characteristics, and stability of epoxy-phenolic coatings on metals

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Polymer-metal adhesion is key to the coating stability of many systems in biomedical, automotive, food packaging, and electronics manufacturing. Epoxy resins, nowadays under scrutiny due to their BPA precursor, find widespread applications in most of these systems due to their excellent mechanical performance, good chemical resistance, and strong adhesion to metallic substrates. Notwithstanding their extensive use, the exact origin of epoxy resins' excellent adhesive properties is not well understood. In order to come up with safer, equally performing resin candidates, one needs to understand the origins of the interfacial adhesion of epoxy coatings to metals. We will report the results of a study examining the origins of the adhesion of epoxy and phenolic resins and coatings on different types of metals by combining a theoretical and practical approach. We also investigate the effect of the metal passivation treatment and surface elemental composition on coatings adhesion. By decoupling the effect of the different functional groups, we find that an increase in the ratio of epoxide-to-hydroxyl groups in the resin leads to better spreading and higher interfacial adhesion energy. The practical adhesion results measured through mechanical means qualitatively correlate with the adhesion energies and binding strength of the resins. The results suggest a key role for the epoxide groups in sustaining the resin's adhesion by bonding with the metal surface. This bonding is attributed to the homopolymerization reaction of the highly reactive epoxide group promoted by active hydrogen on the metal oxide surface. Using XPS analysis and surface free energy characterization, the polarity and surface elemental composition of the substrates are correlated to the different interfacial adhesion energies of the resins. The findings can be used as a fundamental guidance to tailor next generation safer resins which will retain the excellent functional properties of their epoxy-phenolic counterparts.

Mon-Q1-05

Asymmetrical Flow Field-Flow Fractionation detects oligomerization of *Bacillus subtilis* SufS and SufU

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Protein biochemistry is progressing rapidly towards the need to quantify more complex solution-state interactions *in situ*. The distribution of configuration states in multi-step protein interaction pathways in solution are challenging to study using traditional biochemistry techniques. Asymmetrical Flow Field-Flow Fractionation (AF4) is a natural fit to rapidly perform protein separations as an upstream preparation technique and as a downstream orthogonal approach to study complex, multi-step protein pathways. AF4 is an excellent technique for protein separations in part because it is gentle and can thus be used to explore the formation of protein complexes. Early work in AF4 focused on establishing reliable method development protocols while more recent work has evolved to increase the speed and efficiency of the technique. A robust theoretical foundation makes AF4 a powerful analytical tool for samples as the measured retention times are readily transformed into hydrodynamic sizes. This allows the use of a simple UV detector to monitor the elution of separated protein species. SufS and SufU are part of the SUF reaction pathway for iron-sulfur cluster biosynthesis, a ubiquitous and essential cellular process in all kingdoms of life. The SUF pathway is a target for antibacterial treatments because it is essential for pathogens including *S. pneumoniae* and *M. tuberculosis*, but the oligomeric nature of this pathway is unclear. Here, we evaluate the SufS-SufU cysteine desulfurase proteins in the resting state, and show peaks associated with the SufU, SufS, and SufS-SufU complex using online UV detection. We developed a protein standard ladder to evaluate the repeatability of our method and compared the diffusion coefficient (D) of Suf proteins to established protein standards values. Our retention time and D results support the configurations predicted by literature using biochemical assays and protein crystals of SufU, SufS and the SufS-SufU complex, and bring new insights for mixed SufS-SufU samples.

Mon-Q1-06

Patchy Colloidal Clusters with Broken Symmetry

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Colloidal clusters are prepared by assembling positively charged cross-linked polystyrene (PS) particles onto negatively charged liquid cores of swollen polymer particles. PS particles at the interface of the liquid core are closely packed around the core due to interfacial wetting. Then, by evaporating solvent in the liquid cores, polymers in the cores are solidified and the clusters are cemented. As the swelling ratio of PS cores increases, cores at the center of colloidal clusters are exposed, forming patchy colloidal clusters. Finally, by density gradient centrifugation, high-purity symmetric colloidal clusters are obtained. When silica−PS core−shell particles are swollen and serve as the liquid cores, hybrid colloidal clusters are obtained in which each silica nanoparticle is relocated to the liquid core interface during the swelling− deswelling process breaking symmetry in colloidal clusters as the silica nanoparticle in the core is comparable in size with the PS particle in the shell. The configuration of colloidal clusters is determined once the number of particles around the liquid core is given, which depends on the size ratio of the liquid core and shell particle. Since hybrid clusters are heavier than PS particles, they can be purified using centrifugation.

Mon-Q1-07

Bicontinuous Nanostructure Quasi-Solid Polymer Electrolytes with Efficient Ion Transport Channel for Lithium-Ion Batteries

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Quasi-solid polymer electrolytes [QSPEs] are alternative next-generation electrolytes for replacing traditional liquid electrolytes in Li-ion batteries. However, to apply in practical use, enhancing the ionic conductivity with enough mechanical strength is essential. For optimizing ionic conductivity and mechanical strength, introducing the nanostructure can separate the ion transport channel and non-ion transport phase which provides mechanical strength, but both two regions coexist. Here, we report the bicontinuous nanostructure QSPE with using microemulsion. Surfactant, hydrophilic (ionic liquid) with 1M LiTFSi, and hydrophobic (cross-linker) make a long-term thermodynamically stable and transparent ternary water-free microemulsion. Then, bicontinuous nanostructure QSPEs are obtained by uv cured of microemulsion solution. Small Angle X-ray analysis shows a bicontinuous nanostructure and spacing distance [*d*] from 36.5Å to 54.3Å along with the surfactant concentrations. The highest ionic conductivity and lithium transference number at high *d* are evaluated as 1.4mS/cm and 0.56 at room temperature while the mechanical strength is ~0.8MPa. To use in a Li-ion batteries system, the $LiFePO_4$ half-cell exhibits stable cycle capacity retention and retention over 100 cycles (141mAh/g, 94%, and coulombic efficiency is 99%). These state-of-the-art bicontinuous QSPEs demonstrates that ion channel can accelerate Li-ion mobility.

Mon-Q1-08

Biophysical Function of Pulmonary Surfactant in Liquid Ventilation

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Liquid ventilation is a mechanical ventilation technique in which the partial or total lung is filled with oxygenated perfluorocarbon (PFC) liquids rather than air in conventional mechanical ventilation. PFCs are hydrocarbons in which all or most of the hydrogen atoms are replaced with fluorine. PFC liquids are an ideal medium for liquid ventilation because of their high solubility of oxygen and carbon dioxide, and large density (1.7-1.9 g/mL) that facilitates delivery of oxygen to the distal lung. Liquid ventilation holds great promise in treating premature newborns and adults with acute lung injury and acute respiratory distress syndrome by mitigating ventilator-induced lung injury such as regional hyperoxia, barotrauma, and volutrauma. An important physicochemical property of PFC liquids is their low air-liquid surface tension of 14-18 mN/m, which makes PFC long regarded as a replacement of natural pulmonary surfactants. However, during liquid ventilation, the entire or partial air-water surface of the lung is replaced with an oil-water interface between water and the PFC. Surface activity of this oil-water interface and the biophysical function of pulmonary surfactant at this oil-water interface are largely unknown. We have systematically studied the dynamic surface activity of a natural pulmonary surfactant at the PFC-water interface using a novel experimental methodology called constrained drop surfactometry (CDS), recently developed in our laboratory. CDS is capable of simulating the intra-alveolar microenvironment of liquid ventilation under physiologically relevant conditions. Using CDS, we found that (1) the PFC-water interface has an interfacial tension of 58 mN/m, which is significantly higher than the surface tension of PFC liquids. Hence, PFC does not behave as a surfactant replacement in liquid ventilation. (2) Pulmonary surfactant adsorbs to the PFC-water interface to decrease the interfacial tension to an equilibrium value of ~9 mN/m, which is much lower than the equilibrium surface tension of surfactant at the air-water surface, i.e., ~24 mN/m. (3) Pulmonary surfactant decreases the interfacial tension from ~9 mN/m to ~1 mN/m during dynamic compression-expansion cycling that mimics normal tidal breathing. These findings have novel implications in better understanding the physiological and biophysical functions of the surfactant film at the PFC-water interface, and may offer new translational insights into the development of liquid ventilation.

Mon-Q1-09

A Bioinspired Elastic Hydrogel for Solar-Driven Water Purification

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Providing reliable access to clean and safe water is a major global challenge in the 21st century. Therefore, producing potable water from contaminated sources in a sustainable, low-energy approach is of paramount importance to address the water scarcity problem. Inspired by nature, a solar absorber gel (SAG) is developed to purify water from contaminated sources using only natural sunlight. The SAG is composed of an elastic thermoresponsive poly(N-isopropylacrylamide) (PNIPAm) hydrogel, a photothermal polydopamine (PDA) layer, and a sodium alginate (SA) network. Remarkably, the SAG can purify water from various harmful reservoirs containing small molecules, oils, metals, and pathogens, using only sunlight. The SAG relies on solar energy to drive a hydrophilic/hydrophobic phase transformation at the lower critical solution temperature. Since the purification mechanism does not require water evaporation, an energy-intensive process, the passive solar water-purification rate (a water purification rate of 7.18 kg m−2 h−1) is the highest reported. This discovery can be transformative in the sustainable production of clean water to improve the quality of human life.

Mon-Q1-10

Understanding the roles of surface tension and elasticity in electrospinning ultrafine fibers

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Electrospinning is a processing technique to prepare polymeric ultrafine fibers with potential profitable applications in filtration and biomedical scaffolding. Complex interactions in the polymer-solvent system influence the production of high quality (smooth) fibers and limit the types of materials that can be electrospun. One such complexity is the relationship between the surface tension and electric stress; electric stress must be able to overcome a solution's surface tension to achieve the formation of fibers and not break up into droplets during the process. In this work we examine the impact of surface tension on electrospinnability using extensional rheology, aiming to understand the interplay of solution elasticity and surface tension in maintaining a fiber morphology under application of electric stress. We use conventional polymers for electrospinning, poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA), in water with the surfactant Triton X-100 added in small amounts (0.1 wt%) to reduce the high surface tension of water. At low polymer concentrations where fibers were not attained for the polymers in water (high surface tension), smooth fibers were achieved in the case where surfactant was added. We tie this observed change in the electrospinning processing window to the extensional viscosity at the solution composition where we first observe fibers. To further demonstrate the advantage of utilizing a surfactant in this ultrafine fiber processing method, a PEO/sodium alginate solution dissolved in water was also studied. Sodium alginate is a biopolymer that is notoriously unable to form smooth fibers as the surface tension of solutions are high and chain entanglement is low. The addition of a carrier polymer, like PEO, has previously been shown to increase its spinnability by increasing entanglement through interactions like hydrogen bonding between PEO and sodium alginate, however, the solutions must still be fine-tuned to achieve fibers with high sodium alginate contents. The addition of Triton X-100 can broaden the spinnability of sodium alginate even further by decreasing the surface tension and allowing a broader range of concentrations to form smooth fibers. By understanding how the surface tension lowers the elasticity needed to electrospin fibers, we can design more complex formulations and ultrafine fibers with greater functionality.

Mon-Q1-11

Peptide-directed struvite growth for enhanced electrochemical nutrient recovery

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Efforts to recover nitrogen and phosphorous from wastewater have intensified as fertilizer demand grows while sources of phosphate rock become depleted. At the same time, discharge of these nutrients in high concentrations from wastewater treatment plants have led to harmful eutrophication of receiving waters. Precipitation of struvite (MgNH4PO4 6H2O) from wastewater is a promising solution to these issues since struvite can capture N and P from liquid streams and then be land-applied as a slow-release fertilizer. However, current methods of struvite precipitation require the use of expensive additives. Furthermore, other ions, especially divalent ions, can alter the resulting precipitate into a less desirable form. In this work, a common dental peptide was explored as a method to control and increase growth of struvite crystals at neutral pH. Cysteine-capped peptide was attached to a gold mesh substrate in a range of loadings (5-27ug/cm^2). Chronoamperometry was conducted by first placing the peptide-loaded mesh in a batch struvite reactor filled with synthetic wastewater at pH 7.1 and then applying a range of potentials (0.5-0.99V) to the magnesium anode. White precipitates were observed and characterized as struvite by XRD. Struvite crystal morphology was investigated by SEM. We report that a peptide loading of 19 ug/cm^2 led to a nearly 14% increase in struvite yield compared to bare Au with no peptide attached. Furthermore, longer, dendritic struvite crystals formed in the presence of peptide compared to orthorhombic crystals which formed without peptide. These results indicate that the peptide alters local supersaturation, leading to an increase in directional crystal growth. By demonstrating the utility of peptides for increasing struvite precipitation at neutral pH, our findings improve the viability of electrochemical struvite precipitation for a wider range of wastewater pHs and highlights how peptides can modulate crystal growth.

Mon-Q1-12

STM Investigations into the Self-assembly of Proline

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Scanning tunneling microscopy, through the observation of molecular clusters and monolayers on surfaces, provides direct experimental evidence as to how intermolecular interactions result in the self-assembly of extended structures. A detailed understanding of the interplay of interactions will result in improved understanding and prediction of the behavior of self-assembling systems, with implications in a wide range of disciplines ranging from crystal engineering to supramolecular chemistry to protein secondary and tertiary structure. We present experimental results on the self-assembly of proline, as well as the results from computational modeling. Pulse deposition of proline on Au(111) reveals that it forms chain structures and pentamer clusters. The chains are chiral, as would be expected from an enantiopure adsorbate; however, the pentamers on the surface appear racemically mixed. Comparison of self-assembled structures to related molecules reveals similar behavior for proline, indole-2-carboxylic acid, and indoline-2-carboxylic acid, but substantial differences are observed for pyrrole-2-carboxylic acid.

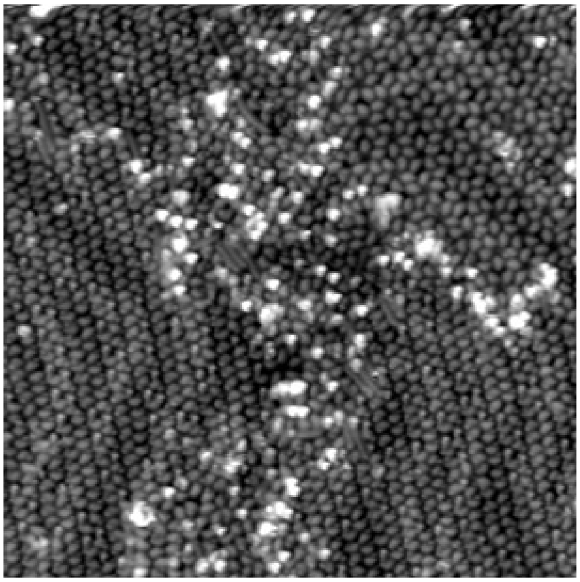

Figure 1. STM image of proline on Au(111). The image shows two configurations: a pentamer formation (top right), and a chain formation (bottom left).

Mon-Q1-13

Evaluating the structure-property relationship of chemically bound PFSA-VDF with polyoxometalate additives and expanded-PTFE reinforcements

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Fuel cell vehicles (FCVs) have been a promising technology to replace internal combustion engine (ICE) vehicles. The technology has been studied and enhanced throughout the emerging need for renewable energy vehicles and succeeded in commercializing a light-duty vehicle that can replace daily commuting vehicles. However, the advantage of the FCVs to both electric vehicles and ICE vehicles can be emphasized when the technology can be adopted to the heavy-duty vehicles such as large trucks for the logistics. Perflourosulfonic acid (PFSA) membranes and ionomers are the current benchmark material that was used on already commercialized light-duty FCVs such as Toyota Mirai and Hyundai Nexo. PFSA membranes are well-known for their robust mechanical and chemical stability with high proton conductivity. However, due to the aggressive environment that can accelerate chemical and mechanical stress during the fuel cell operation, the durability of the PFSA membrane has been a significant challenge for heavy-duty vehicle applications. The radicals that were formed as a byproduct of fuel cell reaction can go through multiple polymer chain scission processes and lead to chemical degradation. Also, mechanical stresses that are applied during fuel cell operation can lead to electrical shorting and pinholes on the membrane. Therefore, both mechanical and chemical durability need improvement for heavy-duty fuel cell vehicles. In this work, we utilize PFSA-VDF terpolymer, where the vinylidene fluoride (VDF) monomer group will be utilized to chemically bind the heteropoly acid (HPA) for radical decomposing catalyst and expanded-PTFE for mechanical integrity for the membrane. The immobilization of HPA can be used as a radical decomposition catalyst that will not migrate. Also, e-PTFE reinforcement will be used to support that the mechanical durability of the membrane can be obtained. Understanding the structure-property relationship between PFSA-VDF-HPA and e-PTFE can provide insight into optimally designing the more robust and highly durable proton-exchange membranes without sacrificing performance. The structure-property relationship will be investigated using a set of composite membranes with different ratios of PFSA-VDF-HPA and e-PTFE. The morphology of the bulk membrane will be analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Furthermore, the entirety of the bulk membrane morphology will be investigated using x-ray scattering equipment such as x-ray diffraction (XRD) and small-angle x-ray scattering

(SAXS). Lastly, the mechanical and chemical durability will be tested using a lab-scale fuel cell station using open circuit voltage (OCV) and humidity cycling method under accelerated stress condition (AST).

Mon-Q1-14

Biophysical Properties of the 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 water evaporation. Dysfunction of the TFLL leads to dysfunctional tear syndrome, with the dry eye disease (DED) being the most prevalent eye disease affecting 10-30% of the world population. The DED is a multifactorial ocular disease characterized by damage of corneal epithelia, inflammation of ocular surface, eye discomfort and visual disturbance, as a result of compromised tear film stability. To date, except for treatments alleviating the dry eye symptoms, effective therapeutic interventions in treating the DED are still lacking. It is estimated that the DED directly and indirectly causes a $55 billion annual economic burden in the United States alone. We have studied the biophysical properties of a model TFLL using a novel experimental methodology called the constrained drop surfactometry (CDS), recently developed in our laboratory.[1,2] 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 that represent the two predominant polar lipid classes in the natural TFLL. Using CDS,[1] atomic force microscopy,[2] and molecular dynamics simulations,[2] we have systematically studied the surface activity, interfacial rheology, polymorphism, and collapse mechanisms of the model TFLL. Our data suggest a distinctive composition-functional correlation for polar lipids in the TFLL.[1,2] These findings have novel implications in better understanding the physiological and biophysical functions of the TFLL, and may offer new translational insights to the treatment of DED. Reference 1. Xu X, Li G, Zuo YY, Biophysical properties of tear film lipid layer I. Surface tension and surface rheology. Biophys. J. 121 (2022) 439-450. 2. Xu X, Kang C, Rui S, Zuo YY, Biophysical properties of tear film lipid layer II. Polymorphism of FAHFA. Biophys. J. 121 (2022) 451-458.

Mon-Q1-15

Microfluidic high pressure measurements of carbon dioxide hydrate phase equilibria

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Gas hydrates are crystalline water structures that trap guest molecules at high pressures and low temperatures. Hydrates have been studied for different energy applications, including gas storage and water desalination, but they also pose a significant problem in oil and gas pipelines. The formation of hydrate plugs is an increasing challenge in the transportation and sequestration of carbon dioxide when water is also present in the stream. It is therefore important to know the equilibrium conditions at which hydrate formation is possible. Due to the slow formation rates of gas hydrates, equilibrium measurements have previously taken several days to complete. Additionally, most previous equilibrium studies were unable to perform measurements of the present phases. Here, microfluidics is used to address both problems in the measurement of carbon dioxide hydrate phase equilibria. The water content of the carbon dioxide phase is measured at hydrate-forming conditions and compared to computer models and previous literature. Raman spectroscopy is utilized to measure the phases, ensuring there are no metastable phases present. The use of microfluidic reactors can allow for quick equilibrium measurements, and this equipment can even be extended to other measurements, such as hydrate formation rate. Acknowledgements: DOE-BES (award# DE-SC0022162) for funding (LW).

Mon-Q1-16

Tailoring nanocrystal optical properties with near-field interactions for next-generation computing

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The exponential increase in global energy demand from technology threatens to limit the growth of future computing capabilities, highlighting the critical need to rethink computing strategies. One promising paradigm for next-generation computing devices involves transmitting and storing information via light. Devices built on these principles require nanometer scale precision over macroscopic areas to execute the processes necessary for computing. Nanocrystals are a promising building block for these next-generation devices, due to their size- and composition-dependent optical properties that can facilitate resonant light-matter interactions. However, realizing these devices requires the capability to control long-range nanocrystal order and their local structures, which has remained a challenge. The strong light-matter interactions that form the basis for next-generation computing may also offer the ability to control the particles themselves. Here, we explore how the near-field light-matter interactions can modify and tune nanomaterial structure and thus their optical properties by investigating the relationships between nanomaterial composition and incident electromagnetic fields. In the future, we anticipate that these techniques can be applied to printed arrays of nanoparticles to tune macroscopic optical properties for the production of next-generation computing devices.

Mon-Q1-17

Role of surface energy for drop-wise dust removal off of solar panels

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The accumulation of dust on solar cells hinders power generation. Dust can absorb or scatter much of the incoming light on solar panels, reducing the amount of light entering the solar cells, especially in regions that receive little to no rainfall. Here, we report the impact single water droplets have on the redistribution of dust and their impact on solar cell performance. It was hypothesized that the coffee ring effect, the re-deposition of particles that are suspended within the droplet upon impact, results in greater light transmittance into the solar cell. The power output of the solar cell was measured before and after the droplet was deposited and dried. It was found that the amount of power increase in the solar cells was greatly dependent on the substrate regarding its hydrophobicity and the approximate contact angle between the droplet and substrate. On polyethylene terephthalate (PET), a hydrophilic substrate, the droplet marginally increased the efficiency of the solar cell at low amounts of dust but decreased the efficiency of the solar cell at higher amounts of dust due to a lack of dust redistribution. For the two other substrates (bare glass, semi-hydrophobic; treated glass, hydrophobic), the opposite was found, creating a correlation between higher hydrophobicity and greater increased light transmittance.

Mon-Q1-18

Using single particle ICP-MS to track plastic particles through soils: A new way of quantifying the transport of nano- and microplastics in terrestrial environments

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Over the last several decades, significant research has been devoted to the transport and fate of plastics in the world's oceans. Only very recently has it been discovered that, in fact, perhaps even more particulate plastic is contaminating Earth's terrestrial environments. Current methods for the detection, characterization, and quantification of nanoplastics (<1000 nm) and microplastics (1-1000 µm) (NMPs), in the environment are expensive, and they require significant time and effort to separate NMPs from soils. This makes it difficult to study the transport of environmentally relevant NMPs in these environments. A new option that provides rapid, accurate and inexpensive NMP analysis in laboratory studies is single particle ICP-MS (sp-ICP-MS). Combined with manufactured, metal-tagged NMPs, sp-ICP-MS can be used to track and determine the particle sizes of the tagged NMPs. Careful selection of a metal tag allows us to track tagged particles of large polydispersivity and irregular shapes through virtually any matrix, so long as the metal added to the NMPs is not present in the background. We demonstrate the use of this technique in the laboratory using saturated sand column experiments to track the movement of two NMP compositions, hydrophobic polystyrene (PS) and hydrophilic polyvinylpyrrolidone (PVP). Both NMP compositions were produced by cryomilling metal-doped plastic coupons to create environmentally representative, metal-tagged NMPs ranging in size from tens of nanometers to several microns. We show that smaller particles of both polymers exhibit greater transport than larger particles, which are filtered out in the sand column. The hydrophilic properties of the PVP allow it to transport much more effectively than the hydrophobic PS particles. Furthermore, the addition of humic acid to the carrier solution improves the colloidal stability of both NMP suspensions resulting in much greater elution from the column than in deionized water or a modified hard water (ionic strength=5 mM). Our observations have major implications for the transport potential of NMPs in organic rich terrestrial environments such as agricultural soils receiving biosolids.

Mon-Q1-19

PERFUSABLE 3D BIOPRINTED GELATIN METHACRYLATE SCAFFOLDS FOR TRABECULAR MESHWORK MODELING AND GLAUCOMA STUDIES

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Glaucoma is a progressive optic neuropathy characterized by loss of peripheral vision and ultimately leading to irreversible blindness. In 2020, approximately 80 million people were affected by the condition worldwide and the incidence only continues to rise. The leading cause of primary open-angle glaucoma (POAG), the most common type of glaucoma, is an increase in intraocular pressure (IOP) which is primarily induced by increased production or poor outflow of aqueous humor (AH). The trabecular meshwork (TM), located at the iridocorneal angle, is a major drainage site for the outflow of AH from the anterior chamber to the Schlemm's canal. It is made up of a complex network of cells and extracellular matrix (ECM) resulting in a tortuous submicron sized pores capable of filtering the AH as it passes. Current in vitro approaches for modeling the TM are focused on flat, 2D culture systems that do not capture the complexity and morphology of the actual three-dimensional ECM. To develop a more accurate model, we have cultured human TM (hTM) cells on 3D-printed gelatin methacrylate (GelMA) scaffolds in static and dynamic 3D environments. We have demonstrated that GelMA hydrogels allow cell proliferation and the expression of important marker genes in hTM cultures. We are now advancing this technology towards 3D bioprinting to create more complex architectures. We have successfully bioprinted multilayered GelMA scaffolds, and quantified hTM cell viability when cultured on the scaffolds. We have also quantified ECM deposition and remodeling using immunohistochemistry and quantitative polymerase chain reaction (qPCR) techniques. In addition, we tested the hydrogels' ability to withstand continuous perfusion culture conditions for up to 72 hours, with and without hTM cells embedded within the structure. This work is helpful in gaining a better understanding of hTM cell biology, and in the future we aim to contribute to the development of novel antiglaucoma therapeutics.

Mon-Q1-20

Thixotropy of High Solids Suspensions with Variable Surface Tension and Viscosity

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High solids suspensions undergo microstructure deformation under applied stresses above the yield stress, which are commonly encountered during processing and shaping of these materials. If the suspension is non-thixotropic, the viscosity will not return to its equilibrium viscosity after an applied stress; often due to the formation of irreversible heterogeneities from particle movement, which compromises the materials properties. Interfacial and surface forces have a direct impact on suspension thixotropy and can be tuned by modifying the composition of the suspensions. However, the relationships between formulation factors and changes in particle spatial distribution have not been fully characterized for high solids suspensions, defined here as >60 vol% solids. Herein, changes in the particle spatial distribution are examined via thixotropy and investigated as a function of binder viscosity and surface tension. Model suspensions of inert glass particles are employed, and formulation components are isolated and modified systematically to deconvolute formulation-rheology relationships. The total solids content was kept consistent at 61.4 vol% of a bimodal distribution of small and large glass spheres. The suspension binder was 30 vol% polyvinylpyrrolidone (PVP) dissolved in variable solvents and surfactants. PVP molecular weight and the solvent system were modified to investigate the roles of viscosity and surface tension, respectively. A FlackTek Speedmixer was used to combine formulation components into a homogeneous mixture and suspension rheology was measured in a TA Instruments Discovery HR-3 Hybrid Rheometer with a parallel plate cross-hatched geometry. Elucidating the role viscosity and surface tension have on suspension thixotropy will help enable the rational design of high solids suspensions that maintain a homogeneous particle distribution throughout processing.

Mon-Q1-21

Polyelectrolyte Complex Hydrogels with Controlled Mechanics Affect Mesenchymal Stem Cell Differentiation in Growth Plate Injuries

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The growth plate is a complex cartilage structure in long bones that mediates growth in children. When injured, the formation of a “bony bar” can occur which impedes normal growth and can cause angular deformities or growth arrest. Current treatments for growth plate injuries are limited and result in poor patient outcomes, necessitating research towards novel treatments that can prevent bony bar formation and stimulate cartilage regeneration. This study investigated alginate-chitosan polyelectrolyte complex (PEC) hydrogels as an injectable biomaterial system to prevent bony bar formation. Biomaterial properties including stiffness and degradation were quantified, and the effect that material properties had on mesenchymal stem cell (MSC) fate was quantified in vitro. Specifically, this study aimed to elucidate the effectiveness of biomaterial-based control over the differentiation behavior of MSCs towards osteogenic or chondrogenic lineages using biochemical metabolite assays and to quantitative real time PCR (qPCR). Further, the PEC hydrogels were employed in a rat physeal injury model to determine their effectiveness at preventing bony bar formation in vivo. Results indicated that material properties significantly affected the differentiation tendency of MSCs in vitro, and the PEC hydrogels show promise as an injectable biomaterial for physeal injuries.

Mon-Q1-22

Exploring the electrical conductivity of fluid suspensions of conductive colloidal particles

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Understanding the mechanism of charge transport in suspensions of conductive particles can enhance the development of next-generation materials for use in emerging energy storage technologies like semi-solid flow batteries and capacitive deionization. However, there remains no theoretical framework with which to quantitatively describe the mechanism of electrical conductivity in these suspensions. In this poster, we describe the preliminary efforts to probe the contributions of particle motion in facilitating electrical transport in dense particle suspensions of conducting nanoparticles. The suspensions are prepared by dispersing functionalized noble metal core-shell nanoparticles in silicone oil. The particle diffusivity was assessed using dynamic light scattering and compared to the electrical diffusivity determined through alternating current impedance spectroscopy measurements. Our results show that conductivity in such suspensions is linked to the complex interplay between particle dynamics, loading, and the properties of the suspending fluid.

Mon-Q1-23

Engineering plasmonic nanocrystals for efficient CO2 reduction

Matthew Crane, Sara Russo

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Climate change has evolved from an emergent issue into a rapidly escalating threat. The increase in atmospheric CO2 is driving rising global temperatures, ocean acidification, and radically changing climate patterns highlighting the critical need for new sustainable energy production technologies. Of particular interest is the pursuit of a one-step process for converting CO2 into liquid fuels with high selectivity and low energy input simultaneously addressing climate change and energy demand. Central to this challenge is minimizing the energy required to break the strong carbon oxygen bond. Recently, plasmonic metal nanomaterials have attracted significant interest due to their ability to perform chemical transformations at ambient conditions using solar irradiation by leveraging localized surface plasmon resonances (LSPR). These LSPRs enhance optical absorbance in nanocrystals and focus light near the surface of these particles to drive selective chemical reactions at mild conditions. One could envision tuning plasmon resonances to engineer reaction selectivity towards desired products for efficient distributed chemistries. However, the mechanism of LSPR-enhanced chemical reactions remains elusive, which limits their design. Here, we investigate reactions on plasmonic nanoparticles by tuning their compositions to elucidate the underlying mechanisms.

Mon-Q1-24

Characterization of Complex Coacervate Environments that Stabilize Reactive Redox Dyes

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Complex coacervates are biphasic liquid-liquid systems that can form when polyelectrolytes of opposite charges are mixed in an aqueous salt solution. These systems consist of a polyelectrolyte rich dense phase and a lean phase with a lower polyelectrolyte concentration. This study demonstrates the novel ability of coacervates to stabilize redox active species in a reduced oxidation state under conditions where the reduced molecule is not normally stable. Specifically, a coacervate system of poly(sodium-4-styrenesulfonate) (PSSNa) and polydiallyldimethylammonium chloride (PDADMAC) has been shown to facilitate the reduction of the redox dyes potassium indigotetrasulfonate (ITS) and methylene blue. Fluorescence data indicates that the redox dyes form aggregated complexes within both the dense and lean phase of the coacervate and that very little dye exists in the monomer form once the reduction reaction is complete. Fluorescence data has shown the reduced ITS to be stable in the coacervate matrix for over a year under atmospheric conditions. Cyclic voltammetry data shows that the reduction potential of the ITS in the lean layer of the coacervate is lower by 143 mV relative to the reduction in oxygen free aqueous solution. This shift in the reduction potential corresponds to a decrease of 27.6 kJ/mol in the Gibbs free energy of reduction for ITS and indicates that reduction of the ITS is more favorable in the coacervate environment. Attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR) was employed to calculate the stochiometric ratios of polyelectrolytes in the dense and lean phase of the coacervate matrix. These studies showed that the control coacervate did not have a 1 to 1 stoichiometry that is often assumed for complex coacervate systems despite behaving as a free-flowing liquid with two distinct phases. Addition of redox dyes and reducing agents moved the system towards a 1 to1 stoichiometry but the system did not obtain a 1 to 1 stoichiometry. The lack of a 1 to 1 stichometry between polyelectrolytes in the dense and lean phase suggests that charge overcompensation may play a role in the complex coacervate formation.

Mon-Q1-25

Elucidating Coverage Control for Defect-Mediated Covalent Surface Functionalization of Ordered Mesoporous Carbon

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Defect-mediated (DM) activation by organolithium reagents is one of a few methods for installing carbon-carbon bonds onto carbonaceous surfaces. Organolithiums undergo deprotonation-lithiation reactions at multiple disbursed C-H sites and with carbometallation at electrophilic surface regions. The resulting “activated” surface is nucleophilic in character and is used to perform subsequent grafting. No study to date has attempted to establish control on the extent of DM grafting on OMC surfaces or study the effects of various synthetic conditions. The three-dimensional pore structure of OMC embodies structures found in 2-D graphene, 1-D CNTs, and 0-D C60. However, the mesoscale pore features of nanocasted OMC are larger and therefore cannot be proxied with DM phenomena studied on other carbon allotropes. We present physicochemical characterization data for aminated OMC surfaces prepared by organolithium activation followed by bromoalkylamine addition. Changes in OMC pore size, synthetic max temperature, and activating agent identity were studied. Results from nitrogen sorption, low-angle X-ray diffraction, infrared spectroscopy, thermogravimetric and elemental analyses illustrate new concepts for covalently modifying mesoporous carbon surfaces by organolithium activation.

Mon-Q1-26

Dynamics of Magnetic Helical Particles in Biologically Relevant Fluids

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Magnetic helical particles can be actuated by the torque induced from the continuous misalignment of particle magnetization with a rotating magnetic field. The coupling between applied torque and translational motion of particles with helical geometries make such particles an ideal model system for studying microparticle dynamics. Both the experimental application and theoretical modeling of the dynamics of these particles has been primarily conducted in Newtonian fluids. The number of studies which extend this analysis to more complex, biologically relevant fluids, are limited to proof of concept experimental studies. This limitation has restricted the use of these particles in biomedical applications, such as biomolecular detection and drug delivery, as many of the fluids and environments encountered in the body are heterogeneous and non-Newtonian. In this work we study the transport of helical particles in model shear-thinning and viscoelastic fluids, to represent biological fluids (blood, mucus, etc.). Helical particles, nominally 12 µm long and 8 µm in diameter, were laser printed using two-photon lithography and made magnetic by incorporating paramagnetic iron-oxide nanoparticles into the photoresist. We characterized their translational response to rotating magnetic fields (~5 mT) as a function of frequency (~0-200 Hz), in solutions containing low concentrations of xanthan gum (a polysaccharide) to model shear-thinning fluids and high concentrations of xanthan gum to model viscoelastic fluid behavior. We compare our experimental results to fluid mechanical modeling of the helical motion of the particles using power law, Carreau and Oldroyd-B rheological models. Rheological properties of the fluids were measured using a parallel plate rheometer and fit with the aforementioned models as input parameters into our calculations. Our results provide an early framework for understanding and improving the locomotion of rotating micro-particles biologically relevant fluids.

Mon-Q1-27

Stability of Protein Corona Formation with Mixed Monolayer Functionalized Gold Nanoparticles

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Nanoparticle technology is a promising area of research with potential use in medical technology, e.g. biosensing, drug delivery, and cancer therapeutics. The formation, structure, and stability of the NP-protein corona plays an important role in nanoparticle-biological interactions. Thiol functionalized gold nanoparticles (AuNPs) were utilized in the present research to investigate the stability of the nanoparticle-protein corona for mixed vs. pure monolayers using UV-Vis absorbance spectroscopy. The mixed ligand nanoparticles displayed the most stable corona formation when tested with BSA (bovine serum albumin), ESA (Equine Serum Albumin), and HSA (human serum albumin) in KCl at physiological concentrations. We suspect that this was due to the large number of energetically favorable protein arrangements closer to the mixed nanoparticle surface. Ion-specific (so-called Hoffmeister) effects on the stability of the NP-BSA corona were investigated as well. Divalent ions demonstrated lower corona stability and greater tendency to aggregate compared to monovalent, symmetric ions across all nanoparticles. DLS characterization of NP-protein corona size and zeta potential, along with TEM and additional analysis are planned for the near future.

Mon-Q1-28

The Effect of Solution Viscosity and Functionalization Chemistry on Acoustic Cavitation Threshold of Silica Nanoparticles

Talaial Alina [1], Evan Mueller [1], Jennifer Cha [2], Andrew Goodwin [3]

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The creation, growth, and collapse of a bubble induced by sound energy is known as acoustic cavitation. Therapeutic acoustic cavitation applications use high input pressures to raise the local temperature in a biological environment, which can ablate diseased tissue but also harm nearby healthy cells. Ultrasound contrast agents should be optimized to generate cavitation events without harming biological environments where ablation is not desired. Solid ultrasound contrast agents, such as phospholipid coated, hydrophobically modified mesoporous silica nanoparticles (PL-HMSNs), have recently been developed to permit acoustic cavitation at low input pressures while minimizing off-target effects. PL-HMSNs experienced more than five-fold greater acoustic activity than those of unmodified mesoporous silica nanoparticles (MSNs) and showed propulsion through an agarose hydrogel model. However, there has been minimal investigation of the effect of viscosity, found in different ranges in biological environments, on nanoparticle cavitation. In an initial exploration of this problem, the lipids 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy(polyethylene glycol)-2000] (DSPE-PEG2K-methoxy) were added to hydrophobically modified MSNs immersed in water/glycerol mixtures of varying viscosities. Then, the input pressures for high intensity focused ultrasound (HIFU) were increased to generate cavitation on these nanoparticles. Higher input pressures were required to facilitate cavitation when solution viscosity was increased. These findings may improve understanding of input pressures required to generate cavitation on solid ultrasound contrast agents in viscous environments such as saliva, blood, or mucus.

Mon-Q1-29

Acoustically Active Nanoparticles for Hydrophobic Drug Release

Taylor R. Ausec, Evan N. Mueller, Talaial B. Alina, Jin Gyun Lee, Jennifer N. Cha, Andrew P. Goodwin, C. Wyatt Shields IV

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Ultrasound is promising for on-demand drug delivery because of its selective spatiotemporal control over release and clinical compatibility. Many systems utilize lipid bilayer-coated microbubbles as a drug carrier due to their sensitivity to ultrasound waves and their ability to transport drugs within the lipid bilayer. Despite success in the lab, their clinical translation has often been limited by short-lived stability in solution and low drug loading capacity. To address these challenges, we have engineered the interface of mesoporous silica nanoparticles to hold a high concentration of hydrophobic drugs for triggered release. The particles used in this work are phospholipid-stabilized, hydrophobically modified mesoporous silica nanoparticles (PL-hMSNs), which can generate cavitation events in response to high intensity focused ultrasound (HIFU). Mesoporous silica nanoparticles are a popular drug carrier because they are biocompatible and have high surface area. We make PL-hMSNs using a simple, three-step process. Mesoporous silica nanoparticles (MSNs) are synthesized using a base-catalyzed reaction which yield monodisperse particles with a hydrodynamic diameter of 130 nm. The surfaces of the MSNs are then modified with an alkyl silane, which produces a contact angle for a layer of deposited particles of about 145°. Lastly, drug is loaded, and a phospholipid monolayer is added to the surface of the particles through a chloroform injection technique, which increases the uptake of hydrophobic drug and improves the solubility of the particles in aqueous media. In an acoustic field, PL-hMSNs show a half maximal signal response at an input voltage of 600 mV. The maximum signal produced by PL-hMSNs in an acoustic field was ten times greater than that of PBS, which is sufficient power for PL-hMSNs to release loaded drug into solution. When these particles were exposed to HIFU, drug release was triggered from the particles. The high drug loading capacity of PL-hMSNs allows for more efficient delivery of hydrophobic molecular therapies to disease sites as compared to existing nanocarriers. Ultrasound-mediated spatiotemporal control over drug release is possible due to the acoustic activity of PL-hMSNs, which can reduce off-target side effects of drugs such as chemotherapies.

Mon-Q1-30

Enzyme Prodrug Therapy and Cellular Trafficking of Photocrosslinked Nanoparticle-Affibody Complexes

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The chemical functionalization and labeling of cell surface proteins has gained significant interest in recent years for therapeutic applications. Despite major advancements in cell labeling or tagging in in vitro studies, challenges remain in translation to in vivo applications. Ultimately, labeling specific cells in vivo for therapy will require methods to have both selective targeting of cells and tissue while avoiding the inherent transient nature of standard protein-receptor interactions. Our group has previously shown that covalent conjugation, using UV-dependent photoreactions, of affibody-enzyme proteins to cell receptors yields enhanced retention on cell surfaces while preserving protein function. To adapt this to clinically relevant settings, our group formed multivalent upconverting nanoparticle-affibody-enzyme complexes that were shown to have increased tumor accumulation in in vivo settings upon using near-infrared irradiation to induce crosslinking. The affibody allows for targeting and covalent photo-crosslinking to cellular Epidermal Growth Factor Receptors while the enzyme, cytosine deaminase, enables a therapeutic effect. We showed that the nanoparticle-protein complexes could be used to significantly reduce tumor growth in mouse models, demonstrating the potential of adapting these particles to therapeutic settings. To further analyze these results, we are seeking to understand the cellular trafficking and fate of a photo-crosslinked nanoparticle-protein complex. While much research has been done to analyze the variety of cellular fates of an endocytosed nanoparticle, the effects of photo-crosslinking a protein-functionalized nanoparticle to cells remains to be seen. These findings may lead to a greater understanding of the potential therapeutic uses of crosslinked nanoparticle complexes.

Mon-Q1-31

Direct Investigation of the Impact of Cellulose Rheology Modifiers on Internal Microstructure of Drying Coatings

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The evolution of microstructure in drying coatings is essential to the final film properties. Understanding this process and the microstructure during drying is a common question in the coatings industry. There is often a separation between the predicted film and the final applied film. There are few techniques that are able to provide this information in situ. This study focuses on tracking fluorescent silica particles that behave as surrogate pigment or rheological modifiers using high-speed laser scanning confocal microscopy to give the time evolution of microstructure as a function of the formulation. Specifically, the addition of a cellulose-based rheology modifier is examined to understand the impact of rheology modifiers on the drying process and resulting microstructure. Using the 3D particle locations, the evolution of this microstructure allows thorough statistical analysis, resulting in simulation-like detail from physical experiments.

Mon-Q1-32

Aqueous thermal field-flow fractionation for the characterization of polymer colloids with low amounts of acidic comonomer

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Polymer colloids synthesized via emulsion polymerization are employed at large scale in a wide range of well-established applications such as coatings, adhesives, home, and personal care along with many emerging applications including medicine, biotechnology, and energy. The worldwide market size for emulsion polymers is estimated at USD 25.5 billion in 2021 and is projected to reach USD 38.9 billion by 2026, with a CAGR of 8.2%. In addition to financial value, the shift from solvent to waterborne dispersions has yielded large and measurable sustainability benefits. The stability of polymer colloids during production, transportation and formulation to final products is often an important aspect during product design and scale up. The incorporation of acidic comonomers into the polymer colloids during emulsion polymerization provides an avenue to manipulate the stability through electrostatic stabilization. Analysis of colloidal surfaces with low acid moieties and obtaining their distributions is challenging and requires a separation step. Thermal field-flow fractionation (ThFFF) is a chromatography-like technique that utilizes a thermal “field” or gradient to separate particles based on size and composition. The primary separation mechanism is based on the ratio of an analyte’s thermal diffusion coefficient (DT) to its translational diffusion coefficient (D). ThFFF has been previously demonstrated to be sensitive to surface composition including acidic surface functionalities containing more than 9% acid. This work aims to examine ThFFF’s sensitivity to subtle changes in low acid moieties (< 3 %) on the surface of polymer colloids. Latex particles composed of butyl acrylate-methyl methacrylate-acrylic acid (BA/MMA/AA) with a range of 0 to 3 % AA were used as a model system. Under aqueous conditions (AqThFFF), salts and/or surfactants are needed to improve retention. Specifically, the effects of adding tetrabutylammonium perchlorate (TBAP) and the surfactant mixture FL-70 to the carrier liquid were examined. The presence of only TBAP in the ThFFF carrier liquid yielded well retained colloids and a trend of increasing retention with decreasing acid content. However, FL-70 alone and FL-70 with TBAP both resulted in decreased retention of the model colloids. The measured retention times and D values (obtained by dynamic light scattering) allowed subsequent calculation of DT values. The DT values were significantly different for colloids containing 0, 1, 2 and 3 % acidic comonomer. The results demonstrated that AqThFFF could be a technique to separate these latex particles based on

differences in surface charge, and to characterize the surface charge distribution with low amounts of acidic comonomer.

Mon-Q1-33

Magnetic Steering and Trapping of Nanodisc-Macrophage Complexes

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University of Colorado Boulder Chemical and Biological Engineering

For decades, cancer patients have struggled with systemic toxicity from drugs such as chemotherapies and immunotherapies due to their inability to specifically interact with diseased cells in the body. Adoptive cell transfers have emerged as a solution to this problem due to their ability to interact specifically with diseased cells. However, adoptive cell transfers accumulate in various tissues throughout the body, including both healthy and diseased sites. Currently, there exists no clinical treatments to remotely control the location of adoptively transferred cells after they are administered. To address this challenge, we have developed magnetically responsive microdiscs that securely attach to the surfaces of cells and enable their remote steering in physiological environments using gradient magnetic fields. We used macrophages as our cell of choice due to their therapeutic potential in a variety of diseases [1]. While macrophages typically phagocytose most free particles in their vicinity, particle geometry can be adjusted to avoid internalization. A spherical particle will be phagocytosed almost immediately, while a thin, flat nanodisc will remain bound to the outside of the macrophage for days, frustrating any efforts to internalize it [2]. We fabricated hexagonal discs 10 microns in diameter with an average thickness of 250 nanometers using soft lithography, in which we used spin-coating to distribute a mixture of superparamagnetic iron oxide nanoparticles (SPIONs), poly(lactic-co-glycolic acid) (PLGA), and drug in chloroform across an elastomeric template. After the chloroform evaporated, PLGA with entrapped SPIONs and drug was deposited on the template surface for microcontact printing and extraction. We then attached the discs to macrophages ex vivo. Following these procedures, we demonstrated stable binding and phagocytosis resistance over several days using fluorescent confocal microscopy. We then demonstrated magnetically mediated steering and trapping of the macrophages with attached nanodiscs in capillaries at physiological flow rates. We used a magnetic field strength varying of 20-300 mT and capillary diameters of 50-500 microns to steer and trap the cells against the capillary wall to compare the efficiency of trapping in a variety of fluid flow velocities up to 2 mm/sec. We quantified the trapping efficiency of disc-cell complexes as a function of magnetic field strength and fluid flow. Our experiments reveal that there is a high rate of retention once cells are trapped, highlighting their potential to localize in regions of the body exposed to high magnetic field gradients. Such nanodisc-macrophage complexes have the potential to release drugs locally and sustainably in a tissue of interest to treat disease, reducing toxicity and bolstering current adoptive cell transfer processes.

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Mon-Q1-34

Miniaturized Magnetically Actuated 3D Printed Langmuir-Blodgett Troughs

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We will show the design of 3D printable silicone inks which allow for the fabrication of magnetically responsive three-dimensional floaters on water. The 3D printed structures exhibit programmable magneto-capillary deformation with shape-driven reconfiguration in response to an externally applied magnetic field. The interplay between interfacial tensional force along the air/liquid interface and the orthogonally applied magnetic force results in lateral motion of the printed soft architectures as capillarity keeps the objects afloat. We have shown how the specific spatial anisotropy in the printed architectures forces them to actuate in a predetermined direction. We will further show how this actuation methodology can be used to measure the surface pressure of proteins adsorbed on air/liquid interfaces in a Langmuir-Blodgett trough and its dependence on protein concentration. The magnetically responsive structures are composed of cured polydimethylsiloxane (PDMS) microbeads embedded with 40 wt. % neodymium-iron-boron (NdFeB) microparticles. The PDMS microbeads are then capillary bridged by small volumes of uncured PDMS liquid precursor. The structures can be utilized as probes for analyzing shear and dilatational rheology of different protein adsorption layers, by acting as miniaturized Langmuir-Blodgett troughs on the interface. We will demonstrate how actuator designs with a working area of approximately 1 cm^2 are capable of compressions greater than 30% of their original area. These soft magnetically responsive actuators are inexpensive compared to commercial Langmuir-Blodgett troughs and are easily constructed. Therefore, these soft structures have potential applications in the fields of interfacial rheology, optics, nanoparticle coatings, and soft robotics.

Mon-Q1-35

Transport Dynamics of Magnetically-Driven Particles in Dilute and Dense Systems

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[1] Department of Chemical and Biomolecular Engineering, Lehigh University, PA, USA[2] Polymer Science and Engineering, Lehigh University, PA, USA

Magnetically responsive Janus particles have been a fascinating subject for the soft matter and complex systems communities in recent years due to the anisotropic nature of the particles, which leads to sometimes unpredictable or unexpected behaviors. Though on a very dilute scale, these unique particles have been studied extensively, pseudo-dilute to dense systems have rarely been studied due to the scalability of Janus particle production, particularly through the physical vapor deposition (PVD) approach usually taken for production of magnetically responsive Janus Particles. The use of Automated Langmuir-Blodgett deposition allows the roll-to-roll production of particle monolayers leading to orders or magnitude increases in Janus particle production, which in turn allows for the study of increasingly large or increasingly concentrated systems. Here we demonstrate the production of large quantities of granular scale (50 micron) ferromagnetic Janus particles and present a number of examples of magnetoresponsive systems. Specifically, we focus on the introduction of shear to these systems through the direct application of rotational torque to Janus particles via an external rotating magnetic field. These systems of rotating magnetic Janus particles lead to some interesting collective behaviors, demonstrating phenomenon such as enhanced transport, instabilities and dynamic heaping.

Mon-Q1-36

Characterization of Sodium Doped Silicon Clathrates through Electron Paramagnetic Resonance

Joseph Briggs [1], Yinan Liu [1], Ahmad Majid [1], Carolyn Koh [1], Craig Taylor [2], Meenakshi Singh [2], Reuben Collins [2]

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Much of the research into quantum materials has been centered around diamond Si, due to the large depth of knowledge and it being extensively studied for electronics. However, d-Si is close to its optimal limit due to its indirect bandgap, and different more ideal allotropes of Si have been theoretically proposed. One silicon allotrope that has been proposed are silicon clathrates, due to their open framework, direct or near direct bandgap, and decreased density compared to d-Si. Silicon clathrates are cage like inclusionary compounds that are made up of a silicon lattice with interstitial “guests” sitting inside of the cages of the form MxSi136, 0<xIn this study we examine these films utilizing continuous wave and pulsed electron paramagnetic resonance to extract information about silicon clathrates for use in quantum application. EPR gives insight into the levels of sodium and their placement and interactions within the silicon cages. Through pulsed-EPR spectrum we have been able to gain insight into the relaxation time and coherence time of low sodium doped type-II silicon clathrates. This work was supported by National Science Foundation (2114569).

Mon-Q1-37

Interfacial Dynamics of Phospholipids Membranes and Their Interactions with Nanoparticles

Gary Min Chiang Ong, Brianna Icamen, Younjin Min

University of California, Riverside. Chemical and Environmental Engineering.

Phospholipids are major components in lipid membranes in living cells which serve important biological functions. Because of their amphiphilic nature, phospholipids can, in aqueous environment, self-assemble into the bilayer structures present in cell membranes such as lung alveoli and myelin sheath. Interactions of such cell membranes with nano-objects have been important topics in the fields of colloids and biophysics, as well as biomedical fields in past decades. Given that nanoparticles (NPs) can serve as not only drug delivery carriers but also toxic foreign objects in contact with cell membranes, this work seeks to answer questions pertaining to fundamental understanding of the complex molecular interactions in NPs-phospholipid systems at different length scales, in particular, focusing on lung surfactant system. In this study, pristine and hydrophobically modified silica NPs were selected to model various types of engineered nanoparticles (ENPs). Monodisperse ~50 nm silica NPs were synthesized via a modified Stöber method and surface of silica NPs were modified with alkyl silanes of varying chain length and polarity. 1,2-Dipalmitoyl-sn-glycero-3-phosphorylethanolamine (DPPE), one of the major components of lung surfactant layers, was chosen as our model phospholipid molecule. The extent of surface modification was determined using transmission Fourier transform infrared spectroscopic measurements and contact angle studies. It was found that the presence of nanoparticles strongly influences the fluidity, rigidity, and pressure-area isotherms of phospholipid layers. In addition, surface hydrophobicity of nanoparticles was shown to strongly control the interfacial dynamics of such phospholipidic layers. We anticipate fundamental knowledge gained through this study would provide new insights into not only understanding the subsequent retention, translocation, and clearance of inhaled ENPs and the sequential processes associated with the nanoparticle toxicity but also designing effective drug delivery carriers systems.

Mon-Q1-38

Highly aligned carbon nanotube and graphene composite through use of mechanical shear forces

Sunghoon Park, Hyunwoo Kim, Ji-Hwan Ha

Soongsil University

Highly aligned carbon nanotube (CNT) and graphene polymer composites were fabricated via a roll-to-roll milling process; the alignment of the CNT/graphene could be controlled by varying the speed of the rotating rolls. The effect of filler alignment on the polymer matrix was morphologically observed and quantitatively characterized using polarized Raman spectroscopy. To provide a more detailed comparison, the composites with alignment in the transverse direction and random alignment were fabricated and tested. Enhanced mechanical and electrical properties were obtained for the aligned CNT/graphene composite, which can be attributed to the efficient electrical network and load transfer, respectively. In addition, a cyclic stretching test was conducted to evaluate the piezo-resistive characteristics of the aligned CNT/graphene composites. The composites with an aligned filler configuration showed an exceptionally high degree of strain sensitivity compared to the other composites.

Mon-Q1-39

Investigating partial coalescence of single droplets against oil/water interface under dynamic conditions

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Investigating partial coalescence of single droplets against oil/water interface under dynamic conditions Partial coalescence has its relevance in a wide variety of physical phenomenon[1] as well as industrial applications[2]. Its significance has been highlighted in understanding meteorological aspects such as raindrop formation, taste perception in food emulsions, refining operations in crude oil separation and so on. Partial coalescence events have been previously reported[3,4] to occur when a drop of oil/water, rising or falling through water/oil merges with its own reservoir, given the conditions are appropriate. In this scenario, several self-similar events leading to the formation of multiple generation of daughter droplets have been recorded before complete merging (coalescence) into its identical bulk fluid is eventually accomplished. In this work, we attempt to gain an insight into the complex phenomenon of partial coalescence in emulsions when the primary droplet collides at the surfactant stabilized interface of the two liquids, under dynamic conditions. This is achieved by changing the distance covered by the primary drop in the ambient liquid. The dynamic interfacial tension data measured using pendent drop method ensures equilibrium coverage of surfactants on the droplet surface before release and therefore substantiates the chosen ageing time of the primary droplet on the dispenser tip. We capture the effects of varying dynamic conditions on the size and lifetimes of each daughter droplet generated in the process which ultimately dictates the overall stability of the coalescence event. In addition, the effect of the concentration of surface-active species is also explored.

References:

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Mon-Q1-40

Spectro-Nanoscopy of Ultrathin Films of Organic and Biological Specimens via Infrared Photo-induced Force Microscopy (IR PiFM)

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Ultrathin films of organic, inorganic, and biological molecules are utilized in many processes involved in production of nano-medicine, biosensors, and semiconductor devices. A non-invasive analytical technique that can verify the chemical and structural integrity of such thin films is presented in this paper. Infrared photo-induced force microscopy (IR PiFM) combines the two well-known techniques – atomic force microscopy (AFM for microscopy) and infrared absorption spectroscopy (IR for spectroscopy) – into one instrument to provide both structural imaging and IR spectro-nanoscopy with ~ 5 nm spatial resolution [1]. Three samples, two with ~30 nm thick peptoid film, each before and post annealing, and a monolayer film with less than 3 nm thickness, were prepared for IR PiFM analysis. Si substrates were cleaned with UV ozone, and the peptoid solution was spun coat to get ~ 30 nm thin films (sample 1: as-deposited thin film). The thin films were then annealed at 150 °C for 30 min (sample 2: annealed thin film). After annealing, the excess (i.e., ungrafted) peptoids were rinsed away by repeated sonication in a good solvent N-methyl pyrrolidinone and isopropanol, then annealed at 100 °C for 10 min to remove residue solvent (sample 3: monolayer). On the thicker peptoid films, the IR signature associated with the peptoid film (acquired by FTIR) was clearly observed in PiF-IR spectra at every location while the spectral image at the amide I band (1633 cm-1) showed a mostly uniform peptoid film. In addition to the IR peaks associated with the peptoid, additional peaks associated with common airborne organic contaminants were observed as well. On the monolayer sample, spectral mapping at the amide I band and local PiF-IR spectra revealed that only nanometer-scale fragments of peptoid had managed to graft onto the Si substrate as shown in Figure 1. Detailed analysis of the PiF-IR spectra and PiFM images will highlight the exceptional spatial resolution and sensitivity of IR PiFM and its usefulness in the analysis of ultrathin films of organic and biological specimens.

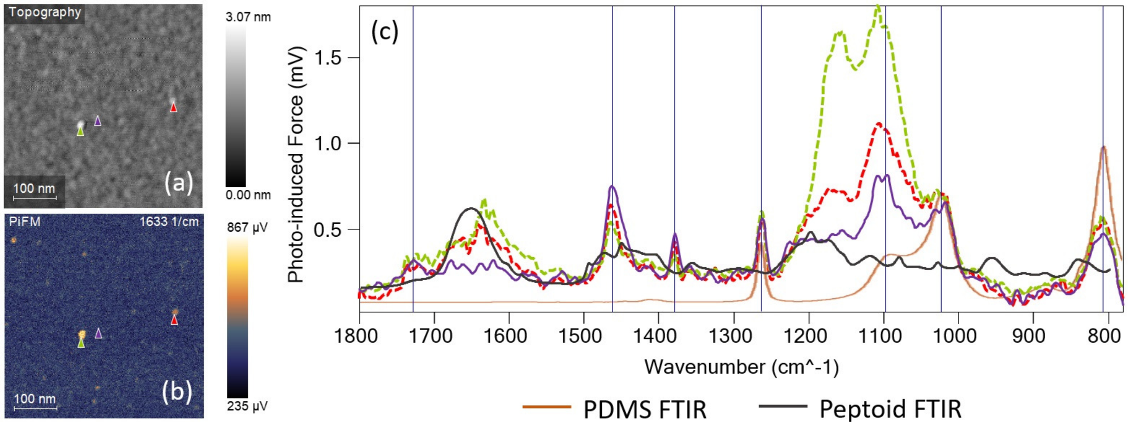

Figure 1. AFM topography (a), PiFM image at 1633 cm-1 (b), and PiF-IR spectra along with FTIR spectra for the peptoid and PDMS (c). The green and red dashed PiF-IR spectra are acquired on particles that are 1.8 nm and 1.2 nm tall, respectively, demonstrating the single-molecule-level sensitivity of PiFM. The PiFM image (b) shows that there are even smaller peptoid fragments remaining that are difficult to distinguish in topography due to the roughness of the substrate. The vertical lines denote the PiF-IR peaks that are attributable to contaminants. References: [1] D. Nowak et al., Sci. Adv. 2, e150157 (2016).

Mon-Q1-41

Mines/NREL Nexus: X-ray Photoelectron Spectroscopy Characterization of Polymer Electrolyte Membrane Fuel Cell and Water Electrolyzers

Jayson Foster, Department of Chemistry, Colorado School of Mines, USA

Mon-Q1-42

Mines/NREL Nexus: Transmission Electron Microscopy and Energy Dispersive Spectroscopy to Analyze Catalyst Layer Degradation of Fuel Cell Cathode Catalyst Layers

Matt Coats, Department of Chemistry, Colorado School of Mines, USA

Mon-Q1-43

Mines/NREL Nexus: Stability and Durability of CO2 Reduction to Formate Electrochemical Systems

Leiming Hu, Chemistry and Nanoscience Center, National Renewable Energy Laboratory, USA

Mon-Q1-44

Mines/NREL Nexus: Supported MoO_x Catalysts for Aldol Condensation

Matt Rasmussen, National Renewable Energy Laboratory, USA

Mon-Q1-45

Mines/NREL Nexus: Characterization of CO_2 Binding on Alkaline Metal Oxide Sorbents and DFMs for Combined Capture and Conversion

Chae Jeong-Potter, Catalytic Carbon Transformation & Scale-Up Center, National Renewable Energy Laboratory, USA

Mon-Q1-46

Mines/NREL Nexus: Synthesis and (Mis)-Characterization of Morphologically-controlled VS_2 for Electrocatalysis

Logan Wilder, National Renewable Energy Laboratory, USA

Tuesday, July 12th | 08:00 - 09:00 | Z2-Plenary Lecture 2

Mon-Z2-01

Light-harvesting Applications of Earth-abundant Nanoparticles

Naomi Halas

Rice University

Tremendous advances in nanoparticle chemistry have been made with noble metal nanocrystals, inspiring a research challenge: can we also synthesize, in controlled ways, metal nanocrystals from more earth-abundant metals? Much of our recent research efforts have allowed us to develop synthetic routes towards Al nanocrystals. Not only are Al nanocrystals unique in their use of a catalyst to lower the valency of their alane reactant, initiating growth, but the catalyst can also play a surprising and unexpected role in con-trolling nanocrystal morphology by associating with specific crystalline facets of the growing nanocrystal.

Al, as well as Cu, can serve as an optical frequency antenna in “antenna-reactors” that promote plasmonic photocatalysis, which also exploits the catalytic transition metals as reactive sites. This combination has been shown to drive chemical reactions of fundamental and also mainstream industrial interest, such as methane reforming, at far lower temperatures than are required by conventional thermocatalysis. But catalytic reactive metals (e.g., Pd, IR, Pt, Ru) are the rarest metals found on the earth’s crust. Can we begin a shift towards more abundant reactor metals as well? Preliminary studies on earth-abundant antenna-reactors provide some very interesting opportunities for performing cata-lytic chemistry in new ways on some unexpected antenna-reactor combinations.

Tuesday, July 12th | 09:30 - 11:30 | A4-Active Matter

Tue-A4-01

Active Janus and Patchy Particles Near Boundaries

Ilona Kretzschmar

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Janus particles, i.e., particles with two distinct halves, have been heralded as new materials for assembly, drug deliver, autonomous motion, and emulsion stabilization since deGennes' 1991 Nobel lecture. Janus particles, i.e., particles with a 50% surface coating, are a specific subset of patchy particles that can have any number of material patches on their surface. Our laboratory has spent the past 17 years developing methods to make a versatile set of Janus and patchy particles with magnetic, photonic, and catalytic properties and studying the behavior of such particles in electric and magnetic fields as well as at and near boundaries. In this talk, our research contributing to understanding the behavior of such particles in the vicinity of solid/liquid, liquid/liquid, and air/liquid interfaces will be discussed. The talk will discuss various swimming mechanisms and then focus more closely on self-diffusiophoresis exhibited by systems with Pt-catalyzed H_2O_2 decomposition. Specifically, probing the impact of activity on the Janus/patchy particle/boundary interaction will be highlighted. Support for this work has been provided by the National Science Foundation CBET, HRD, and DMR as well as the Air Force Office of Scientific Research.

Tue-A4-02

Chemically active colloids near osmotic-responsive interfaces

William Uspal

Mechanical Engineering, University of Hawai'i at Manoa

Active Janus particles self-propel by catalyzing the decomposition of molecular “fuel” available in the surrounding solution. The resulting self-generated chemical gradients drive phoretic flow in an interfacial layer surrounding the particle, leading to directed swimming motion. Generically, the same interfacial mechanism should also drive chemi-osmotic flows along any nearby container walls, providing an additional contribution to motion of the particle and of the solution. Nevertheless, this mechanism has been largely overlooked in most active particle research. Here, we consider two systems in which osmotic-responsive interfaces play an essential role. In the first system, we consider, via theory and experiments, the distribution of small tracer particles around a Janus particle in the vicinity of a planar wall. Experimentally, we observe that, under certain conditions, the catalytic cap of a particle is surrounded by a tracer-free exclusion zone. We build a theoretical model that comprehensively accounts for contributions to tracer motion from flow and chemical gradients, and show that tracer motion cannot be explained without accounting for the osmotic response of the surface. In the second system, we study theoretically how to chemically pattern a solid surface in order to control particle motion. We show that the chemi-osmotic response of a patterned surface can effectively align and spatially localize active colloids.

Tue-A4-03

Active Janus Particle Behavior at Oil/Water Boundaries

Baseemah Rucker, Ilona Kretzschmar, Alexander Couzis

The City College of New York

Janus particles (JP) are asymmetrical particles with each hemisphere having a unique surface composition. The JP in focus is a silica particle with a smooth platinum (Pt) cap on one side. When placed in an aqueous solution of hydrogen peroxide (H2O2), the Pt reacts with the H2O2 and produces water and oxygen on one side of the particle, propelling it forward in the opposite direction. This JP is active without the presence of a magnetic, electric or acoustic field, making it an autonomous swimmer with a chemical motor. Micromotors have become of recent interest of researchers and industry professionals for applications in drug delivery, wastewater treatment and sensors. JPs are fabricated by depositing Pt on top of silica monolayers in a physical vapor deposition machine (PVD). During the deposition, the Pt is deposited normal to the surface of the silica particles. The top half of the silica particles shield the bottom half of the silica particles leaving the top half Pt and the other half silica. The Pt surface and silica surface have different wettability properties making the JPs amphiphilic. An observation cell was designed to observe JP behavior at an oil/water boundary. A hexadecane droplet was placed on the bottom of a swimming basin of JP and water. From a top view, the oil/water boundary was clearly defined, and the JPs interaction with the boundary could be observed. The oil phase and water phase lay next to each other on the same X-Y plane, so gravity in the Z direction does not affect the JP's interaction with either phase. Here we are reporting on the behavior of JPs at an oil/water boundary including the JP position at the oil/water boundary, the guidance of active JPs along the perimeter of the oil droplet, and the effect of JP activity on the JP interactions with the oil/water boundary. Having a greater understanding of the behavior of micromotors in a variety of environments will supply the knowledge needed to engineer guided JP systems.

Tue-A4-04

3D-Printed Layers for Smart Actuations

KENAN SONG

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Polymers and nanoparticles are the most widely used class of raw materials in 3D printing. While 3D printing can build complex shapes, eliminate material wastes, and be cost-effective, there are still limitations in controlling manufacturing resolutions and precision, e.g., managing smart behaviors via multimaterial printing in one-step processing. This hinders in realizing the ultimate potential of 3D printing in broad applications, such as structural composites, thermal exchanging, electronics, optical metasurfaces, and biomedical implants. Here, we report a new in-house developed 3D printing mechanism – multiphase direct ink writing (MDIW), for unique layering textures that are efficient in smart behaviors, especially actuating performances. The MDIW uses two incompatible polymer solutions and nanoparticle dispersions for producing multilayered composite structures within the printing plane, in contrast to the layers usually reported along the out-of-plane normal directions in general additive manufacturing. The mechanism was demonstrated using different polymer and nanoparticle (e.g., polyvinyl alcohol (PVA) and thermoplastic polyurethane (TPU), plus carbon nanotubes (CNTs) and iron oxide (Fe3O4) particles). A lamella-mimicking composite structure was fabricated producing 4 – 512 alternative layers within each printing line (e.g., a size of ~mm for the single printing line). The intrinsic shear force in the nozzle helped in the preferential orientation of particles and provided microstructural changes. The composite lamella with 64 alternative layers produced the best mechanical property improvement (5 times increase in young's modulus, 3 times growth in ultimate tensile strength) as compared to the pure polymer samples. The composite also improved the smart actuations that can be stimulated via temperatures, moisture, and composite dimensions.

Tue-A4-05

Probing Surface-Adsorbate Interactions and Energetics through Active Particle Dynamics

Benjamin Greydanus, J. Will Medlin, Daniel Schwartz

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Introduction Adsorption of solute molecules at the liquid−solid interface is of central importance in liquid-phase heterogeneous catalysis. Reactant adsorption from solution onto the catalytic surface is typically required to initiate the reaction. Moreover, other solute species (and in some cases the solvent) can adsorb on the surface and compete with the reactant for catalytic active sites. Furthermore, the unique properties of different metals can have large impacts on catalysis, including by altering binding strengths of adsorbates. These energetics are commonly studied in vacuum; however, the presence of solvent can have dramatic impacts and the effect of surface composition on the adsorption energies in water is poorly understood. Here, we show the utility of self-propelled active particles for quantification of the affinity and saturation coverage of adsorbates onto a metal surface under steady state reaction conditions. We exploited the dependence of peroxide-fueled active motion on solute concentration to quantify adsorption on available metal surface sites. This approach is particularly attractive as it helps capture one of the most salient aspects of catalysis, i.e., the competitive in situ interactions of the adsorbate, peroxide, and metal surface under steady state reaction conditions in an aqueous phase. Importantly, this approach is broadly applicable to adsorbates with a very wide range of surface affinity, and measures adsorption in a way that is directly relevant to catalytic activity.

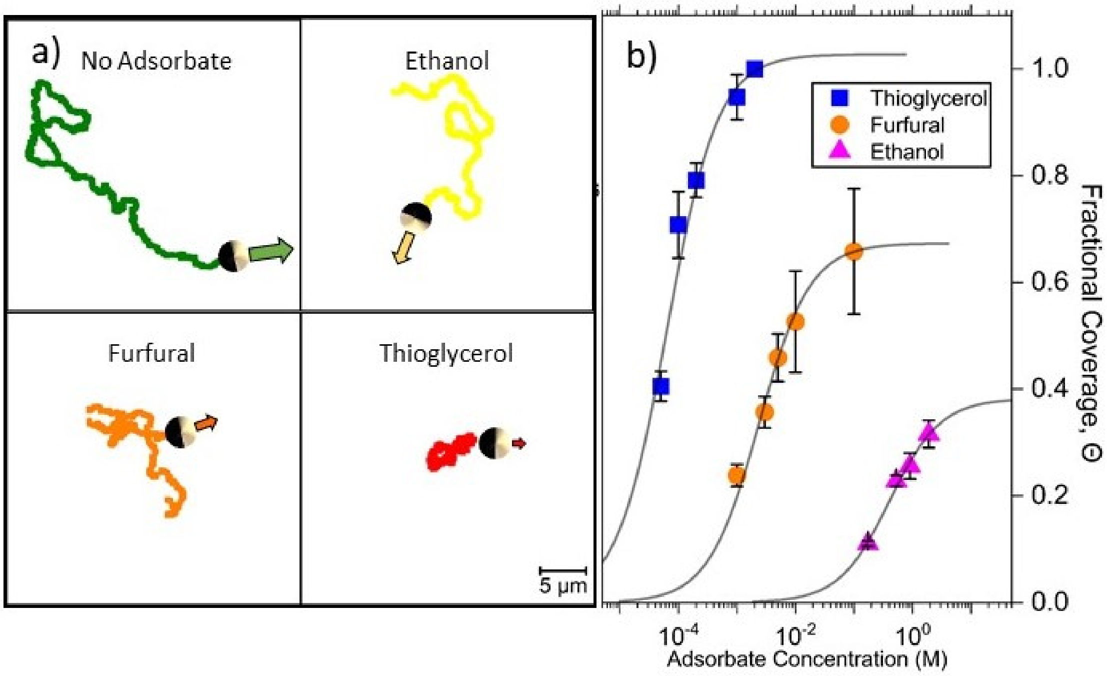

Figure 1. a) Influence of different adsorbates on particle trajectories and b) adsorption isotherms derived from adsorbate-mediated attenuation of active particle motion

Methods and Results Active 1 um fluorescent polystyrene particles were synthesized by sputtering a thin layer (~5 nm) of metal (Pt, Pd, and PdAu alloys) onto one hemisphere of the particle. The motion of the particles in the presence of different organic adsorbates in a 10% H_2O_2 solution was measured and the observed attenuation of velocity was used to construct Langmurian adsorption isotherms, allowing for extraction of the affinity and saturation coverage of each adsorbate. The affinity of thioglycerol towards the Pt was the highest of the measured adsorbates, followed by furfural and then ethanol (Ka 16.6±4.3, 0.47±0.04, and 0.0011±1e-4, respectively). We note that these extracted affinities range over more than 4 orders of magnitude, showcasing the broad applicability of this technique. Comparison of the isotherms at different temperatures allowed for extraction of the enthalpy of adsorption for furfural and ethanol onto the Pt surface under reaction conditions: –ΔH: 69 kJ/mol for furfural and 23 kJ/mol for ethanol. Furfural was further used to probe the relative affinity and energetics (i.e. scaling relations) between the metals. The affinity of the metals towards furfural adsorption showed good agreement with the relative oxophilicity of each metal (Pd>PdAu alloys>Pt). **Significance** Adsorption of solute molecules onto metal surfaces has important implications in catalysis and this work shows that important parameters and salient energetics of this process can be captured using active particles. This technique is effective over a wide range of adsorbate concentrations (nearly 4 orders of magnitude), requires only a microscope equipped with a camera, and accurately captures in situ phenomena that are directly relevant to catalysis.

Tue-B4-01

Effects of Nanoscale Confinement on Adsorption, Transport, and Forces

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Confinement of dissolved species to very small spaces can lead to changes in the behavior of molecules due to the surface electrical potential. In this talk, I will describe several examples of how this confinement affects colloidal phenomena. In the first instance, diffusion within the confined space can be hindered. We have examined the diffusion of the dianion, fluorescein, in a thin film between two glass walls in aqueous solution. Owing to charging of the walls, the diffusion is hindered when the Debye length is similar to or larger than the dimensions of the confined space. In the second instance, I will discuss how surfactant aggregation is affected by confinement. In bulk solution, aggregation occurs at the critical micelle concentration. A surface electrical potential can lead to a change in the critical concentration for aggregation of charged surfactant. When the surfactant is confined between two interfaces, the surfactant is subject to the overall field from both interfaces. In this work, I will describe both how this leads to aggregation at a low concentration, and how the aggregation affects the interpretation of surface forces measurements. For example, aggregation can lead to a change in the double-layer interaction that is a function of confinement.

Tue-B4-02

Surface Forces Sculpt Nanoscopic Mesas in Micellar Foam Films

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A complex interplay of curvature-dependent capillary pressure and thickness-dependent disjoining pressure influences topography of ultrathin supported and freestanding films of soft matter. The confinement-induced structuring and layering of supramolecular structures like micelles provide non-DLVO oscillatory structural contributions to disjoining pressure. In micellar foam films, the oscillatory structural disjoining pressure drives drainage via stratification, associated with coexisting thick-thin flat regions and stepwise thickness evolution. Stratification in micellar foam film proceeds by nucleation and growth of thinner domains at the expense of surrounding thicker film. Often brighter halos arise around growing domains, before creating a necklace with one, two or more bright spots. Even though such brighter regions were attributed in publications to a possible formation of thicker non-flat regions including nanoridges, the experimental and theoretical characterization of nanoscopic topography have remained longstanding challenges. Here, we show the use of IDIOM (interferometry digital imaging optical microscopy) protocols for visualizing and analyzing the nanoscopic thickness transitions in stratifying micellar foam films, with exquisite spatial (thickness < 10 nm, lateral < 1 μm) and temporal resolution (< 1 ms). We discern the nanoridge at the moving front and analyze the topographical instability leading to formation of nanoscopic mesas that can grow and often coalesce with other mesas along the moving front. Finally, we provide a theoretical model based on thin film equation amended with supramolecular oscillatory structural disjoining pressure and show that the shape and size evolution of nanoridges and mesas can be captured quantitatively.

Tue-B4-03

Atomic Force Microscopy as a Tool for Molecular and Macromolecular Interactions with Metal-Organic Frameworks

Joey Palomba [1], Keith Brown [2], Verda Saygin [2]

[1] U.S. Army DEVCOM Soldier Center[2] Boston University, Dept. of Mechanical Engineering

Metal-Organic Frameworks (MOFs) are 2- and 3-D porous materials with metal nodes and organic ligands with great promise based on their high internal surface areas and chemical customization. However, these materials are approaching their third decade of scientific interest and prominence with only a short list of industrial applications. To bring MOF research closer to application environment of relevance, new tools need to be developed to analyze the (super)molecular interaction in ambient or system-relevant conditions and in polymer composites. In this work, new atomic force microscopy (AFM) tools are developed to use mechanical properties such as weight and adhesion force to better understand chemical interactions in pores and at interfaces. By using AFM, not only can new, precise measurements be made, but also this tool can be applied in a variety of controlled sample environments and is easily adaptable to high-throughput experimentation. Starting with simple small molecule/polymer-MOF interactions, this work aims to use established design principles for MOF chemical diversity to investigate libraries of materials and correlate results to application-specific performance.

Tue-B4-04

Brownian Dynamics simulations of shear-induced clustering of electrostatically-stabilized colloidal suspensions with hydrodynamic interactions

Marco Lattuada

University of Fribourg Department of Chemistry

In this work, the aggregation kinetics of charged polystyrene particles exposed to shear flow has been investigated using Brownian Dynamics simulations with the Rotne–Prager-Yamakawa (RPY) approximation of the long-range Hydrodynamic Interactions (HI) over a wide range of particle volume fractions (Φ), Peclet number values (Pe), which measures the relative importance of shear forces with respect to diffusion, and surface potentials (ψ_0). The strength of the repulsive electrostatic interactions has been quantified by means of the Fuchs stability ration (W). It has been observed that, for high values of W and low Pe number values, the aggregation rate is insensitive to the shear rate $\dot{\gamma}$, being the process dominated by repulsion forces among particles, similarly to what is observed under reaction-limited cluster aggregation (RLCA) regime. As the values of Peclet number increase, the resulting shear is sufficient to overcome the energy barrier to aggregation resulting in a sharp increase in the aggregation dynamics and radius of gyration, consistently with the available experimental results and theoretical predictions1. Similar results have been obtained as particle concentrations increases under a given shear rate $\dot{\gamma}$ and for a specific W. Simulations predict that the larger the volume fraction, the higher the collision rate, and the more intense is the disturbance in the flow field induced by particles, which promotes the mobility of the clusters and enhances the resulting aggregation rate. It was also observed that for high values of the Pe number, the curve describing the dimensionless time evolution of the number concentration of clusters for different Φ are almost overlapping throughout the whole simulation time, most likely indicating a similar aggregation mechanism, where concentration instead of shear rate plays a predominant role in determining the process dynamics. Furthermore, in the early stages of the process, when aggregation occurs mostly between primary particles and small clusters, simulations neglecting HI and employing a pure BD algorithm lead to faster aggregation kinetics if compared to the method which includes the long-range hydrodynamics contributions. However, in the subsequent stages, the process is dominated by particle-cluster and cluster-cluster interactions and the long-range hydrodynamics term becomes predominant, resulting in a rapid increase of the aggregation rate and radius of gyration after a given time. This indicates that the inclusion of long-range HI can reveal unique features of the phenomenon and provide a more exhaustive description of the complex interplay between DLVO-interactions and hydrodynamics under shear flow conditions.

Tue-B4-05

Towards Constructing the Potential Landscape of a Colloidal Ellipsoid with Scattering Morphology Resolved Total Internal Reflection Microscopy (SMR-TIRM)

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Nano/microscale colloidal particles exist in various applications, such as paints, milk, and blood. Their properties are influentially affected by the relevant surface interactions between the particles and the boundaries. To measure such colloidal interactions, Total Internal Refraction Microscopy (TIRM) is one of the techniques that could be employed, and herein, we will present our recent progress on developing a TIRM variant, called Scattering Morphology Resolved Total Internal Reflection (SMR-TIRM), which was conducted to anisotropic colloidal particles. SMR-TIRM experiments were performed on our customized rotatable apparatus with a series of no-backlight 8-bit images taken for every 10° of azimuthal angles (φ) on different particles. For an ellipsoid with a specific orientation, like the conventional TIRM, SMR-TIRM uses the total integrated light scattering intensity (I) to track the separation distance (h) between the particle and boundary in the Brownian fluctuation. It further utilizes the morphology of light scattering to resolve the orientation of ellipsoid by using 2D Gaussian analysis to quantitatively measure the angles (M_φ) and aspect ratios (M_{AR}) of the morphologies. We found an empirical equation to demonstrate the relationship between the M_φ and the φ of the ellipsoid, and M_{AR} was used to assess the polar angle (θ) of the ellipsoid. The summarized result suggests the scattering morphology dependence on the orientation of an ellipsoid, which was then combined with our previous simulation results to tentatively construct the potential energy profile.

Tuesday, July 12th | 09:30 - 11:30 | C4-Colloids, Macromolecules, and Surfaces in Life Science

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Tue-C4-01

Engineering Interfaces Between Polycations and Therapeutic Nucleic Acids: Do the Same Design Rules Apply for DNA and Ribonucleoproteins?

Ramya Kumar [1], Ngoc Le [2], Felipe Oviedo [3], Mary Brown [4], Theresa Reineke [2, 3]

[1] Chemical and Biological Engineering. Colorado School of Mines[2] Chemistry, University of Minnesota[3] Nanite, Inc[4] UIC, University of Minnesota

Synthetic polymers are rapidly emerging as promising alternatives to viral delivery of therapeutic nucleic acid payloads such as DNA, RNA and ribonucleoproteins (RNP). Whether structure-function trends that are identified for a specific nucleic payload can be reapplied to other cargo types remains an unresolved question. In this work, we identified effective vehicles for plasmid DNA (pDNA) by screening a chemically diverse polymer library consisting of 43 unique structures. We discovered that a polymer previously identified for RNP delivery (P38) also emerged as the lead structure during screening studies for pDNA delivery, suggesting considerable overlap in the design rules for RNP and pDNA payloads. Through statistical learning tools we identified structural drivers for internalization, toxicity and transfection efficiency for both RNP and pDNA payloads and established that pDNA delivery is less reliant on hydrophobic interactions than RNPs. In addition to mediating transient transfection efficiently, P38 also co-delivered RNPs and pDNA donors to effect homology-directed repair (HDR) at higher rates than JetPEI. Our approach yielded a versatile transfection reagent that delivers multi-modal cargoes to accomplish challenging therapeutic objectives such as HDR.

Tue-C4-02

Temperature-induced pearlescence in multi-layered hydrogel capsules

Medha Rath [1], Allison Fear [2], Taylor Woehl [2], Srinivasa Raghavan [2]

[1] Department of Chemistry and Biochemistry[2] Department of Chemical and biomolecular engineering

Pearlescent and opalescent materials, or more generally materials displaying structural color, are ubiquitous in nature and derive their unique optical properties from interference or diffraction of light within the hierarchical material structure. A quintessential example of a material that exhibits pearlescence is nacre, which is composed of alternating layers of calcium carbonate microplates and biopolymer. Most attempts to prepare synthetic structural materials have involved forming nanocomposites with hierarchically arranged inorganic micro or nanoparticles in an organic polymer phase. Here we demonstrate multi-layered hydrogel capsules that exhibit reversible, temperature induced pearlescence. The hydrogel capsule consists of a millimeter sized liquid water core surrounded by a ~100 µm thick layer of crosslinked alginate, which is then coated by a ~100 µm outer layer of poly(N-isopropylacrylamide) (PNIPA). Generally, PNIPA becomes turbid upon heating above its lower critical solution temperature (LCST) of 32°C; however, when integrated as a thin outer shell onto the multilayered capsule the PNIPA exhibits distinct pearlescence. We quantified the pearlescence of the capsules using optical reflectance measurements and demonstrated that they showed reflectance similar to a natural pearl. We identified a critical PNIPA layer thickness, above which the capsule displays turbidity and below which they displayed pearlescence. This work provides a new method for synthesizing all-polymer materials exhibiting temperature induced structural color, which could find applications in the cosmetics and coating industries.

Tue-C4-03

Enhancing protein crystal nucleation using in-situ templating on bioconjugate-functionalized nanoparticles and machine learning

Caroline McCue, Henri-Louis Girard, Kripa Varanasi

MIT, Department of Mechanical Engineering

The manufacturing of recombinant proteins for applications ranging from cancer treatments to vaccines traditionally relies on chromatography-based purification processes which account for a significant portion of manufacturing costs. Although protein crystallization has been proposed as an alternative route to purify proteins at a lower cost, slow nucleation kinetics and high protein concentration requirements are major barriers for using crystallization as a viable strategy in downstream protein purification. Here, we demonstrate that nanoparticles functionalized with bioconjugates can result in an in-situ template for inducing rapid crystallization of proteins below their supersaturation concentrations. We use a microbatch crystallization setup to show that the supersaturation threshold of proteins is lowered by the presence of functionalized nanoparticles. Furthermore, we use a custom machine-learning-enabled emulsion crystallization setup to rigorously quantify nucleation parameters. We show that bioconjugate-functionalized nanoparticles can result in up to seven-fold decrease in induction time and three-fold increase in nucleation rate of model proteins compared to those in control environments. We thus provide foundational insight that could enable crystallization to be used as a purification step in protein manufacturing by reducing both the protein concentration and the time required to nucleate protein crystals.

Tue-C4-04

Differentially crosslinked silicone particle system for multimodal drug release to skin

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[1] Department of Chemical and Biological Engineering, University of Colorado Boulder[2] Department of Advanced Organ Bioengineering and Therapeutics, Section: Engineered Therapeutics, University of Twente[3] Biomedical Engineering Program, University of Colorado Boulder

Colloidal particles provide a means by which different types of drugs can be released at prescribed rates to match various physiological processes. We describe a dual particle system capable of regulating the release of small molecule drugs at well-defined rates. Drug release is mediated by the crosslink density of the particles, which are made from different types of silicone elastomers. To apply this system, we embed the particles into a tissue-adhesive hydrogel and release drugs to the skin. While many implanted drug reservoirs aim to degrade over time, this hydrogel is designed as a flexible, biostable, and fully removable unit to deliver drugs locally and sustainably while remaining adherent, after which it can be painlessly peeled off. Use of a detachable hydrogel also enables the incorporation of a range of synthetic particle types to guide drug release without dependence on particle degradability, long-term biocompatibility, repeated injections, or accumulation in tissues. To demonstrate dual release using these engineered silicone particles, we encapsulate and release two drugs used for melanoma immunotherapy. Specifically, we release resiquimod (a macrophage-targeting drug) and palbociclib (a T cell-targeting drug) at different rates by adjusting the crosslink density of each type of particle. To release resiquimod quickly (over several hours), low crosslink density silicone (LCDS) particles were prepared from polydimethysiloxane using a homogenization synthesis technique. To release palbociclib slowly (over several days), high crosslink density silicone (HCDS) particles were prepared from silicon alkoxide and alkoxysilane monomers using a nucleation and growth technique. The differential drug release afforded by these engineered particles was designed to match the associated cell activation timescales in innate and adaptive immunity, respectively. Following a series of *in vitro* and *ex vivo* studies, we show that this system can be used to sustainably polarize macrophages toward an anti-tumor phenotype better than free drug administration (i.e., by the sustained activation of proinflammatory markers such as iNOS, CD86, and MHCII) and that the hydrogels can remain attached to skin for several days without generating toxicity. This system is compatible with standard dermatological procedures, such as by affixing the hydrogel within a surgical bed or a microneedle-treated site. Additionally, by embedding microparticles with well-defined crosslink

densities, it is possible to achieve multimodal drug release in a manner that is fully decoupled from the bulk properties of the hydrogel. While we show differential release of two drugs at well-defined rates, the tunable nature of these particles offers the potential to address a variety of topical uses such as treating actinic keratosis, dermatitis, and carcinoma or delivering analgesics and antibiotics.

Tue-C4-05

Processing of lipid nanoparticles for RNA encapsulation

Navid Bizmark [1, 2], Satya Nayagam [1], Dawei Zhang [1], Tom Colace [3], Jane Wang [3], Robert Prud'homme [1]

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Lipid nanoparticles (LNPs) have recently emerged as effective vehicles for ribonucleic acid (RNA) delivery in vaccine formulations. LNP-based RNA vaccines for COVID-19 are among the most recent and critically important examples of such advanced formulations. While there has been extensive research on lipid structure, lipid formulations, and RNA modifications to optimize performance, there has been less work on how processing affects LNP structure and properties. In this work, we have used a Confined Impinging Jet and a Multi-Inlet Vortex Mixer to produce LNPs using Flash NanoPrecipitation (FNP). In these turbulent mixers (Reynolds number>5000), an organic solvent stream—containing the lipids—and an aqueous anti-solvent stream which may contain RNA are rapidly mixed. Through this scalable process LNPs are formed only at the proper compositions and flow rates of the fluid streams. We have explored the effects of buffer pH, ionic strength, and lipid concentrations on the key properties of LNPs, including size, zeta potential, and colloidal stability. We show how these parameters can be tuned to produce 60 to 80 nm LNPs—an optimal size for the best in vivo practices. Moreover, we have maximized the loading of RNA in LNPs under controlled electrostatic and steric interactions. These findings are critical to produce RNA-loaded LNPs, and further develop therapeutic formulations.

Tue-C4-06

Microgel-reinforced hydrogel with ultra-high lubricity for oral therapeutic application

Olivia Pabois, Jing Hu, Anwesha Sarkar

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Xerostomia, or dry mouth resulting from salivary flow/lubricity reduction/absence, affects at least 1 in 10 adults, with rates as high as 80% in institutionalised elders. This condition, which can be a side effect of cancer-related radiations or polymedication, has a detrimental impact on the ability to eat/speak, ultimately causing malnutrition and affecting the quality of life of elders. Inspired by the human saliva structure1, we have developed2 and patented3 an innovative, super-lubricious colloidal formulation, composed of a proteinaceous microgel-reinforced biopolymeric hydrogel. The capacity of our lubricant to provide both hydration and fluid film lubrication was assessed by tribology, using both smooth and 3D-textured elastomeric surfaces, the latter being a biomimetic emulation of the real human tongue surface4. This surface replicates the size and spatial distribution of fungiform/filiform papillae, thus mimicking the human tongue roughness, stiffness, and hydrophobicity. The viscous and adsorption properties of the formulation were characterised using, respectively, rheology and quartz-crystal microbalance with dissipation monitoring, and its mesoscopic structure was resolved by combining small-angle X-ray/neutron scattering with atomic force and transmission electron microscopy. Our formulation was found to reduce drastically the friction between mouth-mimicking surfaces in contact, resulting in friction coefficient values as low as 0.01, and to perform strikingly better than the naturally lubricating human saliva, therefore demonstrating its high potential to work as an effective salivary replacer. Structural studies suggest our microgel-reinforced hydrogel is composed of biopolymeric nanofibrils-coated spherical proteinaceous particles exhibiting a 300 Å radius, and its remarkable lubrication performance is due to an optimal synergy between the two electrostatically binding components: the efficiently adsorbing microgel particles, promoting boundary lubrication, and the highly viscous hydrogel, generating hydrodynamic lubrication. The superior lubrication properties of our innovative technology make it also interesting for other applications, such as optimal mouthfeel-providing fat mimetics to address the ever-increasing global obesity challenge. Acknowledgements: The European Research Council is acknowledged for its financial support (under the European Union's Horizon 2020 research and innovation programme (Grant agreement n° 757993 and 890644)) for this work.

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Tuesday, July 12th | 09:30 - 11:50 | D4-Self and Directed Assembly

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Tue-D4-01

Dynamic pathways in reconfigurable anisotropic colloidal assembly

Michael Bevan

Chemical & Biomolecular Engineering Johns Hopkins University

We report the reconfigurable assembly of different shaped anisotropic colloidal particles including dynamic pathways between different states. Assembled configurations include a variety of liquid, liquid crystalline, crystalline, and glassy states with novel and technologically useful multifunctional properties. Microscopy experiments are performed using AC electric fields to control the quasi-two dimensional assembly of disks, ellipses, squares, rectangles, rhombuses, and other curved/stretched variants of these shapes. By tracking particle positions and orientations, we compute in real-time a number of order parameters based on local symmetries within configurations; we then use order parameters vs time as reaction coordinates to capture stochastic dynamic pathways between states. For the specific case of rectangular prism particles with rounded corners, we demonstrate dynamic reconfiguration pathways: (1) between stable fluid, nematic, and crystalline states, (2) temporarily sampling metastable binematic and string-fluid states, (3) passing through transient tetratic and smectic states, and (4) navigating around dynamically arrested glass states. By dynamically changing AC electric field amplitude and frequency, reconfiguration rates are optimized by jumping between free energy landscapes that control assembly pathways, which we show is orders of magnitude faster than diffusion limited evolution on a single landscape at fixed conditions. Our results demonstrate the ability to control the dynamic assembly of diverse microstructures of anisotropic particles to enable previously unattainable particle based materials and devices exploiting their reconfigurable properties.

Tue-D4-02

Decoding the metabolic response of whole cell sensors using machine learning analysis of self-assembled surface enhanced Raman scattering sensors.

Regina Ragan

University of California, Irvine Department of Materials Science and Engineering

Whole cell biosensors provide ultra-sensitive detection of environmental conditions and have the advantage of directly providing phenotypic information. In particular, whole cell biosensors using bacteria can be engineered to be responsive to different toxins or antibiotics. Specifically, we incorporate Pseudomonas aeruginosa and Escherichia coli (E. coli) in surface enhanced Raman scattering (SERS) sensors fabricated using low-cost solution phase processing to amplify analyte signals in aqueous solution. As many cellular metabolites have aromatic rings, they have high Raman cross-sections. The performance of our developed SERS sensors composed of optimized architectures of Au NP clusters with chemically defined nanogaps have the capacity for single molecule detection limits of resonant molecules and have been integrated in microfluidic devices. Bacterial responses to stress are critical to their survival in dynamic and challenging environments. Stresses can be general, such as from nutrient deprivation, or specific, such as from targeted antibiotic activity. Regardless, they result in rapid and profound shifts in metabolite concentrations within cells to maintain homeostasis. Yet metabolomics approaches introduce an enormous parameter space, e.g., the E. coli metabolome contains over 2600 different metabolites. We overcome this challenge with SERS sensors able to reproducibly, sensitively, and rapidly (on the scale of minutes) collect large data sets for analysis with machine learning (ML) algorithms. Just as one can smell the difference between coffee and chocolate amongst multiple odors, SERS+ML rapidly measures and classifies spectral features of metabolite response. Analysis of SERS data using a generative model, the variational autoencoder, is able to identify metabolic fingerprints associated with antibiotic efficacy in ESKAPE pathogens. Greater than 99% accuracy is achieved with unsupervised Bayesian Gaussian Mixture analysis using just a single spectrum from each class (requiring 10 min of data acquisition) representing different antibiotic exposure conditions. In addition, the stress response of E. coli enables sensitive quantification of heavy metal ion concentrations in water across a dynamic range of six orders of magnitude from concentrations as low as 0.5 pM for arsenic Ⅲ and 6.8 pM for chromium Ⅵ. These limits of detection are approximately 100,000 times lower than the U.S. Environmental Protection Agency regulatory limits.

Tue-D4-03

Assembly of colloidal clusters with homochirality under combined electric and magnetic fields

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Research involving anisotropic particles has shown great potential in applications ranging from colloidal assembly and microrobot design to medical therapy and drug delivery. In particular, the assembly of chiral colloidal clusters has potential applications in sensors to detect chiral molecules or metamaterials with exotic optical properties. As we have previously reported, applying electric fields can assemble dielectric dumbbell-shaped particles into chiral clusters. However, we typically obtained right- and left-handed clusters with almost equal populations, which is understandable since they are energetically equivalent. To make homochiral clusters, we applied the layer-by-layer (LBL) method to coat Fe3O4 magnetic nanoparticles (MNP) on the dumbbell-shape polystyrene dimer particles, which are responsive to both electric and magnetic fields. The advantage of the LBL method allows us to coat multiple layers of MNP on the dimer particles to tune the magnetic response. When we apply an AC electric field perpendicular to the substrate, the particles assemble into chiral clusters with opposite chiralities. However, when we superimpose an in-plane circularly rotating magnetic field, the chirality of the particles changes according to the rotating direction of the magnetic field. We find that by controlling the direction of the magnetic field, we can reversibly switch the chirality and rotation of the clusters. The chiral cluster will experience self-rotation under AC electric field due to the electrohydrodynamics (EHD) and induced rotation under the rotating magnetic field. Two rotation effects can be additive or competitive depending on the rotating direction. To gain a more fundamental understanding of our experimental observations, we also conduct Brownian Dynamics simulations in which Lennard-Jones, dipolar, electrohydrodynamic, and magnetic forces are involved. The impact of a variety of tunable parameters, including the field strength, frequency, and particle aspect ratio, have been investigated. They compare favorably with our experimental observations. Our method provides a convenient route for producing chiral colloidal clusters with single-handedness.

Tue-D4-04

Designing multicomponent polymer colloids for self-stratifying films

Piyush Singh [1, 3], Michaeleen Pacholski [4], Junsi Gu [4], Yoo Kyung Go [2], Cecilia Leal [2, 3], Kshitish Patankar [5], Ray Drumright [5], Simon Rogers [1, 3], Charles Schroeder [1, 2, 3]

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Aqueous polymer colloids known as latexes are widely used in coating applications. Multicomponent latexes comprised of two incompatible polymeric species organized into a core-shell particle morphology are a promising system for self-stratifying coatings that spontaneously partition into multiple layers, thereby yielding complex structured coatings requiring only a single application step. Developing new materials for self-stratifying coatings requires a clear understanding of the thermodynamic and kinetic properties governing phase separation and polymeric species transport. In this work, we study phase separation and self-stratification in polymer films based on multicomponent acrylic (shell) and acrylic-silicone (core) latex particles. Our results show that the molecular weight of shell polymer and heat aging conditions of the film critically determine the underlying transport phenomena, which ultimately controls phase separation in the film. Unentangled shell polymers result in efficient phase separation within hours with heat aging at reasonable temperatures, whereas entangled shell polymers effectively inhibit phase separation even under extensive heat aging conditions over a period of months due to kinetic limitations. Transmission electron microscopy (TEM) is used to track morphological changes as a function of thermal aging. Interestingly, our results show that the rheological properties of the latex films are highly sensitive to morphology, and linear shear rheology is used to understand morphological changes. Overall, these results highlight the importance of bulk rheology as a simple and effective tool for understanding morphology changes in multicomponent latex films.

Tue-D4-05

Electric-Field Assembly of Two-Dimensional Colloidal Quasicrystals

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Quasicrystals are a type of aperiodic material with long-range orientational order. Lacking periodic unit cells, colloidal quasicrystals are predicted to exhibit distinctive optical, electrical, and mechanical properties that differ from those of traditional crystals. However, most quasicrystals are formed from atomic constituents, as in metal alloys, and there are only a few examples of quasicrystals formed from micron scale constituents, making the formation and dynamics of quasicrystals difficult to directly observe in experiments. To address these challenges, we report simulation and theory of electric-field directed assembly of colloidal quasicrystals confined to a surface. In previous experimental work, we found that polystyrene colloids in deionized water spontaneously organized into two layers near an electrode surface when subjected to an external electric-field, forming a variety of intricate ordered phases, including hexagonal bilayer and sigma phases. These structures were found to be in quantitative agreement with Monte Carlo simulations in which isotropic colloids confined to two layers interact via Lennard-Jones and dipolar interactions. By tuning the concentration, dipolar strength, and number ratio of particles in the upper layer to particles in the lower layer, we observe several unique structures previously found in experiments. We find that by equilibrating at high temperature, followed by gradual annealing, quasicrystals can be assembled over a range of parameters. We characterize the quasicrystals by several means, including the scattering patterns, global orientational order, local coordination, and phason strain. We find excellent agreement between the parameters obtained from our simulations compared to those of an ideal Schlottmann quasicrystal. The theoretical energy landscapes of ideal quasicrystals, sigma, and hexagonal phases are determined, and the resulting phase diagrams compare favorably with our simulation results. Our simulation results allow observation of quasicrystal assembly while providing a framework to assembling micron-scale quasicrystals in the laboratory.

Tuesday, July 12th | 09:30 - 11:30 | E4-Electrokinetics and Microfluidics

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Tue-E4-01

Recent Advances in Capillary-flow Driven Analytical Devices

Chuck Henry

Colorado State University

A major push in the field of sensor development is production of very cheap and easy to use sensors that require minimal external equipment. Microfluidic Paper-based Analytical Devices (mPADs) have received significant attention in this field because they are cheap (costing pennies per device), easy to use, and can carry out a wide range of chemical assays. mPADs are normally made from porous hydrophilic materials patterned with hydrophobic materials to create flow barriers to direct flow from a sample inlet through sample pretreatment zones to a detection zone. Furthermore, functional elements like electrodes can be readily integrated to provide additional functionality and assay selectivity. Despite their advantages, mPADs are frequently limited to long analysis times due to slow capillary flow and poor limits of detection for naked eye measurements. Our group has recently reported the development of capillary flow driven microfluidic devices that use channels formed using laser patterning in polyester films and double-sided adhesive combined with paper-based pumps and reagent storage systems to enhance the performance of mPADs. This talk will focus on this new system and its applications for point-of-need diagnostics.

Tue-E4-02

Investigation of Novel Core-Shell Microparticles with Degradable Shells for Controlled-Delivery Applications

Whytneigh R. Duffie [1], Tsvetanka S. Filipova [2], Timothy M. Brenza [1, 3], Katrina J. Donovan [3, 4, 5], Travis W. Walker [1, 3, 5]

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The use of advanced multi-functional microparticles is immensely important for applications (e.g., biological, dental, energetic, sensor) that require adjustable, predictable, and controlled release of functionalized packages. The unique core-shell structure of a microcapsule rather than a homogeneous microsphere offers protection of high-value cargoes from the surrounding environment until the core is later released in a controlled manner. The thickness, morphology, and composition of the outer-shell of the microcapsule can be adjusted for controlled-release of the inner-core material under conditions that are specific to the targeted application of the microcapsule. An unlimited variety of substances can be employed as the core and shell materials of the microcapsule; however, delivery of a functional core that is induced by simultaneous chemical degradation and mass loss of the outer-shell material provides precise release mechanisms that are suitable for advanced applications that require precise delivery. Crosslinkable polymeric systems that are based on anhydrides are promising candidates for shell materials with their surface-eroding mechanism and their ability to selectively and efficiently polymerize the material at high resolutions. In this work, a synthesis protocol was developed to produce unique, bio-compatible, surface-eroding anhydride-based oligomers that later react to form crosslinked networks upon exposure to UV light. A double flow-focusing PDMS microfluidic device will be utilized for continuous droplet formation to most precisely control the size, composition, and uniformity of the multi-phase (liquid/liquid/liquid) emulsions before photo-polymerization of the degradable polymeric outer shell (liquid/solid/liquid). By controlling the channel geometries, the viscous and interfacial properties of the working fluids, the overall flow rate, and the flow rate ratios of the phases that are involved, the diameter of liquid cores, the thickness of shells, and the overall size of the particles can be controlled. These parameters, along with the chemical composition of the outer shell material, will affect the release profile of the inner liquid core, which determines the applicability of the resulting microcapsules to advanced delivery applications. In-depth analysis of the degradation rates and erosion mechanisms with a novel and adaptable flow apparatus can be coupled with previously explored methods of analysis to provide insight into the complex mechanisms that take place during erosion of the microcapsule shell. Given the high flexibility of material selection for the anhydride-based degradable shells that are provided by the novel synthesis technique, microcapsules with shells of different resin formulations can demonstrate nearly identical release kinetics by select differences in shell thickness.

Tue-E4-03

Incircle Theory Predicts Equilibrium Particle Positions for Microfluidic Inertial Focusing Across Arbitrary Cross-Sectional Geometries

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The passive hydrodynamic alignment of microparticles to distinct, well-defined lateral and longitudinal locations by fluid inertia has become well known as microfluidic inertial focusing. While inertial focusing in rectangular and circular channels has been studied extensively, non-rectangular studies have only recently begun to emerge with improvements in microfabrication technologies. In this study, we describe a fabrication method for non-rectangular geometries using femtosecond laser pulses to produce acute tip angled triangular microchannels. Our examination of complex particle ordering in acute triangles has revealed a unique scaling between inertial fluidic phenomena and cross-sectional incircle positioning. We have observed that the radial distribution of inertially focused particles in all rectangular and non-rectangular geometries considered assumed a consistent radial position at $0.6r_i$ when normalized within the incircle focusing region. Angular components scaled with alterations in vertex angles. Throughout this study, we dissect incircle positional effects on inertial behavior and derive a theory that encompasses our observations into a broad theoretical framework that can be applied across various microenvironments. Scaling analysis was used to delineate the parameters necessary to accurately evaluate fluidic inertia within non-rectangular microchannels. Our incircle theory quantifies observed shifts in parabolic velocity maxima within non-rectangular cross-sections and provides generalizations for particle Reynolds numbers within the cylindrical focusing region to streamline comparisons of inertial focusing behavior, particle size limitations, and concentration effects among non-uniform geometries. We show that geometry constrained particle overlap of basin of attraction boundaries in non-rectangular cross-sections can be exploited to antagonize the passive transition from conventional to single position inertial focusing, independent of particle size and without the need for external manipulation. In this work, we demonstrate the applicability of our microfluidic inertial focusing incircle theory for theoretical optimization and simplification of the parameters necessary to achieve desirable, empirical inertial focusing outcomes.

Tue-E4-04

Simultaneous characterization of thermophoresis and fluid properties using multiple particle tracking microrhology.

Maria Chiara Roffin [1], Nazrin Hasanova [1], Xuanhong Cheng [2, 3], Kelly Schultz [1], James Gilchrist [1]

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Thermophoresis is the migration of particle in a fluid driven by a temperature gradient. The applications of this phenomenon are numerous especially in biomolecular separation, despite no agreement has been found on the underlying physics. In fact, existing literature has conflicting experimental results and descriptions of the fundamental mechanism of thermophoresis. The work presented here develops a process to measure thermophoresis of dispersed fluorescent tracer particles and simultaneously measure the local rheological properties of the continuous phase using multiple particle tracking microrheology (MPT). MPT measures the Brownian motion of the embedded probe particles and, using the mean squared displacements, relates it to the rheological properties of the fluid. We developed a method to characterize the particle motion induced by a unidirectional thermal gradient and, at the same time, measure the independent Brownian fluctuations perpendicular to the thermophoretic motion to measure the rheology. In Newtonian fluids, this technique validates the local temperature profile that drives the thermophoretic motion as correlated by the known temperature dependent viscosity. Rayleigh-Bénard recirculation phenomenon interfere with measurement of the thermophoretic motion, thus parallel experiments in microgravity on the International Space Station are being designed. Moreover, these techniques will be extended to particle thermophoresis in non-Newtonian fluids. A better understanding of the relationship between thermophoresis and the material properties will allow for optimization of microfluidic device designed for effective and efficient bioseparation. A timely application is the advancement of devices used for the viral diagnostic tools enabling the implementation of the thermophoretic enrichment methods for virus detection.

Tue-E4-05

Flow-driven "waltzing" of RBC-like disks in microfluidic flow

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We report flow induced "waltz"-like synchronized tumbling /rotation of red blood cell (RBC) pairs under moderate volume fraction (3 to10 %) and confined simple shear flow, conducted with a computational model with lattice Boltzmann fluid coupled with biconcave discs matching RBC elasticity. Without attractive interactions between the particles, hydrodynamicinteractions (HI) is the main driving force to the spontaneous formation of waltzing pairs, in addition to crystalline-like layer formation. Furthermore, HI between RBC and the wallboundary result in cross-stream migration to the flow centerline with zero velocity, leading to localized waltzing RBC pairs exhibing crystalline-likeorder. We further examined how RBC doublet formation increases the tumbling rotation period and reduces the suspension intrinsic viscosity. The fraction of doublet pairs is highly correlated with the intrinsic viscosity.

Tue-F4-01

Multiple nanoemulsions: leveraging interfacial mechanics to scale up production while scaling down size

Matthew Helgeson

Department of Chemical Engineering, University of California Santa Barbara

Multiple emulsions – i.e., droplets within droplets – have opened new frontiers of “designer” emulsions where chemistries and processes can be compartmentalized to control encapsulation and chemical reactions within droplets, providing utility in consumer formulations, pharmaceuticals and particulate materials design. However, most existing processes for multiple emulsions are limited to producing large droplets at low throughput (e.g. microfluidics) or droplets with significant size and morphology dispersity (e.g. bulk mechanical emulsification). Here, I summarize several recent successes in the development of scalable processes to produce multiple nanoemulsions, and the interesting colloid and interface science they rely upon [1]. In particular, we focus on single-step emulsification methods that combine high-energy emulsification with co-surfactant systems that simultaneously possess ultra-low interfacial tension and frustrated spontaneous curvature. Using a simple modification of the Helfrich model for the interfacial free energy to include the thermodynamics of co-surfactant mixtures, we show that such a situation leads to the thermodynamically metastable formation of nanodroplets with multiple internal interfaces. Predictions of the model are consistent with experiments, which indicate a “state diagram” that contains a wealth of preferred droplet structures including uniform, core-shell and multi-shell morphologies. We show that the geometry and properties of these multi-phase nanodroplets can be finely tuned through co-surfactant formulation, and ultimately demonstrate the ability of multi-nanoemulsions to serve as templates for multi-phase nanoparticles with a number of potential applications. [1] T. Sheth, S. Seshadri, T. Prilezsky and M.E. Helgeson, “Multiple Nanoemulsions”, Nature Reviews Materials, 2020, 5(3): 214-228. DOI: 10.1038/s41578-019-0161-9

Tue-F4-02

Patterning wettability in complex microfluidic channels for very large-scale generation of double emulsions

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Spatially controlling the wetting properties of microfluidic channels is critical for the controlled and stable formation of multi-order emulsions (e.g. double emulsions). Existing patterning methods, which rely on selectively delivering fluid to particular regions of the chip, suffer from low spatial resolution, scalability, and cumbersome procedures. These challenges make it difficult to reliably produce chips to generate multi-order emulsions, and impossible to translate these techniques to parallelized chips that contain 1000s of devices on a single chip. Here, we present a method to pattern the wettability in highly parallelized microfluidic chips with micrometer resolution. Our patterning strategy takes advantage of the robust photolithography process and uses a silane chemistry compatible with the harsh chemical and temperature environments inherent to wafer-level micro-fabrication. We first demonstrate this approach on single-channel silicon-and-glass devices, forming both W/O/W and O/W/O emulsions. The technique is extended to pattern wetting properties in a 2100-channel parallelized double emulsion chip, enabling the production of double emulsions at an industrial-relevant scale. We also show that this patterning strategy can be leveraged to pattern wettability in polymer-based microfluidic devices. Moreover, using a PFPE (perfluoropolyether)-PEGDA (poly(ethylene glycol) diacrylate) polymer mixture, we show that the microscale wettability pattern in the Si wafer can be transferred to a polymer device replicate, enabling a one-step patterning of a polymeric device. The alteration of the polymer surface properties is verified by contact angle measurements, vapor condensation experiments, and time-of-flight secondary ion mass spec. We demonstrate the generation of double emulsion with patterned polymer devices as well. While our study focuses on patterning wettability for droplet generation in microfluidics, the method can be further extended to pattern different surface functionality in complex microfluidic devices for separation of multiphase flow systems, biological cell patterning and wall-free flow control, etc.

Tue-F4-03

Electroacoustic analysis of nano-emulsion- and nanoparticle-doped hydrogels

Reghan J. Hill, Jiyuan (Jessica) Wu

McGill University

The size, charge and mobility of emulsion drops and nanoparticles dispersed in hydrogels are challenging to measure in situ, owing to, for example, optical opacity, non-ergodicity, and high nano-particle concentration. In this talk, we will examine recent progress in the application of electrokinetic sonic amplitude (ESA), customarily used for colloidal dispersions, to study this general class of soft viscoelastic solid. First, we will examine the application of a recently developed theory for the dynamic mobility of SDS-stabilized oil-in-water nano-emulsion drops to polyacrylamide hydrogels doped with SDS-stabilized hexadecane. From an independently determined SDS-adsorption isotherm, this furnishes an in-situ electrokinetic drop size and linear-viscoelastic properties of the hydrogel. Next, we will examine progress in interpreting the ESA of uncharged and charged polyacrylamide hydrogels, which may contain charged clay nanoparticles. Here, the challenge is to unravel the contributions of polymer and nanoparticle change, as well as their counterions, to the ESA signal. This will be aided by reference to measurements of the electrical conductivity of the hydrogels and of their monomer-solution counterparts.

Tue-F4-04

Phase separation of water-in-oil nanoscale emulsion using electrostatic space charge injection

Sreedath Panat, Vishnu Jayaprakash, Simon Rufer, Kripa Varanasi

Department of Mechanical Engineering, Massachusetts Institute of Technology

Refinement of crude oil, especially oil-water separation, is one of the most complex steps in oil and gas processing industry. Crude oil extracted from the underground contains significant amounts of water in the form of emulsified droplets. Gravity-based separation of water drops from oil is impractical due to small droplet sizes, especially when they are nanoscale. Conventional electro-coalescers using immersed electrodes for oil-water separation limit their applied electric field strength to mitigate electrical shorting, making them ineffective for coalescing nanoscale droplets. Therefore, to further promote coalescence and enhance the efficiency of separation of water from oil, environmentally toxic chemicals such as demulsifiers are mixed with crude oil which end up in the effluent that reaches water bodies including the ocean and fresh water. In this work we propose a significantly more effective electro-coalescence method based on electrostatic space charge injection that drastically enhances the rate of phase separation of nanoscale emulsions and eliminates the use of toxic demulsifiers. We demonstrate that by introducing a space charge emitter electrode that provides an air gap between the electrode and the emulsion, we can avoid droplet-mediated electrical shorting and apply ~8 times stronger electric field, resulting in much faster phase separation of water in oil nanoscale emulsions at different water cuts ranging from 2%-20%. We visualize the droplet chaining and coalescence events and demonstrate that the rate of oil-water separation scales with the square of applied voltage, showing that the enhanced electric field quadratically enhances the rate of electro-coalescence. Last, we design a practical embodiment for our approach; a flow-through corona-demulsifier that enables rapid, continuous oil-water separation of nanoscale emulsions.

Tue-F4-05

Particle Capture by Swelling Droplets

Gesse Roure, Robert Davis

University of Colorado Boulder

Froth flotation by small air bubbles has been traditionally used in industry to capture fine minerals and other hydrophobic particles. This method, however, is not efficient for capturing very small particles. The present work is motivated by a new agglomeration process that overcomes this lack of efficiency. It consists of mixing a particle suspension and saltwater-filled droplets covered with semi-permeable oil layers. These droplets expand due to an osmotic flux of water caused by the presence of salt inside the droplets. To better understand the physics underlying this novel particle capture method, we focus on the investigation of binary interactions between droplets and particles. To this end, our current work investigates the dynamics of a rigid spherical particle and a semi-permeable spherical drop that expands due to osmosis in an external, pure-extensional flow field. The expansion of the droplet is governed by an expansion-diffusion problem, which is coupled to the set of dynamical equations governing the relative particle trajectory. By performing multiple trajectory simulations, we calculate the transient collision efficiencies, which can be used to determine the collision kernel for population dynamics. We also use these simulations to better understand the evolution of the microstructure by calculating the transient behavior of the pair distribution function. Our results indicate that the presence of drop expansion improves the collision efficiency of the system, especially for very small particles, which are the most difficult to capture by froth flotation. Moreover, although the presence of slow salt diffusion inside the drops can mitigate this improvement, the contribution of expansion to the collision efficiency may still be considerable, even in the absence of hydrophobic forces.

Tuesday, July 12th | 09:30 - 11:30 | H4- Geochemical and Environmental Systems

Tue-H4-01

Nanoparticle release from surfaces into environmental systems – detection and discrimination from natural colloids

Kevin Wilkinson, Madjid Hadioui, Ibrahim Jreije, Agil Azimzada, Nesrine Amiri

Department of Chemistry, University of Montreal

Paints and coatings represent one of the major applications of nanoparticles (NPs). While it has been previously shown that NPs are released from painted surfaces, there is still a lack of experimental data on their release rates under natural conditions and on the size distributions of the NPs following release. In this study, we were able to quantify NP release from painted surfaces under natural weathering conditions in order to identify the main seasonal factors that contribute to increased release. First, an analytical methodology using a highly sensitive single particle inductively coupled plasma mass spectrometer (SP-ICP-MS) was developed that improved the size detection limit (SDL) of the technique down to < 20 nm for $\mathrm{TiO2}$ NPs and < 5 nm for $\mathrm{CeO2}$ NP. Precipitation (rain, snow) was collected after it came into contact with painted panels that were exposed to natural weathering. NPs that were released from the paint, as well as those pre-existing in the precipitation were thoroughly characterized with respect to their size distributions, particle number concentrations and total metal content. Fewer NPs were released during the summer than the winter, in spite of the fact that there was more precipitation in the summer. Controlled lab weathering experiments revealed that NP release was significantly enhanced for wet surfaces, particularly, when the samples underwent freeze-thaw cycles. The results also indicated that NP release and loss (i.e. through agglomeration, sedimentation or sorption, etc.) are dynamic processes that are a function of the physical and chemical properties of the external medium. Although NP release is a primary determinant in environmental risk, subsequent NP behavior leading to losses or re-suspension can be equally critical. The fate of the NP was evaluated for controlled weathering experiments. Finally, recent work using single particle time of flight ICP-MS to discriminate natural colloids from engineered NP will be discussed.

Tue-H4-02

The Goldilocks Zone: Finding the Size Limits for Characterizing Polydisperse Microplastic Samples by sp-ICP-MS coupled to Field Flow Fractionation.

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Anthropogenic and natural nanoparticle (NPs)s, be they metal, plastic or organic, are an under-measured contaminant class that has the potential for an outsized influence on natural systems. Their intermediate size, between their dissolved and bulk counterparts, lead to unique environmental mobility and reactivity. Environmental NP generation via mechanical, chemical, and/or biological processes all produce similar trends in size distribution that make analytical comparison difficult, and conclusions hard to reach. Single particle inductively coupled mass spectrometry (sp-ICP-MS) is one of the premier tools for quantifying metal-bearing particles in environmental media. The technique relies on the concept of a threshold value, which sets the lower limit for what magnitude of signal is counted as a particle. When measuring synthesized nanoparticle standards, this threshold value is generally set at a value far below that of the particles. However, in real-world environmental samples, the presence of dissolved ions or small, unresolved particles can lead to a threshold that excludes some of the actual particle size distribution. The major effect is that it obscures or distorts the measured size distribution, making analytical comparisons between samples with different thresholds difficult. To date, most of the sp-ICP-MS literature has not fully addressed the difficulty of comparing similarly shaped size distributions that may also differ in threshold. New methodology is needed so that particle size distributions can be compared more precisely. Using a metal-doped plastic substrate that has been milled to < 1-5 um, we demonstrate the pernicious effect of high thresholds on both a sample's observed particle size distribution and its measured particle numbers. Dilution and plots of size distribution in log space can be used to demonstrate that the observed threshold is caused by “unresolved particles” as opposed to dissolved ions. Plotting size distributions in log space is also demonstrated to effectively distinguish between monodisperse and polydisperse samples regardless of threshold. Taking this concept one step further, we demonstrate the usefulness of these ideas in using sp-ICP-MS as a detector for the separation of polydisperse, metal-doped, microplastic samples by field flow fractionation (FFF). Variations in threshold are demonstrated to affect the observed FFF separation and artificially improve the separation. However, with careful application of dilutions to collected fractions, we can fill in data missing due to threshold issues and create a more complete picture of

the separation. These same techniques can be used in the analysis of environmental particles by sp-ICP-MS to extend the range of the observed particle size distribution.

Tue-H4-03

Characterization of Polymeric Nanoparticles by Asymmetric Flow Field – Flow Fractionation (AF4)

Stacey Louie, Marfua Mowla, Haoran Wu, Sheyda Shakiba

Department of Civil and Environmental Engineering, University of Houston

Polymeric nanoparticles are of rapidly emerging interest in the environment. This class of nanoparticles includes nano- and microplastics pollution, as well as biodegradable or bio-based nanomaterials for beneficial agricultural applications. Polymeric nanoparticles present unique analytical challenges beyond metal and metal oxide nanomaterials. For example, new methods are required to achieve separation and selective quantification of nanoplastics, given the ubiquitous presence of natural organic matter and inorganic colloids in environmental samples. Further advancements are required to simultaneously monitor the uptake and release of both incidental pollutants and intentionally delivered active ingredients, such as agrochemicals, from the nanoparticles. This study presents the development and application of new approaches based on asymmetric flow field – flow fractionation (AF4) to address these analytical challenges. First, the coupling of AF4 with online total organic carbon (TOC) detection is validated for separation and detection of a multimodal mixture of polystyrene nanoplastics (50, 100, 200, and 500 nm in diameter) in samples containing humic acids and clays. The AF4-TOC method enabled more selective and robust quantification of the various sizes of nanoplastics compared to other AF4 detection modes (UV absorbance, refractive index, and fluorescence staining and detection). In addition, multi-detector AF4 approaches are developed to evaluate the release of fluorescent compounds (as model active ingredients) from biodegradable poly(lactic-co-glycolic acid) (PLGA) nanoparticles. The combination of AF4 separation with simultaneous online detection of the active ingredients (by fluorescence) and polymeric nanoparticles (by UV or TOC) provided a more accurate and direct analysis of loading and release compared to conventional release assays. Furthermore, the unique capability to determine distinctive release rates across the entire nanoparticle size distribution provided key evidence of the mechanism of release, e.g. diffusive release, surface desorption, or particle degradation. These analyses are specifically applied to distinguish the localization of hydrophilic versus hydrophobic active ingredients in the nanoparticles, as well as to identify the mechanisms by which changes in environmental conditions (pH and temperature) trigger a more rapid release. In conclusion, these studies demonstrate the high value of AF4-based methods to support emerging analytical needs and mechanistic studies on polymeric nanomaterials in the environment.

Tue-H4-04

The impact of biofilms and biosurfactants on the dispersibility of microplastics

Amber Pete, Michael Benton, Bhuvnesh Bharti

Cain Department of Chemical Engineering Louisiana State University Baton Rouge, La

The accumulation of plastics in the aqueous environment is a well-known problem. In recent years, many publications have highlighted the impact of both macro and microplastics in the environment. Microplastics are defined as plastics smaller than 5 mm in size. Microbial attack begins almost immediately after a plastic enters the aqueous environment, but biofilm formation is quicker on microplastics due to the increased surface area for attachment. Biofilm-covered microplastics significantly impact the fate of these microplastics. Biofilms can lead to increased sorption of environmental pollutants. Additionally, biofilms are often mistaken for diatoms and phytoplankton and ingested by organisms and thus enter the food web. Previously, it was believed that biofilms also influence the vertical transport of microplastics. This study adds polyethylene microspheres to cultures of marine bacterium Alcanivorax borkumensis and two cyanobacteria, Anabaena sp. and Synechococcus elongastus. We find that the Anabaena and A. borkumensis formed biofilms on the microplastics but only increased dispersibility in the microplastics cultured with A. borkumensis. We find that the increased dispersibility is likely due to the high biosurfactant production by A. borkumensis, which reduces the surface tension of the plastics and leads to their dispersal. We find that biosurfactants play a more prominent role in the dispersibility of the plastics than the biofilm formation does, as previously reported. By understanding how the interaction of microorganisms with microplastics influences the fate of the plastics in the aqueous environment, we can increase our understanding of the long-term effects of these pollutants.

Tue-H4-05

Weathering of Microplastics

Philip Brahana, Ahmed Al Harraq, Bhuvnesh Bharti

LSU: Cain Department of Engineering

Microplastics have become ubiquitous in nature and a part of our everyday life, however their environmental fate remains poorly understood. As microplastics age and endure weathering, their surface chemistry can be altered. An accelerated weathering experiment was performed on microscopic polyethylene particles in the laboratory over a 10-day period. During this period, a change in wettability was observed, which resulted in a shift of the particles to a hydrophilic state and an overall increase of their dispersal in the water column. This change in wettability can be attributed to the destruction of hydrophobic surface groups through the photo-degradation process. To study changes in adsorption, we compared the uptake of two common pollutants onto the microplastic substrate: (1) positively charged malachite green molecules and (2) negatively charged arsenite molecules. We observed an increase in the adsorption of malachite green molecules onto weathered particles, but no significant adsorption of the arsenite molecules throughout the weathering process. This is because during weathering, the magnitude of the negative charge on the PE particles and thus results in electrostatic attraction and repulsion between the malachite green and arsenite molecules, respectively. This finding provides insight on both the transport and dispersibility of MPs in the environment, as well as further understanding their toxicity to human health.

Tue-I4-01

Multi-scale simulations of networking-forming mixtures of colloids and telechelic polymers

Ronald Larson

Department of Chemical Engineering, University of Michigan

We use multiple scales of simulation: molecular dynamics, Brownian dynamics (BD), self-consistent field theory, and population balance equations, to describe the rheology of latex particles linked by bridging telechelic polymers into a reversible network. We use molecular dynamics to determine the binding free energy of hydrophobic end groups to methacrylate latex surfaces. We then use the binding free energy along with Brownian dynamics simulations of polymer chains resolved at the level of a Kuhn step, to determine the gap-dependent transition time for a polymer bridge between two surfaces to a loop with both hydrophobes on the same surface. Combining this transition time with self-consistent field theory (SCFT), which gives the equilibrium ratio of loops to bridges, allows us to deduce the slow gap dependence of the loop-to-bridge transition time. The inverses of these transition times are then used as rate coefficients for reversible loop-bridge transitions in population-balance equations. These are combined with Brownian dynamics simulations of colloid motion, to provide predictions of the linear rheology of colloid-polymer networks, with relevance to latex paint rheology.

Tue-I4-02

Impact Dynamics of Droplets Containing non-Brownian particles on Liquid Films

Boqian Yan, Xiaoyu Tang

Department of Mechanical and Industrial Engineering, Northeastern university

Droplet impact on surface is ubiquitous in many industrial applications, such as inkjet printing and spray coating. Rich phenomenon and impact outcomes including bouncing, merging, and splashing have been observed due to the intrinsic complexity stemming from the interplay of surface tension, viscous effect and inertial effect. Impact dynamics of Newtonian droplet on solid and liquid surfaces have been studied extensively. Non-Newtonian fluids add another layer of complexity which gives rise to more intricate behaviors. In this talk, I will present our experimental study of non-colloidal suspension droplets impacting on liquid films. Richer phenomenon compared to that with Newtonian liquids have been observed and discussed in terms of a regime map in the Weber number-volume fraction space. Scaling analysis will be discussed to understand the controlling mechanism.

Tue-I4-03

Stability of Carbon Black Slurry used in Flow Battery Applications

KangJin Lee, Mohan Das, Matthew Pitell, Christopher L. Wirth

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Western Reserve University, Cleveland, Ohio 44106, United States

Carbon black particles act as an additive that conducts electrons in the slurry used in electrochemical flow batteries. Stability of the carbon black slurry is a critical parameter for its storage and the efficient functioning of the battery. As a result of particle aggregation, sedimentation and deposition onto the device surface, carbon black concentration changes throughout the flow geometry. This not only prevents electrodes from being recycled but also increases the probability of flow channels being clogged. Modifying the carbon black slurry formulation and the flow behavior with addition of a surfactant would improve the suspension stability and the performance of the flow battery. Matching the typical flow battery formulation, we suspended carbon black particles in 1M H_2SO_4 in concentrations ranging from 1-5 vol%. Sedimentation kinetics of the process were measured by tracking the height of the sedimentation bed over time in a cuvette using an in-house camera set-up. Our study reveals that while initial concentration of the carbon black suspension exhibits different sedimentation kinetics, the final packed bed volume fraction is independent of the initial slurry concentration. We attribute this to the formation of a stable gel phase due to the interparticle attractions between the carbon black particles. Furthermore, we modify the interparticle attractions by adding a nonionic surfactant (Triton X-100) above, at, and below the critical micelle concentration (CMC) and study the effect on sedimentation kinetics and gelation volume fraction. Finally, we propose a phase diagram identifying the stable and unstable regimes as a function of particle volume fraction and surfactant concentration.

Tue-I4-04

Stabilization of Suspensions of Silica and Titania Particles Against Both Agglomeration and Sedimentation Using a Double-Chain Cationic Surfactant

An-Hsuan Hsieh, Elias Franses, David Corti

Charles D. Davidson School of Chemical Engineering, Purdue University

Aqueous vesicle dispersions formed from a cationic double-chain surfactant didodecyldimethylammonium bromide (DDAB) are shown to stabilize suspensions of silica and titania particles against both agglomeration and sedimentation. The densities of these particles were accurately determined via densitometry of the particle suspensions. The heights of the settling fronts of the particle suspensions in water were monitored to measure the settling velocities, v_{sed}, of each suspension. The diameters of the particles d_{sed} were determined from v_{sed} and the use of Stokes' law. Silica particles with nominal diameters of 500, 750, and 1000 nm were found to have d_{sed} = 450, 695, and 827 nm, respectively, indicating that no particle agglomeration occurred in water. DDAB vesicle dispersions for DDAB weight fractions w_D = 0.010, 0.020, and 0.027 were prepared via stirring followed by sonication, and then aged for 10 days. The particle suspensions were mixed with the aged DDAB dispersions, with final values of w_D = 0.009, 0.018, and 0.025. The particle settling fronts were monitored to obtain v_{sed} within the DDAB vesicle dispersions. At w_D = 0.009, v_{sed} was independent of time, implying that d_{sed} remained constant during sedimentation. Hence, the presence of the DDAB vesicles at this w_D caused no particle agglomeration. Stokes' law and v_{sed} were also used to estimate the viscosities of the DDAB vesicle dispersions at the shear stresses induced by the settling particles. Using silica suspensions with d_{sed} = 695 nm, the viscosities of the DDAB dispersions were estimated to be 1.35 cP at w_D = 0.009 and 5.02 cP at w_D = 0.018. For this particle size, the shear stress exerted by a particle is ca. 0.005 Pa. For w_D = 0.025 and d_{sed} = 695 nm, no settling of the silica suspension was observed for at least 10 days, indicating that these particles were stabilized against both agglomeration and sedimentation. Moreover, the determined value of v_{sed} = 0 suggests that the viscosity for this w_D at low shear stresses (ca. 0.005 Pa) was practically infinite. Nevertheless, all of these DDAB vesicle dispersions remain flowable at the higher shear stresses (ca. 1 Pa) that develop during the flow of the bulk dispersions through small capillaries, even when the DDAB dispersions stabilize the particle suspensions against sedimentation. The DDAB dispersions at high values of w_D therefore exhibit properties similar to a soft gel with a yield stress lower than ca. 0.1 Pa. For d_{sed} = 827 nm and w_D = 0.018, some particles sedimented much faster than expected for monodisperse sizes, suggesting that agglomeration occurred, probably due to depletion forces induced by the vesicles, an effect analogously generated by micelles (Yang et. al, J. Colloid Interface Sci., 2015, 450, 434-445). For d_{sed} = 827 nm and w_D =

0.025, neither particle agglomeration nor sedimentation was detected, evidently because of the very high viscosity of the DDAB dispersion at low shear stresses. Overall, DDAB vesicle dispersions can stabilize many types and sizes of particles against both agglomeration and sedimentation, while still retaining desirable properties for various practical applications.

Tue-I4-05

In situ generation of colloidal particles at oil-water interfaces: A spontaneous emulsification approach

Mario Cordova, Hossein Hejazi

Department of Chemical and Petroleum Engineering, University of Calgary

Interfaces between two immiscible fluids are abundant in many science and engineering areas, including improved oil production, underground soil remediation, wastewater treatment, and emulsion formation [1]–[3]. Colloidal particles, when placed at liquid-liquid interfaces, can affect the interfacial properties such as reducing the interfacial tension and enhancing the interfacial viscoelasticity [4]–[9]. The particle adsorption at the interface can provide a certain degree of control over the interface stability and rigidity [10]–[12]. A common approach to generate colloidal particles is performing interfacial or bulk reactions by the use of emulsions as templates [13], [14], where emulsion droplets act as the reaction sites [15], [16]. In this work, colloidal particles are generated "in situ" at the oil-water interface via spontaneous emulsification. A sodium silicate solution mixed with ammonium bicarbonate is placed in contact with a heptane solution containing aggregates of a non-ionic surfactant “Polysorbate 80 (Span-80)”. Subsequently, the interaction of surfactants with the adjacent aqueous phase promotes the spontaneous formation of aqueous based emulsions. The emulsified aqueous phase undergoes a sol-gel reaction in which sodium silicate colloids link together into branched chains and form extensive 3D networks throughout the liquid medium. The reaction ends up with the formation of a solid-like material which is comprised of a solid backbone that entraps water. The transformation of the aqueous phase fosters the formation of silica particles at the oil-water interface. SEM micrographs and confocal images of dried drops reveal the origination of colloidal size particles. The detection of particles in the evaporated drop region occurs when the aqueous and oleic phases have been in contact for 24 hours. We show that the beginning of the gel formation is commensurate with the time of emergence of particles at the interface. This unique particle generation route is conducted via spontaneous emulsification and does not require an alcoholic medium to produce particles at the oil-water interface. The production of colloidal particles with no mixing opens the window for the fabrication of innovative materials via interfacial phenomena. The in situ fabrication of materials may benefit particle-laden interfaces applications such as, coating, printing and enhanced oil recovery.

Tue-J4-01

Designing Nanoparticle Surface Chemistry and Interfacial Rheology for Highly Stable Gas-in-Water Foams at High Salinity

Keith Johnston [1], Xiongyu Chen [1], Chang Da [1], Pinkeng Wu [1], Daniel Hatchell [2], Hugh Daigle [2]

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The design of surface chemistries on nanoparticles (NPs) to stabilize gas/water foams with concentrated electrolytes, especially with divalent ions, has been elusive. At these conditions, the relationships between the interfacial rheology of NP laden gas-brine interfaces and NP adsorption and interparticle interactions are not well understood. Herein, we design binary ligands on the surface of silica NPs whereby the primary ligand provides steric stabilization in bulk brine and at the air-brine interface, whereas a second ligand raises the hydrophobicity to promote NP adsorption. The level of NPs adsorption at steady state is sufficient to produce an interface with a relatively strong elastic dilational modulus $E' = d\gamma/d\ln A$. However, the interface is ductile with a relatively slow change in E' as the interfacial area is varied over a wide range in compression and expansion cycles. With these favorable properties, highly stable nitrogen/water (N2/brine) foams are formed with CaCl2 concentrations up to 2% from 25°C to 90°C. The viscoelastic gas-brine interface arrests coarsening (Ostwald ripening) with little change in foam bubble size for days. With the addition of a liked-charged surfactant to the NP solution, the foams are also highly stable, but may be formed at a much lower shear rate than in the case of NPs alone. Unlike the case for most previous studies, the NP amphiphilicity was essentially independent of the surfactant concentration given the very low adsorption of the surfactant on the like-charged NP surfaces. The concept of tuning of nanoparticle surfaces with binary ligands to achieve both colloidal stability and high interfacial activity was also found to be successful for designing highly stable CO2-in-brine foams. Unlike the case for the N2-in-brine foams, the intermolecular interactions between CO2 and the surface ligands influenced the interfacial properties. The ability to design NP laden viscoelastic interfaces for highly stable foams, even with high divalent ion concentrations, is of fundamental mechanistic interest for a broad range of foam applications including mobility control in CO2 sequestration and enhanced oil recovery.

Tue-J4-02

Surface Tension and Viscoelastic Properties of Ultra-thin Liquid Crystal Films at the SmA-N Transition by Surface Light Scattering Spectroscopy

Angelo Visco [1], Huda Alwusaydi [1], Anthony Smart [2], William Meyer [3], Alexander Belgovskiy [3], Jay Mann [4], Elizabeth Mann [1]

[1] Physics, Kent State University, Kent, OH[2] Scattering Solutions, Inc., Costa Mesa, CA[3] Scattering Solutions, Inc., Cleveland, OH[4] Chemical Engineering, Case Western Reserve University, Cleveland, OH

We present a preliminary study by surface light scattering spectroscopy (SLSS) of surface properties of thin films of 8CB (4′-Octyl-4-biphenylcarbonitrile) at the air/water interface over a temperature range that covers the bulk smectic A phase and its transition to the nematic phase. SLSS uses light scattered from thermally-excited capillary waves to deduce surface tension, viscosity, and surface visco-elastic properties [1]. The amplitude of thermal capillary waves, which exist at any fluid interface, is controlled by the surface response function to be generally less than a nanometer [2][3]. Historically, such measurements have been difficult and the potential of the SLSS technique had not been fully realized. Scattering Solutions Inc. has designed an improved optical system to overcome former limitations of signal quality, accessible wave vectors, and ease of use. We compare surface tension measurements from SLSS with simultaneous measurements from a standard Wilhelmy plate technique on the same surface. We compare our measurements of surface visco-elasticity at an air/film/water interface with previous measurements [4] on a free-standing smectic liquid crystal film (air/film/air) by dynamic light scattering. References: [1] D. Langevin, Light Scattering by Liquid Surfaces and Complementary Techniques (Surfactant Science) (CRC Press, 1991). [2] W. V. Meyer et al., Appl. Opt. 40, 4113 (2001). [3] J. Adin Mann, Jr et al., Appl. Opt. 40, 4092 (2001). [4] S. Pardaev, Light Scattering Studies of Defects in Nematic/Twist-Bend Liquid Crystals and Layer Fluctuations in Free-standing Smectic Membrane, Ph.D, Kent State University (2017).

Tue-J4-03

The Role of Janus Particle Amphiphilicity on the Rheological Properties of the Air/Water Surface

Elton L. Correia, Dimitrios V. Papavassiliou, Sepideh Razavi

Chemical, Biological & Materials Engineering, University of Oklahoma

Research on particles with anisotropic surface properties, i.e., Janus particles, has gained significant attention due to the possibility of novel applications such as assembling functional structures, design of active nanomotors, and biological sensing and imaging. Janus particles are also of interest for interfacial applications, as they can adsorb to interfaces stronger than homogeneous particles and their surfaces can be tuned to serve added functionalities. Interfaces are routinely subjected to deformations that produce compression/expansion and shear stresses. Therefore, it is important to understand the impact that the Janus character brings to interfaces. Specifically, the characteristics of both faces are important as those control how the particles are interacting at the interface, which ultimately affects the resulting interfacial microstructure. In this study, we fabricated 1μm Janus particles with a hydrophilic silica core and a thin (10nm thick) gold cap. The particles are further modified with different thiols to achieve a varying degree of Janus amphiphilicity. We analyze the impact of the Janus degree of amphiphilicity on the interparticle interactions at the air/water interface, and the response of such particle-laden interfaces to applied stresses. Our results show that by controlling the degree of amphiphilicity, one can drastically change the resulting microstructure, which in turn affects the response to different stresses.

Tue-J4-04

Effect of Polarizability on the Interfacial Tension of Liquids and Fluids

Raymond Sanedrin [1], Nusrat Ahmad [2], Aleksey Baldygin [1, 2], Prashant Waghmare [2]

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According to de Gennes, “A liquid spreads completely if it is less polarizable than solid [1].” The extent of interaction of a drop of liquid deposited on a surface at equilibrium has been well established for various liquid-solid combinations, such as between polar-polar, polar-nonpolar, and nonpolar-nonpolar. The surface tension of the liquid and surface free energy of the solid greatly play a role on the final equilibrium contact angle [2]. Herein, we show similar hypothesis for liquid-fluid interface. A wide range of liquid-vapor combinations, polar-polar, polar-nonpolar and nonpolar-nonpolar were investigated and we show the impact of the polarizability of the surrounding saturated vapor phase on the equilibrium surface tension of the liquid-vapor combination. Furthermore, we show that the molecular weight (MW) of both phases (drop and surrounding saturated vapor) influences the activity of the molecules at the liquid-vapor interface. As an example, for both nonpolar liquid and vapor, only when the MW of the vapor was lower than the MW of the liquid, surface activity at the liquid-vapor interface was observed. [1] de Gennes, Pierre-Gilles, Françoise Brochard-Wyart, and David Quéré. “Capillarity and wetting phenomena: drops, bubbles, pearls, waves”, Springer Science & Business Media, 2013. [2] Jin, Ming, Frank Thomsen, Thomas Skrivanek, and Thomas Willers. "Why Test Inks Cannot Tell the Whole Truth about Surface Free Energy of Solids." Advances in Contact Angle, Wettability and Adhesion 2 (2015): 419-438.

Tue-J4-05

Green synthesis of thin poly(cyanoacrylate) films: patterned coatings, liquid packaging, and gas encapsulation

Manos Anyfantakis [1], Venkata Jampani [2], Miha Skarabot [2], Urban Mur [3], Miha Ravnik [3], Ulrich Jonas [4], Jan Lagerwall [1]

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Thin polymer films are key elements in a variety of applications, ranging from coatings to sensing technologies. Their production is typically based on either wet chemistry relying on organic solvents, or chemical vapor deposition involving low pressure and/or high temperature, often requiring elaborate equipment. Although such strategies are able to deliver planar films with well-controlled properties, the fabrication of films of arbitrary shape, desired in numerous emerging technologies, remains challenging. We here introduce a new, green concept comprising a minimal system and a straightforward method to produce thin films of cyanoacrylates, the main ingredient of superglue and surgical adhesives. Our system comprises water, ordinary surfactant and cyanoacrylate monomer. Upon exposure of a surfactant-laden air-water interface to vapors of cyanoacrylate, anionic polymerization is initiated by water. At the same time, water acts as a precipitation solvent for the polymer chains, confining their growth to the fluid interface. The surfactant molecules promote uniform polymer growth by stabilizing the growing chains, resulting in a homogeneous, thin poly(cyanoacrylate) film. Under appropriate conditions, centimeter-sized films with thickness variations of less than 10 nm are formed. The thickness is accurately programmed by adjusting the reaction time; values of 50-500 nm are reproducibly achieved in a timescale from a few minutes to one hour. We highlight the application potential of this new technology for making and exploiting thin polymer films on demand with three paradigms. First, by patterning the shape of the fluid interface and by modulating the film thickness, we produce planar films of arbitrary size, shape, and color (resulting from thin-film interference). Second, by applying the polymerization scheme to liquid entities of different forms, we demonstrate the in-situ packaging and manipulation of aqueous specimens. These include liquids containing reagents that can be consequently used for carrying out drop-based chemical reactions, and biological samples containing living organisms that are not harmed by the interfacial polymerization. Third, by forming bubbles that we in turn polymerize, we show the in-situ encapsulation of various gases. Solid soap bubbles allow for easy handling of the enclosed gas that can be released at will, for instance to initiate a chemical reaction. The advantages of this new concept are its simplicity, water-based nature, and its generic applicability to various cyanoacrylates and surfactants. These unique features, combined with the biodegradable and biocompatible nature of poly(cyanoacrylates) may open an avenue for a plethora of advanced packaging, photonics, and biotechnology applications.

Tuesday, July 12th | 09:30 - 11:30 | K4-Rheology and Dynamics

Tue-K4-01

Magnetoresponsive Janus Particle Suspensions: Modulation of Optical Transmittance and Transport Dynamics in Dense Systems

James Gilchrist, Samuel Wilson-Whitford, Jinghui Gao, William Buckley, David Kramer

Department of Chemical and Biomolecular Engineering, Lehigh University

Janus particles, having two hemispheres of surface properties, have long been studied since they were proposed by de Gennes. They are not commonly used in industrial processes because of the lack of ability to produce them on a large scale. Specifically, the most common fabrication method is to create monolayer coatings that are functionalized through physical vapor deposition. One key limitation is the ability to coat large areas of particles. This talk will introduce our Automated Langmuir Blodgett (ALB) coating process that allows roll-to-roll coating of nanometer to micron-scale particles. This method will be discussed in light of creating large area particle arrays for functionalization of magnetic Janus particles and our initial results into making pilot plant-scale quantities of particles. Two specific applications utilizing bulk suspension properties of magnetic Janus particles will be explored. In both examples, the individual particles are responsive, yet in aggregate behave as active systems dissipating energy at the particle scale that display complex behavior. The first investigates light transmittance of suspensions of Janus particles ranging from 1 - 50 microns in diameter subjected to both uniform and non-uniform oscillatory magnetic fields. 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. The second will investigate dense piles of these particles that become individual rollers. Upon actuation of a rotating magnetic field, these particles spontaneously heap and have kinematics that include a boundary layer flow that behaves as poured granular media.

Tue-K4-02

Viscosity Measurements of Gas Hydrate Slurries in Water Continuous Systems

Ahmad Afif Abdul Majid, Hannah Stoner, Jose Delgado-Linares, Carolyn Koh

Center for Hydrate Research Department of Chemical & Biological Engineering Colorado School of Mines

Gas hydrates are crystalline structures that trap small gas molecules (such as methane, ethane, and propane) inside hydrogen bonded water cages. These structures form at high pressures and low temperatures. Due to this formation condition, gas hydrates could form and plug oil and gas flowlines. It is reported that hydrate formation is the number one flow assurance concern in offshore oil/gas production lines. Traditionally, the method to deal with hydrates in flowlines uses complete avoidance whereby hydrate formation is prevented by injection of thermodynamic hydrate inhibitors. This method is uneconomical for maturing fields, especially those with high water content (water continuous system). In the 2000s, there was a shift in hydrate mitigation strategies to a technique called hydrate management. Now, gas hydrates are allowed to form but their properties are managed to prevent hydrate plugging. An important parameter that is needed while using this strategy is the viscosity profile of gas hydrate slurries at various conditions. In this work, in situ viscosity profiles of gas hydrate slurries were measured using a high pressure rheometer with a four-blade vane impeller. Measurements were conducted using two different model systems: (1) non-emulsified and (2) emulsified systems with commercial surfactants. Tests were conducted at a constant temperature of 4 ºC, constant shear of 800 s-1 and using an isochoric method with initial pressure of 1000 psig of methane. The water content was varied from 80 to 100 vol.% water. Results of this investigation showed that the relative viscosity of a hydrate slurry increases with hydrate volume fraction. Additionally, it was observed that for non-emulsified systems, the oil layer acted as a mass transfer barrier that prevented extensive formation of gas hydrates. The authors acknowledge funding support from DOE-BES Award Number DE-SC0022162.

Tue-K4-03

Piezoelectric response arises from frictional network in dense suspension

Hojin Kim [1, 2], Stuart Rowan [1, 3, 4], Heinrich Jaeger [2, 5]

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Control of interparticle constraints and frictional contacts has provided new ways to tune shear thickening behavior of dense colloidal suspensions. However, direct evidence of frictional contacts is still lacking on account of the technical difficulties in detecting their formation during shear in-situ. By measuring viscosity and conductance simultaneously in dense suspensions of piezoelectric particles, we found that shear-thickening correlates with a clear conductance enhancement due to piezoelectricity arising from stress-activated interparticle friction. The role of frictional contacts in driving shear thickening behavior is demonstrated by varying the degree of thickening, from continuous to discontinuous, with particle volume fraction and shape. The changes in conductance measured at constant stress can furthermore serve as direct signature of the spatiotemporal evolution of particle configurations. Importantly, shear-induced piezoelectricity also opens up new possibilities for mechano-activated chemistries that operate with a specific, targeted stress.

Tue-K4-04

Viscoelastic creep and recovery in dense suspensions of rough colloids

Yug Chandra Saraswat, Lilian Hsiao

North Carolina State University

Creep and yielding in dense colloidal suspensions are considered to arise from the slow relaxation of cage dynamics and interparticle friction. The objective of this study is to elucidate the mechanism through which interparticle friction affects the slow recovery and rate-dependent creep rheology of dense suspensions. We use dense suspensions composed of fluorescent colloids with tunable roughness suspended at high volume fractions ($0.6 \leq \phi \leq 0.63$) in a refractive index-matching squalene. The hard sphere-like poly (methyl methacrylate) colloids are synthesized with a grafted layer of poly (12-hydroxystearic acid), and roughness is induced by adding a crosslinking molecule during the nucleation step of the synthesis. Confocal laser scanning microscopy is used to determine the particle shape and volume fraction in the solvent to account for swelling. Dense suspensions are loaded onto a stress-controlled rheometer equipped with a parallel plate geometry, which applies constant shear stresses above and below the yield stress of the bulk material. For suspensions at 2% below the maximum packing fraction, rough colloids exhibit lower strain deformation and enhanced viscoelastic recovery. Suspensions of rough colloids are more solid-like in nature, exhibiting 70 – 90% less strain deformation compared to smooth colloids suspended at the same jamming distance, for applied stresses that are within the linear regime (0.0075 Pa – 0.01 Pa). In the nonlinear stress regime (2 – 5 Pa), suspensions of rough colloids exhibit 20 – 30% lower strain than the smooth colloids. The strain recovery of suspensions of rough colloids display twice as much strain recovery as the suspensions composed of smooth colloids at all stresses. These results suggest that the geometric frustration caused by surface roughness generates long-lived contacts between nearest neighbor colloids, and that the slow relaxation of these contacts are responsible for enhanced elasticity, solid-like minimal deformation, and higher viscoelastic recovery at a given applied stress.

Tue-K4-05

Enhanced linear viscoelasticity of rough colloids in dense suspensions

Lilian Hsiao, Shravan Pradeep, Alan Wessel

Chemical & Biomolecular Engineering, North Carolina State University

We report the linear rheology for dense suspensions of sterically stabilized smooth and rough colloids interacting as hard particles. Small amplitude oscillatory measurements reveal that rough colloids at high volume fractions exhibit enhanced storage and loss moduli that are orders of magnitude greater than smooth colloids. Frequency-concentration superposition is used to collapse the viscoelasticity data onto a master curve, where shift factors point to a more elastic microstructure and reduced cage volume for rough particles. A combination of mode-coupling theory, hydrodynamic modeling, and activated hopping theory shows that rough particles with significantly reduced localization lengths become trapped in their glassy cages for extended periods of time as compared to hard spheres. High-frequency data show that rough colloids, but not smooth colloids, display a transition from a free-draining to a fully lubricated state above the crossover volume fraction, and furthermore exhibit glassy and gel-like behavior. Scaling analyses support the idea that lubrication forces between interlocking asperities are enhanced, leading to rotational constraints and stress-bearing structures that significantly elevate the viscoelasticity of dense suspensions. The results provide a framework for how particle surface topology affects the linear rheology in applications such as coatings, cement, consumer products, and shock-absorbing materials.

Tuesday, July 12th | 09:30 - 11:30 | M4-Wetting & Adhesion

Tue-M4-01

Innovation at Interfaces: From Energy to Biomedical Applications

Kripa Varanasi

Massachusetts Institute of Technology

Interfacial interactions such as wetting and adhesion play an important role in multiple industries. In this talk, I will summarize how surface/interface chemistry, morphology, thermal, electrical, and magnetic properties can be engineered across multiple length scales for significant efficiency enhancements in a wide range of processes. I will discuss many novel concepts such as symmetry breaking and self-peeling in droplet hydrodynamics, tailoring interfacial friction for efficient dispensing of viscous products and enhancing flow assurance, photo-thermal traps for anti-icing, and engineering charge transfer to enhance droplet retention for reducing agricultural run-off to solve important problems at the Water-Agriculture Nexus. In parallel, I will also discuss engineering bio-interfaces for enhancing the bioprocessing value chain: from bioreactors to injections. We will describe non-invasive approaches to prevent foam build-up in bioreactors, protein purification and a new methodology to inject highly viscous drug formulations subcutaneously using core annular flows. Manufacturing and scale-up approaches, robust materials and processes, and entrepreneurial efforts to translate these technologies into useful products and markets will also be discussed.

Tue-M4-02

LaMer Keynote: Multicomponent, multiphase thermodynamics with interfacial curvature

Nadia Shardt [1, 2], Janet A. W. Elliott [1]

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A two-dimensional interface supplemented with surface excess properties is a mathematically convenient representation of the region between two bulk phases. Gibbsian composite-system thermodynamics can be used as a tool to understand systems with interfaces. For example, it can be used to show that the equilibrium properties of bulk phases differ when the interface between them is flat or curved; the effect of interfacial curvature becomes particularly important as the radius of curvature approaches the nanoscale. However, our understanding of the effect of interfacial curvature on the properties of multicomponent systems is incomplete. In this presentation, advances are presented on three topics: (i) predicting surface tension as a function of temperature and composition for a wide array of mixture types, (ii) predicting phase diagrams of vapor–liquid systems as a function of radius of curvature for multicomponent droplets and bubbles, and (iii) predicting a liquid drop's contact angle on physically rough or chemically heterogeneous surfaces. First, we propose a new equation for the surface tension of multicomponent systems that can be applied to mixtures containing both subcritical compounds (e.g., organic and aqueous mixtures) and supercritical compounds (e.g., carbon dioxide); we validate our proposed equation against experimental data spanning a wide range of temperatures, pressures, and compositions. Second, we develop an activity-coefficient model to calculate the vapor–liquid phase diagram of nonideal systems with nanoscale radii of curvature, making use of our newly-developed surface tension model. Finally, in deriving equations for contact angle, we conclusively demonstrate that the properties at the circumference of a liquid drop dictate its contact angle on a substrate—that is, the line fraction on a chemically heterogeneous surface and the line roughness on a physically rough surface. As a whole, this work contributes new thermodynamic tools for understanding processes under the influence of interfacial curvature, which can be applied to the atmosphere (e.g., cloud microphysics) and to industrial processes (e.g., catalysis).

Tue-M4-03

Enhanced Evaporation from Droplets on Porous Coatings

William Ducker, Mohsen Hosseini

Dept. of Chemical Engineering and Center for Soft Matter and Biological Physics, Virginia Tech,
Blacksburg, Virginia, 24061, USA

Evaporation is important in a diverse range of applications, including removal of solvent to purify solutes, removal of solutes that were used to deliver dissolved substances, in cooling, in renewable energy schemes, and in drying surfaces. Our research group is particularly interesting in rapid drying of surfaces to reduce the longevity of pathogenic microbes that are a source of disease transmission. Here we will describe how a porous coating can rapidly increase the rate of evaporation of water droplets from surfaces. The effect is not small; thin coatings can lead to up to an 8´ increase in evaporation rate. The evaporation is a function of the film thickness, among other factors. The mechanism of the rate increase, and the relationship to wettability will be discussed.

Tue-M4-04

Dropwise condensation on biphilic patterned surfaces with multiple thermal conductivities.

Huy Tran, Ziwen He, Min Pack

Department of Mechanical Engineering at Baylor University

Recent investigations have been interested in dropwise condensation on biphilic patterned surfaces to enhance the heat transfer performance in the heat exchanger and condenser, but the understanding of the optimum design is still under progress. This study experimentally observed the drop departure rate and the heat flux at a constant subcooling temperature to find ideal area fraction and channel width of the dropwise condensation region on the patterned surfaces. The ideal point is influenced by the decrease in area fraction of dropwise condensation side with the increase in heat transfer rate. This study also expected that with lower dropwise region's channel width, the heat transfer also increase due to large drop departure rate.

Tue-M4-05 Withdrawn

Predicting contact angle hysteresis via micro-scale interface dynamics on random and periodic rough surfaces: Effect of roughness area fraction

Pawan Kumar [1], Paul Mulvaney [2], Dalton J. E. Harvie [1]

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Surface wetting refers to the phenomena of spreading of a liquid on a solid in the presence of another immiscible liquid or gas. Separation of metal ores, water repellent surfaces, enhanced oil recovery, efficient lab-on-a-chip devices etc., are some of the applications where surface wetting plays an important role. On rough surfaces, the wetting exhibits a hysteresis in the static contact angle (CAH). With the advancement in microfabrication techniques, hysteresis on surfaces possessing structured roughness has been explored to some extent, however the wetting behaviour on randomly structured surfaces remains largely unexplored. Here we measure the CAH for de-ionized water droplet on surfaces having randomly distributed and hexagonally arranged cylindrical pillars with different area fractions. Each pillar has a diameter of 10-micron and aspect ratio of unity. To ensure that the inherent surface is chemically homogeneous and hydrophobic, a monolayer of octadecanethiol (ODT) is deposited before measurement. Experimental findings are also compared against a unique numerical model that is based on a novel roughness scale mechanical energy balance. The numerical model is developed in the open-source software Surface Evolver and utilizes the concept of free energy minimization. We find that for both randomly distributed and periodic pillars, the macroscopic advancing contact angle increases with pillar area fraction, showing a logarithmic dependence that is in good agreement with the experiments. Further, for a given area fraction a randomly structured surface generally produces a lower advancing contact angle than a structured surface. Extending our results, we also show numerically that on a hexagonal surface (or a structured surface in general), the contact angle is different depending upon the direction of interface advance relative to the orientation of the roughness structure, suggesting the potential of the tool for designing directional wetting surfaces. This combined experimental and numerical study shows that contact angle hysteresis can be quantitatively predicted on surfaces with known roughness topography, opening new possibilities in the optimisation and design of the many processes and devices that depend upon wetting behaviour.

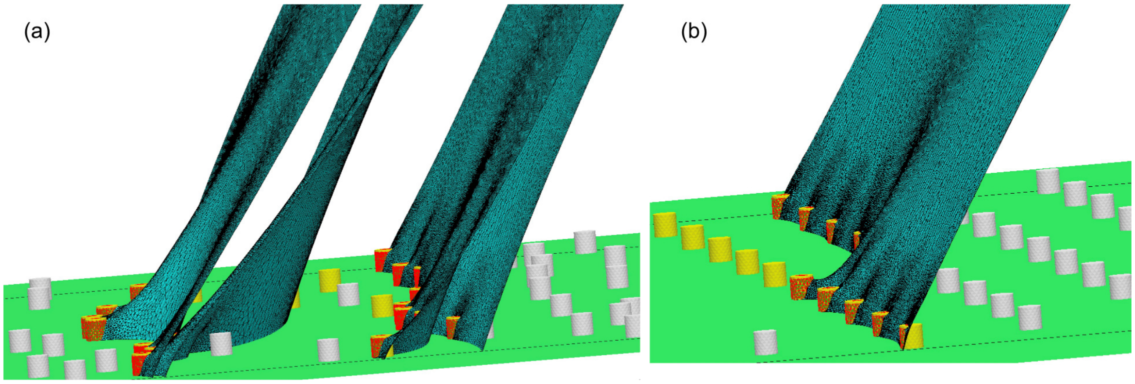

Figure: (a) Shows four equilibrium interface morphologies of a liquid/gas interface as it advances over a surface textured with randomly distributed cylindrical pillars. (b) Liquid/gas interface advancing with a zipping contact line motion on a surface with hexagonally arranged cylindrical pillars. For both cases the (flat) Young's angle is 112 degrees, the area fraction of pillars is 0.02 and their aspect ratio is 1.

Tuesday, July 12th | 09:30 - 11:30 | N4-Connecting the Dots

Tue-N4-01

Ambitions to connect the dots – perspective from a modeler working in consumer goods

Peter Koenig

Corporate Functions, Data and Modeling Sciences, The Procter and Gamble Company.

As chemists in the consumer goods industry, we have the mission to not only explore molecular mechanisms but to explain and predict how these chemical technologies will make a difference for delivering affordable, safe, and sustainable products that perform to delight consumers. This requires a keen understanding of mechanisms and drivers beyond the molecular scale. To bridge from the molecular scale to commercially relevant predictions is a challenge that requires connecting dots on multiple levels, including industrial-academic collaborations, business propositions, identifying the right mechanisms and drivers that connect performance to physical properties, colloidal scale and ultimately molecules. I will provide examples of molecular, surface, rheological and colloidal models to bridge into and beyond the mesoscopic gap. These models describe consumer relevant phenomena such as product dispensing and spreading, tribology and stability.

Tue-N4-02

Microemulsion Applications in the Oil and Gas Industry

Lirio Quintero

Baker Hughes

Microemulsion technologies for multiple applications have been increasing in the oil industry during the last few decades and can be categorized in three groups of technologies. The first group of technologies involves cleanup processes in wells and surface facilities, such as wellbore cleanup, near-wellbore remediation/stimulation, flow-back recovery in shale gas wells, cement spacers, oil-based drilling fluid displacement to water-based fluid, oil removal from drilling cuttings, etc. The second group involves formulations of single-phase microemulsions to have two or more immiscible products used in production operations in one single-phase fluid in order to optimize process operations (e.g. combination of solvent-based demulsifiers with water clarifiers to treat crude oil-water production fluids). The third and oldest group of applications is enhanced oil recovery, where a surfactant formulation that forms a microemulsion with the crude oil is injected into the reservoir to displace the oil bank and increase oil recovery. Microemulsion formulations for these applications need to have very low interfacial tension and high oil solubilization. The success of those formulation depends on the proper selection of additives and systematic studies of Winsor phase behavior of the microemulsion systems. A very important point for the oil industry is that surfactant companies, universities and research institutes have greatly expanded the knowledge about phase behavior of microemulsions and have made available more efficient surfactants for microemulsion formulations. The target formulations need to exhibit phase behavior type Winsor III, Winsor IV or a Winsor I system on the borderline of Winsor III system depending on the specific application, temperature and composition parameters (o/w ratio, oil type, water composition, surfactants, and other components such as linkers). This presentation includes microemulsion formulation methodology, discussion of ultra-low interfacial tension, wettability alteration, fluids compatibility, cleanup evaluation, as well as relevant field data. The following applications will be discussed: (1) near-wellbore cleanup to remove formation damage (e.g. paraffins and asphaltenes deposits, scales deposits, sludges) in oil and gas wells; (2) microemulsion formulations for surfactant flood in enhanced oil recovery; (3) spacers for displacement of oil-based fluid to water-based fluid during the construction of oil wells; (4) formulations of single-phase microemulsions for crude oil-water effluent treatment.

Tue-N4-03

Innovation in Interfacial and Colloidal Science at Dow

Carol Mohler [1], Chris Tucker [1], Dan Miller [2], Michael Tate [3], Chris Nelson [1], Yifan Dong [4]

[1] Core R&D, The Dow Chemical Company, Midland, MI 48674[2] Core R&D, The Dow Chemical Company, Collegeville, PA 19426[3] Dow Industrial Solutions, Midland, MI, 48674[4] Dow Packaging & Specialty Plastics, Lake Jackson, TX 77541

Colloidal and interfacial science plays a critical role in driving innovation in a wide variety of technically challenging applications in the chemical industry. This includes the development of stable complex agricultural formulations, stabilization of home/personal care products, new surfactants for emulsification and cleaning in high electrolyte or cold water conditions, and delivery of actives in oilfield applications, to mention only a few examples. The molecular characteristics of interfaces, particularly those buried between phases, are also key in developing new adhesives for production and recycling of multilayer films for packaging, more environmentally friendly surfactants for emulsification or solubilization of oils, and effective flocculants and dispersants for inorganic scale and pigments. Since many of these technical challenges are interdisciplinary, Dow often leverages academic and government partnerships to accelerate fundamental understanding and guide the development of novel technical solutions. High throughput robotic technologies have also proven to be useful to rapidly characterize and develop complex multicomponent formulations. This presentation will highlight capabilities and examples of ongoing research and technical challenges in interfacial and colloidal science at Dow.

Tuesday, July 12th | 13:00 - 14:40 | A5-Active Matter

Tue-A5-01

Morphogenesis of growing bacterial communities in polymeric environments

Sebastian Gonzalez La Corte, Tapomoy Bhattacharjee, Brianna Royer, Ned Wingreen, Sujit Datta

Princeton University

Many bacteria live in polymeric environments, such as mucus in the body, exopolymers in the ocean, and cell-secreted extracellular polymeric substances (EPS) that encapsulate biofilms. However, most studies of bacteria focus on cells in polymer-free fluids. How do interactions with polymers influence the behavior of growing bacterial communities? To address this question, we experimentally probe the growth of non-motile *Escherichia coli* in solutions of chemically-inert polymers. We find that, when the polymer is sufficiently concentrated, the cells grow in striking “cable-like” morphologies—in stark contrast to the compact morphologies that arise in the conventionally-studied polymer-free case. Experiments and agent-based simulations indicate that these unusual community morphologies arise due to a polymer-induced entropic attraction between pairs of cells. These results suggest a pivotal role of polymers in regulating microbe-host interactions through physicochemical interactions, e.g., potentially by promoting bacterial exposure to external biochemical groups that protect the host against pathogens. More broadly, this work helps to uncover quantitative soft matter principles governing the morphogenesis of diverse forms of growing active matter in polymeric environments.

Tue-A5-02

Bacterial Locomotion in Nematic Liquid Crystals

Ameya Gajanan Prabhune, Nuris Figueroa-Morales

Department of Physics at University of Colorado Boulder

Several flagellated bacterial species exhibit a ‘run-and-tumble’ locomotion pattern in fluids. Peritrichous bacteria form a bundle of synchronously rotating flagella that propels them forward (run) until they stop and reorient (tumble). While bacteria stochastically determine their new orientation in isotropic fluids, in anisotropic environments the direction of lowest viscosity is the preferred direction for bacterial movement. Here, we use nematic phase liquid crystals (NLC) and *B. subtilis* with stained flagella to observe the speeds and flagella orientation of bacteria inside anisotropic media. Our experiments show that a significant fraction of bacteria swimming inside NLC forms two flagellar bundles at opposite ends of the cell body. We use the intensity of flagella bundles to define the quantity “Asymmetry” for bacteria inside NLC, given by the ratio of difference and sum of flagella on opposite ends. It ranges from zero to one, with zero indicating a perfectly symmetric bacterium with equal flagella on either side and one indicating a bacterium with only a single bundle. Using this definition, we observe that maximum bacteria speeds inside NLC are proportional to their average Asymmetry for the swimming trajectory. Based on our observations, we hypothesize that opposing flagella bundles work against each other and decrease bacterial speeds. Further, we have observed periodic acceleration and deceleration of bacterial speed along their trajectory, independent of their respective Asymmetry. These oscillations indicate that they cannot sustain high swimming speed for long periods inside anisotropic media. Overall, our research could one day be used to improve liquid-crystal-based biosensors and understand bacteria behavior in biological anisotropic media.

Tue-A5-03

Soft Microbots with Tunable Traction

Yan Gao, Ela Springer, David Marr, Ning Wu

Department of Chemical and Biological Engineering, Colorado School of Mines, Golden,
Colorado, United States of America 80401

Microbot-based drug delivery has attracted increasing attention due to the potential for targeting and avoiding side effects associated with systemic delivery. Most approaches to data have relied hard materials with issues of biocompatibility and difficulty in incorporating drugs within a rigid matrix. Here we introduce a soft microbot based on magnetic Pickering emulsion droplets that can not only rapidly roll along surfaces but also due to its intrinsic deformability, exhibits traction significantly higher than their rigid counterparts. We show that the magnetic particle distribution at the microbot interface can be tuned with the external field, strongly influencing the translation speed. Finally, and because these microbots are stabilized with Pickering particles, we demonstrate that they can be destabilized and used to deliver their contents to a desired location.

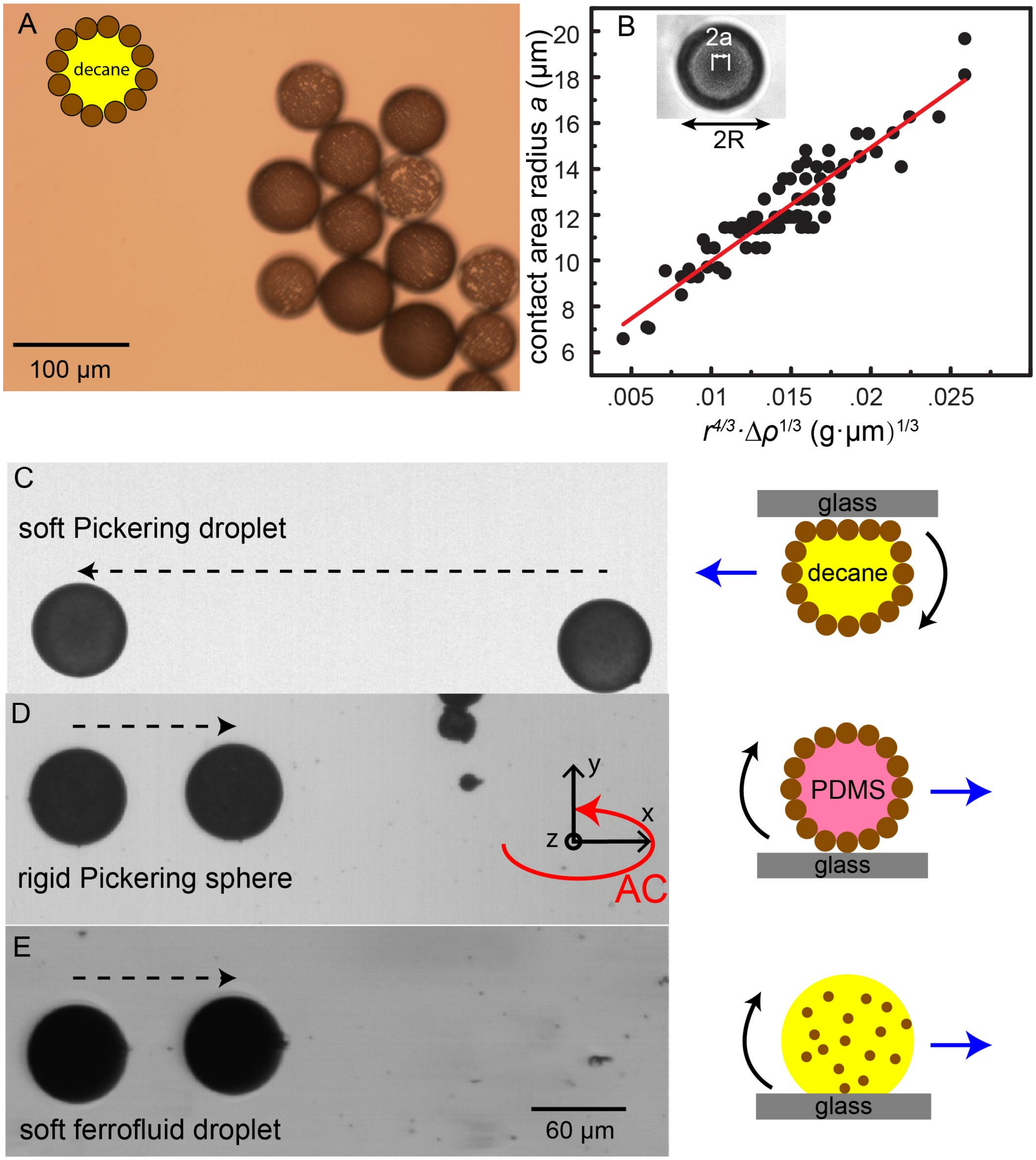

Figure 1. A) Fabricated Pickering decane-in-water emulsion droplets are partially or fully covered by 1 µm particles (latex-Fe3O4 composite microspheres). B) The radius of contact area a of Pickering droplets depends on their size R. Circles: experimental measurement. Line: Hertzian model based on Eq. (1). Inset: the optical image of a deformed droplet. C)-E) Rolling of three different types of µbots (soft Pickering droplet, rigid Pickering sphere, and soft ferrofluid droplet) over 10 seconds under a circularly rotating magnetic field along the x-z plane. The black arrows indicate the rotational direction, while blue arrows represent the translational direction.

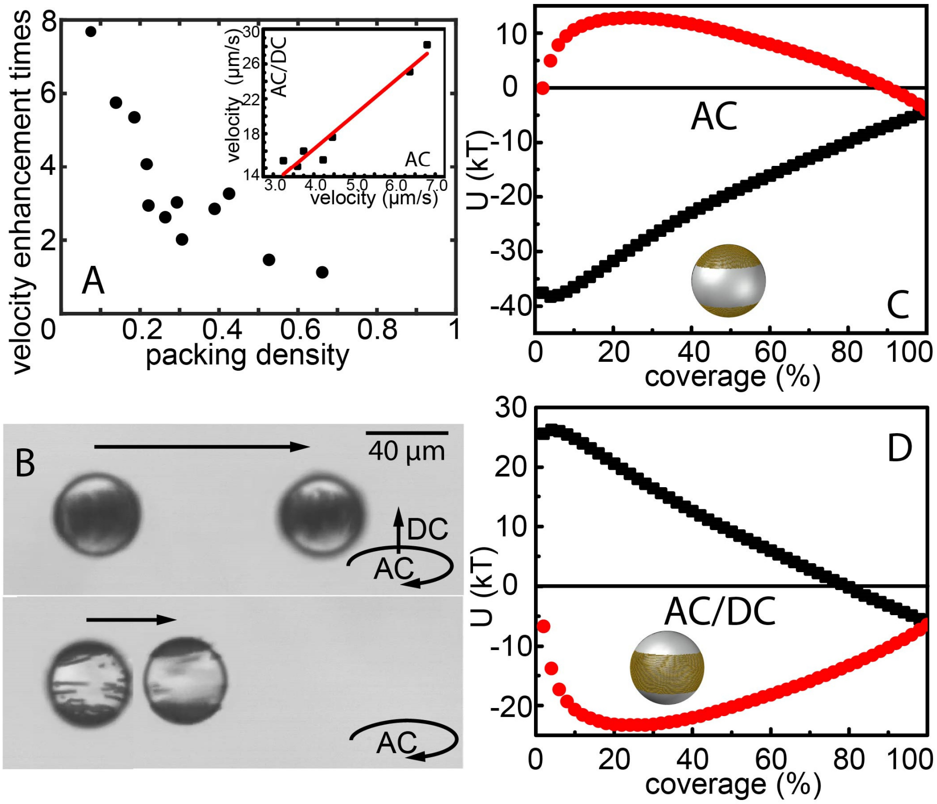

Figure 2. A) Velocity enhancement upon addition of a DC field showing a strong packing density dependence. Inset: Measured velocities at 30 % coverage. B) Surface particle redistribution upon addition of a DC field. C) Predicted total magnetic interaction energy of particle packing at the droplet surface under a 3 mT AC rotation field and under. With 3D model of magnetic particle packing at poles. D) 3 mT AC/DC combined fields. Black dots are packing from the poles to the equator and red dots are packing from the equator to the poles. With 3D model of magnetic particle packing at equator.

Tue-A5-04

Urease-powered micromotors from double emulsion-templated microcapsules

Jessica O'Callaghan, Daeyeon Lee, Daniel Hammer

1. Chemical & Biomolecular Engineering, The University of Pennsylvania

Catalytic microswimmers are artificial systems that self-propel from the conversion of chemical energy into mechanical force. Despite their demonstrated application in fields such as environmental remediation or microrobotics, their implementation in biomedicine remains limited since the materials they rely on are often toxic or have limited bioavailability. Enzyme-powered micromotors have emerged as an attractive alternative since the catalysts they rely on are biocompatible. Moreover, numerous enzymes have been shown to increase the motion of micron-sized particles, including in our lab, where the activity of entrapped catalase was shown to induce large-scale random motion of surface-adherent polymersomes. Despite these exciting outcomes, the fundamental aspects underlying the motion behavior of enzyme-powered motors is still largely unknown; this is even further complicated by the heterogeneity in structure and number of catalytic elements that occurs when using conventional particle assembly approaches. In this study, we prepare uniform micron-sized particles templated from water-in-oil-in-water (W/O/W) double emulsions droplets assembled in a capillary microfluidic device. The assembled particle is a hollow microcapsule made of poly(lactic-co-glycolic acid) (PLGA), a polymer with excellent biocompatibility and tunable biodegradability. PLGA stabilized droplets rapidly assemble into shells with high mechanical rigidity due to fast evaporation of the organic solvent. Moreover, the size of PLGA-containing double emulsions and that of resulting microcapsules can be tuned by osmotic annealing, which depends on the ratio of solute in the inner and outer phases of the double emulsion. We demonstrate the use of these annealed capsules by directly attaching the enzyme urease to the shell through carbodiimide chemistry. We then examine their motion in solution in response to enzymatic turnover. Consistent with previous reports, our initial findings suggest that a minimum number of asymmetrically distributed enzymes is required to induce self-propulsion. Our work is the first of its kind to demonstrate motion of uniform particles prepared by double emulsion microfluidics. Moreover, it offers unique advantages to existing methods for robustly screening differences between the thermodynamic and kinetics properties of enzymes and the effects such properties have on observed particle motion.

Tue-A5-05

Magnetically powered chitosan milliWheels for rapid translation and delivery of anti-TNF

Matthew Osmond [1], Ellie Korthals [2], Keith Neeves [2], David Marr [1]

[1] Department of Chemical and Biological Engineering, Colorado School of Mines[2] University of Colorado, Denver

Background: Inflammatory bowel disease (IBD) is mediated, in part, by an overexpression of tumor necrosis factor-a (TNF) by mononuclear cells in the intestinal mucosa. Intravenous delivery of anti-TNF antibodies is problematic; up to one-third of patients are non-responders. Oral delivery of anti-TNFs has thus far been hampered by degradation of in the harsh gut environment. Objective: To engineer magnetically powered hydrogel particles we call milliWheels that can roll on mucus and provide a protective and sustained release of anti-TNF. Methods: Iron oxide nanoparticles were suspended in a chitosan hydrogel crosslinked with genipin. The gel was pressed through a sieve to produce milliWheels. The velocity of rolling milliWheels over glass and mucus secreting cells was measured under the influence of a 10 mT magnetic field rotating at 5 to 20 Hz. milliWheels were loaded with 10 µg/ml anti-TNF and showed sustained release over one week. The permeability of TNF treated gut epithelial cell monolayers (Caco-2) was measured with or without the presence of milliWheels. The expression of occludin was measured as a marker of tight-junction cohesion in response to the presence of anti-TNF and the milliWheels. Results: Sieve based fabrication yielded irregular 75-150 µm milliWheels, that rolled at >500 µm/s over glass and mucus coated cells. Depending on crosslinking density and pH of release media, milliWheels release ~10% to 80% of their payload over one week. In a model of the gut epithelium the anti-TNF milliwheels reduce the effect of TNF treatment on permeability. The expression of occludin was measured to increase in response to the presence of anti-TNF and the milliWheels. Conclusions: milliWheels are a potential strategy to deliver biologics for the treatment of IBD; they translate over mucosal surfaces at high speed, protect therapeutic proteins from the gut environment, provide sustained release directly to the inflamed epithelium, and provide measurable defense against the effects of TNF.

Tue-B5-01

Depletion Forces and Gelation of Aqueous Colloidal Suspensions Containing Associating Mixtures of Polymers and Surfactants

Robert Tilton

Department of Chemical Engineering, Carnegie Mellon University

Inter-particle depletion forces act in parallel with van der Waals attraction and electrostatic double layer repulsion when charged colloids are suspended in solutions of nonadsorbed macromolecules, micelles, nanoparticles, or other “depletants”. The depletion force is the deepest attractive minimum in a longer range oscillatory structural force associated with the redistribution of depletants in the inter-particle gap and the bulk solution as the inter-particle spacing changes. The interaction strength depends on the osmotic pressure of the solution. Accordingly, it is commonly observed that the magnitude of depletion forces in polyelectrolyte solutions is greater than that in comparable nonionic polymer solutions due to the counterion contribution to osmotic pressure. This presentation will discuss the synergistic strengthening of depletion forces between charged silica surfaces in aqueous solutions of nonionic Pluronic poly(ethylene oxide – b – propylene oxide – b – ethylene oxide) triblock copolymers caused by their noncovalent complexation with sodium dodecylsulfate (SDS) anionic surfactants. Charged complexes formed by Pluronic-SDS association provide a pseudo-polyelectrolyte effect, whereby sodium counterions contribute to the macromolecular osmotic pressure, and complexes yield stronger depletion forces than either the polymer or the surfactant on their own. Forces were measured by the colloidal probe atomic force microscopy technique and interpreted in terms of the size and charge of complexes as determined from dynamic light scattering and ion-selective electrode analyses. Interest in colloidal forces is typically motivated by their effects on colloidal aggregation. Observations of strengthened depletion forces in Pluronic/SDS mixtures are correlated with shifts in the phase diagram for gelation of colloidal silica suspensions induced by a combination of electrostatic double screening and depletion forces induced by SDS, Pluronic, or their mixtures in solution. For an equivalent ionic strength, SDS solutions favor silica colloidal gelation more than the simple electrolyte NaCl does, due to the combined effects of double layer screening and depletion forces induced by SDS micelles. Introducing Pluronic polymers to form Pluronic-SDS complexes further promotes gelation, which may be attributed to the strengthened depletion forces.

Tue-B5-02

Optically Driven Assembly of Colloidal Sodium Yttrium Fluoride Nanocrystals Through Hydrodynamic Surface Roughness

PETER PAUZAUSKIE [1, 2], R. Greg FELSTED [3], Jaehun Chun [2], Gregory K. Schenter [2], Alexander B. Bard [3], Xiaojing Xia [4]

[1] Materials Science & Engineering, U. Washington[2] Pacific Northwest National Laboratory[3] Chemistry Department, U. Washington[4] Molecular Engineering Program, U. Washington

The growth of bulk crystals via the oriented-attachment (OA) of nanoscale, colloidal building blocks has been of interest as one of the important “non-classical” mechanisms underlying the synthesis of materials. Understanding how specific crystals assemble into well-defined structures promises to provide significant advances in the design of materials having complex composite structures. In this presentation single-beam near-infrared laser-tweezers are used to generate local electromagnetic fields capable directing the assembly of cubic sodium yttrium fluoride (NaYF) nanocrystals with rough surfaces and a non-stoichiometric composition of $Na_{0.5-x}Y_{0.5+x}F_{2+2x}$ where $0 < x < 0.5$. Experiments show that pristine NaYF nanocrystals assemble irreversibly in a linear chain containing up to 10 nanocrystals. Control experiments with NaYF nanocrystals coated with ethylenediaminetetraacetic acid (EDTA) molecules do not show appreciable assembly. Using a boundary element method with an integral representation of the Stokes flow via a hydrodynamic Green’s function, we demonstrated that the nanometer-scale root-mean-square surface roughness of the pristine NaYF nanocrystals (originating from the complex composition and synthesis of NaYF) can significantly reduce the colloidal hydrodynamic lubrication force between pairs of crystals as the crystals approach each other. This observation, in contrast to that between crystals with smooth surfaces (i.e., NaYF nanocrystals with EDTA coating) can be overcome with a sufficiently strong optical force from laser tweezers to force the crystals into assembly by contact. This work demonstrates that the local optical force in combination with a reduced hydrodynamic lubrication force is responsible for the assembly colloidal NaYF nanocrystals, despite appreciable colloidal forces such as electrostatic and van der Waals forces. This combination of experiment with theory highlights the importance of the surface roughness of colloidal nanocrystals during non-classical crystal growth under nonequilibrium conditions, and can provide insights into the aggregation of other colloidal entities such as viral particles.

Tue-B5-03

The effect of surface chemistry on interfacial behaviors and dynamics of ionic liquids under nanoconfinements

Monica Iepure, Amy Lu, Younjin Min

Chemical and Environmental Engineering University of California, Riverside

Ionic liquids (ILs) have emerged as a new class of room temperature liquid salts that have a plethora of potential applications in industry owing to their unique properties such as their negligible volatility, high thermal stability, and the ease of their structural tunability. Current research, however, has been mainly focused on the behavior of ionic liquids in bulk while many of industrial applications require to confine ILs at nanometer scales.

Here, we present interfacial behaviors and dynamics of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-methyl-3-octylimidazolium tetrafluoroborate, confined in gaps comparable to their molecular dimensions. Porous alumina membranes were synthesized using a conventional two-step anodization process in order to emulate nanoconfined geometries. The achieved pore sizes of alumina membranes were confirmed by scanning electron microscope with a range of 30 – 100 nm. The interfacial areas of porous alumina membranes were then hydrophobically modified with phosphonic acids of varying carbon chain lengths (hexylphosphonic acid, decylphosphonic acid, tetradecylphosphonic acid and octadecylphosphonic acid) and thus, degree of corresponding hydrophobicity. The successful conjugation (surface modification) was qualitatively as well as quantitatively characterized by transmission Fourier transform infrared spectroscopic measurements. Water contact angle was increased from 19 to 109°, also confirming that the surface of alumina membranes was modified with different degrees of hydrophobicity. The homogeneous surface modification was revealed by the atomic force microscopy with a surface roughness of 15 ± 1.4 nm, and further surface characterization was done by measuring the elastic modulus and adhesion force of respective surfaces with surface modifications. The breakdown of continuum behavior of ILs was further evidenced in aids of dynamic scanning calorimetry which allowed us to quantitatively identify changes in their thermal, dynamic as well as relaxational properties of ILs confined in alumina porous membranes with different degrees of hydrophobicity. We anticipate our findings obtained from these unique combination of experimental approaches lead to new fundamental insights on the drastic changes of physicochemical properties of confined ILs with surface modification, delivering crucial perspectives for the applications where the space restriction is present such as supercapacitor, lithium batteries, and active lubrication. The atomic force microscopy additionally revealed homogeneous surface modification.

Tue-B5-04

Investigation and Analysis of Scattered Light from the Deformation and Adhesion of Synthesis Oil-in-Water Microcapsules

Hairou Yu [1], Jiarui Yan [2], Christopher Wirth [1]

[1] Department of Chemical and Biomolecular Engineering, Case School of Engineering, Case Western Reserve University[2] Department of Chemical and Biomedical Engineering, Washkewicz College of Engineering, Cleveland State University

Measuring the adhesion and deformation of healthy RBCs from a boundary is of great importance to the diagnosis and treatment of diseases like sickle-cell disease. However, the complexity of the bio-material and deformation ability makes it difficult to analyze. The strategy herein is to utilize synthetic microcapsules with an enclosed oil-core and a solid polymer shell that interacts with a boundary as the analog to investigate the adhesion and deformation of red blood cells. This phenomenon is not only crucial to RBC adhesion but also generally influential when soft and hard surfaces come into contact. Microcapsules are synthesized via a Pickering emulsion, which consists of cinnamon leaf oil stabilized by calcium carbonate nanoparticles in water. The shell is formed through the ion-exchange reaction and cross-linking process by sodium alginate and calcium ions. To image and measure the size of microcapsules, fluorescent tag Nile red is added in cinnamon oil to represent the size of the oil core. The size distributes from 4.3 to 5.3 μm depending on the fabrication time, and the zeta potential is around −20 mV regardless of the fabrication time. The Brownian fluctuation between the capsule and the glass substrate is measured by Scattering Morphology Resolved Total Internal Refraction Microscopy (SMR-TIRM) as it offers high energy and spatial sensitivity. The fluctuations in total scattered light intensity directly result from the fluctuations in separation distance, typically at a resolution of a few nanometers, as the evanescent wave decays exponentially with distance. The scattering light morphology of an anisotropic colloidal particle systematically changes with orientations and positions away from the substrate. We aim to analyze the mean square displacement, potential energy profile, and morphology changes in scattering light to study the adhesion and deformation of liquid containing microscale capsules interacting with solid boundaries.

Tuesday, July 12th | 13:00 - 14:40 | C5-Colloids, Macromolecules, and Surfaces in Life Science

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Tue-C5-01

Zwitterionic Materials and Surfaces for Biomedical and Engineering Applications

Shaoyi Jiang

Meinig School of Biomedical Engineering Cornell University

An important challenge in many applications is the prevention of unwanted nonspecific biomolecular and macromolecular attachment on surfaces from implants and drug delivery carriers to marine coatings. We have demonstrated that zwitterionic materials and surfaces are highly resistant to nonspecific protein adsorption and microorganism attachment from complex media. Typical zwitterionic materials include poly(carboxybetaine), poly(sulfobetaine), poly(trimethylamine N-oxide), and glutamic acid (E) and lysine (K)-containing poly(peptides). Unlike poly(ethylene glycol) (PEG), there exist diversified zwitterionic molecular structures to accommodate various properties and applications. Unlike amphiphilic PEG, zwitterionic materials are super-hydrophilic and non-immunogenetic. In this talk, I will discuss interfacial properties and phenomena associated with zwitterionic materials for applications in implants, stem cell cultures, medical devices, drug delivery carriers and marine coatings. With zwitterionic materials and surfaces, results show (a) no capsule formation upon subcutaneous implantation in mice up to one year, (b) expansion of hematopoietic stem and progenitor cells (HSPCs) without differentiation, (c) no anti-coagulants needed for artificial lungs in sheep, (d) no antibodies generated against zwitterionic polymers; (e) long-term resistance to marine biofoulants I will also discuss recent developments on immunomodulating materials and surfaces and their applications.

Tue-C5-02

Transparent Coatings based on Polydopamine that Kill Drug-Resistant Pathogens within Minutes

Saeed Behzadinasab [1], Myra Williams [2], Mohsen Hosseini [1], Leo Poon [3], Alex Chin [3], Joseph Falkinham [2], William Ducker [1]

[1] Department of Chemical Engineering, Virginia Tech, USA[2] Department of Biological Sciences, Virginia Tech, USA[3] Centre for Immunity and Infection, Hong Kong Science Park, Hong Kong, China

Microbes can be transferred to humans by contact with contaminated solid surfaces where they cause disease and human suffering. Treatment of such infectious diseases also costs billions of dollars annually in the U.S. alone. A traditional method of reducing the spread of disease by contact is to disinfect the surface with 70% ethanol or frequently wash hands. An engineering way of stopping this transmission route is to utilize surface coatings that rapidly kill microbes. Transparent coatings that are antimicrobial are highly desired for this purpose because transparent coatings preserve the aesthetics of the solid objects. In many cases, such as for cell phones or touch screens, the transparency is necessary for functionality of the object. Here, we have fabricated two transparent surface coatings that inactivate germs within minutes. We used polydopamine (PDA) as the adhesive in each coating. PDA has the advantage that the monomer, dopamine, can be easily sprayed onto surfaces, where it polymerizes into a conformal film on all parts of the object. We fabricated the first coating (PDA/Cu2O) by depositing a suspension of both dopamine and Cu2O particles. Spontaneous polymerization of dopamine into PDA bound the Cu2O particles to the solid. For our second coating (PDA/Cu), we first made a layer of PDA, then used electroless deposition to deposit thin layer of copper. We kept a low density of Cu2O, and thin layers of Cu or PDA to maintain the transparency of the coatings. In only 10 minutes, the PDA/Cu2O coating killed 96.82% of methicillin-resistant Staphylococcus aureus (MRSA) and 99.94% of Pseudomonas aeruginosa (P. aeruginosa). Also, the coating inactivated 99.88% of SARS-CoV-2 (COVID-19 virus) within 1 hr. The PDA/Cu coating killed 99.18% of MRSA and >99.99% P. aeruginosa, within 10 minutes, and inactivated 99.98% of SARS-CoV-2, within 1 hr.

Tue-C5-03

Mechano-bactericidal effect of cicada wing replica formed through electrohydrodynamic instability in secondary mode

Dae Joon Kang

Department of Physics, Department of Quantum Biophysics and Biomedical Institute for Convergence, Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16419, Republic of Korea

Cicada wings composed of densely packed nanostructures have been extensively studied due to their outstanding properties such as high transparency, superhydrophobicity, and bactericidal activity. Nevertheless, conventional fabrication techniques pose a great challenge to replicate the nanostructure of cicada wings due to their unique and distinctive structural features such as high aspect ratio, compactness, and conical shape. In this work, we present a new way to accurately replicate the nanostructure of the cicada wing by exploiting the electrohydrodynamic (EHD) instability in the polymer film. The rapid evolution of EHD instability in the secondary replication mode leads the film fluid to fully penetrate into the cicada wing and generate both the shape structure and wing replica with excellent feature uniformity at a large scale as shown in Figure 1. The quality of the cicada wing replica is reliably maintained because our replication protocol allows the water-soluble mold to be produced by the dissolution step instead of the demolding step. Moreover, the mechano-bactericidal activity inherent in the natural cicada wing is confirmed on the surface of the wing replica produced by our method. Therefore, we believe that our replication method offers a promising opportunity to both obtain a faithful replica of biological surfaces and explore various applications based on unique structural properties.

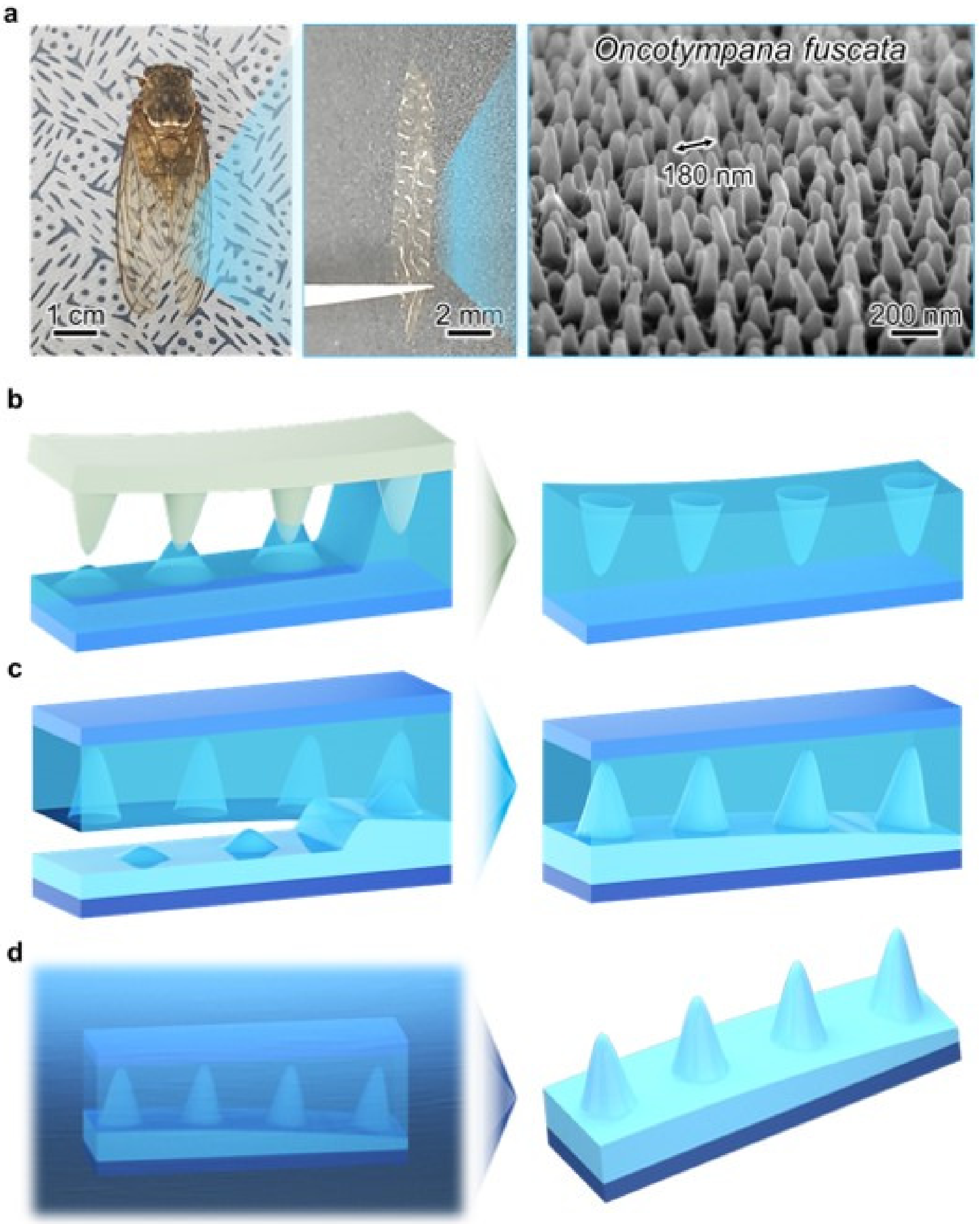

Figure 1. Cicada wing nanostructure replication protocol: (a) Digital photographs of a cicada (Oncotympana fuscata) and its wing membrane (left and middle). SEM image of wing membrane surface (right). (b) In the secondary replication mode of EHIP process, a natural wing surface is inversely replicated, producing nanohole array on the water-soluble film. (c) With the as-fabricated master mold, a positive replica of cicada wing nanostructure is formed through the secondary mode. (d) After EHIP process, the assembly composed of the positive replica and master mold is immersed into water. Consequently, the positive wing replica is obtained without structural damages.

Tue-C5-04

Transparent Anti-SARS-CoV-2 and Antibacterial Silver Oxide Coatings

William Ducker [1], Mohsen Hosseini [1], Alex Chin [2], Leo Poon [2], Myra Williams [3], Joe Falkinham [3], Saeed Behzadinasab [1]

[1] Dept. of Chemical Engineering and Center for Soft Matter and Biological Physics, Virginia Tech, Blacksburg, Virginia, 24061, USA[2] School of Public Health, LKS Faculty of Medicine, The University of Hong Kong, Hong Kong Special Administrative Region, Hong Kong, China.[3] Department of Biological Sciences, Virginia Tech, Blacksburg, Virginia, 24061, USA

Transparent antimicrobial coatings can maintain the aesthetic appeal of surfaces or the functionality of a touch screen while adding the benefit of reducing disease transmission. We fabricated an antimicrobial coating of silver oxide particles in a silicate matrix on glass. The matrix was grown by a modified Stöber sol-gel process with vapor-phase water and ammonia. A coating on glass with 2.4 mg of Ag2O per mm2 caused a reduction of 99.3% of SARS-CoV-2, >99.5% of Pseudomonas aeruginosa, Staphylococcus aureus and methicillin-resistantStaphylococcus aureus compared to the uncoated glass after one hour. We envisage that screen protectors with transparent antimicrobial coatings will find particular application to communal touch screens, such as in supermarkets and other check-out or check-in facilities where a number of individuals utilize the same touch screen in a short interval.

Tuesday, July 12th | 13:00 - 14:40 | D5-Self and Directed Assembly

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Tue-D5-01

Electric Field driven Assembly and Energy Transfer in Rare Earth doped Microspheres

Ruchi Patel, James Dorman, Bhuvnesh Bharti

Cain Department of Chemical Engineering, LSU

Active Luminescent Colloids can be promising functional materials as a combined virtue of their ability to perform controlled dynamic functions while exhibiting optical tuning via energy transfer. This work investigates the assembly and energy transfer in multicolored rare-earth photoluminescent microspheres, via the application of in-situ electric fields. Colloidal silica with average diameters ~ 2 μm were synthesized using a modified Stöber process as the core material. Eu^{+3} (red fluorophore) and Bi^{+3} (green fluorophore) doped YVO$_4$ shells of ~30nm thickness were deposited on the silica core by a simple sol-gel chemistry. The high surface-to-volume ratio of the nanophosphors on the colloidal bulk is exploited in being able to maximize luminescence while also allowing for energy level hybridization of the Bi^{+3} - VO4^{-3} pair. The two core-shell microspheres were assembled using an alternating current (ac) electric field and were characterized using in-situ electric field photoluminescence (PL) and fluorescence microscopy. The results help us identify the role of external forces on the assembly, and dynamic energy transfer between PL responsive colloids, and thus provides a framework for the design of 'soft' optoelectronic materials.

Tue-D5-02

Iridescent and reconfigurable grating structural color from colloidal crystals self-assembled by direct current electric fields

Tianyu Liu

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Similar to the brilliant coloration of natural organisms such as butterflies and chameleons, self-assembled colloidal crystals can display structural colors due to constructive interference of light diffracted by their microscale ordering. Multilayer colloidal crystals with building block sizes in the range of 0.1 to 0.3 µm produce reflective structural colors by Bragg's reflection. On the other hand, colloids with larger particle size, 0.5-1.3 µm, show rainbow-like, angular dependent color under conditions of off-axis transmission. This coloration arises due to a grating diffraction mechanism. Grating diffraction structural color is potentially applicable to materials and products because its properties are distinguishable from Bragg structural color. The differences include color for off-axis transmission and the micron-scale building blocks of the self-assembled crystals. Here we pursue a fundamental study of structural color in self-assembled colloidal crystals for the purpose of clearly delineating the relationship of such structural color to microstructural properties, including the particle size, packing density, packing configuration, and layer thickness. We self-assemble poly-crystalline colloidal arrays with fine grain size by application of a dc electric field to an initially dilute suspension of colloids in a thin liquid cell. Grating diffraction structural color properties such as angular dependence, saturation, and brightness were found do depend sensitively on the particle size and layer thickness. We find the color band becomes broader and shifts to a higher scattering angle as the particle size is reduced. Furthermore, multiple scattering occurs in thick multilayer crystals, which results in the loss of color saturation and brightness. Based on Mie theory and structure factor, we construct a light scattering model that predicts the structural colors of the experiments. Taken together, the studies provide insight into grating diffraction structural color as a potential application of colloidal self-assembly and which could be used in applications requiring off-axis transmissive color, including displays and coatings.

Tue-D5-03

Long-range Transport and Directed Assembly of Charged Colloids under Aperiodic Electrodiffusiophoresis

Kun Wang, Samuel Leville, Behrouz Behdani, Carlos Silvera Batista

Chemical Biomolecular Engineering, Vanderbilt University

The aim of this study is to examine the transport of charged colloids under uniform low frequency AC fields. AC electric fields are an important tool in directed assembly and propulsion of charged colloids. However, it has been customary to assume the electrodes behave as ideally polarizable at frequencies of approximately 1 kHz. Therefore, the effect of Faradaic processes in AC colloidal electrokinetics remains unclear. Herein, we use confocal microscopy and ratiometric analysis to show that AC fields applied in media of low conductivity induce significant pH gradients that can persist at frequencies as high as 10 kHz. The shape of the pH profiles depend on the frequency and amplitude of the applied signal. In some cases, the pH reaches a maximum value at distances tens of microns away from the electrode surface. Under these conditions, particles experience aperiodic electrodiffusiophoresis. In those cases, charged particles respond by migrating towards to the point of highest pH with velocities that were much higher than those due to sedimentation and Brownian motion. The focusing of particles reveals the existence of an effective potential well that is conducive to a phase transition. For once at the focusing position, particles begin to assemble into 2D aggregates. At this point, depending on frequency, field strength and ionic conductivity, particles form 2D crystals with different levels of order. These results have significant implications for the fundamental understanding of AC colloidal electrokinetics. It provides new possibilities for separation strategies and field directed assembly.

Tue-D5-04

Staged assembly of DNA-coated colloids programmed by acoustic waves

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Self-assembly of DNA-coated colloids (DNACCs) is of great interest and importance for realizing the programming of material manufacturing at the micro/nano-scale. So far, such programmability has been extensively explored in the internal design of DNA sequences or colloids geometry for assembling different crystal structures. However, the assembly of DNACCs-based materials with more intended morphologies other than crystals is also important and remains challenging. In addition, DNACCs are known to show a strong tendency to be kinetically trapped due to the stochastic nature of self-assembly. External fields such as electric and magnetic can be introduced to direct the self-assembly of colloids effectively. Typically, such external-field-directed self-assembly allows to be equipped with open- or closed-loop control strategies to account for design uncertainty and mitigate disturbances. However, the most widely used AC electric fields do not apply for DNACCs. DNACCs assembly requires saline buffer while AC electric fields need to work in low ion concentration. Magnetic fields work in saline buffer but require specific material properties of the DNACCs, limiting the properties of the assembled materials. In this work, we use acoustic waves to externally program the assembly of DNACCs in a highly robust and precise manner in a microfluidic device. We show a staged assembly strategy to realize sequential assembly of DNACCs under different acoustic frequencies from stage to stage to produce hierarchical structures. By programming the frequency, amplitude and phase of the acoustic waves at each stage, we demonstrate flexible assembly of DNACCs (such as head-to-head, layer-by-layer, spatial control) into final structures with different intended morphologies, which is challenging using DNA alone. Since the driving force at each stage is based on nonspecific acoustic radiation, our approach can be adopted for most colloidal systems without specific requirement on particle or medium properties.

Tue-D5-05

Rotational dynamics in a back-and-forth rotating magnetic field

Dana Lobmeyer [1], Aldo Spatafora-Salazar [1], Lucas H. P. Cunha [1], Kedar Joshi [2], Sibani Lisa Biswal [1]

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Rotating magnetic fields (RMFs) have become a useful tool in directing the two-dimensional assembly of magnetic colloids. While RMFs assemble particles by producing an effectively isotropic attractive interaction, they have also been shown to produce a collective rotational motion in large particle systems. To suppress this rotational motion while maintaining isotropic interactions, a back-and-forth field has been used, where the rotating field changes direction every other period. However, effectively isotropic interactions in the back-and-forth field have not been verified. In this work, we probe a two-particle system of superparamagnetic particles to elucidate particle-particle interactions in the back-and-forth field. Through experimental rotational dynamics, we showcase anisotropy in the particle-particle interactions, thereby refuting the claim that isotropic interactions are maintained under this type of field. We present the preferred alignment of these particle pairs in the direction tangential to where the field turns around, thereby creating an angular trap. Lastly, we elucidate the presence of lateral interactions that cause the field to appear to have isotropic interactions in larger particle systems. Understanding how colloidal assembly is impacted by relatively small changes in the directing magnetic field paves the way for fine tune control at the colloidal scale.

Tuesday, July 12th | 13:00 - 14:40 | E5-Electrokinetics and Microfluidics

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Tue-E5-01

Enhanced diffusiophoretic transport in mixtures of polymers and surfactants

Angela Yang, Yingqi Yi, Aditya S. Khair, Stephen Garoff, Robert D. Tilton

Carnegie Mellon University, Department of Chemical Engineering

Diffusiophoresis is the deterministic transport of a colloid in a solute gradient. It often provides faster transport rates than diffusion and does not require external driving forces such as pumping for transport. Diffusiophoresis of charged colloids in gradients of ionic solutes is sensitive to the difference between the anion and cation diffusivities. The current understanding of diffusiophoresis is limited to gradients of simple electrolytes or ionic surfactants. Diffusiophoresis is expected to be important in applications of complex fluid formulations, which often involve polymers in conjunction with surfactants. Anionic surfactants may associate with nonionic, water-soluble polymers to form charged complexes. In this work a polymer/surfactant solute system of Pluronic P123 water-soluble triblock copolymers and sodium dodecyl sulfate (SDS) anionic surfactants is used to drive diffusiophoresis of negatively charged polystyrene colloidal particles in a microfluidic channel that enables quantitative comparison of transport rates among different systems. Results from this work demonstrate that solute gradients involving Pluronic/SDS complexes increase the initial rate of colloid transport and prolong the duration of diffusiophoresis compared to that in gradients of SDS alone. It is hypothesized that this is largely due to the greater size of the complexes relative to either monomeric SDS or SDS micelles. The complexes provide a lower effective diffusivity of the anionic species and a greater difference between the anionic and cationic species diffusivities.

Tue-E5-02

Impact of surface heterogeneity on diffusiophoresis of colloids in a mixture of electrolytes and non-electrolytes

Arkava Ganguly, Ritu Raj, Ankur Gupta

Department of Chemical and Biological Engineering, University of Colorado Boulder

Concentration gradients of electrolytes and non-electrolytes can induce a motion in colloidal particles through diffusiophoresis and the proportionality constant that relates included velocity with concentration gradient of solutes is referred to as the diffusiophoretic mobility. Over the last decade, there has been significant interest in controlling the diffusiophoretic motion of colloids through surface modification. Yet, the theoretical treatment of diffusiophoresis assumes that the diffusiophoretic mobility is a lumped parameter and overlooks the surface heterogeneity commonly present in experimental systems. Here, we overcome this limitation by systematically deriving diffusiophoretic mobility in a mixture of electrolytes and non-electrolytes while incorporating heterogeneous properties of the colloidal surface. We perform singular perturbation analysis on Poisson-Nernst-Planck equations and the modified Stokes equation in the limit of thin double layers. We derive an expression for the leading order diffusiophoretic velocity as well as the first-order correction. We show that for special scenarios, our derived results reduce back to expressions previously reported in literature. Our analysis reveals that even for particles with net neutral charge, there can be salient electrolytic diffusiophoresis due to surface heterogeneity. Overall, the results described here provide a convenient way to predict diffusiophoretic motion of patchy colloids in a mixture of electrolytes and non-electrolytes.

Tue-E5-03

Diffusiophoresis and diffusioosmosis in microfluidic systems: Surface-flow-driven phenomena in the presence of flow

Suin Shim

Princeton University

Diffusiophoresis is the spontaneous motion of colloidal particles induced by a concentration gradient of solutes. Since common materials for microfluidics usually have a nonzero surface potential, electrolyte gradients that drive particle motion can also generate diffusioosmotic flow along the channel walls. Therefore, even in the absence of imposed flows, particles can further transport by the diffusioosmotic slip-driven flow. In typical microfluidic experiments with solute gradients, diffusiophoresis of particles, diffusioosmotic flow, and (if nonzero) imposed liquid flow coexist with various magnitudes [1]. I will present two systems that show such combined influences, and discuss how the observed particle behaviors represent different components of diffusiophoresis, diffusioosmosis and microfluidics. In particular, one, two, and three dimensional particle behaviors in the channels with and without imposed flows are studied with experiments and theoretical models. [1] S. Shim, *Chem. Rev*. 2022, **122,** 7, 6986–7009

Tue-E5-04

Drop deformation during diffusiophoresis

Brian McKenzie [1, 5], Henry Chu [2], Stephen Garoff [3, 5], Robert Tilton [1, 4, 5], Aditya Khair [1, 5]

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Diffusiophoresis refers to the motion of a colloidal particle in a solute concentration gradient, animated by particle-solute interactions. We analyze the diffusiophoretic motion of a viscous drop in a gradient of neutral solute. In a spatially uniform gradient, the drop experiences no tendency to deform, regardless of the magnitude of the interfacial tension at the interface of the drop and suspending fluid. Next, we consider a non-uniform gradient, where the ambient solute concentration takes the form of a quadrupole around the drop centroid. The additional quadrupolar gradient superimposed on the uniform gradient does not alter drop translation, because of symmetry, but it does induce a deformation in the drop shape, which is spheroidal to first order in the capillary number. Whether the drop becomes prolate or oblate depends on whether the solute-drop interaction is attractive or repulsive. Therefore, our work shows that, in principle, a drop could undergo deformation during diffusiophoresis in a non-uniform solute gradient.

Tue-E5-05

Programmable Two-Dimensional Diffusiophoretic Banding of Colloidal Particles

Ritu Raj, C. Wyatt Shields IV., Ankur Gupta

Department of Chemical and Biological Engineering, University of Colorado Boulder

Diffusiophoretic processes utilize solute concentration gradients to influence the transport of colloidal particles in microfluidic applications. As solute concentration gradients can be introduced in microfluidic devices without relying on an external field, diffusiophoresis provides a means for non-invasive control of particle transport across a wide range of useful applications. For example, diffusiophoresis has been exploited to deliver colloidal particles to dead-end pores, develop membraneless water filters and to measure the zeta potential of particles. A key distinguishing features of diffusiophoresis, that makes it amenable for the aforementioned applications, is that particles tend to concentrate in a particular region in response to an induced concentration gradient. This phenomenon is known as colloidal banding. Till date, the majority of theoretical and experimental investigations study the banding of colloidal particles in response to one-dimensional concentration gradients. However, widespread adoption of diffusiophoresis into microfluidic devices requires an improved understanding of the response of colloids to two-dimensional concentration gradients. In this work, we investigate how the spatial arrangement of solute sources and sinks affects the diffusiophoretic motion of colloidal particles, where multiple sources and sinks interact with each other to create a net solute concentration field that influences the motion of the particles. We performed numerical computations, utilizing a finite volume scheme to resolve the concentration field, to predict particle trajectories and found that an increase in asymmetry, both spatial and geometric, of the sources and sinks, enhances colloidal banding. We quantified the time required to achieve sufficient banding, explored the effect of geometrical arrangement on the banding structures, and also probed the effect of solute wall permeability on the trajectories of particles. We then model particle distribution using a continuum approximation in order to characterize quantitative measures of the distribution. Overall, our results advance fundamental understanding of colloidal banding in two dimensions and widen the design space available for utilizing diffusiophoretic processes in microfluidic applications.

Tuesday, July 12th | 13:00 - 14:40 | F5-Emulsions, Bubbles & Foams

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Tue-F5-01

Pickering liquid crystal emulsions with long-term colloidal stability and enhanced sensitivity to amphiphilic analytes

Oscar Pineres-Quinones [1], David Lynn [2], Claribel Acevedo-Velez [1]

[1] Department of Chemical Engineering University of Puerto Rico-Mayaguez[2] Department of Chemical and Biological Engineering University of Wisconsin-Madison

Liquid crystal (LC)-in-water emulsions provide a versatile approach for designing droplet-based sensors that can detect and report the presence of amphiphilic analytes in aqueous environments. The practical utility and potential application of LC emulsions in these contexts is limited, however, because the bare LC droplets that comprise them are not colloidally stable for prolonged periods. This presentation will describe our recent studies aimed at designing LC droplet-based sensors with improved colloidal stability, tunable sensitivity, and selectivity to aqueous amphiphilic analytes. Our approach makes use of so-called “Pickering emulsions” created by the adsorption of nanoparticles to aqueous/LC droplet interfaces. We designed Pickering LC emulsions that remain colloidally stable for at least three months. The nanoparticle-stabilized LC droplets in these emulsions respond to and report on the presence of aqueous amphiphiles (e.g., surfactants), as evidenced by bipolar-to-radial changes in LC droplet configurations that are similar to those observed in bare-droplet LC emulsions and can be readily observed and quantified, in real time, using polarized light microscopy. This approach also provides means to tune the sensitivities of the nanoparticle-stabilized LC droplets to amphiphilic analytes. Overall, our results demonstrate that Pickering stabilization provides a useful strategy to substantially improve the colloidal stability and shelf-life of LC emulsions and tune the sensitivities of the nanoparticle-stabilized LC droplets, thus increasing the potential practical utility of these droplet-based sensors as platforms for the detection and reporting of chemical and biological analytes.

Tue-F5-02

Influence of physical structure and size of silica particles of varying wettability on the demulsification of surfactant stabilized oil-in-water emulsions

Anirban Ghosh, Michael Miranda, Clint Aichele

Oklahoma State University

Oil and water separation is a challenge faced by many industries. Oily wastewater is generated by many industries such as metallurgy, food industries and petroleum industries. One major source of oily wastewater is produced water. More than 20 billion barrels of produced water are generated each year in the US. The presence of hydrocarbon components and surfactants in produced water may lead to the formation of stable Oil in Water (O/W) emulsions. Silica nanoparticles have been used for carrying out demulsification in surfactant stabilized emulsion systems. This work seeks to probe the influence of the structure and size of silica particles on the demulsification of O/W emulsions. Silica particles of different sizes were chosen and modified to achieve a varied range of wettability. Fumed silica and spherical silica of two types were chosen to bring about variations in shape and size. The wettability of the silica particles was varied using a silane modification process. The hydrophilicity of the silica nanoparticles was used as an indication of the wettability of the silica particles. Model emulsions were prepared using cyclohexane as the oil phase. Emulsion properties were analyzed with and without the addition of modified silica particles over time. Bottle tests and microscopic tests were performed to analyze the properties of the emulsions. Bottle tests were used to understand the macroscopic separation of oil and water. Microscopic coalescence behaviour was probed by optical imaging techniques. Emulsion properties were found to remain constant over the experimental time without the addition of nanoparticles.

Tue-F5-03

The influence of asphaltenes structure and aggregation on water-in-oil emulsion stability

Nataira Pagan Pagan [1], Thao Vy Nguyen [1], Sibani Lisa Biswal [1], Amanda Marciel [1]

[1] Rice University[2] Rice University

Defined by their solubility class, asphaltenes represent the most polar, aromatic, and heaviest fraction of crude oil. They are known to strongly adsorb at oil-water interfaces forming viscoelastic films that confer solid-like mechanical properties that stabilize water-in-oil emulsions. The formation of these emulsions leads to undesired flow assurance problems for the oil and gas industry that require demulsification to prevent operational challenges and costs. Given the heterogeneity in chemical composition, structure, and molecular weight of natural asphaltenes, it remains challenging to identify how their aggregation, precipitation, and diffusion behavior at oil-water interfaces promote stability. To address this challenge, we use small-angle X-ray scattering (SAXS) to investigate the structure and aggregation behavior of asphaltenes with varying solvents and concentrations. The direct connection between structure and macroscale stability is important for understanding the interfacial properties of asphaltenes and their role in driving the emulsification process. This work contributes to providing insights for designing energy-efficient demulsification strategies.

Tue-F5-04

Stable CO2/Water Foam with Ultralow Concentration of Amine-Coated-Nanoparticles and Surfactant

Xiongyu Chen [1], Chang Da [1], Daniel Hatchell [2], Hugh Daigle [2], Keith Johnston [1]

[1] UT-Austin, Department of Chemical Engineering,[2] UT-Austin, Department of Petroleum Engineering

CO2-in-water foams at elevated temperature, pressure and salinity are typically very unstable since the CO2 bubbles undergo rapid coalescence and coarsening. We have designed a system of like-charged surfactant and surface-modified nanoparticles to make ultra-stable CO2 foam at 60 °C, 15 MPa and an extreme salinity (230 g/L TDS) with an very low nanoparticle concentration (0.05 wt%). We modified the silica nanoparticle surface by covalently bonding two amines: one primarily for interfacial activity and another primarily for colloidal stability in brine. The nanoparticles were characterized with thermogravimetric analysis, NMR and conductimetric titration. The nanoparticle size was measured by dynamic light scattering in brine at 60 and 80 °C for 2 weeks. The foam stability was measured with optical microscopy at 60-80 °C and 15 MPa. In the presence of only 0.05 wt% nanoparticles, the initial foam bubble growth rate was similar to the surfactant only condition. However, after the initial fast bubble coalescence and coarsening, the nanoparticle interfacial concentration increased sufficiently to decrease the bubble growth rate by 2 orders of magnitude. The surfactant adsorption on the liked-charged nanoparticle is low, making the nanoparticle amphiphilicity relatively independent of the surfactant. The tuning of the nanoparticle surface for both colloidal stability in brine and high amphphilicity at the CO2-water interface over a wide range of surfactant concentration and with an ultralow nanoparticle concentration is novel and of great interest for both fundamental advancement and practical applications, for example mobility control in CO2 sequestration and oil recovery.

Tue-F5-05

Stabilization of ethanol-based Pickering foams

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Aqueous foams are encountered in many commercial products used in our everyday lives and are widely studied. However, the formation and stabilization of foams using high alcohol content (>75%) solvents such as ethanol is still a scientific challenge. Herein, we report a new class of Pickering foams based on high ethanol content showing long-term stability by using natural fatty acid crystals. The 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 thermostimulable high ethanol content foams. These foams can be used as a new formulation strategy 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.

Tuesday, July 12th | 13:00 - 14:40 | H5-Geochemical and Environmental Systems

Tue-H5-01

Atmospheric Aerosol Particle Liquid Phase Transitions and Ice Nucleation using Microfluidics

Cari Dutcher, Margaret House, Priyatanu Roy

University of Minnesota

Atmospheric aerosols, which are suspensions of solid and liquid particles in our atmosphere, are one of the major contributing factors to our climate, yet are a leading source of uncertainty in climate modeling. Part of this uncertainty arises from the highly complex nature of individual aerosol particles: the chemical composition and thermodynamic phase of aerosol particles evolve dramatically with changes in the ambient environmental conditions. The resultant composition and phase inform the particle’s optical properties, species uptake and partitioning, and activation to cloud condensation or ice nuclei. In this work, recent advancements using laboratory microscale flows will be highlighted for measuring droplet phase transitions, including liquid-liquid phase separation (LLPS) and ice nucleation (IN), will be presented. Microfluidics offers the advantage of rapid and monodisperse droplet generation with precise temperature control and minimal solid-surface contact during experiments. Temperature and relative humidity dependence of LLPS and crystallization for model aerosol droplets with varying salt and organic composition is explored. It is observed that temperature has a significant effect on some systems while having no effect on others depending on the organic to inorganic ratio (OIR) as well as the identity of the organic and inorganic phases. IN results of model biological ice nucleating particles, Snomax, along with bulk and sea surface microlayer sea water samples obtained from a simulated waveflume experiment (SeaSCAPE) are studied in static and high-throughput droplet microfluidic platforms. Automated detection and classification of frozen droplets from liquid drops was implemented through machine learning with a deep neural network.

Tue-H5-02

Characterization of Sub-Micron Mineral Dust Aerosols in Snow by Single Particle Inductively Coupled Plasma Mass Spectrometry

Aaron Goodman [1], Alex Gundlach-Graham [2], Shaun Bevers [1], James Ranville [1]

[1] Colorado School of Mines[2] Iowa State University

Although natural atmospheric nanomaterials are ubiquitous and highly influential in environmental systems, they have only recently begun to be studied. We analyzed sub-micron and nano-scale Mineral Dust Aerosols (MDA) in wet deposition (snowfall) from two storms in Colorado, USA using single particle Inductively Coupled Plasma Mass Spectrometry (spICP-MS). We found high particle number concentrations (PNCs) of MDA (up to 10^8 particles/mL) and observed an order of magnitude difference in number concentrations related to storm strength and meteorological conditions. We applied novel data processing to Particle Size Distributions (PSDs) obtained with spICP-MS and determined that all PSDs followed the Pareto Distribution (inverse power law) seen in literature, despite differences in number concentration. We characterized multi-element MDA particle types with single particle ICP-Time-of-Flight MS (spICP-TOFMS) using particle type-specific detection limits based on both crustal abundance ratios and Poisson distributed noise associated with particle detection. We supplemented this approach with an unsupervised hierarchical clustering algorithm applied independently to all samples. Both methods of analysis confirmed that MDA largely followed elemental crustal abundance ratios, with a minor class of titanium-rich particles identified. Particle compositions obtained through spICP-TOF-MS were validated using Automated Scanning Electron Microscopy, and confirmed that the lower size detection limits, and high throughput capability of spICP-MS analysis enabled superior characterization of MDA. We conclude that particle size and composition of MDA can be effectively analyzed in wet deposition by spICP-MS, and while there is uncertaintly in quantifying absolute particle number, relative particle numbers between samples can be assessed. Characterization of nano-scale MDA can be used to better understand particle dynamics in the atmosphere, which can affect climate. Analysis of natural particle composition informs studies related to nanogeochemical cycling and can be used to further advance methods of detecting engineered nanomaterials in the environment.

Tue-H5-03

Biophysical Inhibition of Pulmonary Surfactant by E-Cigarette Aerosols

Yi Zuo

Department of Mechanical Engineering, University of Hawaii at ManoaDepartment of Pediatrics, University of Hawaii

With an increasing prevalence of electronic cigarette (e-cigarette) use, especially among youth, there is an urgent need to better understand the biological risks and pathophysiology of health conditions related to e-cigarettes. A majority of e-cigarette aerosols are in the submicron size and would deposit in the alveolar region of the lung, where they must first interact with the endogenous pulmonary surfactant. To date, little is known whether e-cigarette aerosols have an adverse impact on the pulmonary surfactant. We have systematically studied the effect of individual e-cigarette ingredients on an animal-derived clinical surfactant preparation, bovine lipid extract surfactant, using a combination of biophysical and analytical techniques, including in vitro biophysical simulations using constrained drop surfactometry, molecular imaging with atomic force microscopy, chemical assays using carbon nuclear magnetic resonance and circular dichroism, and in silico molecular dynamics simulations. All data collectively suggest that flavorings used in e-cigarettes, especially menthol, rather than nicotine, play a predominant role in inhibiting the biophysical function of the surfactant. The mechanism of biophysical inhibition appears to involve menthol interactions with both phospholipids and hydrophobic proteins of the natural surfactant. These results provide novel insights into the understanding of the health impact of e-cigarettes and may contribute to a better regulation of e-cigarette products.

Tue-H5-04

Functionalization of mesoporous carbons derived from pomelo peel as capacitive electrodes for preferential removal/recovery of copper and lead from contaminated water

Jiming Lu [1, 2], David Harbottle [1], Zhenghe Xu [2], Prashant Mishra [1], Timothy Hunter [1]

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Water is a valuable resource that is needed to sustain life, but is also essential in many engineering processes, which unavoidably leads to large volumes of water being contaminated. To achieve safe discharge and also recover valuable “pollutants”, better performing sorbents are needed to rapidly and efficiently decontaminate water and generate minimal secondary wastes. Bio-sorbents derived from pomelo peel were functionalized with pyrrolic-N (BNC-5 electrode) and pyridinic-N (BNC-6 electrode) to enhance electroadsorption and selectivity of Pb2+ and Cu2+. The interaction between soft acid ions (Pb2+) and soft base sites (pyrrolic-N) contributed to a strong chemisorption that elevated the electroadsorption capacity to ~2.0 mmol g-1 for Pb2+ at an applied voltage of 1.2 V. With fast removal kinetics (0.077 g mg-1 min-1 of Pb2+), the BNC-5 sorbent exhibited comparable characteristics to other N-doped sorbents prepared using graphene. The large adsorption-desorption hysteresis of BNC-5 in responding to the applied electric voltage confirmed the chemisorption effect. The results showed only 32.4% of adsorbed ions being desorbed from the sorbent by reducing the applied voltage to 0 V, but almost complete desorption (98.5% of adsorbed ions) being achieved at –0.8 V. When operated in adsorption-desorption cycle mode, BNC-5 after ~400 cycles maintained a capacity retention ≥ 80%. After 400 cycles, the electrode capacity was almost fully restored (98.7%) by only mild chemical washing (0.1 M HNO3) of the sorbent and the cycling performance maintained. The study demonstrated over 1200 cycles the robustness of sorbent and hence the potential to successfully convert waste into high-performance materials for large-scale remediation strategies using CDI.

Tuesday, July 12th | 13:00 - 14:00 | I5-General aspects of Colloids and Interface

Tue-I5-01

Magnetically responsive nanodiscs for spatial control of cell-mediated immunotherapies

Nicole Day [1], Chris Orear [1], William Wixson [1], C. Wyatt Shields IV [1, 2]

[1] Department of Chemical and Biological Engineering, University of Colorado Boulder[2] Biomedical Engineering Program, University of Colorado Boulder

Adoptive cell transfers (ACTs), such as chimeric antigen receptor T cell (CAR T-cell) and tumor-infiltrating lymphocyte therapy, are methods that involve injecting healthy cells into patients to treat disease. This form of therapy is rapidly growing in popularity due to the ability of cells to interact with diseased cells more specifically than small molecule drugs or injected particles. However, ACTs lack methods to control the function and localization of cells within the body after injection. Thus, there remains a need to guide the activity and accumulation of adoptively transferred cells at diseased sites. To address this challenge, we have developed a singular technology with multifunctionality for regulating the activity and transport of macrophages in physiological environments. Our magnetically responsive nanodiscs are designed to stably attach to the surfaces of cells, whereby they evade phagocytosis due to their high aspect ratio [1]. This allows the nanodiscs to remain bound to macrophages for several days and release drugs to cell surface receptors. Macrophages are functionally plastic cells and can revert their phenotypes rapidly in the presence of certain environmental cues; therefore, stable binding of the nanodiscs is necessary to maintain an inflammatory phenotype in the carrier macrophages and sustain the production of cytokines to other cells in the diseased tissue. Nanodiscs are made using microcontact printing of poly(lactic-co-glycolic acid), which allows for the incorporation of superparamagnetic iron oxide nanoparticles (SPIONs) and drugs into the discs. We show that nanodiscs can encapsulate and release resiquimod, a small molecule drug that can treat solid tumors by driving the phenotype of their carrier cell towards an inflammatory state. Macrophages bound to resiquimod-containing nanodiscs maintained their phenotypes for several days, as indicated by the increased production of inflammatory cytokines and increased expression of inflammatory markers, as compared to controls. Release of cytokines by activated macrophages can also stimulate nearby immune cells and generate an anti-tumor response. To improve control over ACT localization, encapsulated SPIONs enables guided accumulation in diseased tissues using gradient magnetic fields. Magnetic trapping of the macrophage-nanodisc complexes at specific sites (e.g., a solid tumor) promotes localized treatment by the carrier macrophages and the therapeutic payload. To demonstrate the spatial control of macrophage ACTs using bound magnetic nanodiscs, we studied their trapping in artificial blood vessels in vitro. We show efficient magnetic trapping of under typical venous flow (4.5 cm/s) in physiologically representative capillaries. Encapsulation of SPIONs also enables real-time monitoring of macrophage-nanodisc complex accumulation, as SPIONs can be used as a tracer for magnetic particle imaging (MPI), a non-invasive imaging modality with high precision. Regions with high levels of complex accumulation will be detectable by MPI and the success of magnetic trapping used as an indicator of therapeutic success. The combination of sustained macrophage activity and magnetic trapping and the potential for monitoring *in vivo* using MPI highlights the promise of magnetic nanodiscs to improve the performance of ACTs in a range of therapeutic contexts. Reference: [1] Champion, J.A. & Mitragotri, S. (2006). Proc. Natl. Acad. Sci. U.S.A., 103(13), 4930-4934.

Tue-I5-02

Finding and analyzing DNA aptamers for gold nanosphere targets

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Single-stranded oligonucleotide ligands called aptamers for numerous biological targets ranging from proteins to whole cells have been identified in countless studies. Aptamers that bind with high affinity and specificity for material targets, however, are far less explored but present numerous opportunities for the processing, functionalization, and utilization of the resulting biointerfaces. Aptamer sequences for a particular nonnucleotide target are typically identified using an evolutionary-based screening approach called "Systematic Evolution of Ligands by EXponential Enrichment" (SELEX). Despite its popularity, SELEX itself is a labor-intensive process with pitfalls such as its propensity to introduce sequence bias and side products to the screening process. We previously reported a nonevolutionary screening approach we call CompELS (Competition Enhanced Ligand Selection) to rapidly and reliably identify single-stranded DNA aptamers for two model material targets, planar {111} gold and gold nanorods. Here, we have expanded our CompELS screening platform to a third gold-based target, namely gold nanospheres. Following aptamer selection against our nanocolloidal target, we evaluated winning sequences to identify base segment consensus as well as any shared and unshared patterns in their predicted secondary structure elements such as hairpins, internal loops, and bulges. Lastly, we compared winners across all three gold targets to identify any shared sequence or secondary structure motifs. As aptamers continue to be pursued as potential ligands or capture agents in the biology and bioengineering community, our ongoing and future efforts include adapting our unconventional screening approach to enable faster and easier aptamer identification for challenging material as well as biological targets.

Tue-I5-03

Interaction of articular cartilage precursor films with synovial fluid at the interface

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The articular cartilage extracellular matrix (AC-ECM) is a complex macromolecular network that regulates the proper function of synovial joint locomotion together with synovial fluid. Changes in the AC-ECM or synovial fluid composition and physical properties lead to debilitating diseases, such as osteoarthritis, with over 30 million adults living with it in the United States alone. Among several AC-ECM components identified at the surface of articular cartilage are collagen type I (Col-I), collagen type II (Col-II), and fibronectin (Fn). However, their individual and synergistic roles in mediating synovial fluid components adsorption, their contribution to the assembly onto load-bearing and wear protecting films on the surface of the AC-ECM, and how they retain SF components have yet to be investigated. We developed a platform to model the articular cartilage surface to address this knowledge gap. First, Col-I, Col-II, or Fn precursor films were grafted onto gold substrates using self-assembled monolayers (SAMs) of amine-terminated thiols. These SAMs allowed us to use surface chemistry to control the adsorption and grafting density of the AC-ECM components. First, we used X-ray photoelectron spectroscopy to confirm the grafted SAM thin film and its chemical composition. Next, we optimized concentrations of Col-I, Col-II, or Fn that formed a thin film were grafted onto glutaraldehyde-activated SAM/gold substrates. Finally, film formation kinetics and adsorption of synovial fluid components as a function of underlying precursor film composition was monitored by Quartz Crystal Microbalance with Dissipation (QCM-D) at physiologically relevant temperature (37oC), pH (7.4) and ionic strength (150mM). The experimental data was used to obtain viscoelastic properties (viscosity, density, storage modulus) of the films using Gordon-Kanazawa model. Our findings indicate that Fn plays a crucial role in binding and retaining of SF components, which we hypothesize is necessary for controlling robust lubrication and wear protection of the articular surfaces. Also, our proposed AC-ECM surface model allows for a quantitative, molecular comparison of how the major components of cartilage surface contribute to synovial fluid film nanomechanics, which is disrupted in the altered synovial joint environment in joint pathologies.

Tue-J5-01

Functionalized iron oxide (Fe3O4) nanoparticles as a new type of recyclable hydrate dispersant

Yuanxing Zhang, Ning Wu, Amadeu Sum

Chemical Engineering Colorado School of Mines

The agglomeration of gas hydrates in flowlines may disrupt the normal operation and even block them, causing enormous financial loss. The current solution is to inject low-dosage hydrate inhibitors or surfactant-like anti-agglomerant. The concerns about using such chemicals are mainly about the cost, toxicity, and environmental impact. More recently, nanoparticles have been investigated to be a potential candidate for dispersing small hydrate particles and allowing them to flow in a slurry form. In this work, we coated 20 nm iron oxide particles with different hydrophobicity and studied their impact on hydrate dispersion. The response of iron oxide nanoparticles to the magnetic field was also utilized for recycling. Both on a microscopic scale with in-situ observations at ambient conditions and on a macroscopic scale with high-pressure rock-flow cell experiments, we explored the performance of nanoparticles with different extent of surface modifications. With proper surface modifications, the iron oxide nanoparticles prevented small hydrate particles from agglomeration. Furthermore, we investigated efficient particle recycling strategies with a magnetic field. The nanoparticles were fully detached from the oil-water interface by adding a tiny amount of surfactant (0.5% to the water phase). After drying, they can be readily reused, reducing the cost and minimizing environmental concerns.

Tue-J5-02

Modulation of slippage at brine-oil interfaces by surfactants: The effects of surfactant density and tail length

seokgyun ham [1, 3], Arun K. Narayanan Nair [2], shuyu sun [2], Rui Qiao [1, 3]

[1] Department of Mechanical Engineering, Virginia Tech[2] Department of Earth Science and Engineering, King Abdullah University of Science and Technology[3] The Center for Soft Matter and Biological Physics, Virginia Tech

In multiphase flows, slippage often occurs at fluid-fluid interfaces. Such slippage can affect overall fluid transport when the slip length is comparable to the characteristic dimension of the flow, e.g., in oil recovery from nanopores. Slippage at the fluid-fluid interface has been studied in many works, but the effects of interfacial impurity on the slippage are poorly understood. In this work, we use molecular dynamics simulations to study the slippage at brine–oil interfaces in the presence of two surfactants. Nonylphenol and phenol, a hydroxyl group attached benzene ring with a nine carbon-tail and one without a clear tail, are selected to probe how the density and the tail length of surfactant affect the interfacial slippage. In the absence of surfactant, a slip length of 1.2 nm exists at brine–decane interfaces. As either surfactant is introduced to brine–decane interfaces, the slip length initially decreases linearly. Nonylphenol with modest surfactant densities (~0.5 nm -2) can eliminate positive slippage at brine-oil interfaces, while high loading of phenol (~1.3 nm -2) is required to flip the sign of the slip length. As the surfactant density at brine-oil interfaces increases, the decrease of slip length slows down, and eventually, the slip length saturates at -1.4 and -0.5 nm for nonylphenol and phenol, respectively. The evolution of the slip length with surfactant density and the impact of surfactant tail length on slip length are understood by clarifying the nanoscale structure and flow of interfacial fluids and surfactants.

Tue-J5-03

Effect of surface rheology on viscous fingering

Jiayu Li, Harishankar Manikantan

Department of Chemical Engineering University of California, Davis

Surfactants such as fatty acids, alcohols, proteins, and particles generally stabilize fluid interfaces against rupture and coalescence. However, interfacial instabilities occur even in the presence of surfactants. These instabilities are often undesirable and present challenges in common industrial processes involving multiphase flows. We investigate, for the first time, the impact of interfacial rheology on the Saffman-Taylor or viscous fingering problem and demonstrate the stabilizing role of surface viscosity. We use linear stability analysis to show that surface viscosity slows the growth of unstable protrusions and results in thicker fingers. We quantify the growth of the instability in realistic ranges of fluid and geometric parameters, and illustrate the quantitative changes that are predicted to occur when a typical surface-viscous surfactant is present in a multiphase fluid displacement problem. We use these insights to also propose qualitative changes that might occur in flow in porous media when surface-attached microparticles that behave as surfactants might be present at the fluid-fluid interface.

Tue-J5-04

A sub-phase exchange cell for studying fluid-fluid interfaces with optical microscopy

Benjamin Appleby [1], Arpit Mishra [1], David Goggin [2], Joseph Samaniuk [1]

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Microscopy studies of thin film dynamics at fluid-fluid interfaces are challenging to perform, especially with in-situ changes to sub-phase chemistry that are intended to mimic processing or biological changes that can influence film stability in emulsions, phospholipid films, or foams. There are many materials with bulk properties that depend on interfacial films, including oil-water emulsions in food and petroleum applications, hydrate plugs in the oil and gas industry, and biological materials where phospholipid mono- and bilayers are present. Altering bulk chemistry can influence film structure, and this in turn can change bulk properties. Applications of the sub-phase exchange cell are potentially many, including altering the salinity or pH in the bulk phase around biological films to understand the connections between film structure and chemistry, observing the mechanisms of action of anti-agglomerate agents on hydrate films, and observing metal film etching for thin film transfer. We developed a sub-phase exchange cell that we have tested experimentally and simulated in COMSOL Multiphysics to determine the operating conditions that will yield desired concentration changes in the bulk sub-phase. A challenge for any sub-phase exchange cell is understanding the influence of flow rate and cell geometry on final bulk phase composition, and our presentation will include these details. The presentation will also include the design of the sub-phase exchange cell, the results of simulations, and the use of the cell in observing the etching of copper films for the purpose of transferring thin films to a fluid-fluid interface. In particular we will discuss our work transferring monolayer graphene from a copper film to an air-water interface by exchanging a water sub-phase with ammonium persulfate.

Tue-J5-05

Importance of the hydrophobic phase on interfacial properties of polyelectrolyte surfactant aggregates at fluid/fluid interfaces.

Michal Roguski, Lynn Walker

Carnegie Mellon University

Steady-state and mechanical properties of oil/water interfaces with adsorbed rod-like polyelectrolyte-surfactant aggregates - pCTVB [poly (cetyltrimethylammonium vinyl benzoate)] were characterized over a range of concentrations orders of magnitude below and above the critical aggregation concentration. By comparing to a previous study at the air/water interface, the role of the hydrophobic phase in determining interfacial properties is explained. The cationic surfactant, CTA+ drives the adsorption to the interface, significantly reduces the interfacial tension (Π_max=γ_0-γ_CAC ~ 40 mN/m) and can be partially removed by exchanging the bulk phase with deionized water. The negatively charged polyelectrolyte, polyvinyl benzoate (pVB-) adsorbed to the interface contributes to its high dilatational modulus (E*~100 mN/m) and forms an irreversibly adsorbed insoluble film. Aggregate rearrangements at the interface at a timescale longer than that of adsorption are also observed. This work presents the importance of the hydrophobic phase in determining the interfacial properties of polyelectrolyte surfactant aggregates at fluid/fluid interfaces.

Tuesday, July 12th | 13:00 - 14:40 | K5-Rheology and Dynamics

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Tue-K5-01

Rheo-XPCS study of training and memory of nanocolloidal soft glasses subjected to oscillatory shear

Yihao Chen [1], Simon Rogers [2], Suresh Narayanan [3], James Harden [4], Robert Leheny [1]

[1] Johns Hopkins University[2] University of Illinois at Urbana-Champaign[3] Advanced Photon Source, Argonne National Labs[4] University of Ottawa

We present a study combining x-ray photon correlation spectroscopy with in situ rheology to investigate training and memory effects in soft glasses composed of bi-disperse nanocolloidal silica particles subject to periodic shear. During a training process consisting of a rectangular wave of strain, the x-ray speckle patterns undergo an evolution in which the degree of correlation in the microstructure between adjacent strain cycles steadily increases to a plateau. Simultaneously, the shear stress exhibits a steadily evolving hysteresis. The number of cycles required to reach the plateau increases approximately linearly with the scattering wave vector, indicating a process in which microscopic reversibility is reached at progressively shorter length scales during the training. Memory of the training is illustrated by applying a set of reading strain oscillations with different amplitudes to a well-trained glass. Both the degree of correlation in the microstructures and the change in stress between adjacent reading cycles vary non-monotonically with the reading amplitude, with the correlation showing a peak at the training amplitude.

Tue-K5-02

Aging and transient memory in colloidal gels with time-varying attraction

Yihao Chen [1], Qingteng Zhang [2], Subramanian Ramakrishnan [3], Robert Leheny [1]

[1] Dept. of Physics & Astronomy, Johns Hopkins University[2] X-Ray Science Division, Argonne National Laboratory[3] Dept. of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering

We present a combined rheology, x-ray photon correlation spectroscopy (XPCS), and modeling study on gel formation and aging of suspensions of nanocolloidal spheres with volume fractions of 0.20 and 0.43 and with a short-range attraction whose strength is tuned by changes in temperature. Following a quench from high temperature, where the colloids behave essentially as hard spheres, to a temperature below the gel point, the suspensions form gels that undergo aging characterized by a steadily increasing elastic shear modulus and slowing, increasingly constrained microscopic dynamics. The aging proceeds at a faster rate for stronger attraction strength. When the attraction strength is suddenly lowered during aging, the gel properties evolve non-monotonically, in a manner resembling the Kovacs effect in glasses, in which the modulus decreases and the microscopic dynamics become less constrained for a period before more conventional aging behavior resumes. Eventually, the properties of the gel following the decrease in attraction strength converge to those of a gel that has undergone aging at the lower attraction strength throughout. The time scale of this convergence increases as a power law with the age at which the attraction strength is decreased and decreases exponentially with the magnitude of the change in attraction. A model for gel aging in which particles attach and detach from the gel at rates that depend on their contact number qualitatively reproduces these trends following a decrease in attraction strength. The model reveals that the non-monotonic behavior following the decrease results from the dispersion in the rates at which the populations of particles with different contact number adjust to the new attraction strength.

Tue-K5-03

Obtaining Structural Information of Carbon Black in Carbon Black/PVDF Suspensions with Rheo-Dielectric Measurements

Qingsong Liu, Jeffrey Richards

Department of Chemical and Biological Engineering, Northwestern University

Lithium-ion battery technology plays a central role in the wide-spread adoption of renewable energy and electrical vehicles due to improved large-scale manufacturing techniques. To further improve the performance and reduce the cost of lithium-ion batteries, a fundamental understanding of the relationships linking battery performance to the structural characteristics of the battery components is required. In particular, the lithium-ion battery porous electrode has a complex microstructural structural hierarchy that depends sensitively on how it is processed. The origin of the process sensitivity of porous electrodes is the presence of high structured carbon black (CB) used as conductive additives. Controlling electrode structure during processing requires understanding the structure of CB agglomerates that form in the coating fluid in response to deformation (such as shear) and the influence of other slurry components such as the polymer binder poly(vinylidene difluoride) (PVDF). We used rheo-dielectric measurements to show that the addition of PVDF modifies the structure of CB agglomerates through the indirect effect on the solvent viscosity. Simultaneous impedance measurements were conducted on these CB/PVDF suspensions in shear flow as a function of carbon and PVDF composition. We found that the CB agglomerate size information can be derived from normalized suspension viscosity through rheological measurements. Additionally, the further validation of such size information is evident in the dielectric strength of the relaxation process obtained from impedance measurements. We anticipate that this finding will chart a pathway towards a framework of predicting dielectric properties of such suspensions from their rheological properties.

Tue-K5-04

Three-Dimensional Technique for Probing Flow Kinematics of Falling Liquid Films Provides Real Time Sag Measurements.

Marola W. Issa [1], Hairou Yu [1], Maria C. Roffin [2], James F. Gilchrist [2], Steven V. Barancyk [3], Reza Rock [3], Christopher L. Wirth [1]

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Automotive coatings generally have dual role, which is to protect and decorate. In industrial topcoat applications, coating defects often arise during the flash stage which is roughly the 10-minute interval immediately following application. During flash, the solvents evaporate, and polymer crosslinking can be initiated. Fundamental understanding of the rheology of such complex systems is crucial for avoiding defects such as sag. Sag is a gravity driven phenomena that leads to material accumulation downstream and results in a non-uniform surface appearance. Our benchmarking experiments utilized a new technique, called Variable Angle Inspection Microscopy (VAIM), to non-invasively measure sag through the volume of an arbitrarily oriented thin film. Flow kinematics were investigated by measuring the velocity of silica particles in non-evaporative systems of known viscosities. The coating films were ~140 µm thick oriented at angles between 5° and 10° relative to gravity. Probe particles were tracked at speeds as high as ~100 µm/s. The flow field was well-resolved in ~10 µm thick slabs. Generally, VAIM measurements were highly reducible. Velocity profiles were predicted with a known model. The agreement between the measured and model velocities validated the effectiveness of this new method in relating material properties and flow regimes. Ongoing effort works to explore complex systems of acrylic based model clearcoats. Polymer molecular weight and initial solid content were observed to affect the rate of solvent evaporation. Evaporation of the film, represented by the decay in thickness over time, showed an exponential decrease throughout the dehydration process. The rate was observed to be inversely proportional to the polymer molecular weight. Evaporation rate was highest for the lowest molecular weight polymer. The added complexity in evaporative systems is predicted to affect the kinematics of falling liquid films. Tracking probe particles throughout the volume of film via VAIM will provide fundamental understanding of the drying process where particle velocities are expected to decrease in regions of film where polymer networks originate and propagate.

Tue-K5-05

A Computational Investigation of The Dynamics and Rheological Properties of MR Fluids

Mingyang Tan [1], Joshua A. Adeniran [2], Travis W. Walker [1, 3, 4]

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A magnetorheological (MR) fluid is composed of magnetic microparticles and a carrier fluid. When subject to an external magnetic field, the magnetic interactions between the magnetic microparticles cause a change of the microstructures; thus, the viscosity can be changed by several orders of magnitude. In this study, a particle-mesh-Ewald method is implemented to efficiently calculate the magnetic forced, and accelerated Stokesian dynamics (ASD) is applied to simulate the dynamics and calculate the rheological properties under different external magnetic fields. The dependence of the rheological properties on the strength, direction, and frequency of the external field is discussed.

Tuesday, July 12th | 13:00 - 14:40 | L5-Surface science and catalysis

Tue-L5-01

Faceted materials for sustainable energy applications

Raiven Balderas [1, 2], Amy Settle [1, 2], Davis Conklin [2], Hien Pham [3], Peter Metz [4], Katharine Page [5], Abhaya Datye [3], Brian Trewyn [1, 2], Derek Vardon [1, 2], Ryan Richards [1, 2]

[1] Department of Chemistry, Colorado School of Mines, Golden, CO 80401, USA[2] National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO 80401, USA[3] Department of Chemical and Biological Engineering and Center for Microengineered Materials, University of New Mexico, Albuquerque, NM 87131, USA[4] Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA[5] Materials Science and Engineering Department, University of Tennessee, Knoxville, TN 37996, USA

Material design and synthesis has made tremendous impacts in the scientific community by unleashing a material's true potential via enhanced properties and applications. Over the years, advanced synthetic strategies have emerged and expanded to not only control the size and shape of nanoparticles, but to also control the preferential growth of surface facets paving the way for new materials with facet-dependent properties. Metal oxide (111) facets as compared to their potentially more stable counterpart facets (e.g. (100), (110)) have recently exhibited enriched chemical properties owing to their unique surface arrangement. As a result, metal oxide (111) faceted surfaces have found use in applications such as catalysis, sorbents, batteries, etc. A common and unfortunate issue in catalysis, is catalyst deactivation, and thus research in improving catalyst stability remains prevalent to this day. Solid base metal oxide catalysts such as MgO offer utility in a wide variety of applications from pharmaceuticals to fuels. The (111) facet of MgO, as compared to its counterpart facets, has shown enhanced and unique properties highlighting the significance of surface exposed facets. Carbon coatings have emerged as a promising modification to impart metal oxide catalyst stability. To tackle the research pursuit of catalyst stability, we have applied a carbon coating to MgO(111). The application of a carbon coating led to an array of several fundamental questions of which we have preliminary studied: (i) the ability of carbon coated metal oxides to allow the oxide to retain its innate catalytic behavior, (ii) the effects of carbon coatings on the physiochemical properties of metal oxide surfaces, and (iii) the extent to which metal oxide faceting plays a role in the catalytic activity and inherent characteristics. To address these questions, this work has examined the synthesis, characterization, and catalytic activity of carbon coated derivatives of MgO with different surface facets. We studied the condensation of 2-pentanone, a model methyl ketone for condensation studies. This reaction has industrial and sustainable relevance as methyl ketones can be biomass-derived and converted into both dimer and trimer products, the former of which resembles precursors suitable for diesel and the latter of which resembles common jet fuel molecules upon oxygen removal. Our findings highlight the catalytic efficacy of MgO(111), provide insight into carbon coating for catalyst stability, and pave the way for continued mechanistic investigations. Future work includes exploring the synthesis of faceted titanium dioxide for hydrodeoxygenation studies.

Tue-L5-02

Joining methanation and direct air capture at low temperatures using amine grafted ruthenium catalysts

James Crawford, Matthew Yung, Michael Griffin

National Renewable Energy Laboratory

Closing carbon cycles is essential for reaching net zero emissions by 2050. The US alone consumed 850 trillion liters of methane in 2020. Methane is largely sourced from hydraulic fracturing of shale, an energy intense and environmentally disruptive process. An impressive effort from both academia and industry has resulted in the development of dual functional materials (or DFMs) capable of capturing atmospheric CO2, and with the addition of H2 and heat, forming methane (methanation). Under the assumption that H2 is sourced from renewable processes, and methane is fully combusted back to CO2, one can imagine a closed carbon loop. One challenge faced by traditional DFMs is high-temperature methanation (300°C+), largely owed to the strong chemisorption of CO2 to the alkaline oxide component. In the following work, a focus on low-temperature methanation using finely divided ruthenium active sites is explored. Support and synthesis considerations including templating method, washing, calcination, and reduction are considered to promote an optimal low-temperature methanation catalyst. In future work, amines will be grafted to the low-temperature catalyst surface, promoting direct air capture. These materials will be characterized for their stability under reaction conditions with hopes of demonstrating stable, low-temperature, high selectivity methanation sourced from atmospheric CO2.

Tue-L5-03

Bayesian Force Fields for Nanoparticle Heterogeneous Catalysis

Cameron Owen [1, 2], Jin Soo (David) Lim [1, 2], Yu Xie [2, 3], Lixin Sun [2, 3, 4], Boris Kozinsky [2, 3, 5]

[1] Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA USA[2] Materials Intelligence Research Group, Harvard University, Cambridge, MA USA[3] Harvard John A. Paulson School of Engineering and Applied Science, Cambridge, MA USA[4] Microsoft Research, Cambridge, Cambridgeshire UK[5] Robert Bosch LLC Research and Technology Center, Cambridge, MA USA

Quantitative understanding and control of interfacial reactions between the gas-phase and solid surfaces are crucial for improving numerous catalysis and energy conversion systems. Examples of these interfacial phenomena include H_2 exchange and CO adsorption, both of which are important industrial processes and lead to markedly different nanoparticle behaviors. This work demonstrates a collection of robust many-body Bayesian force fields (FFs) trained with an on-the-fly active learning framework implemented using Gaussian process regression in the FLARE code [1]. The active learning module uses molecular dynamics (MD) simulations of low-index surfaces and nanoparticles both with and without gaseous exposure to sample important configurations and calls on density functional theory (DFT) only when the predictive Bayesian uncertainty exceeds a threshold. The trained Bayesian FFs are uncertainty-aware, meaning that the user is able to determine whether the final production MD simulation is sampling atomic environments outside of the training set. These uncertainty-aware Bayesian FFs are then used to perform large length-scale and long timescale MD simulations to study the dynamics of the pure, free-standing metal nanoparticle systems (e.g., Pt, Au, CuPt, and PdAu), as well as reaction mechanisms under gaseous exposure (e.g., H_2 and CO). These MD simulations are compared to experimental observations, including spectroscopic analyses of particle shape, dopant distribution for bimetallic particles, and morphological evolution both under and in the absence of gaseous exposure. [1] J. Vandermause et al, NPJ Computational Materials 6 (2020).

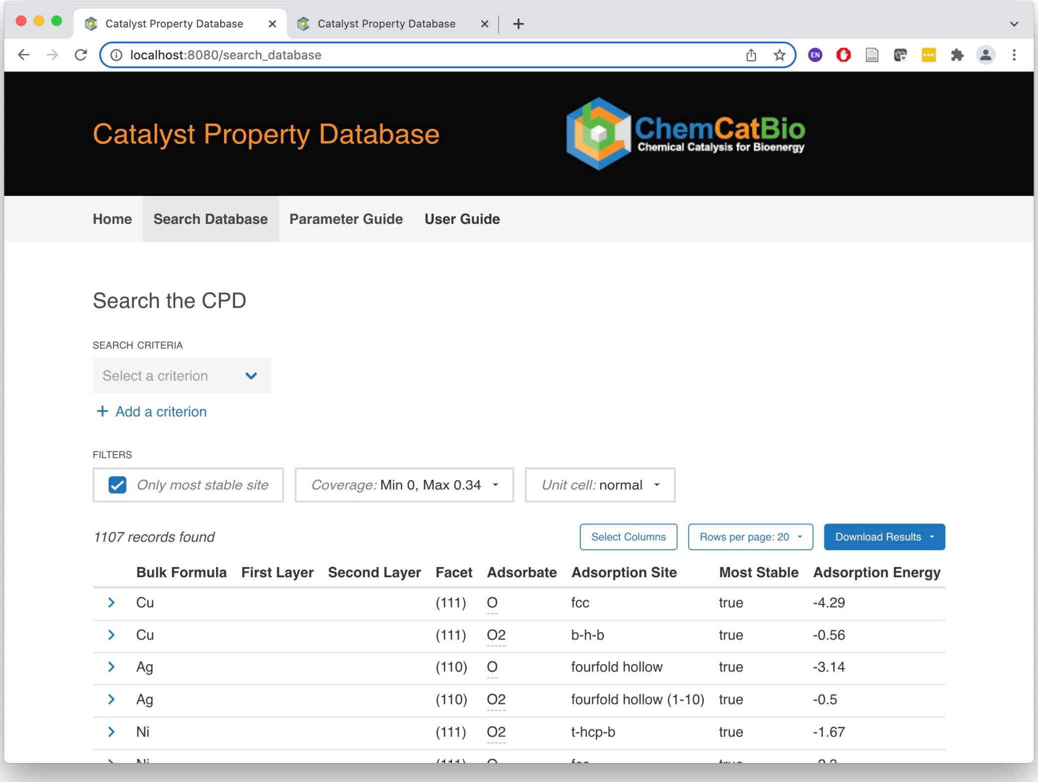
Tue-L5-04

Making Surface Science and Catalysis Data Accessible for Faster Research: Progress with the Catalyst Property Database

Kurt Van Allsburg [1], Sean Tacey [1], Carrie Farberow [1], Qiyuan Wu [1], Nalinrat Guba [2], Alicia Key [2], Rachel Hurst [2], Tom King [3]

[1] Catalytic Carbon Transformation and Scale-Up Center, National Renewable Energy Laboratory, Golden, CO, USA[2] Computational Science Center, National Renewable Energy Laboratory[3] Strategic Energy Analysis Center, National Renewable Energy Laboratory

There is growing awareness among scientists that making research data more findable, accessible, interoperable, and reusable (FAIR) can make research more efficient. Sharing research data facilitates benchmarking, analysis, and discovery, leading to new insights and better methods. And given the limited time and resources available to meet the urgent challenge of mitigating climate change, new and faster research is critical. Despite all this, the fields of catalysis and surface science remain packed with examples of duplication of effort, where researchers found it challenging enough to find and/or apply past results that it was easier to simply calculate or collect similar data again. How can this be? In the Chemical Catalysis for Bioenergy Consortium (ChemCatBio), our goal is to accelerate research by providing resources. To address the challenges in finding and applying data for catalysis, we have created the free Catalyst Property Database (CPD; https://cpd.chemcatbio.org). The CPD aims to gather catalysis-centric information into a centralized, searchable resource, facilitating literature searches, benchmarking, and advanced analyses. It currently focuses on density functional theory-computed adsorption energies for intermediates on catalytic surfaces. This presentation will detail the motivations, development, and features of the CPD. Upcoming additions including reference species interconversion and a new catalyst deactivation mitigation resource will be discussed, along with future plans for new data types and interoperability with other data resources. The authors believe that the continued gap between the promised benefits of data utilization and the actual state of data application/reuse pointed out in the first paragraph is mainly attributable to a lack of resources in the broader context of surface-centric chemical information. While the Materials Project has made admirable contributions in the area of bulk solids and we and others have contributed domain-specific resources that are more surface-focused, we believe there is still a broader gap in surface science data resources. Accordingly, this presentation will conclude by prompting discussion on how the researchers in surface science and catalysis fields can better collaborate to harness data for faster discovery.



Catalyst Property Database

Search the CPD

SEARCH CRITERIA

Select a criterion

+ Add a criterion

FILTERS

☑ *Only most stable site*

Coverage: Min 0, Max 0.34

Unit cell: normal

1107 records found

Bulk Formula	First Layer	Second Layer	Facet	Adsorbate	Adsorption Site	Most Stable	Adsorption Energy
Cu			(111)	O	fcc	true	-4.29
Cu			(111)	O2	b-h-b	true	-0.56
Ag			(110)	O	fourfold hollow	true	-3.14
Ag			(110)	O2	fourfold hollow (1-10)	true	-0.5
Ni			(111)	O2	t-hcp-b	true	-1.67

Figure 1. The Catalyst Property Database, which makes it easy to search previously published research results. A wide range of searchable parameters helps users find the right data quickly.

Tue-L5-05

Understanding interactions between different types of sites on surface-modified metal catalysts

Will Medlin

University of Colorado Boulder

A major objective for modern research in heterogeneous catalysis is developing materials integrating distinct active sites that are capable of efficiently catalyzing different types of elementary reaction steps within an overall cycle. For example, reactions of oxygenated derived from biomass, of many post-consumer plastics, and of CO2 often rely on efficient dissociation of molecular hydrogen (for which Pt group metals are effective catalysts) and C-O bond activation (which often involves sites capable of acid-base catalysis). Proximity between the different types of active sites is important, but it is often challenging to develop multifunctional catalysts that have truly independent sites. That is, the presence of one material at the surface influences the properties of the other. This presentation will describe several approaches for preparing bifunctional materials for C-O bond activation reactions, typically via combining a supported metal catalyst with organic materials capable of acid-base chemistry. The adjacency of these sites can strongly influence properties such as site accessibility, geometry, and electronic structure. This presentation will focus on the importance of these interactions in driving selective catalysis, including possibilities where beneficial synergistic effects can be realized.

Tuesday, July 12th | 13:00 - 14:40 | M5-Wetting & Adhesion

Tue-M5-01

Realization of Anisotropic Wettability through Secondary Electrohydrodynamic-induced Hybrid Structures for Fog Collection

Dae Joon Kang

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The study of plant surfaces, such as rice or bamboo leaves, has led to great efforts to produce anisotropic arrays of micro/nanoscale features to study anisotropic droplet dispersal. Nevertheless, precisely controlling the density and continuity of three-phase contact lines for anisotropic wetting remains a major challenge without resorting to chemical modifications and costly procedures. In this work, we have investigated the secondary electrohydrodynamic instability in polymer films to generate secondary nanoscale patterns between micrometer-sized grooves by controlling the time scale parameter, $1/\tau_m$ ($> 10^{-4}$ s^{-1}). We have shown experimentally that anisotropic wettability can be easily controlled morphologically without chemical modifications. Thus, anisotropic hydrophilic surfaces produced by secondary phase instability of polymer films are advantageous for both condensation and droplet removal. As a result, they outperform the water collection efficiency of conventional (isotropic) hydrophilic surfaces in water collection applications (~200 mg-cm^{-2}-h^{-1}) with excellent durability.

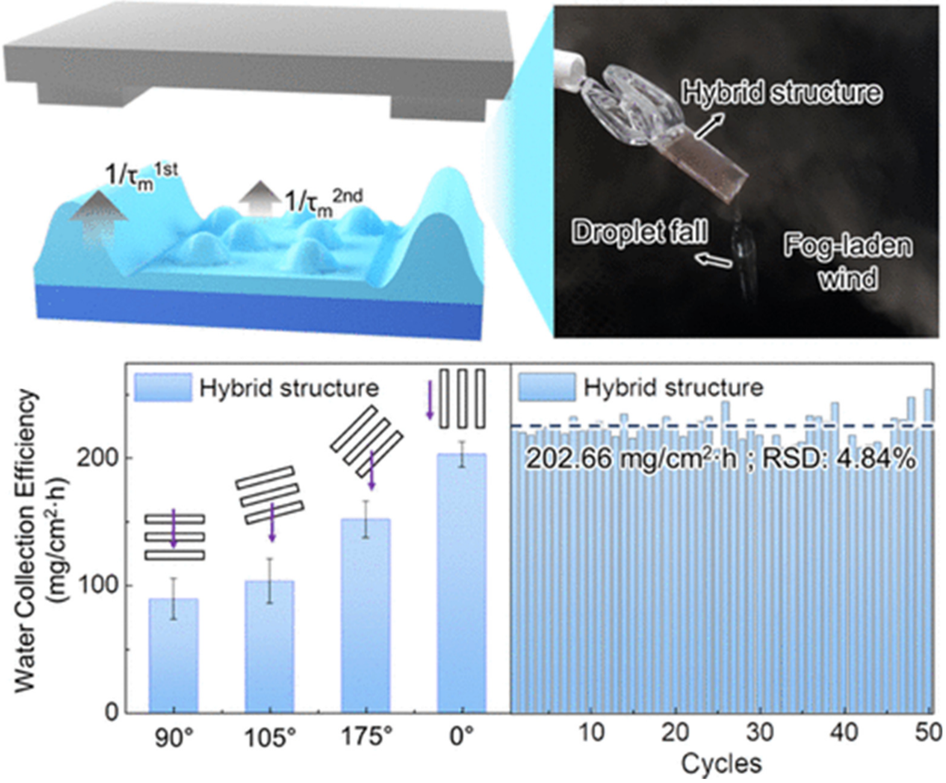

Figure. Fog collection based on secondary electrohydrodynamic-induced hybrid structures with anisotropic hydrophilicity.

Tue-M5-02

Hydrophobically Modified Silica-Coated Gold Nanorods for Generating Nonlinear Photoacoustic Signals

Evan Mueller [1], Maju Kuriakose [2], Saheli Ganguly [1], Ke Ma [1], Marco Inzunza [2], Todd Murray [2], Jennifer Cha [1], Andrew Goodwin [1]

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Photoacoustic imaging has become a popular technique in the diagnostic imaging because it can utilize light at larger penetration depths and better resolution than optical coherence tomography or fluorescence imaging. This makes it a very powerful tool that can be used in medical diagnostics. To achieve higher photoacoustic responses than what is available with endogenous contrast agents, many exogenous contrast agents have been developed, such as plasmonic nanoparticles and Near-IR dyes. However, these agents are still limited to relatively low responses and poor stability, which limits the benefits for photoacoustic imaging in scattering media. The ability of agents to induce cavitation events in response to laser irradiation would both increase signal and provide a high response. In this work, silica coated gold nanorods with a longitudinal plasmon peak of 750-800 nm were lipophilically modified to facilitate the formation of cavitation nuclei on the rod's surface along with providing a high degree of stability. It was found that the lipophilically modified silica coated gold nanorods were able to achieve nonlinearity at pulse radiant exposures greater than 8 mJ/cm2. At radiant exposures of 21 mJ/cm2, the photoacoustic response was 13-15 times higher than unfunctionalized gold nanorods without deformation to the nanorods. The higher responses were attributed to the formation of solvent vapor due to the roughly equivalent response of the lipophilically modified nanorods in degassed water, with the hydrophobic modification of the silica facilitating the nucleation of cavitation events. The concentration of the samples was also investigated, and it was found that the photoacoustic response was greater for samples with higher concentrations than ones that were lower increasing at a roughly linear rate, providing a means to be able to determine the concentration of the rods within an in vivo setting. It was also found that the lipophilically modified silica coated gold nanorods were more resistant to dissolution in aqueous media, showing stability for more than one month in PBS. Finally, the photoacoustic response was found to be 2x higher in bovine serum albumin and human peripheral plasma compared to water and phosphate buffer solution.

Tue-M5-03

Characterizing the Hydrophobicity of Nanoparticles: From Qualitative to Quantitative Methods

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The hydrophobicity of nanoparticles (NPs) is one of the most important physicochemical properties that determine their agglomeration state under various environmental and biological conditions. When studying nano-bio interactions, the hydrophobicity of NPs plays a predominant role in mediating the biological response and toxicity of the NPs. Although many methods have been developed to qualitatively or quantitatively determine hydrophobicity, there is not yet a scientific consensus on the standard of characterizing the hydrophobicity of NPs. In this presentation, we will summarize existing methods for qualitatively and quantitatively characterizing the hydrophobicity of NPs.[1] Emphasis will be given to two novel methods recently developed in our laboratory. One is an optical method, called the maximum particle dispersion,[1,2] which is capable of quantitatively determining the surface free energy of NPs. Its measuring principle is the manipulation of colloidal stability by controlling van der Waals interactions between particles dispersed in a series of suspending liquids of different surface tensions. The other method is called the relative dye adsorption method, which qualitatively characterizes the hydrophobicity of NPs by measuring the relative partitioning of hydrophobic and hydrophilic dyes onto the NPs.[3] Characterization results obtained with both methods showed excellent agreements. The maximum particle dispersion method holds great promise to be developed into an easy-to-use and cost-effective standard method for quantitatively characterizing the hydrophobicity of NPs. **References** 1. Li G, Cao Z, Ho KK, Zuo YY, Quantitative determination of the hydrophobicity of nanoparticles. *Anal. Chem.* 94 (2022) 2078-2086. 2. Cao Z, Tsai SN, Zuo YY, An optical method for quantitatively determining the surface free energy of micro- and nanoparticles. *Anal. Chem.* 91 (2019) 12819-12826. 3. Li G, Ho KK, Zuo YY, Relative dye adsorption method for determining the hydrophobicity of nanoparticles. *J. Phys. Chem. C.* 126 (2022) 832-837.

Tue-M5-04

Pattern deposition of colloidal particles following the de-wetting of a solid substrate by a volatile carrier liquid

Ofer Manor, Ekhlas Homede, Mohamed Abo Jabal, Anna Zigelman

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The capacity of nanoparticles to self-arrange to various structures and their unique physical properties has made these building blocks essential in a broad range of applications and scientific disciplines. One of the most common methods to deposit particles atop a solid surface is to employ a volatile carrier liquid. Following the deposition of the suspension, comprising colloidal particles in a carrier liquid, the liquid evaporates, during which it de-wets the solid surface, leaving behined particulate deposits. We attempt to introduce a useful approach toward the fabrication of colloidal (nanoparticle) structures atop a solid substrate and a strategy to predict the deposit morphology following the evaporation of a carrier liquid. In laboratory, we alter the energy barriers to particle-particle and to particle-substrate attachments to result from colloidal surface forces. Different energy barriers to particle attachments render different macroscopic to nanoscopic morphology of the particulate deposits following the convective self-assembly of the particles in the volatile carrier liquid that de-wet the solid substrate. We show that by tuning the energy barriers, we render the morphology of the particulate deposits homogenous or patterned at the macroscale and comprising small or large particle aggregates at the nanoscale. To realize the physics of this problem, one must connect contributions to the morphology of the particulate deposit from the macro-scale convective flow in the volatile carrier liquid, from the nano-scale surface forces in the dispersion, and from the thermal motion of the particles. We identify the midway agents that facilitate a connection between the macroscale and nanoscale mechanisms: These are the mechanisms of particle coagulation in the liquid bulk and particle adsorption to the substrate. By embedding theorems for the rates of particle coagulation and adsorption in a long wave approach for the mass and momentum transport in the volatile dispersion and by compering theory to experiment, we show that the deposit morphology is determined to leading order by two dimensionless numbers. One is the ratio between the rate of particle adsorption and the rate of liquid evaporation. Another is the ratio between the rate of particle coagulation and particle convection. The magnitudes of both numbers are closely connected to the surface forces in the dispersion and to the rate of liquid evaporation.

Tue-M5-05

Nanoparticle-laden liquid droplets: From wetting dynamics to the deposition of surface submicrometric droplets

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Controlled transport of liquid droplets on solid surfaces is of critical importance in many practical applications, such as self-cleaning surfaces, coating, and drug delivery. Non-adhesive liquid drops levitate on solid surfaces; therefore, they are highly mobile and directed towards desired locations by external stimuli. Although research on liquid-repellent surfaces has proliferated, existing methods for creating long-ranged liquid transport are still limited to creating surface roughness or coating the liquid droplets. Here, we create non-contact aqueous drops on hydrophilic surfaces in an oleic environment and develop a new approach for depositing nanodroplets on solid surfaces. A glass surface is buried under an oil phase that contains a high concentration of Span 80 surfactants, and a droplet of silica nanoparticle dispersion is released on the solid surface. We study the effect of surfactant concentration in oil and nanoparticle concentration in water and find a plethora of droplet spreading regimes from fully wetting to non-wetting depending on the surfactant concentration. In high surfactant concentrations, an oil film is trapped within the surfactant assemblies on the solid surface and prevents the direct contact of droplets with the solid surface. Thus, the drop is in a fully non-wetting condition, and it can be used as a carrier to deposit nanoparticle cargoes at desired locations. Besides, the presence of surfactant assemblies, i.e., micelles in the oil phase, forms spontaneous water in oil (W/O) emulsions at the drop-oil interface. The drop moves and leaves a trace of emulsions with encapsulated nanoparticles on the solid. We demonstrate the possibility of local surface patterning and coating the surface with hydrophilic cargoes in a hydrophobic environment. The developed methodology in this study facilitates the nanodroplet patterning in numerous applications, from pharmaceutical polymetric carriers to the formulation of cosmetics, insecticides, and biomedical diagnosis.

Tuesday, July 12th | 13:00 - 14:40 | N5-Connecting the dots

Tue-N5-01

Connecting the DOTs: From foundational science to product development

Yonas Gizaw

The Procter and Gamble Co.

Providing to consumer irresistibly superior product with sustainable competitive advantage is a paramount importance for leading consumer goods product company. Consumers are demanding high performing product with minimum carbon footprint at relatively fair prices, commodity prices are increasing to unprecedent rate, supply chain disruption and commoditization of leading brands requires disruptive innovation at accelerated speed. To accelerate our innovation, we develop foundational knowledge in partnership with several universities, develop mechanisms and models, and work with suppliers to produce high performing molecules and formulate to address the unmet consumer needs. In this presentation, we will cover couple cases studies starting from basic science all the way to product development.

Tue-N5-02

Aspiring to design for delivery

Suzanne D'Addio

Merck & Co., Inc.

The declining success rate for new therapies in the pharmaceutical industry speaks to the growing challenge of addressing complex disease biology with conventional molecules and formulations. Discovery and development of differentiated drug products that address novel targets require out-of-the-box thinking and seamless collaboration across disciplines to question assumptions and drive innovation. Beginning the development process with target product definition (the end product in mind) has been an essential component of inventing new therapies since the implementation of the Quality by Design framework. As pharmaceutical scientists working in Discovery, we must bring to bear risk-based assessments of the impact of formulations on molecules, the performance of formulations upon administration and in vivo, and the interactions which may impact product stability during manufacturing and the shelf life. This talk will highlight practical challenges, outstanding questions, and emerging strategies to characterize and improve the design of drug molecules.

Tuesday, July 12th | 15:10 - 16:10 | A6-Active Matter

Tue-A6-01

Tuning attractive and repulsive interactions between solubilizing oil droplets

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Solubilization is a spontaneous transport process occurring in surfactant-stabilized emulsions that can lead to Marangoni flow and droplet motility. Conventionally, active droplets exhibit self-propulsion and pairwise repulsion due to solubilization processes and/or the solubilization products raising the droplet's interfacial tension. Here, we present emulsions with the opposite behavior, namely that solubilization and/or its products decrease the interfacial tension and cause droplets to attract and cluster. We systematically characterize the influence of oil structure, nonionic surfactant structure, and surfactant concentration on the interfacial tensions and Marangoni flows of solubilizing oil-in-waterdrops. Three regimes corresponding to droplet “attraction”, “repulsion” or “inactivity” are identified and the chemical trends leading to these behaviors are discussed. We believe these studies contribute to a new fundamental understanding of solubilization processes in emulsions and provide guidance as to how chemical parameters can be used to influence the dynamics and chemotactic interactions between active droplets.

Tue-A6-02

Colloidal design of new types of self-propelling active cleaners for efficient microplastics remediation

Haeleen Hong, Rachel Bang, Lucille Verster, Orlin Velev

Chemical engineering, NCSU

With the persistence and toxicity of microplastics dispersed throughout numerous aquatic systems, microplastic removal has received attention as one of the most urgent environmental remediation problems. Conventional water treatment methods such as filtration and centrifugation are impractical for the enormous volume of natural water because of their high cost, low throughput, and disruption to aquatic life. We propose a new remediation technique based on active microcleaners. These microcleaners will remove microplastic particles in the aquatic system by spreading through active motion and having morphology enabling highly efficient capture. The active cleaners are composed of dehydrated and concentrated soft dendritic colloids (SDC). The SDCs are a new class of soft matter introduced recently by our group. Their highly branched hierarchical structure mimicking the nanofiber mats from the legs of the gecko lizards leads to strong adhesion to microplastic particles via van der Waals attraction. The microcleaner SDCs are made of chitosan, a sustainable biomaterial. The dried SDCs particles are infused with a small amount of fatty acid, which when released slowly acts as “fuel” that generates a surface tension gradient which makes the microcleaners self-propel on the water surface by the Marangoni effect. The self-propulsion over long distances will enable the compacted dendrimeric particles to spread over a large area of water before re-hydrating, sinking, and capturing the microparticles. This could dramatically enhance their water remediation efficiency. We first characterized how the microcleaner propulsion is influenced by the kinds of fatty acid “fuel”, its surface tension and solubility, and traversed area. The active cleaners can propel for >400 s at distances >8 m at the water-air interface driven by just 0.1 µl of eugenol at a speed of > 300 mm/s. This rapid propulsion of active cleaner results in fluid shear during re-hydration, which leads to restoring the SDC pristine structure of highly branched dendrimer, after propulsion. The rehydrated dendritic colloid system is able to perform highly efficient microplastics capture and has considerable promise for cleanup applications in diverse aquifer types including saline seawater conditions.

Tue-A6-03

Bubble-based acoustic propellers for sustained corticosteroid delivery in the bladder

Jin Gyun Lee, Ritu Raj, Cooper Thome, Ankur Gupta, C. Wyatt Shields

Department of Chemical and Biological Engineering, University of Colorado Boulder

Interstitial cystitis (IC) is a chronic disorder of the urinary tract that causes discomfort, pelvic pain, frequent urination, and sometimes blood to appear in the urine. Currently, the most widely used treatment to remedy IC is bladder instillation; the medication is usually a steroidal drug that is solubilized in 50 mL of 50% dimethyl sulfoxide (DMSO), which is directly introduced into the bladder and eventually drained out using a catheter. Patients must receive this treatment weekly for 6-8 weeks and hold the liquid in their bladders for several hours each time, which can cause discomfort and have low effectiveness due to the short residence time of the drug. As a potential alternative, we describe an acoustically powered microswimmer that can propel within the bladder, securely attach to the bladder epithelium, and slowly release drugs for several days. The microswimmers are 3D-printed using two-photon lithography to contain a large cavity that holds a gas bubble of a defined size (e.g., diameter of cavity = ~13 μm). When exposed to their resonant frequency (320 kHz), the bubbles oscillate by stable cavitation, driving their rapid propulsion (i.e., ~50 body lengths of microswimmer per second). As a proof-of-concept demonstration, we designed microswimmers with propeller arms to induce non-linear swimming motions in response to applied ultrasound. We show that the microswimmers can swim within C57BL/6 mouse bladder explants. We further show that corticosteroids, a commonly used drug for treating IC, can be encapsulated into the bodies of the microswimmers and slowly released over several days until the microswimmers are washed out. Our results highlight a new potential treatment for IC that leverages ability of the microswimmers to cover large surface areas within the bladder and slowly release drugs over several days.

Tue-B6-01

Interfacial rheology of an oil-water system undergoing spontaneous emulsification

Ekta Sharma, Rochish Thaokar, Vinay Juvekar

Indian Institute of Technology, Bombay, India

Spontaneous emulsification (SE) finds numerous industrial applications such as personal care products, drug encapsulation, enhanced oil recovery, etc. SE involves emulsion formation even at moderate interfacial tension and with almost no energy input. This phenomenon is driven by the migration of surfactant molecules within the system. In this study, paraffin oil containing a non-ionic surfactant Span 80 was used as the organic phase. When this organic phase at concentrations above critical micelle concentration is brought into contact with water, it spontaneously forms water droplets at the interface. These droplets present at the interface form a network and impart elasticity to the interface. The interfacial film formation is a time-dependent phenomenon, and to understand the dynamics, we have performed temporal interfacial rheology. Microscopic investigations of the interface also reveal how the structure evolves at the interface. Interfacial elasticity was measured as a function of time as well as surfactant concentration using an interfacial shear rheometer equipped with bicone geometry. As the concentration of surfactant increases, smaller droplets are formed, resulting in higher elasticity. If we further increase the concentration of surfactant, the formation of multiple planes of the droplets occurs, and its signature is observed in interfacial elasticity. Furthermore, how the addition of salt affects the dynamics of this phenomenon was explored. It was observed that an appropriate amount of salt addition could restrict the formation of droplets and thereby elasticity. In addition, a water-soluble surfactant was added to the system, and the combined effect of the surfactants on interfacial film was observed. Over the last few decades, significant efforts have been made to understand the mechanism of spontaneous emulsification, but it is still not very clear (López-Montilla et al.).

Tue-B6-02

Interfacial Tribology of Hydrophilic and Hydrophobic Surface-Modified PDMS

Emily Schmidt [1, 2], Isabella Miller [2], Lilian Hsiao [2]

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Understanding the frictional behavior between compliant, lubricated elastomers is important for many applications including the development of artificial tissues and prosthetics, soft haptics, and food science. Polydimethylsiloxane (PDMS) is an inherently hydrophobic material that leads to complex interfacial phenomena in water-lubricated contacts. Here, we alter the wetting behavior of PDMS contacts and investigate the effect of surface energy on their interfacial friction. Elastomer tribopairs are synthesized by crosslinking the commercially available PDMS composite, Sylgard 184. The PDMS is rendered hydrophilic with the addition of up to 1 wt.% poly(dimethylsiloxane-ethylene oxide polymeric) (PDMS-b-PEO). The hydrophilic PEO chains in the block copolymer reorient towards the PDMS surface upon water contact, reducing the interfacial free energy of the substrates. Sessile-drop goniometry shows that the contact angles of unmodified PDMS and 1% PEO-b-PDMS modified PDMS are $\theta = 106.31° \pm 4.74°$ and $\theta = 24.43° \pm 1.70°$, demonstrating that water-based lubricants wets 1% PEO-b-PDMS much more than unmodified PDMS. Tribological testing is performed on unmodified and modified PDMS tribopairs using a ball-on-three plates geometry with a steel ball and the elastomer plates, using water as the lubricant. Stribeck curves indicate a reduction of the friction coefficient (μ) in the boundary and mixed regimes for the PEO-b-PDMS modified PDMS. The maximum friction coefficients for unmodified PDMS and 1% PEO-b-PDMS modified PDMS are $\mu = 2.23 \pm 0.28$ and $\mu = 0.76 \pm 0.52$. We hypothesize that the reduction in μ at low sliding speeds for the hydrophilic PDMS is a result of water being trapped into pockets created by surface asperities. To test this hypothesis, we model the wetting energies of the PDMS tribopairs using the Owens, Wendt, Rabel, and Kaeble model, and investigate the correlation of the boundary friction with the interfacial energy and the film thickness.

Tue-B6-03

Evaluating the Impact of carbon microsphere on the Stribeck curve of aqueous lubricant

Samuel Solomon, Noshir Pesika

1. Department of Chemical & Biomolecular Engineering, Tulane University

Previous studies have demonstrated that carbon microspheres can be used as additives to enhance the performance of lubricants due to their ability to function as ball bearings that help to reduce friction and mechanical wear in moving parts. This work aims to investigate the impact that carbon microspheres have on the respective lubrication regimes of the Stribeck curve – boundary, mixed and hydrodynamic. 60 wt% glycerol aqueous mixture is used as the base lubricant and carbon particles (with a mean size of 200 nm) are dispersed in varying amounts to obtain concentrations of 1 - 4mg/ml respectively. The tribological performance of the composite micro-lubricant will be studied on a pin-on-disk tribotester with a silicon wafer as the disk and an uncoated glass lens as the probe. Stribeck curve analysis of the results will be conducted to determine how the plot responds to varying concentrations of micro-lubricant. Wear track analysis will also be carried out using SEM and AFM to confirm the mechanism of lubrication. Since the boundary regime experiences the most asperity contact between the friction pair, it is expected that the particles will play the greatest role in this regime and provide the highest reduction in coefficient of friction than other regimes. This fundamental study will provide further insight into the role of microparticles in lubrication.

Tuesday, July 12th | 15:10 - 16:10 | C6-Colloids, Macromolecules, and Surfaces in Life Science

Tue-C6-01

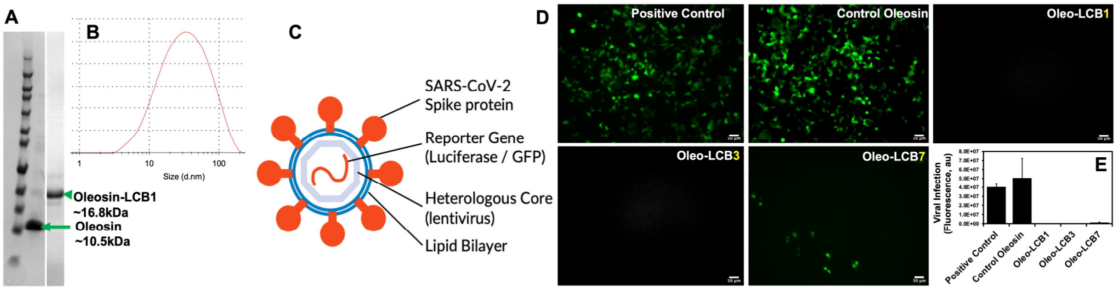
Recombinant Protein Micelles for Inactivation of SARS-CoV-2

Rajarshi Chattaraj, Christina Y. Kim, Daeyeon Lee, Daniel Hammer

Chemical and Biomolecular Engineering, University of Pennsylvania

The emergence of SARS-CoV-2 has led to an urgent need to develop therapeutics, treatments, and vaccines, both against the immediate threat, as well as developing a versatile platform for future treatments. Binding between the receptor binding domain (RBD) of the spike protein on SARS-CoV-2 and the human ACE2 receptor is essential for entry of the virus into the epithelium. SARS-CoV-2 can enter via endocytosis by binding to the ACE2 receptor, and/or via fusion, where, after ACE2-binding, it gets activated by the human proteases like furin, TMPRSS2, and cathepsins,allowing it to fuse at the plasma membrane. A powerful strategy to block viral infection is to use inhibitors such as ACE2-derived or *de novo*-designed short chain peptides and mini-proteins that bind to the S1 protein with high affinity. Here, we have developed micelles purely from a functional recombinant protein called oleosin that will bind and inactivate the Spike S1 protein. Unlike therapeutic antibodies, recombinant proteins can be formulated relatively easily, and unlike free peptides and mini-proteins in many cases, recombinant proteins are uniform, have greater circulation half-life, and can be equipped with multiple functionalities with precision through genetic engineering. Oleosin is found in nature as a stabilizer for fat bodies in plant seeds; it is a rare protein that can be engineered to behave as a free-chain triblock surfactant, capable of assembling into micelles and vesicles, as shown in our lab. Micelles were formed by spontaneous self-assembly of oleosin that was genetically modified with anti-S1 mini-protein and peptide sequences. Because oleosin is a protein, we can precisely incorporate into it different functional moieties at the gene level, eliminating complex post-formulation functionalization chemistry and washing steps involved in other synthetic nanostructures. We cloned S1-binding mini-protein genes called LCB*x* previously designed by David Baker's laboratory (UW Seattle) to the oleosin N-terminus, which we term Oleo-LCB*x*. and expressed them in E.*Coli*. These proteins formed 10-100 nm micelles as verified by dynamic light scattering. To assess inhibitory activity of these micelles, we measured their effect on Reporter Virus Particle (RVP) infection into 293T-hsACE2 cells; the RVPs contain a gene for green fluorescent protein (GFP) and "infection" is reported by GFP-associated fluorescence. Two proteins, Oleo-LCB1 and Oleo-LCB3, completely blocked both wild-type and Delta variant RVP infection into cells at 10 µM. A therapeutic dose response showed reduction in RVP infection at concentrations as low as 5 nM functional protein in micelles. Additionally, to validate the potential

multifunctional nature of a micellar therapeutic, two different concentrations of Oleo-LCB1 and Oleo-LCB3 were co-mixed in the same sample. Certain combinations performed much better than individual molecules at the same concentration, with one combination completely eliminating RVP infection. Ongoing work involves addition of anti-fusogenic functionalities to micellar oleosin for a synergistic approach to block ACE2 receptor and fusion mediated viral infection. Although the immediate concern is to combat SARS-CoV-2 infection, the strategy is modular, in that domains of proteins embedded in the nanostructurescan be swapped with other bioactive domains of different specificity as required as new infectious agents and mutant strains emerge.



A: SDS-PAGE of oleosin variants. ***B***: Dynamic light scattering results of oleosin-LCB-1 micelles at 10 µM in phosphate buffered saline. ***C***: Structure of RVPs. *D-E*. Images (*D*) and analysis (*E*) (n~10) for RVP uptake mediated fluorescence in ACE2 expressing 293T cells. Presence of Oleo-LCB1 and Oleo-LCB3 completely eliminates any viral infection into cells as demonstrated by total lack of fluorescence.

Tue-C6-02

Co-delivery of inactivated H1N1 virus and NKT cell agonist from degradable microparticles for single dose vaccination

Zachary Sparks, Anuj Chauhan

Chemical & Biological Engineering Department, Colorado School of Mines

Purpose: Immune response to antigen can be amplified by co-delivery of agonists such as alpha-galactosylceramide (a-GalCer) which is an agonist for NKT cells. In many cases multiple doses of the antigens are needed to achieve the desired response. We propose to co-deliver multiple doses of vaccine and agonist in a single dose by sustained or pulsatile release from degradable micro-particles. Once injected into the body via an intramuscular injection, the particles may release the vaccine in a controllable manner to achieve the optimal immune response. Methods: The goal of this work is to develop microparticles with sustained or pulsatile release over a few months with sufficient amount of agonist and viral release to drive an immune response. Multiple formulations including PLGA (8-16 kDa or 2-6 kDa) and PLGA (8-16 kDa)/PCL (14 kDa) blend were synthesized using double emulsion solvent evaporation technique to encapsulate 1) inactivated virus (H1N1 influenza A/PR/8/34), 2) inactivated virus and sodium hydroxide, 3) a-GalCer, or 4) inactivated virus and a-GalCer. Polymer molecular weight, polymer hydrophobicity, polymer concentration in the organic phase, and concentration of inactivated virus in the synthesis were varied to investigate the effects on particle loading and particle release characteristics. Particle loadings and release profiles were measured in vitro using enzyme linked immunosorbent assay (ELISA) and liquid chromatography mass spectroscopy (LCMS), and optimized formulations were tested in vivo in mice. Particle size was characterized using optical microscope and SEM. Results: Particle size measurements showed that co-encapsulation of the inactivated virus and a-GalCer agonist yielded larger particles (35.9 ± 8.6 µm) compared to just the virus (29.0 ± 10.1 µm) or just a-GalCer (21.7 ± 4.7 µm) for all formulations. The PLGA50:50 formulation had the highest vaccine loading of 7.5 ± 1.3 µg/mg which is about double the loading for PLGA75:25/PCL particle formulation. The formulations with co-encapsulation of inactivated virus and a-GalCer in PLGA50:50 contained 3.0 ± 0.47 µg/mg vaccine and 6.0 ± 0.28 µg/mg a-GalCer. The release profiles of the inactivated virus loaded particles in PLGA50:50 and PLGA 75:25 formulations were similar with nearly constant rate of release over the duration of ~50 days. Both formulations showed a burst release between 23 and 28 days, but the PLGA50:50 formulation showed a 70% greater burst release of 2.7 µg/mg inactivated virus. Only the PLGA50:50 formulation was used for a-GalCer loaded particles which gave ~38% release through seven weeks. Co-encapsulated virus and a-GalCer PLGA50:50 particles released 100% virus in ~15 days whereas a-GalCer release was only ~49%. Co-

encapsulation with NaOH increased the rate of release due to faster degradation of the particles. The PLGA50:50 8-16 kDa formulation had higher loading (7.5 ± 1.3 μg/mg) and longer release (~50 days) compared to PLGA50:50 2-6 kDa formulation which had loading of 2.8 ± 0.53 μg/mg and release over ~7 days. Based on these findings, if a significant amount of a-GalCer is to be released on a similar time scale as vaccine, then a mix of virus loaded particles and co-encapsulated virus and a-GalCer loaded particles should be used.

Tue-C6-03

Cellulose ester colloidal dispersions as rainfast biodegradable foliar formulations for targeted agrochemical delivery

Mariam Sohail [1], Tahira Pirzada [1], Saad Khan [1], Charles Opperman [2]

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Increased awareness of the long-term impacts of agrochemicals has resulted in the hunt for efficient and sustainable delivery platforms. In order to meet the food demands of an exponentially increasing global population, there is a dire need to establish sustainable technologies for targeted delivery of agrochemicals with minimal environmental footprints. We present an adaptable and bio-friendly controlled release platform consisting of aqueous colloidal dispersions of biodegradable cellulose derivatives synthesized through a simple yet scalable anti-solvent precipitation process (Advanced Functional Materials, 2022, https://doi.org/10.1002/adfm.202108046). We propose utilization of these dispersions as foliar formulations for controlled release of agricultural active ingredients (AI) corroborating their performance through a rigorous diverse spectrum of tests. The biodegradable nature of our polymer particles and use of water as the dispersant medium justify sustainable nature of these formulations. In addition, the adaptability of the dispersions to cater to a range of crops and AI is exhibited through modulation of particle morphology and the particle-AI binding strength. The colloidal dispersions are synthesized through solvent evaporation process from a ternary mixture of cellulose ester (CE)/water/acetone. Fundamental insights in the phase behavior of the ternary system are analyzed via the Flory Huggins model wherein clear demarcation is observed in particle morphology and phase behavior through varying the ester linkages in the cellulose esters. Change in particle size and shape further effects the binding affinities with the model AI as is corroborated through Isothermal Titration Calorimetry (ITC) analysis and release assays. Our results demonstrate that tuning the particle morphology permits both weak and strong binding with the AI thus allowing achieving both slow and fast AI release as required. Furthermore, we have verified the functional performance of the colloidal dispersions through simulated rain tests to validate rainfastness and anti-fungal assays to corroborate AI bioavailability. These results are further complimented with stability analysis, and surface interactions with model leaf surfaces. The potential impact of rainfastness and controlled release formulations can be significant especially in tropical rainy climates where rain induced wash-off necessitates multiple sprays to achieve desired crop yields. This, in turn, increases operational costs in addition to causing environmental pollution, increased pathogen resistance and non-target exposure. CE dispersions as agrochemical formulations can be significant in reducing number of sprays required while maintaining the desired efficacy level. Our study goes the complete wheel starting from a fundamental thermodynamic system analysis of the CE particle formation process and the CE-AI binding interactions to demonstrating the superior rainfastness of the dispersions and the bio-availability of the loaded AI. With their functional performance verified through release and fungal assays, fundamental thermodynamic insights into the dispersion synthesis process and the particle-AI interactions open a window of opportunity allowing tuning particle size and the binding strength of the desired AI. This can allow tailoring of the dispersions to cater to a wide variety of AI, and crops. This ‘lab to leaf’ approach demonstrates the potential of CE dispersions to achieve targeted AI delivering allowing higher efficacy at lower delivery rates.

Tue-D6-01

Thermoresponsive ‘shape-shifting’ diblock copolymer nano-objects: synthesis, characterization and applications

Steven Armes

University of Sheffield

Polymerization-induced self-assembly (PISA) is widely recognized to be a powerful platform technology for the rational synthesis of block copolymer spheres, worms or vesicles in the form of concentrated dispersions. Moreover, the design rules for PISA are generic: this approach works equally well in aqueous solution, polar solvents (e.g. methanol or ethanol) or non-polar media (e.g. n-alkanes, mineral oil or silicone oil). In this talk, our recent results on thermoresponsive ‘shape-shifting’ diblock copolymer nano-objects in aqueous media will be discussed. Their synthesis involves the RAFT aqueous dispersion polymerization of 4-hydroxybutyl acrylate (HBA) using various water-soluble polymer precursors. In each case, a single diblock copolymer of fixed composition can form spheres, worms, vesicles or lamellae simply by varying the solution temperature, which leads to a subtle change in the degree of (partial) hydration of the weakly hydrophobic poly(4-hydroxybutyl acrylate) chains. Each thermally-induced morphological transition is characterized by transmission electron microscopy, dynamic light scattering, small-angle X-ray scattering, ^{1}H NMR spectroscopy and rheology. Moreover, these transitions are fully reversible, which suggests potential applications for vesicle loading and subsequent payload release.

Tue-D6-02

Cross-Linked Polyelectrolyte Complex Nanoparticles for Controlled Release at High Ionic Strength

Xiongyu Chen [1], Jason Zhang [1], Ethan Keller [1], Golnaz Heydari Sangestani [1], Raymond Park [1], Chuxin Lei [2], Guihua Yu [2], Keith Johnston [1]

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Polyelectrolyte complex nanoparticles (PECNP) form due to the electrostatic attraction between oppositely charged polymers and release of counterions. They have many applications in drug delivery, water treatment, coatings and recently in release of chemicals in high ionic strength media including subsurface oil and gas reservoirs. Herein we synthesize PECNPs using polyethylenimine (PEI) and a scale inhibitor poly(vinylsulfonate) (PVS) for controlled release of PVS at high salinity. As ionic strength increases, screening of the charges on the polymers often leads to nanoparticle aggregation at medium ionic strengths and then rapid and extensive PEC dissociation into polyanions and polycations at high ionic strengths. To overcome these limitations, covalent crosslinks were formed over a range of crosslink densities between the polyethylenimine chains. The level of covalent crosslinking of the PEI was tuned to provide stability against rapid PEC dissociation in seawater and to control the release of PVS. Without covalent crosslinking, the PECNP grew from 200 nm to 1 μm in 1 minute in phosphate-buffered saline (1 wt% salinity) and completely dissociated in seawater within 1 minute. The positive surface charge of the PEI on the surface of the PECNPs caused the NPs to strongly adsorb on anionic sandstone mineral surfaces (~10 mg/g rock). The long term release of PVS from the PECNPs on the mineral surfaces may be attributed to PVS interactions with PEI and the mineral surface, which influence PVS transport. The gradual release is of great interest for long term scale inhibition. This fundamental study of PECNP crosslinking to control polyanion release is of interest in a wide range of applications in high ionic strength aqueous solutions, including subsurface brines and also physiological fluids in humans.

Tue-D6-03

Poly (vinyl alcohol)-stabilized polymersomes with strong near infrared absorbance of encapsulated indocyanine green J-aggregates

Mohammed Kawelah [1], Ceren Atila Dincer [1], Sangheon Han [2], Thomas Truskett [1], Konstantin Sokolov [2], Keith Johnston [1]

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Photoacoustic imaging (PAI) with NIR active exogenous agents is a non-invasive imaging modality with high sensitivity and tissue penetration of up to a few centimeters for early stage detection of cancer cells. One of few FDA-approved near infrared (NIR) organic dyes is indocyanine green when in the J-aggregate state (ICGJ). To prevent dissociation of ICG J-aggregates in the blood stream, they have been encapsulated into liposomes and other nanoparticles. Relative to lipsosomes, polymersomes with a stronger and thicker bilayer made by the self-assembly of block copolymers have higher stability in vivo with less cargo leakage. Herein, we synthesize biodegradable polymersomes utilizing self-assembly of the poly(lactide-co-glycolide-b-polyethylene glycol) (PLGA-b-PEG) amphiphilic copolymer to achieve high loadings of stable ICGJ in the aqueous core. Free ICG monomer and small J-aggregates impurities were separated from ICGJ-loaded polymersomes with ultracentrifugation at 50k rpm to achieve a very high level of the ICGJ peak (890 nm) relative to the monomer peak (785 nm). The I890nm/I785nm of 5.0 was well above the level in our previous work of 1.6. However, the I890nm/I785nm decayed overnight suggesting unfavorable interactions of the J aggregates with the polymersome bilayer. When PVOH was added to the aqueous dispersion, the I890nm/I785nm became very stable indicating that the homopolymer strengthened the bilayer and protected ICGJ from the destabilizing sites. Interestingly, PVOH was found to catalyze the formation of ICGJ in the presence of small ICGJ seeds and excess ICG monomer. The relationship between hydrodynamic diameter (DLS) of ICGJ and spectral properties was investigated. Very small ICGJ <10nm can still give similar spectral absorbance as 50nm ICGJ. In the future, these PVOH-stabilized polymersomes can be utilized to co-deliver ICGJ as imaging agent with chemotherapeutic drugs for photo-guided chemotherapy as well as for image-guided cancer surgery.

Tue-D6-04

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 far from equilibrium assembly driven by chemical reactions in the living cells, i.e., dissipative assembly. These out of equilibrium kinetically controlled active structures are in constant exchange of energy and mass with the environment. Here we demonstrate far from equilibrium dissipative assembly of protein hydrogels driven by a redox cycle, which exhibit autonomous behavior and bonding that depend on protein unfolding. Fast oxidation of pendant thiol groups on partially unfolded bovine serum albumin (BSA) formed hydrogels over ~10 minutes, while simultaneous slow reduction of the disulfide bonds by dithiothreitol dissolved the hydrogel over hours. Interestingly, we found that the hydrogel lifetime was regulated by the concentration and type of chaotropic salt, i.e., denaturant, included to unfold the BSA. Experiments showed that increasing chaotropic salt concentration, which encourages protein unfolding, increased the number of solvent accessible thiol groups on the BSA, increased the crosslinking density in the hydrogels, and decreased the hydrogel lifetime. Likewise, decreasing chaotropic salt concentration led to lower crosslinking density and longer hydrogel lifetimes. Despite the decreasing crosslinking density, the hydrogel storage modulus increased as a function of decreasing chaotropic salt concentration, which fluorescence spectroscopy measurements showed was due to enhanced hydrophobic forces. Systematic experiments showed that the increase in hydrogen peroxide reaction rate with thiol groups controlled the hydrogel lifetime.

Tuesday, July 12th | 15:10 - 16:30 | D7-Self and Directed Assembly

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Tue-D7-01

Atomic Stencil-Driven Patchy Nanoparticles for Controlled Self-Assembly

Chansong Kim, Ahyoung Kim, Lehan Yao, Eric Yang, Falon Kalutantirige, Yu-Shen Liu, Xiaoying Lin, Qian Chen

Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign

Herein, we develop an atomic-stencil method to prepare patchy gold NPs (AuNPs) with a superior monodispersity. We are able to achieve a library of facet-specifically decorated patchy NPs. We analyze the surface properties of patchy NPs synthesized with controlled synthesis parameters to prove the underlying mechanism of our strategy and rationalize it by presenting the finely tuned patchy configurations. Moreover, we demonstrate our atomic-stencil method is universally effective for diverse shapes of AuNPs from simple faceted polyhedral to complicated-crystalline spherical NPs. We expect that our study will provide the groundwork for high-quality assembled structures which is crucial for practical applications in diverse areas.

Tue-D7-02

Controlling the synthesis and self-assembly of colloidal gold nanoparticles using robotic automation and artificial intelligence

Huat Thart Chiang [1], Kiran Vaddi [1], Lilo Pozzo [1, 2]

[1] Department of Chemical Engineering, University of Washington[2] Department of Material Science and Engineering, University of Washington

Controlling the self-assembly of particles to fabricate complex and useful materials has been a long-standing challenge due to the large and complex experimental design spaces often associated with this kind of problem. In the bottom-up synthesis of nanoparticles, it is extremely difficult to achieve control of the self-assembly process as it is influenced by both experimental conditions (e.g., reagent concentrations, pH, temperature) as well as temporal manipulations (i.e., the time and order in which the experimental conditions are altered) owing to intrinsic nonlinear competition between nucleation and growth of seed particles in solution. We are interested in the inverse design of materials, where the objective is to assemble molecules and/or particles to obtain materials with a desired structure or property. While there are many ways to approach this problem, we believe that an automated artificial intelligence-driven approach is the most effective. In this talk, we discuss the use of automation tools such as liquid handling robots to synthesize materials and UV-vis plate readers or high throughput SAXS instruments to characterize them. This significantly reduces the cost and time of performing the experiments and allows us to efficiently collect large amounts of data. Spectral characterizations however pose a challenge for data processing such as computing physically meaningful similarity measures. Towards this, we describe a Riemannian geometry-based approach that is advantageous over standard multi-variate statistics for UV-vis spectra or SAXS scattering curves. The generic methodology presented in this talk can be used in many ways depending on the end goal. For example, machine learning models can be trained on data to efficiently predict a spectra response given experimental synthesis conditions. Bayesian Optimization can be used to iteratively suggest new synthesis conditions that eventually lead to a material with the desired property. Finally, causal networks can be generated from data and used for the design of future experiments. To demonstrate our framework, we perform retrosynthesis of colloidal gold nanoparticles intending to synthesize a particle of a targeted structure, size, and dispersity given a target in terms of a spectrum using Bayesian optimization.

Tue-D7-03

Non-orthogonal DNA Coatings for Stepwise Programmed Colloidal Assembly

In-Seong Jo [1], Joon Suk Oh [2], Manhee Lee [3], Etienne Ducrot [1], David Pine [4, 5], Gi-Ra Yi [6]

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Self-assembly of colloidal particles have been investigated as a key strategy to access colloidal superstructures from functional building blocks. To program the assembly, many interactions between particles have been studied, for example, chemical bonds, electrostatic or depletion interactions. DNA has been proven to be the most versatile thanks to the high affinity and specificity between complementary DNA strands as well as the recent developments of DNA synthesis on demand. Colloids coated with DNA strands can then be selectively assembled into various types of colloidal superstructures. The structure formed is dependent on the characteristic of colloidal building blocks - size, shape, and existence/location of the interactive patches. The temperature-dependent binding strength between particles is also a key parameter as the recognition between DNA bases relies on hydrogen bonds. The melting temperature (T_m) that marks the transition between aggregated and dispersed particles is a signature of the chosen DNA sequence, its grafting density, the buffer conditions… When employing simultaneously multiple DNA pairs to reach complex colloidal superstructures, it becomes crucial to program precisely the sequence of their melting temperatures. Here, we report a strategy to program interactions between colloidal particles grafted with complementary sequences by introducing mismatched segments in the sticky-end to pilot the thermal triggering of the interactions. We use colloidal particles coated with high-density DNA brushes of self-complementary sticky-ends (CGT<u>X</u>ACG) with one base pair mismatch in the sequence. Despite the mismatch, the DNA-coated particles can still bind through DNA hybridization and crystallize. We demonstrate that the corresponding T_m can be tuned over a wide range of temperature depending on the nature of the mismatch. Furthermore, this shift of T_m can be finely tuned by the mixing, in the coating, two different types of mismatched DNA strands. In addition, since these interactions have different melting temperatures but are not orthogonal, binary colloidal mixtures can directly form core-shell superstructures by stepwise DNA-mediated colloidal self-assembly in solutions. This demonstrates the possibility to fabricate complex colloidal superstructures made of different crystalline lattices grown on top of each other using mismatched DNA strands, opening the way to the control of the boundary between crystals.

Tue-D7-04

Bottom-Up Fabrication of Large-Scale Gold Nanorod Arrays by Surface Diffusion-Mediated DNA Origami Assembly

Risheng Wang, Shuo Yang, Wenyan Liu, Yuwei Zhang

Chemistry of Missouri University of Science and Technology

Self-assembly of anisotropic metal nanoparticles serves as an effective bottom-up route for the nanofabrication of novel artifacts. However, there still are many challenges to rationally manipulate anisotropic particles due to the size and geometric restrictions. To avoid the aggregation and mis-hybridization from DNA sticky-end-guided assembly in buffer solution, in this work, we utilized a novel surface diffusion-mediated DNA origami assembly method for the fabrication of plasmonic nanomaterials into well-ordered structures through π-π stacking interactions. Highly ordered 1D and 2D arrays of AuNRs were constructed by employing DNA origami frames as scaffolds with the surface mobility of DNA origami in a liquid environment manipulated by divalent (Mg2+) and monovalent (Na+) cations. To facilitate the further manipulation of those patterns, a novel pattern transfer method was introduced to transfer the arrays of AuNRs from a liquid to a dry ambient environment with high yield and minor structural damage. The results demonstrated a cost-effective and reliable strategy of DNA origami-assisted, large-scale assembly of AuNRs for constructing complex superstructures with potential applications in the nanofabrication of plasmonic and electronic devices, and the capability to integrate with many advanced lithography techniques.

Tue-F6-01

Adhesive forces between drops coated with polymer-surfactant complexes measured using a microfluidic platform.

Xiaotong Song [1], Emily Jamieson [1], Joseph Berry [1], Rico Tabor [2], Ray Dagastine [1]

[1] Dept. of Chemical Engineering University of Melbourne[2] School of Chemistry Monash University

Attractive interactions between drops in which aggregation, rather than coalescence occurs, lead to the formation of aggregates, gels or microstructures that then control the phase behaviour, stability, rheology and most importantly function of formulated products (e.g., food, personal care products, pharmaceutical formulations). These forces are often highly system specific and are a function of a number of additive components. Previously, we developed a microfluidic platform to probe surface forces between drops with strong adhesive interactions. For a specific polymer-surfactant (PS) complex we correlated the adhesive interactions observed the microfluidic device with surface forces measured between micro-drop pairs using atomic force miscopy. The microfluidic device forms 1-dimensional structures, i.e. chains of drops, where the stronger the adhesion forces measured via AFM correlated to the formation of longer chains of drops in the microfluidic device. In this talk, we discuss the application and development of these devices to correlate drop adhesion as a function of a range of PS complexes. The evolution of the devices now allows for thousands to tens of thousands of observations allowing for the development of drop chain length distributions to define a system specific adhesive fingerprint. We will discuss results that compare the adhesive behaviour for different polymers as a function of surfactant composition. The device also allows for step changes in solution conditions to observe the responsive nature of many PS complexes to changes in surfactant and electrolyte concentration. We will also touch on a series of benchmark studies including a novel small angle neutron scattering (SANS) study using these microfluidic devices.

Tue-F6-02

Long-term Stability and Characterization of Nanoparticle Stabilized Monodispersed Foams

Nicole Donovan [1], Shuaijun Li [2], Jing Fan [2], Charles Maldarelli [1]

[1] Levich Institute - City College of New York Chemical Engineering Department[2] City College of New York Mechanical Engineering Department

Foams are found in a wide range of applications, such as detergents, food, cosmetic products, and oil recovery. In many of these products and processes, microstructure and stabilization of foams play a critical role in determining their properties and performance. Colloids have emerged as an alternative stabilizing agent to replace traditional surfactants, because of their demonstrated effectiveness in stabilizing foams and the possibility to manufacture particles with eco-friendly materials. It has been theoretically proven that particle laden interfaces provide a larger resistance to foam coarsening due to their ability to irreversibly adsorb and increase the interfacial elasticity, E. If the elasticity, , coarsening will be prevented. However, the relationship between the microstructure and bulk properties of particle-stabilized foams has not been well studied. In this research, we apply microfluidic techniques to produce monodispersed bubbles stabilized by silica nanoparticles whose hydrophobicity is modified by electrostatic adsorption of cetyltrimethylammonium bromide (CTAB). We found that the stability of the foams depends on the concentrations of CTAB and nanoparticles and by tuning the particle hydrophobicity to an optimal value, we produced monodispersed foams of long-term stability against coalescence and coarsening. With SEM, the nanoparticle coverage on the interface is clearly revealed. Furthermore, we characterize the interfacial elasticities and show that for nanoparticle stabilized foams, the elasticity can reach values greater than , therefore supporting that coarsening events can be halted due to high interfacial elasticity. The dilatational rheology of variable continuous phase formulations reveals significantly higher interfacial elasticity than the air-water interface with surfactant (CTAB) alone. Bulk rheological properties of the foams for various air volume fractions are also studied and the nanoparticle & CTAB foam exhibits significantly higher storage and viscous moduli than bulk measurement for CTAB only stabilized foams.

Tue-F6-03

Miscible antifoams: Leveraging evaporative solutocapillary flows for a novel antifoam mechanism

Suzanne G.K. Calhoun [1], Vineeth Chandran Suja [1, 2], Lien Nguyen [1], Gerald G. Fuller [1]

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Foaming is often problematic in non-aqueous fuels and lubricating oils, leading to the use of additives called antifoams. Existing antifoams are solid particles or immiscible liquid droplets requiring specialized high shear machinery for incorporation. These antifoams are prone to gravitational separation, or removal under dynamic operation conditions – rendering them ineffective. A miscible liquid that is effective as an antifoam would overcome these obstacles. Evaporation greatly influences thin film stability, stabilizing or destabilizing depending on the volatility and surface tension of liquid components. A fluid with higher surface tension and higher volatility destabilizes a thin film as it evaporates. We hypothesize that such a fluid would act as a miscible antifoam, leveraging evaporation driven solutocapillary flows. We test this utilizing a custom experimental platform that probes thin film dynamics and foam stability at the single bubble level. We investigate several potential miscible antifoam systems with a range of surface tension deficits and viscosity ratios. With performance equivalent to or better than conventional and the added benefit of ease of use, miscible antifoams have the potential to be groundbreaking.

Tue-F6-04

The morphology and behaviour of mixed oil and water foams in thin film and bulk form

Yuchen Si [1, 2], Tao Li [2], Paul Clegg [1]

[1] Department of Physics and Astronomy, University of Edinburgh [2] Wenzhou Institute, University of Chinese Academy of Sciences

Initially, we investigate a mixture of particle-stabilized oil-based foams and aqueous foams in the form of thin films. In our study, aqueous foams are stabilized by hydrophobic silica particles in a mixture of water and propylene glycol, and oil-based foams are stabilized by partially fluorinated particles in olive oil. These two types of foam do not tend to combine automatically as the oil and aqueous phase repel each other. However, by spinning our composite foams and then sandwiching them between two coverslips, tortuous air channels across large parts of the thin-film samples appear due to space constraints and external forces (Figure 1). Unusually, bubbles are found in aqueous regions, oil regions and sometimes spanning both [1].

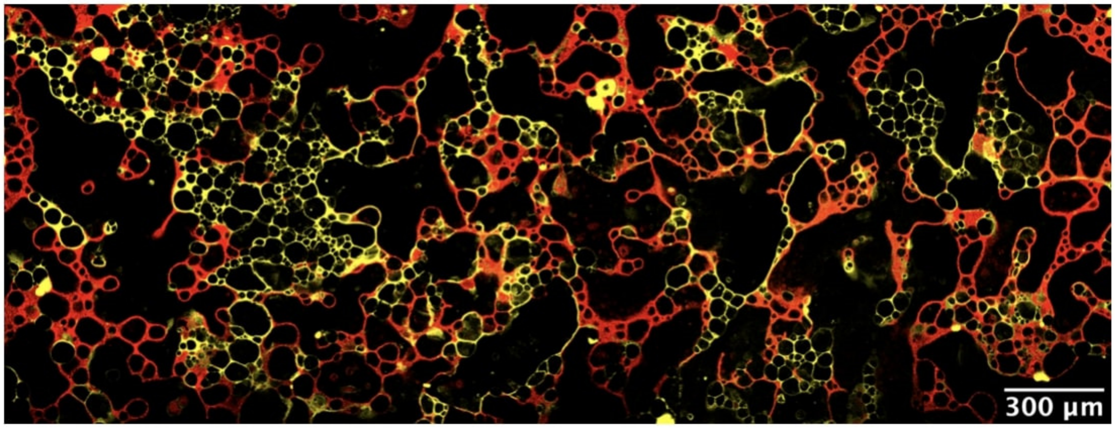

Figure 1 : Thin-film: Confocal micrographs of mixed foam sample: yellow aqueous foam stabilized by silica particles and red olive oil foam stabilized by MP-8T particles [1]. More recently, we have extended our studies to the case of mixed foams in bulk. A new material called ‘an emulsion of particle-stabilized foams’ has been discovered, which is a combination of two types of well-studied colloidal materials: foams and emulsions. Similar to a traditional emulsion, catastrophic and transitional phase inversions occur between oil-in-water (O/W) type and water-in-oil (W/O) type samples. Specifically, we induce catastrophic phase inversion by adjusting the proportions of aqueous foams and oil-based foams, and transitional phase inversion by modulating the volume fraction of propylene glycol in the aqueous phase. An intermediate state (Figure 2b) which is a

mixture of phase-separated O/W (Figure 2a) and W/O (Figure 2c) appears during the transitional phase inversion process. Water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) foam droplets are sometimes observed in O/W and W/O samples respectively. I will present these results alongside prospects for the future and potential applications.

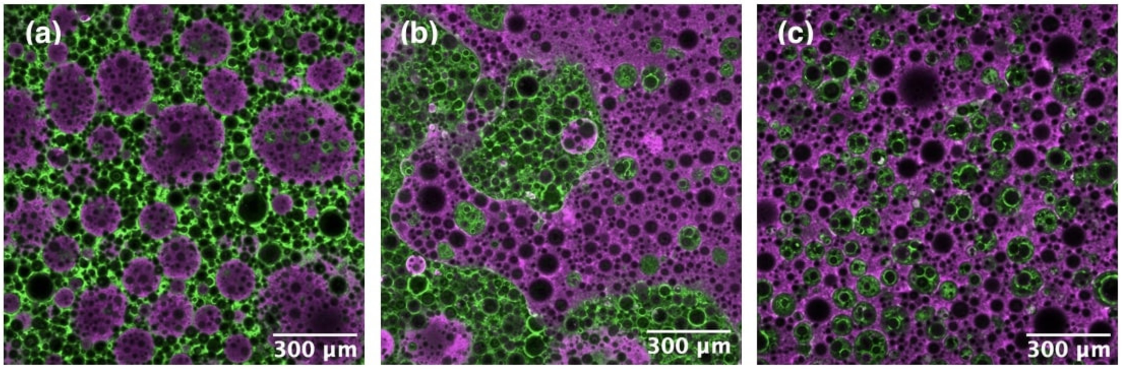

Figure 2 : Bulk: Confocal micrographs showing the transition from (a) droplets of oil foam, through (b) an intermediate state, to (c) droplets of aqueous foam driven by the compositions of the foams. Both foams are stabilised by particles.

References [1] Si Y, Li T, Clegg P S. Mixed Aqueous-and-Oil Foams via the Spinning Together of Separate Particle-Stabilised Aqueous and Oil Foams[J]. Langmuir, 2022.

Tuesday, July 12th | 15:10 - 16:30 | G6-Energy Systems

Tue-G6-01

0D + 1D = 2D-Heterostructures by Electrospinning

Qi Li [1, 4], Feng Yan [1], John Texter [1, 2, 3]

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Advances in electrocatalytic electrodes are resulting from our fabrication of heterostructured multiphase materials of high specific surface area [1,2]. These are needed to realize the full potential of 2D materials and require symmetry-breaking during fabrication. We have discovered [3] how to electrospin and coat 2D materials, for example graphene nanosheets, in randomly oriented networks with network connectivity, so that nanosheet anisotropy is retained in the resulting coatings. This preferred electrospinning is in intermittent competition with a hydrodynamic linear instability driven by spontaneously decreasing of surface free energy. Here we further capitalize on operating close to such an instability boundary between electrospraying and electrospinning. We report electrospinning of a multiphase aqueous suspension composed of 0D nanolatexes (NLs), 1D MWCNTs (multiwall carbon nanotubes), and an aqueous PVA (polyvinyl alcohol) carrier fluid. Rather than a fibrous web of predominantly 1D anisotropy, we obtain a random network of 2D nanomembranes bound by mixtures of NL and PVA. These nanomembranes are μ-films formed by PVA and NL that are remnants of menisci supported by mini-networks of MWCNTs. SEM images suggest a redistribution of NLs that transfers NLs from MWCNT surfaces to the product-2D μ-film surfaces supported between MWCNTs within NL-PVA μ-films (nanomembranes). Approaches to structural tuning, improving electrochemical properties, and directions for future applications include film densification to modify specific surface area, carrier and NL modification to modulate ionic and electrical conductivities, and nanophase doping to create further heterostructures that facilitate support of additional catalytic sites for tandemly cooperative and consecutive reaction catalysis. These observations provide a basis for increasing dimensionality and designing 2D networks based on coupling an instability with colloidal network re-equilibration.

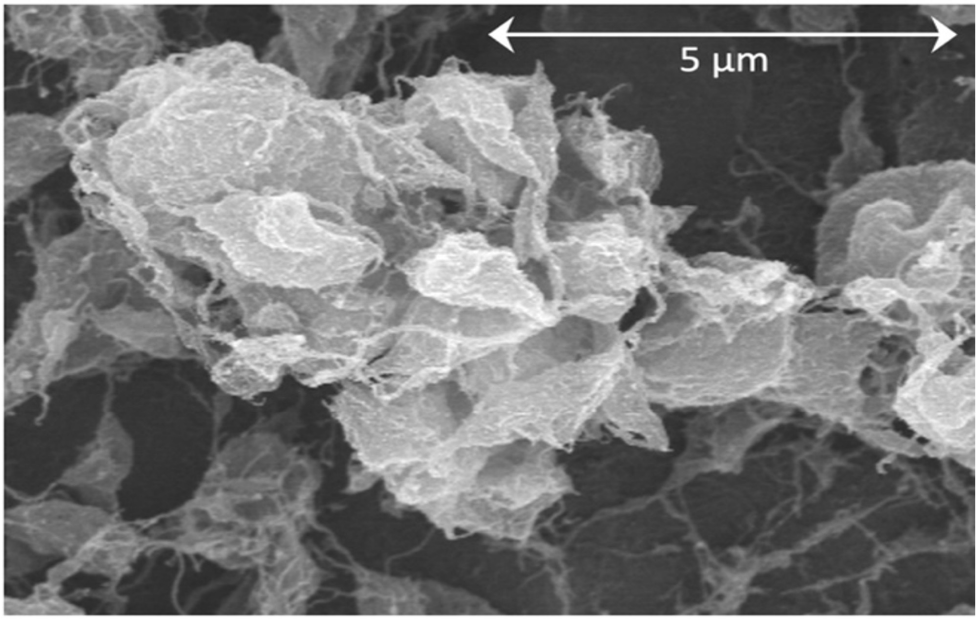

Figure 1. SEM of heterostructured coating References 1. A. K. Geim, I. V. Grigorieva, Nature, 2013, 499:419-425. 2. H. C. Tao, Q. Fan, T. Ma, S. Z. Liu, H. Gysling, J. Texter, F. Guo, Z. Y. Sun, Prog. Mater. Sci., 2020, 111:100637. 3. Q. Li, F. Yan, J. Texter, MRS Adv., 2020, 5:2101-2110.

Tue-G6-02

Manufacturing materials for global scale direct air capture

Ryan Lively

Georgia Institute of Technology

Direct CO2 capture from atmospheric air is gaining increased attention as one of the most scalable negative carbon approaches available to tackle climate change if coupled with geological sequestration of CO2. Furthermore, it can also provide CO2 for further utilization from a globally uniform source, which is especially advantageous for economies without natural sources of carbon-based feedstocks. The creation of robust adsorption materials and their manufacturing into low-cost, energy-efficient devices to meet this global challenge will be the focus of the talk. Engineering novel materials—such as solid-supported amines, metal-organic frameworks, and polymers of intrinsic microporosity—into structured contactor adsorption devices shows promise for direct air capture, where scalability is key. Structured sorbent contactors can help manage kinetic and engineering factors associated with the separation, including pressure drop, sorbent stability, and heating/cooling rates. Monoliths, fiber sorbents, and 3D printed materials will be discussed as the three main classes of existing or emerging structured sorbent contactors. Recent developments in their manufacture; advantages and disadvantages of each structure relative to each other and to pellet packed beds; recent developments in system modeling; and finally, critical needs in this area of research will all be discussed.

Tuesday, July 12th | 15:10 - 16:30 | H6-Geochemical and Environmental Systems

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Tue-H6-01

Experimental Investigation of Low Salinity and Low Salinity Polymer in Marmul Oil Field

Intisar Al Busaidi, Rashid Al Mammari, Dawoud Al Mahrouqi, Mahvash Karimi

Sultan Qaboos University

During recent years, some research studies have been performed on hybrid application of polymer and low salinity water flooding (LSWF). Numerous technical and economic benefits of low salinity polymer flooding (LSPF) have been reported. However, as with any EOR technology, there are various risks involved in using LSPF. Ions exchange between porous media and brine is one of crude oil/ brine/ rock (COBR) reactions that identified as a potential risk in LSPF. To the best of our knowledge, this conclusion was drawn based on bulk rheology measurements, and no explanation was provided on how water chemistry changed in the presence of polymer. Therefore, this study aimed to understand rock/ brine interactions with high and low salinity brine in the absence and presence of polymer with Marmul reservoir cores. Many single core flooding experiments were performed with low and high salinity polymer solutions to investigate the influence of partially hydrolyzed polyacrylic amide with different brine salinities on cation exchange reactions. Ion chromatography (IC), Total organic carbon (TOC), rheological, and pH measurements were conducted for produced aqueous phase. A higher increase in pH and lower polymer adsorption was observed in LSPF compared with conventional polymer flooding. In addition, IC measurements showed that all produced fluids in the absence and presence of polymer showed elevated Ca2+, Mg2+, K+, Cl- and SO42- ions compared to the injected fluids. However, the divalent cations levels, mainly Ca2+, were the highest and remained elevated for several pore volumes in the presence of LSP. The results are in line with rheological measurements where the highest viscosity reduction was recorded with the highest level of Ca2+ production. Despite the viscosity loss due to cation exchange reactions, LSP can be attractive alternative to conventional polymer flooding in Marmul field.

Tue-H6-02

Predicting Nanoparticle Photoreactivity in Mixtures of Protein and Natural Organic Matter

Riya Mathew, Marfua Mowla, Sheyda Shakiba, Stacey Louie

Department of Civil and Environmental Engineering, University of Houston

Macromolecules such as natural organic matter (NOM) and protein ubiquitously present in natural water can influence the photoreactivity and aggregation state of titanium dioxide nanoparticles (TiO_2 NPs) for water treatment applications. The adsorption of macromolecules on TiO_2 surface can suppress the reactivity by scavenging the reactive species generated. However, the photoreactivity in the presence of heterogeneous foulant species, such as NOM and protein, is not fully understood. Most prior studies using reaction models implicitly assume the Langmuir-Hinshelwood model. However, this assumption of Langmuirian surface coverage is not necessarily suitable if the adsorbates do not follow Langmuirian adsorption, e.g. in cases of irreversible adsorption. The objective of this study is to predict the influence of complex mixtures of NOM and protein on the photoreactivity of TiO_2 NPs and evaluate the adequacy of the Langmuir-Hinshelwood model in these systems. To compare the photoreactivity behavior across different adsorbed macromolecules under controlled aggregation states, TiO_2 NPs were immobilized on glass rods. The UV-A photodegradation of phenol was first evaluated with single component coatings of NOM or a model protein, bovine serum albumin (BSA), as well as binary component mixtures of NOM and BSA at various concentrations. In the single component experiments, NOM more strongly suppressed the photoreactivity than BSA, which indicates a higher scavenging of reactive species or reaction rate constant of NOM. A competitive reaction model was then used to predict the phenol photodegradation based on the single component reaction rate constants and the adsorbed layer composition in the NOM-BSA mixtures, as predicted using either of two distinct adsorption models, a Langmuir (equilibrium) or kinetic competitive adsorption model. Here, the Langmuir competitive adsorption model was not capable of predicting the adsorbed layer composition in presence of NOM-BSA mixtures, because NOM adsorbs more quickly and is not displaced by BSA. Hence, the adsorbed layer composition was more accurately predicted by a kinetic adsorption model based on Smoluchowski collision rates. Even in cases where BSA concentration was higher than NOM in mixtures, the reactivity was primarily influenced by NOM. SEC analysis also showed that NOM was preferentially degraded compared to BSA, substantiating that it was favorably adsorbed on the NP surface. Therefore, the NP reactivity was predicted by the competitive model only when using the kinetic adsorption model to estimate surface coverages of NOM and BSA, whereas the Langmuir-Hinshelwood model failed to produce accurate predictions. This study concludes that competitive

reaction models should be carefully derived to reflect the true surface coating composition rather than implicitly assuming a Langmuir equilibrium model.

Tue-H6-03

Gypsum Dissolution Under the Effect of Surfactant with Varying Chain Length and Sulfate Analysis

Galip Yiyen, Kodie Duck, Robert Walker

Montana State University

Gypsum - CaSO4·2H2O - is an earth abundant mineral and one of the primary sources of dissolved sulfate in environmental ground and surface waters. Sulfate concentration in groundwater near open-air coal mines can reach concentrations as high as 5000 mg/L, significantly exceeding levels considered safe for human (250 mg/L) and livestock (3000 mg/L) consumption. In this research, surfactant adsorption and its effects on gypsum dissolution were examined and field-applicable sulfate analysis techniques have been investigated. Vibrational sum frequency generation (VSFG) spectroscopy experiments show that the anionic surfactant SDS (sodium dodecyl sulfate) adsorbs to form a highly ordered, conformal film; shorter surfactants including SES (sodium ethyl sulfate) and SOS (sodium octyl sulfate) also adsorb to the gypsum surface forming a covering with some polar ordering but without an observable film. The cationic surfactant DTAC (dodecyl trimethylammonium chloride), in contrast, shows no net polar ordering implying that these surfactants form disordered aggregates. Conductometric titration support these findings and show that SDS solutions suppress gypsum dissolution by 40% relative to DTAC and pure water solutions. Additional evidence of differences between SDS and DTAC adsorption comes from EDX images. EDX mapping shows that SDS was uniformly able to cover the surface, but DTAC adsorption only occurs at rough areas on gypsum surface forming patches and leaving large expanses of the gypsum exposed to solution. These findings imply that the adsorbed SDS film disrupts water structure at the interface and impedes loss to dissolution.

Tue-H6-04

Investigating the role of surface hydrophobicity on silica scale formation using quartz crystal microbalance

Bridget Anger, Xitong Liu

George Washington University

Mineral scaling in membrane-based desalination is a major contributor to increased operational costs and reduced water production. Silica presents a unique issue due to its amorphous nature, which makes it difficult to remove via physical cleaning. Most conventional forms of scaling mitigation practices, including pH adjustment and antiscalant addition, incur high chemical costs or can be ineffective. A promising method of scale reduction is to alter the surface, as certain properties such as charge, topography, and hydrophobicity may influence the free energy barrier for heterogeneous nucleation. The objective of this work is to examine the direct effect of surface hydrophobicity on silica scale kinetics by using a quartz crystal microbalance with dissipation monitoring (QCM-D) to quantify the deposition of silica. While other studies have noted a potential relationship between surface hydrophobicity and scale reduction, they have not controlled for surface charge or topography/roughness which affect the nucleation process. To control the surface charge and topography, neutrally charged self-assembled monolayers (SAMs) of varying hydrophobicity were used to coat the surface of gold QCM sensors. The SAMs were selected based on the end functional group, and comprised of -OH, -CH3, and -CF3. To focus on the impact of hydrophobicity on heterogeneous nucleation on the surface, the experiments were performed with low oversaturated silica solution where there is negligible bulk nucleation. Under these conditions, the rate of silica deposition over 24 hours was compared with the hydrophobicity of the surface. The hydrophobicity of the surfaces as well as the interfacial free energy were calculated from contact angle measurements taken using a contact angle goniometer. These findings were then compared with classical nucleation theory to understand the mechanism of deposition.

Tue-I6-01 Withdrawn

Size and Shape-Tunable Soft Polymer Nanoparticles via Semimicrofluidic Syntheses

Nikunjkumar Visaveliya

The City College of New York

The softness of polymer nanoparticles is advantageous in a myriad of applications based on their characteristics such as accommodating active components in their cores and revealing flexible surfaces to interact with targeted objects. Controlled structural aspects of the polymer nanoparticles such as size, shape, morphology, internal softness, interior cross-linking, and core composition 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, on the other side, such as stimuli-responsive surfaces, wrinkling, surface porosity, shell-layer swellability, layer-by-layer surface functionalization, surface charge, surface roughness, and textures 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 be 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, the state-of-the-art fundamental characteristics of the polymer nanoparticles are presented through experimental results. We have applied a semi-microfluidic approach where initial emulsification has been formed inside the microfluidic channel and the completion of polymerization conducted externally. Therefore the overall process of the formation of polymer nanoparticles is semi-microfluidics.

Tue-I6-02

Synthesis and Assembly of Roughness-Controlled Janus Colloids

Kennedy Guillot, Michael Benton, Bhunvesh Bharti

Cain Department of Chemical Engineering, Louisiana State University

Patchy colloids are particles with heterogeneous surface properties that have emerged as a versatile building block for colloidal materials. Careful design of these particles has enabled their use as surfactant-like microspheres, as well as components for self-assembly with unusual structural motifs. The Janus configuration, i.e., particles with distinct properties in each hemisphere, has shown much promise since its seminal introduction by de Gennes. The synthesis of Janus particles can be a rigorous process, and do not always provide a scalable mechanism. Here, we developed a facile technique for synthesizing Janus colloids with a hemisphere of controlled roughness. Rough Janus colloids employs the partial degradation of a particle, altering the surface morphology of the affected patch. Here a fraction of the surface area of a polymeric particle is exposed to its good solvent which selectively etches the exposes area. This degradation altered the surface morphology of the particles, creating “rough” Janus colloids. This presentation will highlight the synthesis of these roughness-controlled Janus colloids as well as show initial results of the assembly of these rough-smooth microspheres, driven by depletion interactions.

Tue-I6-03

Engineering a Colloidal Metamaterial comprising of Metamaterial-capped Janus Particles for light harvesting applications in cancer detection and therapeutics

Samhita Kattekola, Ilona Kretzschmar, Alexander Couzis

CUNY City College of New York

A material's response to electromagnetic waves is characterized by its electric permittivity, ε, and magnetic permeability, μ. Metamaterials are non-naturally occurring materials with negative electric permittivity and/or negative magnetic permeability, which endow the materials with interesting optical properties as they can be engineered to reverse the Doppler and Vavilov–Cerenkov effects or modify transmission of light through the material. Therefore, these metamaterials can be found in applications such as perfect lenses, cloaking materials, and emission enhancing coatings among others. A newly developing field within metamaterials is metafluidic metamaterials, which couples the properties of metamaterials and fluids. Our research aims to design a new type of metafludic metamaterial, a colloidal metamaterial comprising metamaterial-capped Janus particles. Spherical particles with a metamaterial cap on one side form hyperbolic metamaterial-capped Janus particles. These particles, when dispersed in a fluid, produce the desired colloidal metamaterial. Utilizing the Janus nature of the particle, one half of the particle can be used to impart colloidal properties such as self-assembly, mobility, and dispersibility while the other half can be used to optimize the desired metamaterial effects. The hyperbolic metamaterial used in our research is fabricated by layering alumina, germanium, and silver. The alternating layers of metals and dielectrics produce a negative electric permittivity tensor that forms the basis of the hyperbolic metamaterial. Such materials have been shown to enhance emissions when fabricated on a flat surface. However, the particle surface used to make the novel colloidal metamaterial is curved and is smaller in scale. The particles have diameters in the 1–4 μm (micron) range. We will report on optical properties and effects of the colloidal metamaterial in comparison with the same metamaterial on a flat surface.

Tue-I6-04

Synthesis of Non-spherical Polymer Particles Using the Activated Swelling Method

Giovanni Russo, Marco Lattuada

Department of Chemistry, University of Fribourg

The preparation of particles with non-spherical shapes is a challenging endeavor, often requiring a significant ingenuity, complex experimental procedures and difficulties to obtain reproducible results. In this work we prove that monodisperse non-spherical polymer particles possessing asymmetric Janus structure can be easily produced by using an activated swelling method in combination with a control of the rate of free radical polymerization through the addition of the inhibitors 4-methoxyphenol (MEHQ) and O_2. Monodisperse non cross-linked polystyrene particles, used as seeds, are activated by the addition of an initiator, which promotes their swelling ability, and then swollen with a monomers mixture (methyl methacrylate, glycidyl methacrylate and ethylene glycol dimethacrylate), before being polymerized in presence of both MEHQ and O_2. Our results show that only when both MEHQ and O_2 are present during the course of the polymerization, the particles shape can be controlled, from spherical to asymmetrical. A variety of particles shapes can be obtained, ranging from dimpled spheres, flattened spheres and Janus particles by varying the swelling ratio, always with excellent monodispersity and reproducibility. By following the shape evolution of these particles by means of a Scanning Electron Microscope, we observed the formation and growth of a single poly(MMA-GMA) patch, producing Janus particles. Depending upon the presence or absence of the inhibitors, a collapse/reshaping of the PS side was observed, resulting in non-spherical shapes.

Tuesday, July 12th | 15:10 - 16:10 | J6-Molecules and Particles at Fluid Interfaces

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Tue-J6-01

Growth mechanism of membranes assembled by complexation between polyelectrolytes and nanoparticles at a water-water interface

Wilfredo Mendez, Kathleen Stebe, Daeyeon Lee

University of Pennsylvania Department of Chemical and Biomolecular Engineering

Complexation between oppositely charged polyelectrolytes (PEs) and nanoparticles (NPs) has been used to assemble functional films and membranes that respond to multiple inputs and stimuli. Complexation at interfaces formed in aqueous two-phase systems has emerged as a powerful method to assemble these functional membranes. Remarkably, membranes formed at these interfaces can grow continuously to thicknesses approaching several millimeters and have shown a high degree of tunability over their structure via modification of solution properties such as ionic strength. To identify the mechanism for the growth of such membranes, we study the interfacial assembly of silica (SiO_2) nanoparticles and polydiallyldimethylammonium chloride (PDADMAC) in Aqueous Two-Phase Systems (ATPS) as a function of NaCl concentrations. Using microfluidics tools that facilitate sequential insertion of a fluorescent and non-fluorescent PDADMAC, we identify a gradual change in the growth mechanism of these membranes as a function of NaCl concentration. When membranes are grown at low ionic strength, newly incorporated PDADMAC chains permeate through the existing membrane and undergo complexation with nanoparticles, leading to a well-stratified structure. As the ionic strength is increased, the complexing species distribute more uniformly across the thickness of the membrane, indicating enhanced exchange between the two species. This mechanism change, we believe, is driven by increased numbers of extrinsically compensated charged groups on the nanoparticles and the polyelectrolytes. This PDADMAC/SiO_2 nanoparticle membranes show tremendous potential for the formation of active membranes, where finite control over the internal structure of the membrane can lead to targeted release of materials and highly selective separation of materials.

Tue-J6-02

Droplet-based Langmuir-Blodgett Film Balance for Studying Self-assembled Monolayers at the Oil-Water Interface

Guangle Li, Yi Y. Zuo

Department of Mechanical Engineering, University of Hawaii at Manoa

Langmuir-Blodgett (LB) films have extensive applications in self-assembled monolayers/multilayers, artificial biomembranes, thin-film materials, and nanotechnology. To date, almost all LB films were prepared with the classical Langmuir film balance, developed by Agnes Pockels, Irving Langmuir, and Katharine Blodgett a century ago. The classical Langmuir film balance has a few limitations, such as film leakage from the barriers and walls, restriction on the film compression rate, and difficulties in precisely maintaining the surface temperature, mostly due to its bulky design. Among all these limitations, LB transfer from the oil-water interface is particularly challenging as it requires stacked oil and water layers in the Langmuir trough. Hence, the LB transfer technique has been prevailingly used to study self-assembly at the air-water surface instead of the oil-water interface. In this presentation, we will introduce a novel droplet-based LB film balance that facilitates the study of self-assembled monolayers at the oil-water interface. This miniaturized LB film balance is based on a novel experimental methodology called constrained drop surfactometry (CDS), recently developed in our laboratory. In conjunction with atomic force microscopy, we will show the benefit of CDS in studying the molecular organization and lateral structure of pulmonary surfactant films self-assembled at the oil-water interface. This new droplet-based LB film balance holds great promise in studying molecular and colloidal self-assemblies at the oil-water interface.

Tue-J6-03

Kinetic-limited adsorption of particles to toluene/water interface

Yu Fu, Joelle Frechette

Department of Chemical and Biomolecular Engineering, University of California, Berkeley

Particle-laden fluid interfaces are promising for use in 2D material design and advanced liquid-based device fabrication due to the stability provided by the particles at the fluid interface. However, manipulation and control of adsorbed particles can be challenging, particularly in the case where the interface gets crowded, since particles need to re-organize at the interface to increase coverage. Therefore, understanding particle adsorption dynamics in the late stage is essential for elucidating kinetic limitations due to the presence of energy barrier between crowded interface and adsorbing particles. In this study we report on the evolution of interfacial tension and particle attachment to the toluene-water interface using home-built microtensiometer apparatus with drop radius below 50 um. Smaller drop size leads to faster diffusion such that diffusive transport can be faster than 2D arrangement at the interface, especially at high interfacial area fraction. We characterize the adsorption dynamic of surfactant coated 3-(trimethoxysilyl) propyl methacrylate (F108-TPM) particles (radius 200 nm). Dynamic of adsorption measured for particle bulk concentrations ranging from 0.05g/L to 1g/L. Higher area fraction can be reached using higher bulk concentration. Dynamic interfacial tension data is also compared with the data from pendant drop tensiometry, where the adsorption is mainly governed by diffusion and occurs over a longer time sale due to the larger drop curvature. The dynamic interfacial tension change is also compared with Ward-Tordai model. The deviations between measurements and the model indicate limitations in the the diffusion-limited assumption as well as the irreversible nature of the adsorption process

Tuesday, July 12th | 15:10 - 16:30 | K6-Rheology and Dynamics

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Tue-K6-01

Characterization of length-scale dependent rheology using bi-disperse multiple particle tracking during cell-material interactions

John A. McGlynn, Kelly M. Schultz

Department of Chemical and Biomolecular Engineering, Lehigh University

hMSCs re-engineer their microenvironments to enable basic cellular processes, including motility and differentiation, during wound healing and tissue regeneration. This re-engineering is inherently length-scale dependent and both structure and rheological properties are important factors in retaining native function of hMSCs. During hMSC-mediated scaffold remodeling single cross-links break on the nanometer scale, cellular extensions pull material and degrade paths through the scaffold to enable motility on the micrometer scale and bulk scaffold degradation occurs on macroscopic scales. We measure length-scale dependent rheology during cell-mediated remodeling of the pericellular region using bi-disperse MPT. Traditionally, MPT uses a single particle size to characterize rheological properties. But in complex systems, MPT measurements with a single size particle can characterize distinct properties that are linked to the materials length-scale dependent structure. By varying probe size, MPT can measure material properties associated with different length-scales. Bi-disperse MPT measures length-scale dependent rheology by tracking a bi-disperse population of particles. 0.5 and 2 micron particles are embedded in the same sample and the Brownian motion of these particle populations are tracked separately using a brightness-based squared radius of gyration. The Brownian motion of each particle size is then related to rheological properties using the Generalized Stokes-Einstein Relation. We measure hMSC-mediated scaffold degradation in a well-defined poly(ethylene glycol) (PEG)-peptide hydrogel scaffold. A 4-arm star PEG-norbornene is cross-linked with a matrix metalloproteinase-degradable peptide sequence after exposure to UV light. An adhesion ligand, CGRDS, is also included in the hydrogel to enable cellular adhesion to the network during motility. We measure that cells preferentially re-engineer their microenvironment across length-scales using enzymatic secretions (irreversible degradation) and cytoskeletal tension (reversible degradation). Using bi-disperse MPT measurements we also identify the area where the cell is applying force by extending particle trajectories and identifying points of intersection. From these measurements, we identify that 2 micron particles are stuck in a loose gel network that has been partially degraded and is being reversibly remodeled by the hMSC. At the same time, 0.5 micron particles are measuring irreversible scaffold degradation due to cell-secreted enzymes and are able to diffuse through the larger network structure cells are pulling on. By characterizing evolving length-scale dependent rheology, new materials can be designed which better mimic native tissue and instruct cell behavior.

Tue-K6-02

High-throughput microscopy and microrheology of phase separating coacervates

Yimin Luo, Mengyang Gu, Chelsea Edwards, Megan Valentine, Matthew Helgeson

University of California, Santa Barbara

Composition, rheology, and morphology are highly coupled during phase separation in kinetically evolving complex fluids. Understanding such processes is often hindered by the difficulty in monitoring compositions and properties in situ, in real time, for a wide range of compositional formulations. Here, we report a high-throughput microscopy platform that allows systematic acquisition of image and video datasets for determination of phase morphology and rheology using minimal sample volumes. Using measurements on a system of mixed polyelectrolytes that undergo complex coacervation, we show that the method can be used to simultaneously map the equilibrium liquid-liquid phase boundary as well as kinetic evolution of morphology and rheology during coacervate formation. We find that microrheology can detect subtle signatures of coarsening and rheological aging, providing sensitive measures of ongoing phase separation. At long times, the quasi-equilibrium rheology of the dense phase is measured in situ, enabling sampling of a large data set involving composition-dependent dense phase properties over a wide composition range. We use this data set to interrogate various scaling models that have been proposed for polyelectrolyte coacervates. Using the resulting data-driven viscosity model that empirically relates dense-phase compositions to the zero-shear rate viscosity, we demonstrate that it is possible to reconstruct the binodal phase boundary and associated tie lines with minimal direct measurements of composition by more invasive methods. Overall, the results demonstrate how high-throughput microrheological measurements can be integrated with downstream data-driven modeling to provide a critical link between material discovery, formulation, and design.

Tue-K6-03

Characterizing phase transitions of microfibrillated cellulose induced by anionic and cationic surfactants

Shiqin He [1], Marco Caggioni [2], Seth Lindberg [2], Kelly Schultz [1]

[1] Lehigh University[2] Procter & Gamble Co.

Rheological modifiers are added to products to tune rheology or induce phase transitions with a small amount of material to reach desired rheological behavior. Microfibrillated cellulose (MFC) is a fibrous colloid, which is a waste product from the paper industry, that is renewable and abundant and could be used as a potential rheological modifier. Current fabric and home care products use hydrogenated castor oil (HCO) as a rheological modifier to induce phase transitions and tune the rheology of products. But HCO has an anionic surface which is only compatible with an anionic surfactant, which limits the use of HCO in some formulations. MFC's surface is non-ionic, making it compatible with anionic, cationic and non-ionic formulations. This makes MFC not only a potential substitution for HCO but also broadens its use in other formulations. But the lack of rheological studies of MFC on structure and property changes during phase transitions has so far slowed its introduction into commercial products. This work modifies the surface of MFC and characterizes the change in structure and rheological properties during phase transition when MFC is contacted with anionic and cationic surfactants. The MFC surface is oxidized using TEMPO oxidation to introduce carboxyl groups to the surface. The oxidized MFC (OMFC) is contacted with an anionic surfactant, sodium dodecyl sulfate (SDS), or a cationic surfactant, benzyldimethyldodecylammonium bromide (BDDAB), to induce gelation. Gelation is characterized using multiple particle tracking microrheology (MPT). In MPT, fluorescent probe particles are embedded in an OMFC sample and their Brownian motion is measured and related to rheological properties. Using MPT, we measure that OMFC has different rheological properties and microstructures during the sol-gel transition when contacted by anionic or cationic surfactants. When OMFC is in contact with an anionic surfactant, the gelation process is gradual and the area of the OMFC sample shrinks during network formation. When OMFC is in contact with a cationic surfactant, the gelation process is fast. OMFC gels the moment it contacts the cationic surfactant and the OMFC sample remains in its original shape without a change in overall area. These two distinct gelation processes indicate that the gelation mechanism depends on the charge of the contacting surfactant. During gelation with anionic surfactant, the OMFC colloidal fibers are able to rearrange while forming a more compact gel. In gelation with cationic surfactant, the rearrangement between the colloidal fibers is limited by fast gelation causing the colloids to remain in relatively the same location but still form a network. This work modifies the surface of MFC and determines that the microstructure and rheological properties of MFC is dependent on the type of surfactant that it interacts with during the sol-gel transition. This will enable the use of MFC as a rheological modifier for diverse formulations in fabric and home care products.

Tue-K6-04

Isolating the yield transition in thixotropic cellulose nanocrystal gels

Elnaz Nikoumanesh, Ryan Poling-Skutvik

University of Rhode Island, Department of Chemical Engineering

Colloidal gels often exhibit strong aging behavior in which rheological properties increase with time after gelation and thixotropy in which the rheological properties depend strongly on shear history. These aging and thixotropic phenomena obscure the yield transition, leading to ambiguous definitions that make it challenging to compare results across different experimental or processing conditions. Here, we explore the yielding of salt-induced gels of cellulose nanocrystals (CNC) and identify a rheological procedure to unambiguously define the yield transition in the presence of aging and thixotropy. The CNC gels are prepared at a volume fraction of 3% CNC to which a small amount of NaCl is added to reach ionic strengths ranging from 10^{-3} to 10^{0} M. The addition of salt immediately destabilizes the CNC to form gels with elasticities that increase with increasing salt concentration. We characterize the aging and thixotropic properties of these gels using linear oscillatory rheology measurements. Additionally, we perform shear start up and oscillatory amplitude sweeps as standard methods to characterize the yield transition. From these measurements, we observe that the yield stress increases with increasing salt concentration but also increases with waiting time between yielding events as the material ages and repairs its internal structure. To quantify these dynamics and to isolate the yield transition, we use a series of creep measurements. As the applied stress increases, the material exhibits a critical transition between solid-like and fluid-like regimes that clearly identifies the yield stress of the material independent from thixotropic or aging effects. Finally, we relate the thixotropy of these materials to the underlying dynamics of the CNC to identify the mechanisms by which these gels break and reform bonds. Our results provide insight into how colloidal particulates form elastic gels and how these gels respond to complex processing deformations.

Tuesday, July 12th | 15:10 - 16:30 | L6-Surface science and catalysis

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Tue-L6-01

Controlling the Photocatalytic Properties of Colloidal Quantum Dots using Surface Ligand Chemistry

Matthew Beard

National Renewable Energy LaboratoryRenewable and Sustainable Energy Institute, University of Colorado, Boulder

Colloidal semiconductor nanocrystals, specifically quantum dots (QDs), are of interest to numerous scientific disciplines due to their highly tunable optical and electronic properties. I will discuss our efforts in controlling the optical and electrical properties of QDs using various ligand chemistries. I will discuss how the ligand dipole moment can impact ligand exchanges, the bandedge position and photoredox catalytic reactions. By taking advantage of ligand-ligand coupling on the QD surface we can construct Janus-ligand shell systems. Which are ligand shells where one half the QD is covered in one type of ligand and the other half with a different ligand. We show that such asymmetric ligand-shells can be used to make artificial pyroelectric films and they form Pickering emulsions in solution. We demonstrated that such emulsions that are photoactive could be used in photocatalytic systems. We have also produced ligand exchange strategies to produce n and p-type PbSe colloidal QDs. We studied electronic impurity doping of colloidal PbSe quantum dots (QDs) using a post-synthetic cation exchange reaction in which Pb2+ cations are exchanged for either Ag+ or In3+ cations. Finally, I will discuss photocatalytic studies using metal-halide (CsPbBr3) nanocrystals doped with a Cu+ transition metal catalyst. The Cu+ binds substrates to the heterogeneous NC surface allowing for a novel two-photon induced N-N bond forming reaction.

Tue-L6-02

Leveraging the Young-Laplace effect in plasmonic nanocrystals for enhanced photothermal catalysis

Matthew Crane

Colorado School of Mines

Nanomaterials have emerged as a promising platform for scalable photocatalysis, including low-cost water purification, efficient CO2 conversion, and nitrogen fixation, due to their high surface area to volume ratios and size-tunable electromagnetic and catalytic properties. In typical solution-phase reactions using these catalysts, global resistive heating of solvents containing reactants and nanocrystals drives chemistry under isothermal conditions. However, temperature constraints due to solvent boiling points limit accessible chemistries as well as reactor designs without complex temperature and pressure management equipment, hindering the distribution of these technologies. As a result, many enticing reactions remain inaccessible to colloidal chemistries. Here, we present a new paradigm for driving colloidal chemistries through local, non-isothermal photothermal heating, rather than global, isothermal resistive heating. To quantify achievable temperatures, we investigate the solution-liquid-solid growth of semiconductor nanowires as a prototypical high-temperature chemistry. We show that plasmonic metal nanocrystals dispersed in solution can act as both light absorbers to locally heat and decompose reactants as well as directors for the solution-liquid-solid growth of semiconductor nanowires. Heat transport calculations combined with thermographic imaging show that the Young-Laplace effect suppresses boiling to enable high temperature nanomaterial growth via collective local heating. These observations are validated by single particle photothermal studies in optical tweezers, which reveal the importance of solvent selection. This local heating, rather than traditional global resistive heating, removes restrictions on synthesis equipment and permits the growth of nanomaterials on the benchtop, without complex reactors. To highlight this advantage, we demonstrate continuous colloidal nanowire growth with this process. Based on insights from single-particle temperature measurements and heat transfer analysis, we conclude with future directions to enhance photothermal chemistries.

Tue-L6-03

Energetics of Reaction Pathways Enabled by N and H Radicals during Catalytic, Plasma-Assisted NH_3 Synthesis

Tsung Wei Liu, Diego Gómez-Gualdrón

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Plasma-assisted catalysis is emerging as an alternative to several thermocatalytic processes. For ammonia synthesis, it could make the process milder, which would help production, decentralization, and compatibility with renewable energy. However, one major obstacle preventing optimization of the plasma-assisted process is the incipient mechanistic understanding of ammonia formation on plasma-exposed catalysts. Here, optical emission spectroscopy is consistent with only a weak effect of the metal on plasma composition and with the presence of small concentrations of plasma radicals in N_2/H_2mixtures in dielectric barrier discharge (DBD) reactors, which are bound to enable new catalystinvolved pathways not considered in previous kinetic models for NH_3 synthesis. Thus, we comprehensively examined, via density functional theory calculations, the energetics (favorability) of 51 reactions on Fe, Ni, Co, Pd, Ga, Sn, Cu, Au, and Ag. Enthalpic barriers for Eley – Rideal (ER) reactions involving N•and H•radicals were found to be negligible and hence supportive of the following: (i) plausible NNH formation and consequent prominent role of the associative pathway to form NH_3(consistent with some experimental reports detecting surface-bound $N_XH_Y$species), (ii) likelihood of N• adsorption taking over N_2*dissociation as the primary source of surface bound N * , and (iii) probable dominance of ER hydrogenation reactions over Langmuir – Hinshelwood ones. The energetics herein presented will allow thoroughly studying the pathway competition in future kinetic models, but numbers calculated here already suggest that the dominant pathway may change with the metal identity. For instance, N_2H_Ydissociation favorability is more likely to become competitive with ER hydrogenation earlier in the hydrogenation sequence the more nitrophilic the metals. Yet, the calculated favorability of ER reactions is also already consistent with the weaker dependence of initial NH_3 turnover frequencies (TOFs) on metal identity compared to the thermocatalytic scenario. With practical implications for computational catalyst screening, TOFs experimentally measured herein for an atmospheric DBD reactor linearly correlate with Δ Erxn for the ER hydrogenation reaction $H\bullet + HNNH_2^* \rightarrow HNNH_3^*$. This descriptor may be robust to exact synthesis conditions, as its correlation with TOFs was maintained for earlier TOF data in a subatmospheric radio frequency reactor.

Tuesday, July 12th | 15:10 - 16:30 | M6-Wetting & Adhesion

Tue-M6-01

Simulations of binary droplets impacting surfaces

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Droplets Impacting with surfaces to achieve desired coatings, or cleaning surfaces are a commonly encountered process in the field of protective coatings. The behavior of a colliding binary liquid droplet is sensitive to the impact velocity, surface wetting properties and the droplet composition. Here we report on detailed modeling (molecular dynamics (MD) and classical density functional theory (cDFT) studies of impacting droplets as well as interfacial surface free energies. The presence of a two components in the liquid drop makes the surface collision a much more complicated problem. During the collision the the kinetic energy of the entire drop is quickly converted into heat. Thus, the temperature varies during the collision and indeed, throughout the droplet. We capture two extreme situations by performing both adiabatic (constant energy) and isothermal (constant temperature(T)) simulations. The type of binary AB fluid mixture is purposely kept simple. That is, we let the AA and BB interactions be identical. Furthermore, we keep the A and B diameters equal and simply multiply the Lorentz-Berthelot energy parameter for the AB cross-interaction by a mixing constant. To mimic demixing, the mixing parameter is varied from on the interval from 0 to 1. Although the mixture is kept simple, interesting phase behavior is observed during the droplet collision. For certain sets of conditions (e.g., T, droplet composition, impact velocity, mixing parameter) the droplet is seen to simply vaporize into a binary gas phase. However, for others the simulation results in a phase separated droplet. That is, a resulting droplet consisting of A rich and B rich regions. These regions, however, do not take off separately (i.e., detach) but rather stay attached. To investigate this curious behavior, we used cDFT to explore the effects of the mixing parameter on the phase diagram of the binary AB mixture. We determined the location of liquid-vapor (LV) and liquid-liquid (LL) phase separation. In addition, we computed the value of the interfacial tensions of the LL and LV interfaces. These can be used to predict when an A rich and B rich droplet will stay attached and when they will detach. Although the colliding droplet represents, initially, a non-equilibrium system, the phase diagram is used to provide insight into the observed phenomena.

Tue-M6-02

Air entrainment dynamics under xanthan gum droplets from dilute to semi-dilute regimes

Ziwen He, Huy Tran, Min Pack

Baylor University

An interstitial air layer is formed upon impact of a liquid droplet on a smooth surface to cushion the motion of the impacting droplet. Although this air-cushioning effect of Newtonian droplets on surfaces has been studied extensively, viscoelastic effects of aqueous polymeric droplets is the focus of this study. Here, we report that for a certain range of Weber number We~*O*(1-10) , the air film profile is a function of the concentration of the xanthan gum droplets. The air film slope increases with the increasing concentration within dilute regime, whereas decreases after the critical concentration within the semi-dilute unentangled regime. The submicron air film is visualized by a high-speed total internal reflection microscopy (TIRM) technique, which displays the altered air film slope accompanied by varieties in the polymer concentration.

Tue-M6-03

Water Content Effects Cyclopentane Hydrate Contact Angle and Film Growth in the Presence of Natural Surfactants

Hannah Stoner, Jon Wells, Chaffin Ross, Jefferson Moak, Jose Delgado-Linares, Carolyn Koh

Center for Hydrate Research - Colorado School of Mines

Gas hydrates are solid inclusion compounds of hydrogen-bonded water cages stabilized by gas molecules. They typically form at high pressures and low temperatures making them a promising natural resource in deep marine sediments and polar caps, while being a nuisance in oil and gas flow lines. Cyclopentane is a convenient low pressure analog to gas hydrates formed in petroleum lines and is used in this study to evaluate the effect that varying water content has on the wettability of the hydrate surface in the presence of natural surfactants. The presence of these natural surfactants creates a highly hydrophobic hydrate surface and delays both the onset and rate of film growth on the water droplet at small concentrations at 0.02 vol% of the oil phase. When the concentration amount of water in the system is increased, dilution of the natural surfactants occurs and the effects of the natural surfactants at the surface are greatly reduced. There may also be a thicker water layer present on the hydrate surface which fills pores. This makes the hydrate surface more hydrophilic based on the measured value of the contact angle. Presence of natural surfactants also exhibits small kinetic inhibition effects based on the reduction of the hydrate film growth rate on the water droplet. Higher hydrate wettability and quicker film growth leads to “stickier” hydrates that are more likely to agglomerate and plug the flowline. This has implications for gas hydrate flow assurance applications that give insight to hydrate mitigation approaches. We would like to thank the NSF for funding from CBET Award #201520 and the CHR Consortium for the facilities used.

Tue-M6-04

Cold Spray of Polystyrene Particles on Various Substrates

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Cold spray (CS) is a solid-state coating technique that has been used since the 1980's for a wide range of applications of metals, polymers, ceramics, and composites on various substrates. During the cold-spray process, particles are accelerated to high speeds (above the speed of sound; Ma > 1) through a converging and diverging nozzle with a pre-heated, high-pressure gas. Upon impact on a substrate, at sufficient velocities, particles deposit to form a non-porous coating on the substrate that is caused by severe plastic deformation of the particle. The bond that forms between the particle and the substrate can be metallurgical, chemical, or mechanical. Cold spray of polymers has been investigated to a lesser extent than metals, and since polymers behave significantly differently than metals during cold spray, many inquiries into the relevant physical behaviors still exist, limiting potential, commercial utilization. Cold spraying of polymers have many potential applications, including surface protection from corrosion, protection from cavitation erosion or mechanical impacts, electronic applications, and biocompatible and antibacterials coatings. However, the deposition efficiency of polymer cold spraying being very low (10%) when compared to metal cold spraying (~100%) limits the viability of these applications. This study focuses on cold spraying of as-is and functionalized polystyrene particles on polymeric and aluminum substrates. A number of different process conditions were investigated to achieve buildup of particles on the substrates. Analysis was performed to characterize the deposition thickness on each substrate. Promising results were obtained with polymeric substrates when the gas temperature and substrate heating was kept around the glass-transition temperature of the as-is PS particles. The deposition on the aluminum substrates is still an ongoing investigation that is mainly focused on the first-layer adhesion, since the first couple of layers of deposited particles plays a key role during the process.

Tuesday, July 12th | 16:45 - 17:45 | Z3-Unilever Award Lecture

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Tue-Z3-01

From hairy nanocelluloses to granular hydrogels: *Colloidizing* bio-based materials for environmental and healthcare applications

Amir Sheikhi

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Soaring population growth, supply and demand imbalance, shortage of ready-to-use remedies, and urbanization have imposed unprecedented challenges to satisfying the world's essential needs. In the **B**io-**S**oft **Ma**terials **L**aboratory (***B-SMaL***), we aim at addressing some of the quintessential challenges of the 21st century in healthcare and environment by developing colloidal systems based on the micro- and nanoengineering of abundant biopolymers. In this talk, I will first explain how the most abundant biopolymer in the world, cellulose, is chemically converted to a newly emerged colloid, called hairy cellulose nanocrystals (HCNC) with fundamentally different colloidal properties compared with conventional cellulose nanocrystals (CNC). I will show how such differences have enabled the applications of HCNC in sustainable development, ranging from rare-earth element recovery and water/body fluid treatment to threshold scale inhibition. I will then discuss how emulsifying gelatin (a derivative of the most abundant protein in the body, collagen) yields an *in situ* forming, bio-orthogonal microporous hydrogel platform with orthogonal stiffness and porosity that is nontrivial to create using bulk hydrogels. Colloidal engineering of this class of microfluidic-enabled modular hydrogels has enabled accelerated tissue repair and 3D bioprinting of tissues. Together, these platforms show the power of bio-based colloids to leverage eminent, cost-effective technologies for improving the quality of modern life.

Wednesday, July 13th | 08:00 - 09:00 | Z4-LaMer Award Lecture

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Wed-Z4-01

Engineering at the Nano-Bio Interface: Protein Corona Formation on Carbon Nanotube-based Sensors

Rebecca Pinals [1], Markita Landry [2]

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Engineered nanoparticles are poised to transform sensing, imaging, and delivery in biological systems due to their advantageous optical and physical properties. Specifically, single-walled carbon nanotubes (SWCNTs) possess tissue-transparent and photostable near-infrared fluorescence that renders them uniquely suited for accessing biological systems. SWCNT-based constructs have been formulated into selective fluorescent probes, such as DNA-functionalized SWCNTs that operate at spatiotemporal scales necessary to capture information on chemical signaling events including dopamine neuromodulation in the brain.1 The critical – and often overlooked – challenge with these nanoscale tools is understanding the fundamental mechanisms of interaction between the nanoprobe and the system they are designed to query. When a nanoparticle enters a biological system, the surface becomes rapidly coated with proteins to form the “protein corona”. Binding of proteins to the nanoparticle disrupts intended nanoparticle functionality and leads to unpredictable in vivo outcomes. A comprehensive understanding of the protein corona remains a paramount barrier to successfully implementing nanotechnologies within biological environments. Herein, I present multimodal characterization of (i) protein corona composition, (ii) driving forces of formation, and (iii) kinetics of protein adsorption on DNA-SWCNTs in relevant biological media. I have optimized a platform to quantitatively characterize protein corona composition formed on nanoparticles by mass spectrometry-based proteomics to determine abundant and differentially enriched vs. depleted corona proteins.2 By varying incubation conditions of DNA-SWCNTs in biofluids, I investigated interactions driving selective protein corona formation. To study the dynamic exchange of biomolecules on the SWCNT surface, I developed a multiplexed fluorescence assay that enables real-time tracking of biomolecule adsorption and desorption events.3 Finally, I extend these studies to inform the development and application of a predictive supervised learning model.4 Understanding the protein corona composition, timescales and driving forces of formation, and dynamics under relevant solution conditions informs design and synthesis of nanotechnology-based tools applied in protein-rich environments. Although corona formation can impair nanobiotechnology efficacy, it also presents an opportunity to create improved protein-nanoparticle architectures by exploiting selective protein adsorption to the nanoparticle surface. I will conclude by discussing how these design principles can be applied to create new nano-bio constructs, specifically, for SARS-CoV-2 spike protein sensing.5 In this work, I develop techniques and analyses to characterize the in situ protein corona and employ this knowledge towards rational design of nanobiotechnologies.

References 1. Beyene, A. G. et al. Imaging striatal dopamine release using a nongenetically encoded near infrared fluorescent catecholamine nanosensor. Science Advances 5, eaaw3108 (2019). 2. Pinals, R. L. et al. Quantitative Protein Corona Composition and Dynamics on Carbon Nanotubes in Biological Environments. Angewandte Chemie International Edition 59, 23668–23677 (2020). 3. Pinals, R. L.,* Yang, D.,* Lui, A., Cao, W. & Landry, M. P. Corona Exchange Dynamics on Carbon Nanotubes by Multiplexed Fluorescence Monitoring. J. Am. Chem. Soc. 142, 1254–1264 (2020). 4. Pinals, R. L.,* Ouassil, N.,* et al. Supervised learning model predicts protein adsorption to carbon nanotubes. Science Advances 8, eabm0898 (2022). 5. Pinals, R. L. et al. Rapid SARS-CoV-2 Spike Protein Detection by Carbon Nanotube-Based Near-Infrared Nanosensors. Nano Lett. 21, 2272–2280 (2021).

Wednesday, July 13th | 09:30 - 11:10 | B7-Colloidal & Interfacial Forces

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Wed-B7-01

Effects of dispersity on the conformation and response of polymer brushes

Jacinta Conrad

Department of Chemical and Biomolecular Engineering, University of Houston

Polymer brushes grafted to surfaces are ideal candidates to manipulate interfacial properties due to their low cost, facile processability, high flexibility, and stimuli-responsive behavior. A critical challenge in tailoring the functionality of these surfaces is in understanding how the brush conformation, dictated in part by the polymer molecular weight distribution, affects the responsive behavior. In this talk I will describe experiments on flat and spherical brushes in which we explore the effects of polymer dispersity on the conformation of polymer brushes grafted to surfaces, and characterize the effects of dispersity on the response to changes in solution pH. These experiments reveal that dispersity can be used as a design parameter to tunably control the responsive behavior of these soft, functional interfaces.

Wed-B7-02

Interfacial Assemblies of Star and Linear Polyelectrolytes

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We report on the effect of the molecular architecture of poly(acrylic acid) (PAA) on its interdiffusion within ultrathin films formed via electrostatic layer-by-layer (LbL) assembly with poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA). Ellipsometry and neutron reflectometry were used to compare the degree of interdiffusion of star or linear PAA within the assembled films. In-situ ellipsometry revealed that when PAA sequential layers were formed on top of pre-assembled wet films, star PAA was more diffusive, with the diffusion coefficient of an 8-arm star polyacid being ~3.5-fold higher than that of its linear counterpart. The difference in the degree of polymer interdiffusion within films of star and linear PAA was also evident in neutron reflectometry experiments performed using deuterated PDMAEMA to provide contrast between layers. Applying a limited-source diffusion model, we observed up to a 10-fold increase in the diffusion coefficient of PDMAEMA in star compared to linear PAA-containing films upon exposure to salt solutions. We suggest that the higher mobility of star polymers results from a smaller number of contacts between PDMAEMA star and PAA linear polymers, and support this conclusion by FTIR measurements of a lower ionization degree of assembled star PAA, and by isothermal titration calorimetry (ITC) studies of interpolymer binding in solution that exhibit a lower PDMAEMA-to-PAA ratio and higher dissociation constants for star PAA/PDMAEMA complexes.

Wed-B7-03

Colloidal Deposition & Detachment: Roles of Polymers, Surfactants, Roughness, and Shear

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This talk will present findings on colloidal deposition and detachment in personal care products due to dilution of polymer-surfactant mixtures, shear flow, and different particle surface roughness morphologies. 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 combination of single component mediated interactions. We then employ a flow cell-microscopy assay for in situ characterization of colloidal deposition and detachment as a function of dilution and shear flow. Results show three deposition/detachment stages as a result of non-equilibrium composition changes during dilution: (1) initial compositions producing depletion attraction normal to substrates with no resistance to shear detachment, (2) intermediate compositions due to polymer-surfactant complexes yield little attraction and in some cases repulsion, and (3) preferential surfactant dilution ultimately results in normal and tangential bridging attraction producing deposition and detachment resistance. The presence of particle roughness, which weakens normal attractive interactions, is also found to produce adhesive torques in the presence of either depletion or bridging attraction to resist shear detachment. All normal and tangential interactions are accurately captured by position and orientation dependent energy landscapes as the superposition of DLVO, depletion, steric, and bridging potentials including a novel approach to model the geometry of rough particle surface morphologies. The success of these measurements and models suggests their validity to investigate and understand new formulation compositions, novel materials, different processing methods, and diverse applications involving particle deposition.

Wed-B7-04

Influence of Charged Residue Identity on Hydrophobic Interactions Mediated by Amphiphilic Helices of α-Peptides

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The hydrophobic interaction governs water-mediated colloidal and biophysical processes such as molecular recognition and protein folding. Both experiment and simulation have contributed to an understanding of hydrophobic interactions of non-polar solutes and surfaces, but hydrophobic interactions encoded by nanoscopic patterns of non-polar, polar and charged groups such as encountered with proteins remain poorly understood. We report single-molecule force measurements on conformationally flexible α-peptides capable of forming parallel coiled-coil dimers to explore how charged residue identity (lysine versus arginine) influences hydrophobic interactions of the single oligopeptides with model non-polar surfaces. We quantify hydrophobic interactions by comparing force measurements performed in aqueous buffer and aqueous buffer containing 60 vol. % methanol, where the latter solvent composition largely eliminates the hydrophobic interaction. We find that the lysine-bearing α-peptides, which display a global segregation of non-polar and lysine-rich domains in an α-helical conformation, exhibit strong hydrophobic interactions (1.00 ± 0.10 nN). We interpret this result to indicate that an α-helical conformation was induced by the hydrophobic interaction of the peptide with the non-polar AFM tip, a conclusion that is supported by ATR-FTIR measurements. Additional support for this interpretation is obtained by using a sequence isomer that cannot adopt a globally amphiphilic α-helical conformation (confirmed by ATR-FTIR to remain largely random coil) and is found to not mediate measurable hydrophobic interactions. In contrast to its lysine counterparts, both amphiphilic and scrambled arginine-containing α-peptides display very weak hydrophobic interactions (0.29 ± 0.02 and 0.17 ± 0.02 nN, respectively), evidenced by their random coil secondary structures measured using ATR-FTIR. Overall, these results reveal that the profound influences of identity of proximal charged and polar groups on hydrophobic interactions, which we previously reported using conformationally rigid β-peptide oligomers, extend to the interactions of α-peptides with non-polar surfaces.

Wed-C7-01

Dynamics of competitive adsorption: proteins and surfactants vying for a spot at the air-water interface

Ankit Kanthe, Charles Maldarelli, Raymond Tu

The City College of New York - CUNY Department of Chemical Engineering

Monoclonal antibodies (mAbs) have become a leading candidate for oncology-based therapeutics due to their unparalleled selectivity towards antigen binding. However, the adsorption of mAbs at the air-water interface is a critical issue in the production and use of antibody-based pharmaceuticals. Air/water interfaces are ever-present during the manufacture (filtration, chromatography) and production (freezing, thawing, filtration and filling) of the drug product, and air/water interfaces continue to be present during the storage, transportation, and administration of therapeutics to the patients. When an air/water interface is created, the antibodies will expose their hydrophobic residues to the gas phase leading to irreversible adsorption, partial unfolding, interfacial aggregation, and recruitment of additional proteins from the solution phase. Taken together, this leads to decreased yields in the native conformation of protein films and shortened shelf life of the mAb-based therapeutic drugs. The pharmaceutical industry uses multicomponent systems to circumvent adsorption issues, adding ‘inert’ surfactants to the mAb formulations. However, the mechanism of the adsorption behavior of a large surface active biomacromolecule in the presence of surfactants is still an open scientific question. This presentation will discuss how we quantify the critical parameters and construct a general model to understand the competitive adsorption process. We also attempt to elucidate the molecular scale behavior of macromolecules adsorbing and unfolding at the air-water interface.

Wed-C7-02

Using Liquid Crystals to Characterize the Deformability of Red Blood Cells Infected by Malarial Parasites

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Red blood cells (RBCs) are efficient transporters of oxygen in our bodies because their high deformability allows them to pass through narrow blood capillaries. However, during certain diseases such as malaria, the deformability of RBCs decreases, leading to pathological consequences. In this presentation, we will describe new approaches based on the use of aqueous liquid crystals (LCs) to characterize the mechanical properties of RBCs at the single-cell level. First, we will show that LC elasticity strains healthy RBCs into complex folded shapes that depend on the mechanical properties of the RBCs. We observe the membrane shear moduli of RBCs from a single donor to vary by more than one order of magnitude, revealing a large cell-to-cell variability. Second, we will describe the use of LC elasticity to characterize the mechanical properties of RBCs infected by the malaria parasite, *Plasmodium falciparum*. Specifically, we will report how the deformability of malaria parasite-infected RBCs changes with the stage of infection. Overall, these observations demonstrate the utility of LC elasticity for studying the mechanical properties of RBCs at the single-cell level.

Wed-C7-03

Cholesterol induced morphological transitions and instabilities

Cain Valtierrez-Gaytan [1], Joseph Barakat [2], Bjorn Solberg [3], Benjamin Stottrup [3], Joseph Zasadzinski [1]

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Phase separation and domain formation is important in lung surfactants (LS) in which a lipid-protein mixture 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 of LS leads to neonatal respiratory distress syndrome (NRDS) in premature infants; NRDS occurs in roughly 30,000 premature births each year when babies are born before the LS system in the lungs is fully developed. The inhibition of LS can be life threatening and can result in acute respiratory distress syndrome (ARDS) which has a 40% mortality rate. Natural LS is composed of many constituents, however to elucidate the role of composition on LS function we focus on dipalmitoylphosphatidylcholine (DPPC), hexadecanol (HD) or palmitic acid (PA), and dihydrocholesterol (DChol). In this work we show the spontaneous evolution of semi-circular domains to extended uniform stripes via a fingering instability at constant surface tension and temperature. In these systems crystalline-like domains grow in a liquid-like matrix due to a competition between interfacial and electrostatic interactions. It was found that semi-circular domains form at low levels of system compression with a crystal stoichiometry of 2:1 DPPC to HD/PA stoichiometry ratio (as indicated by mass balance and x-ray diffraction). The idea is that as this co-crystal nucleates and grows, HD or PA is depleted from the liquid phase and excess DPPC and all the DChol is concentrated in the liquid phase. As the interfacial tension of the system is decreased (and we effectively crosses the DPPC-DChol coexistence phase boundary) the excess DPPC from the liquid phase epitaxially grows on the existing crystal and this causes the line tension of the resultant domains to decrease. This decrease in line tension is sufficient that perturbations of the domain boundary result in fingering instabilities (Mullins-Sekerka theory). The domain shape then transitions towards a stripe phase due to the system now being electrostatically dominated as a function of time at static experimental conditions. It is further shown that this stripe phase is an equilibrium state (supported by continuum theory) and reversibility experiments. Thus, it is effectively shown that a system can spontaneous transition from a kinetically trapped state to an equilibrium state via an instability growth pattern.

Wed-C7-04

Biodegradable polymersomes with encapsulated indocyanine green J-aggregates for highly selective photoacoustic cancer imaging

Mohammed Kawelah [1], Ceren Atila Dincer [1], Sangheon Han [2], Thomas Truskett [1], Konstantin Sokolov [2], Keith Johnston [1]

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Photoacoustic imaging (PAI) is an emerging modality for molecular and functional imaging with high sensitivity and tissue penetration of up to a few centimeters. Amongst many exogenous near-infrared contrast agents, indocyanine green J-aggregates (ICGJ) are one of very few with FDA approval. These J-aggregates undergo rapid dissociation in serum and thus must be protected. Herein, we successfully encapsulated ICG J-aggregates in polymersomes using all FDA-approved materials via self-assembly of poly(lactide-co-glycolide-b-polyethylene glycol) (PLGA-b-PEG) using a double emulsion solvent evaporation method. The surface of these polymersomes was conjugated with a monoclonal antibody using click chemistry to target epidermal growth factor receptors (EGFR) associated with breast cancer cells. The polymersomes have an optimum size range of 80-90nm for enhanced permeability and retention (EPR) effect and rapid cellular uptake and strong NIR absorbance at 890nm with low cytotoxicity in breast cancer cells. The encapsulated J-aggregates inside the polymersomes were stable in 80% fetal bovine serum for more than 24 hours under both neutral and acidic conditions, a sufficient time for photoacoustic imaging. In the future, the polymersomes may be designed for high payloads of targeted chemotherapeutic drugs together with ICGJ for photo-guided delivery to tumor sites as well as for image-guided cancer surgery.

Wed-C7-05

Confinement of triple enzyme cascade in layered double hydroxide-based nanocomposites to prevent oxidative stress

Adél Szerlauth [1], Tamara Madácsy [2], Árpád Varga [2], Dániel Sebők [3], József Maléth [2], István Szilágyi [1]

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In normal physiological conditions, reactive oxygen species (ROS) are balanced by antioxidants [1]. If such a balance is shifted towards ROS, various diseases may develop in human body or in other living creatures. Antioxidant enzymes are produced to prevent ROS-induced illnesses, but their sensitivity to environmental conditions (pH, radiation, temperature, etc.) hinders their applicability and supplementation. Immobilization or encapsulation in/on carrier materials is a promising tool to eliminate this problem. In our study, three antioxidant enzymes, horseradish peroxidase (HRP), superoxide dismutase (SOD) and catalase (CAT) were immobilized on delaminated layered double hydroxide (dLDH) to achieve sufficient and broad-spectrum ROS scavenging activity, while sodium alginate (Alg) and trimethyl chitosan (TMC) were applied to tune colloidal stability (see scheme for the composition) [2,3]. The immobilization was carried out via the sequential adsorption method, in which electrostatic interactions played a major role and were monitored by electrophoretic light scattering. By analysing the resistance against salt induced aggregation in time-resolved dynamic light scattering, remarkably high critical coagulation concentration was determined indicating the applicability of the composite in electrolyte solutions. Small angle X-ray scattering (SAXS) measurements were performed to explore the formation of polyelectrolyte and enzyme layers and it was found that the surface became diffuse rather than formation of rigid layer-by-layer assembly. The adsorption of enzymes was further confirmed by direct stochastic optical reconstruction microscopy (dSTORM) measurements. By labelling the enzymes with fluorescent dyes, dSTORM measurements proved that after incubation with HeLa cells, the composite penetrated trough the cell membrane without any cellular damage by the nanomaterial. Finally, it was unambiguously proved that the developed hybrid material acts as an effective antioxidant agent and that it was effective in preventing DNA double strand breaking processes. Thus, our composite is a promising tool in ROS scavenging and DNA repairing processes both in biomedical and in industrial applications.

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Wed-C7-06

Antioxidant co-immobilized multi-enzymatic colloids by sequential adsorption

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In nature, almost all the reactions in cells are catalyzed by cooperation of various enzymes and enzyme catalysis also has a primal role in biochemical industrial processes. Oxidoreductase enzymes are of special importance for the fight against oxidative stress by keeping the reactive oxygen species (ROS) at an optimum level. Oxidative stress giving rise to damage of cellular components and causes significant loss in the quality of industrial products. In some of the later cases, only peroxidase enzymes are needed, however, when they are used together with superoxide dismutase enzymes, they perform a cascade reaction leading to the complete decomposition of ROS to water and oxygen. Enzymes, on the other hand, are sensitive of any major changes occurring in their surrounding environment. This major drawback can be overcome by immobilization on solid supports, which also offers several technical advantages in the industrial applications [1]. Nanostructured materials provide ideal characteristics for the co-immobilization of different enzymes to obtain multi-enzymatic systems. However, the particle aggregation is a critical issue in these applications, since the experimental conditions influence the charging and the aggregation processes and thus, the colloidal stability of these dispersions [2]. Sequential adsorption method with the application of polyelectrolytes (PE) is a self-evident way to immobilize multi-enzymatic systems in the nanostructures. In this method, the PE multilayers act as a support layer and also a separator between the proteins. On the other hand, they ensure high colloidal stability for the system.

Here we present two example for co-immobilized multi-enzymatic composite system on different support built-up by the sequential adsorption method. On one hand, superoxide dismutase (SOD) and horseradish peroxidase (HRP) was co-immobilized on inorganic titania-nanosheet support by the application of poly-diallyldimethylammonium (PDADMAC) and poly-styrenesulfonate (PSS) to obtain the TNS-PDADMAC-SOD-PSS-HRP composite material [3]. On the other hand, papain (PPN) and HRP enzyme was co-immobilized on sulfate latex (SL) particles, where heparin (HEP) was used as an intermediate PE layer between the enzymes to obtain the SL-PPN-HEP-HRP hybrid material [4]. The enzyme and PE doses were optimized in each step of the sequential adsorption and the colloidal stability and charging properties was also tested in the presence of electrolytes by dynamic and electrophoretic light scattering techniques respectively. The enzymatic activity of the systems was tested by biochemical assays. Although the obtained materials possessed somewhat lower enzymatic activity compared to the bare enzymes, these systems are promising candidate for biomedical and industrial processes, where the bare enzymes usually lose activities due to the harsh conditions.

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Wed-D8-01

Dissipative self-assembly of paramagnetic colloidal suspensions in microgravity

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In microgravity, suspensions of spherical, paramagnetic particles (0.26, 0.48, and 1.02 μm diameters) were subjected to toggled magnetic fields with amplitudes ranging from 627 A/m to 2276 A/m over a frequency range of 0.25 Hz to 20 Hz and a duty ratio range of 0.10 to 0.50. At long experiment times (>50 minutes) five unique microstructure types were identified: unstructured, columns I, columns II, anisotropic, and sheet-like. Especially dynamic, active behavior was observed for aggregates in the anisotropic regime. Aggregates in these fields engage in motion, splitting, merging, ejection, and coalescence: a rich set of terminal-state emergent dynamics which persisted even as durations exceed four hours. Additionally, we find that the transmitted light intensity, a reciprocal measure of the extent of aggregation, exhibits a power-law dependence on time during the initial coalescence. The dynamic microstructures formed in these experiments appear to be unique to the dissipative self-assembly of magnetic colloids in toggled fields, without an obvious analogue to static equilibrium states.

Wed-D8-02

Assembly of Paramagnetic Colloidal Clusters in a back-and-forth rotating magnetic field

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Applying high-frequency rotating magnetic fields (RMFs) to a suspension of magnetic colloids induces an effectively isotropic interaction potential among the particles that drives their organization into two-dimensional (2D) clusters with crystalline order. The clusters of superparamagnetic particles under an RMF acquire an effective circular shape and rotate in the direction of the field. Suppression of cluster rotation can be achieved by applying a “back-and-forth” field, consisting of a rotating field that inverts the direction of its rotation at the end of every period. However, it is unclear if other structural changes occur because of this field. In this work we investigate the impact that such a field has on the assembly of superparamagnetic particles into clusters. In contrast to the conventional RMF, we find that the clusters become anisotropic in shape and display a preferred orientation as the amplitude of the magnetic field increases. The director of the clusters coincides with the tangent direction to the point of inversion of the “back-and-forth” RMF. At long times, we observe that the strength of the cluster alignment can decrease as clusters coalesce laterally with respect to the director and do not realign. The lack of realignment with the director, combined with slower growth kinetics than those found in clusters in a conventional RMF, suggests that the colloidal system is in an arrested state. Our work implies that small changes in external driving have a significant effect on the organization and control of polarizable particles, allowing for novel ways to direct colloidal assembly for the design of structured materials.

Wed-D8-03

Dynamics of Suspensions of Rotating Magnetically-Assembled Chains of Janus Particles

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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.

Wed-D8-04

Magnetic Field-directed Assembly of Biofilm Targeting Superstructures

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The eradication of biofilms formed on difficult-to-access surfaces remains an unresolved challenge across diverse disciplines. Advances in small-scale robotics using responsive nanomaterials provide promising routes to address this challenge. However, to be effective, modalities to eliminate biofilms must address their formation on topographically complex surfaces and must produce forces of sufficient strength to remove these remarkably robust structures. Here, we demonstrate magnetic field-directed assembly of catalytic nanoparticle superstructures extending from a solid boundary to form adaptive macroscale (mm-cm) bristle-like assemblies with tunable motion and mechanical properties for biofilm disruption. Under dynamic fields, the bristles' shape, length, and stiffness can be rapidly tuned to extend, retract, or stiffen in a controlled fashion. These assembled structures scrub the biofilm while exhibiting catalytic activity that generates antibacterial reagents. Furthermore, as the bristle-like nanoparticle structure disrupts the biofilm, it forms superstructures that incorporate biofilm debris, facilitating retrieval of samples. We study the spatiotemporal dynamics of bristle assembly, motion, and cohesive strength. Shear stresses generated by bristles are strong enough to remove highly adhesive biofilms. Notably, the bristles can conform to surfaces with complex topographies, entering angled grooves or extending into narrow crevices, providing a novel topography-adaptive functionality for effective biofilm removal. We apply these dynamic bristle-like structures using programmable motions to target complex 3D geometries of *ex vivo* human teeth with complete biofilm. We envision this nano-robotics strategy for assembling reconfigurable catalytic superstructures will advance current oral care modalities and other fields contending with biofouling on hard-to-reach surfaces.

Wed-D8-05

Sticky and polarizable nanoparticles: processing conditions to achieve anisotropic structure

Kelsey Reed, James Swan, Patrick Doyle

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Anisotropic materials are of interest for a variety of applications ranging from biomedical technologies, to oil and gas operations, to consumer care products, and throughout the food industry. Discovery of novel anisotropic materials and understanding of the processing conditions necessary to achieve a desired structure is thus an active area of soft matter research. We present a simulation study of a novel anisotropic material composed of a mixture of attractive nanoparticles and polarizable nanoparticles, that is formed via a specified processing scheme. It is well known that magnetic nanoparticles in an external magnetic field will polarize and form chains or other structures based on the strength and implementation of the applied field. It is also well known that nanoparticles that interact via attractive short-range potentials will aggregate and form structures dictated by the strength of the interparticle interactions. While both of these systems have been studied in detail separately, to our knowledge there is little work in the area of materials composed of attractive nanoparticles in which some fraction of the particles are also polarizable in the presence of an applied magnetic field. The space of driving forces for self-assembly is two-dimensional: thermal and magnetic, which allows for the scalable design of hierarchical microstructures with tailored material properties. We will present the results from Brownian dynamics simulations of attractive colloids in which some fraction of the particles are also polarizable. We use a mutual dipole model, which accounts for many-body interactions, to model the dipole interactions between magnetic particles and the depletion interaction as the attractive potential between particles. We will describe the processing conditions used to achieve the anisotropic structure and describe quantitatively how the microstructure differs from that of a pure depletion gel. These results highlight the use of simulations to investigate novel colloidal materials formed via specific processing conditions.

Wed-D8-06

The Influence of Viscoelastic and Shear-Thinning Media on µWheel Transport

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Microscale devices that can be transported with remote control, known as microbots, have the potential to be used for targeted drug delivery and noninvasive surgeries to assist in the treatment of conditions such as blood clots, cancer, and cystic fibrosis. For lung-based diseases where mucus biofilms can form a transport barrier, drug delivery via aerosol provides a more direct route than systemic approaches. As a result, many lung diseases are treated with drugs that are aerosolized using a nebulizer. The ideal aerodynamic particle size for deep lung penetration is 1-5 µm. If the particles are too large, they will settle before reaching the lungs and if they are too small, they will be exhaled back out. Our approach utilizes superparamagnetic polystyrene colloidal particles that can come in sizes ranging from 1-5 µm. In the presence of a rotating magnetic field, these colloidal particles can reversibly self-assemble into standing disks resembling wheels, coined microwheels (µwheels). Colloidal assemblies have a distinct advantage here as individual particles can be within this range and µwheel components delivered in the lungs can assemble in situ to perform targeted treatment. Initial studies of µwheels have been conducted in Newtonian media and have shown high velocities (~100 µm/s). For transport through mucus-like conditions, assuming a Newtonian system no longer applies since mucus is a viscoelastic and shear-thinning media and the transport mechanism of µwheels changes. µWheels were rolled in low concentration xanthan gum solutions (0.01-0.05 wt%) actuated by a rotating magnetic field and translation was tracked using particle image analysis. Xanthan gum shows viscoelastic and shear-thinning properties that rheologically mimic mucus. We show that µwheels have significant velocity losses due to traction loss. Viscoelastic fluids will have more slip at a surface than Newtonian media. When a rubber band is pulled apart, the stored elastic energy snaps it back together when released. The same concept applies to viscoelastic fluids. When the media is sheared and deformed, the stored elastic energy will pull additional fluid along with it. µWheels in 0.05 wt% xanthan gum have almost no traction even when rotating over 10 rad/s. We demonstrate that µwheels in lower concentrations have more traction. µWheels can even lose enough traction with the bottom surface to where their translation direction reverses and gains traction from fluid above. We also show that µwheels in 0.05 wt% xanthan gum have low rotation rates. This is because µwheels have a more difficult time trying to rotate due to higher viscous resistance.

Wed-D9-01

Digital alchemy for the inverse design of patchy particles

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Patchy particles are an exciting development for the fields of colloidal and nanomaterials. The ability to tailor interparticle interactions offers the promise of precise control of the self-assembly of patchy particles into structures with desirable properties. Given the many possible “degrees of anisotropy,” the design space of patchy particles is enormous, prohibiting the direct exploration of this space and making inverse design methods a crucial tool for the field. Of the many inverse design methods developed to date, digital alchemy is particularly attractive for patchy particles. Digital alchemy is an extended ensemble method that incorporates particle properties into the thermodynamic ensemble, allowing inverse design via statistical-mechanically-rigorous, on-the-fly updates to interparticle pair potentials. In this work, we extend the digital alchemy framework for the inverse design of patchy particles, and design triblock Janus particles to self-assemble target crystal structures. We provide examples of symmetric triblock Janus particles in 2- and 3-dimensions that self-assemble the open kagome and pyrochlore lattices, respectively. To highlight the generality of our method, we also present the inverse design of asymmetric triblock Janus particles to self-assemble a snub square lattice, whose coordination has a lower symmetry than the kagome and pyrochlore lattices, and therefore requires patches of differing sizes. Surprisingly, particles designed based upon geometric considerations are unable to self-assemble into the snub square lattice, whereas particles designed via our digital alchemy framework do, highlighting the ability of the method to find nontrivial solutions to the design problem. This work shows how digital alchemy can be used to design arbitrary patchy interactions to self-assemble into desired crystal structures, and can be built upon to design patchy particles of arbitrary shape and patch configuration.

Wed-D9-02

Plasmonic Response of Nanoparticle Assemblies

Zachary Sherman [1], Manuel Dominguez [2], Kihoon Kim [1], Jiho Kang [1], Stephanie Valenzuela [2], Murari Singh [1], Benjamin Roman [1], Eric Anslyn [2], Delia Milliron [1], Thomas Truskett [1]

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The optical properties of materials composed of plasmonic nanoparticles can be tailored through the dielectric properties of individual nanoparticles as well as their spatial arrangement. By leveraging structure-dependent properties, self-assembly of plasmonic nanoparticles enables tunable optoelectronic, catalytic, and biomedical technologies. Understanding which material is optimal for a particular application is challenging because there is an enormous number of possible physical parameters and assembled structures to screen. Computational methods have the potential to accelerate this search, but current methods for determining the effective plasmonic properties 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. In this work, we develop a mutual polarization method to rapidly simulate the optical response of nanoparticle materials, allowing for 10^3-10^5 nanoparticles to be probed at a time. The method is well-suited to configurations obtained from molecular simulations, enabling a complete computational framework that predicts both self-assembled structures and their optical properties. We use our mutual polarization method to investigate the plasmonic response of two important classes of nanoparticle assemblies: 1) random binary superlattices and 2) gels. Though these assemblies are impractical to investigate using conventional numerical approaches, the optical properties predicted from our mutual polarization method agree well with corresponding experimental measurements of lab-synthesized assemblies. Using the detailed information available in simulations, we elucidate the structural origins of the experimentally observed changes in optical behavior upon assembly. Our mutual polarization method is therefore a valuable tool for understanding the complicated structure-property relations governing plasmonic nanoparticles and will facilitate design of new optoelectronic materials.

Wed-D9-03

Periodicity of Lamellar and Hexagonally Packed Cylindrical Phases in a Periodic Box

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In all molecular simulations of periodic ordered morphologies (POMs, such as those formed by block copolymers), the periodic boundary conditions (PBCs) limit the periodicity L of POMs to discrete values that must be commensurate with the periodicity imposed by the PBCs. For the commonly used cuboid simulation boxes, although the case of cubic phases (*e.g.*, the body-centered cubic spheres or the double gyroid) is straightforward to analyze, those of lamellae and cylinders are complicated by the various orientations they can have in the box. While one of us proposed a general formula to calculate L of lamellae (*J. Chem. Phys.* **2000**, *112*, 450), that of cylinders has rarely been calculated. More importantly, when L is different from the bulk periodicity L_0 of POMs, the PBCs change the structure and even the stability of POMs obtained in the simulations. Here we first propose a general method for calculating the periodicity of hexagonally packed cylinders in a cuboid box. Based on this, we further propose a global order parameter of the cylindrical phase suitable for the study of phase transitions in molecular simulations. We also show how to choose the lengths of a cuboid box such that regular-hexagonally packed (RHP) cylinders with given L and orientation can fit into the box. Finally, we show how to use pressure tensor, which can be readily calculated in off-lattice molecular simulations, to determine L_0 of both lamellae and RHP cylinders regardless of their orientation.

Wed-D9-04

Competing structural motifs in spherically confined hard tetrahedral particles

Rachael Skye [1], Erin Teich [2], Julia Dshemuchadse [1]

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Directed assembly provides unique opportunities for tuning colloidal particle structures. Controlling the precise particle spacing, structural motifs, and orientation affects the photonic and electronic properties of the assembly. Confinement in a spherical container, such as an evaporating droplet, is a common technique used in directed assembly, allowing for control of the number of particles in a system. Such assemblies are well explored in spherical colloids, but the behavior of anisotropic particles in confinement is not well understood. To address this gap in knowledge, we studied a family of hard, tetrahedral particles related through vertex truncation. Using Monte Carlo simulations, we compressed particles inside a spherical container and analyzed the changes in assembly behavior for systems ranging from 4 particles in a highly-curved container to 10,000 particles in a container with nearly flat walls. We show that the curvature of the wall has a profound impact on the structural motifs exhibited by these tetrahedral particles, favoring interparticle motifs which can pack closely against that wall. The motifs that form near the wall then seed growth of a specific structure into the center of the container, even changing the observed structure entirely for certain shapes. These findings illustrate how confinement can be a powerful technique for affecting both the short-range structure in particle neighborhoods and for controlling long-range crystal structure and even grain orientation of the formed assemblies.

Wed-D9-05

Frank-Kasper Phases of Diblock Copolymer Melts Studied with the DPD Model: SCF Results

Juntong He, Qiang Wang

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For conformationally asymmetric diblock copolymer (DBC) melts A-B, we proposed a model system that can be readily used in dissipative particle dynamics (DPD) simulations and performed the corresponding self-consistent field (SCF) calculations to study the stability of Frank Kasper (FK) phases. This provides the mean-field results needed for direct comparison between the DPD simulation and SCF results, without any parameter-fitting, to unambiguously quantify the fluctuation/correlation effects inherently neglected by the SCF theory but important in the low-molecular-weight DBC melts forming FK phases in experiments. Our SCF calculations of the DPD model are faster and use less memory, both by at least one order of magnitude, than those of the "standard" model, thus giving accurate results. Among the five FK (i.e., A15, C14, C15, Z and σ) phases considered here, C14 is found to be the only stable one; its stability is due to the conformational asymmetry and, in particular, it is stabilized over other FK phases by entropy. Our SCF phase diagrams for the DPD model of conformationally asymmetric A-B are quite different from those for the "standard" model, highlighting the effects of model differences.

Wednesday, July 13th | 09:30 - 11:30 | E7-Electrokinetics and Microfluidics

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Wed-E7-01

LaMer Keynote: Asymmetric rectified electric fields

Aref Hashemi [1], William D. Ristenpart [2], Gregory H. Miller [2]

[1] Courant Institute, New York University[2] Department of Chemical Engineering, University of California Davis

We have discovered that a steady field is induced within liquids by a sinusoidal potential, referred to as Asymmetric Rectified Electric Field (AREF). AREF helps explain several long-standing discrepancies regarding the behavior of particles and electrically induced fluid flows in response to oscillatory potentials, broadly impacts the interpretation of the experiments, and offers new avenues for research in electrokinetics. Additionally, we demonstrate that a non-antiperiodic, zero-time-average, excitation of a spatially symmetric system can yield a net response (e.g., net drift of charged ions). In particular, our theory suggests that swapping the powered (non-antiperiodic potential) and the grounded parallel electrodes of an electrochemical cell alters the system behavior, a prediction verified by our experimental observations on the AREF-induced electrophoresis. As a toy model, we also consider an object atop a flat surface that undergoes a dual-mode horizontal vibration. Our calculations, and subsequent experimental observations, show that the object experiences a net drift if the applied frequencies are the ratio of odd and even numbers (e.g., 1 Hz and 2 Hz).

Wed-E7-02

A quantitative microfluidic study of single- and two-phase flow instability in permeable media

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[1] Department of Chemical Engineering, University of Wyoming[2] Department of Mathematics and Statistics, University of Wyoming

Darcy’s law describes a linear relation between the gradient of field potential and the Darcy velocity. Its multiphase extension imposes Darcy’s law per phase by introducing relative phase permeabilities and capillary pressures, quantities that all depend solely on the local phase saturations. Because local phase saturations are defined over a representative element volume (REV), Darcy’s law and its multiphase extension both assume that sub-REV scale flow dynamics are instantly resolvable at the REV scale and steady states are established instantaneously. Motivated by the widespread adoption of this multiphase extension as the canonical treatment for simulation of flows in large-scale permeable media, this talk presents a series of experimental efforts that invalidate the assumption of the instant resolution of multiphase flow into its steady state and highlight the need for alternative formulations of multiphase flow in permeable media. The experimental work is split into two phases. The first phase of the experimental work is designed with hopeful deductive reasoning: if experiments for single-phase permeable flow disprove the assumption of instantaneous resolution of the flow dynamics and given that unsteady flow dynamics in multiphase flow processes are more complex and are more likely to persist compared to single-phase flow, then the assumption of instantaneous resolution of unsteady flow dynamics is invalidated for all fluid flows in permeable media. The second phase of the experimental work is to study the physical phenomena occurring in multiphase permeable flow that makes it harder to resolve unsteady flow dynamics at the REV-scale. Initially, single-phase flow in a disordered permeable medium is studied using fluorescent particle image velocimetry (FPIV). By introducing tracer particles into the injected fluid, a high-speed camera captures the motion of the tracer particles within the tracked fluid through a microscope. A custom PIV algorithm then calculates a velocity field for each frame in the recorded video. Experiments are repeatedly performed on the same microfluidic device using the same steady-state baseline pressure profile. Video recordings begin at the onset of instantaneous inlet pressure-increases of different magnitudes applied to the microfluidic device, and they continue until new steady flow states are reached. The evolving velocity fields are analyzed for the duration of the transient state. Further analysis shows that the duration of the transient state is weakly but positively correlated with the magnitude of the instantaneous increase of the inlet pressure. The second phase of this study requires two-phase

flow experiments and is concerned with the identification of Haines Jump. Commonly conjectured to be a contributing factor to fingering invasion, Haines Jump refers to the rapid pore displacement that occurs when an interface passes through a narrow throat during drainage. Video recordings are obtained where a saturated fluid phase in the field of view is being displaced by an immiscible phase containing fluorescent tracer particles. A mostly novel collection of algorithms is used to segment the displacement front in all frames and then concatenate them into an evolution graph according to their spatial-temporal proximity. Preliminary results confirm the existence of Haines Jump.

Wed-E7-03

Pore-Scale Approach for Real-Time Evaluation of Absolute Permeability in Microfluidic Porous Networks Using an Analogous Electrical Circuit: Incorporating the Pore Geometry Effect

Meriem Boumedjane

Sultan Qaboos University, Department of Petroleum and Chemical Engineering

Permeability estimation is crucial for providing fundamental information that are required to establish production and injection rates. Several experimental and numerical approaches have been developed to evaluate the permeability of rock reservoirs at the large scales (field- and core-scales). However, the evaluation of the permeability at the micro-scale has remained a challenge because of the small length scale, the variety and the complexity of porous structure of the microfluidic devices. Since permeability is a scale dependent property and due to the increasing usage of microfluidic devices in the petroleum field to visualize the pore events and evaluate Enhanced Oil Recovery (EOR) techniques, the characterization of such quality at the pore scale is highly required. Herein, by the combination of an integrated microfluidic set-up and the analogous electrical circuit we upgraded the conventional methods to provide an accurate, reproducible, and practical on-chip approach to calculate real-time absolute permeability of pore networks. On the basis of the designed fluidic set-up, a sequential flow rate stepping scheme was optimized and used to estimate the permeability of the porous networks after fully saturate them with a fluorescein solution that was driven to the system by a pressure controller. The permeabilities of the micromodels were obtained by applying Darcy's law for laminar flow after estimating the differential pressure across the whole system and the pore networks by measuring the equivalent flow resistances of the fluidic circuit. The method is highly accurate, sensitive, and effectively predicts the absolute permeabilities of the micromodels. The use of a pressure controller and pressure sensors affords the potential of parallelization of the microfluidic set-up and delivers high-throughput compared to the previous proposed techniques. The validation of the approach was based on its independency of the porous medium geology and by providing convergent results between the experimental and computed permeabilities in the microfluidic devices. Moreover, this approach will help in delivering qualitative and quantitative data to understand capillary phenomena and dominant mechanisms of different chemical EOR processes at the pore scale.

Wed-E7-04

Acoustic Microfluidics for Micro/Nano Manipulation

Xiaoyun Ding

University of Colorado Boulder

Manipulating particles from nanometer scale to micrometer and millimeter scale, such as molecules, cells, colloids, droplets, and small model organisms, has been important in biology, chemistry, and medicine. Micro manipulation can be achieved by optical, electromagnetic, mechanical, acoustic approaches or their combinations. The integration of acoustic waves in microfluidic system has demonstrated great potential for manipulation of micro/nano particles and colloids and has gained great attention due to its advantages such as, non-invasiveness, low cost, less requirement on medium, ease to use, miniaturization, and low power consumption. In an acoustic microfluidic system, manipulation typically relies on two main acoustic forces: acoustic radiation force, which is responsible for the motion of particles, and the stokes drag force arising from acoustic streaming, which is responsible for the motion of fluid. In this presentation, I will briefly introduce two of our recent progress in acoustic manipulation 1) manipulation of protein molecules for real-time analysis of protein thermodynamic stability, where we employed surface acoustic waves (SAWs) to unfold proteins and concentrate the precipitated proteins on a microfluidic chip by capitalizing the novel coupling of acoustic heating and acoustic forces; 2) Manipulation of internal structure of complex colloids, where the orientation of the internal structure of disk-in-sphere endoskeleton droplets could be reversibly manipulated by simply using different frequencies of acoustic wave, which changes the balance between the primary and secondary radiation forces responsible for the disk orientation. Both tasks are challenging and rarely reported yet and may provide avenues for directed assembly of novel hierarchical colloidal architectures and intracellular organelles or intra-organoid structures.

Wed-E7-05

Tunable Ionic Perm-selectivity for Dynamic Control of Preconcentrated Molecule Plugs

Barak Sabbagh [1], Sinwook Park [1, 2], Gilad Yossifon [1, 2]

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Passage of an electric current through a permselective medium (e.g., ion exchange membrane, nanochannel) results in regions of depleted and enriched ionic concentrations at the opposite sides of the membrane interfacing an electrolyte solution, due to imbalanced ion transport. This phenomenon is termed ionic concentration polarization (ICP). ICP has been the focus of intensive research in the past decade in relation to lab-on-a-chip microfluidic applications and mainly has been used for highly enhanced immunoassay bioanalysis and sensing by the preconcentration of analytes[1]. Upon the application of an electric field, a preconcentrated plug of the charged analyte forms at the outer edge of the depletion layer due to counteracting advection and electromigration ion fluxes. ICP-based preconcentration can continuously accumulate charged molecules of a sample solution and operate under a wide range of electrolyte conditions. However, one of the main drawbacks of current ICP-based preconcentration systems is the inability to precisely and dynamically control the location of the preconcentrated biomolecule plug to ensure its overlap with the surface-immobilized molecular probes. Recently, we have demonstrated a novel method to control the location of the plug by using a series of tunable nanochannel that can be easily obtained on-demand by using microvalves made of a soft elastomer (PDMS)[2]. However, using nanochannels with high hydrodynamic resistances caused a low throughput and respectively relatively low preconcentration factor. Herein, we have overcome this challenge, while maintaining all the advantages of a tunable geometry, by integrating a cation exchange membrane (CEM) on the entire microchannel bottom surface. The CEM replaces the need for nanochannels and enables increased throughput by reducing the hydrodynamic resistance. We have shown that despite the fixed CEM coating along the entire microchannel, only where the microvalve has been deformed the interplay of ionic transport between the bulk solution beneath the microvalve and the CEM causes a generation of ICP and preconcentration plug. Although the microvalve doesn’t fully block the microchannel, the ionic current through the CEM is sufficient to trigger the ICP while the remained micro-size gap allows the solution to flow freely. This behavior was examined in various operation conditions (e.g., microvalve deformations, ionic strengths, and applied voltages) and verified with a numerical model.

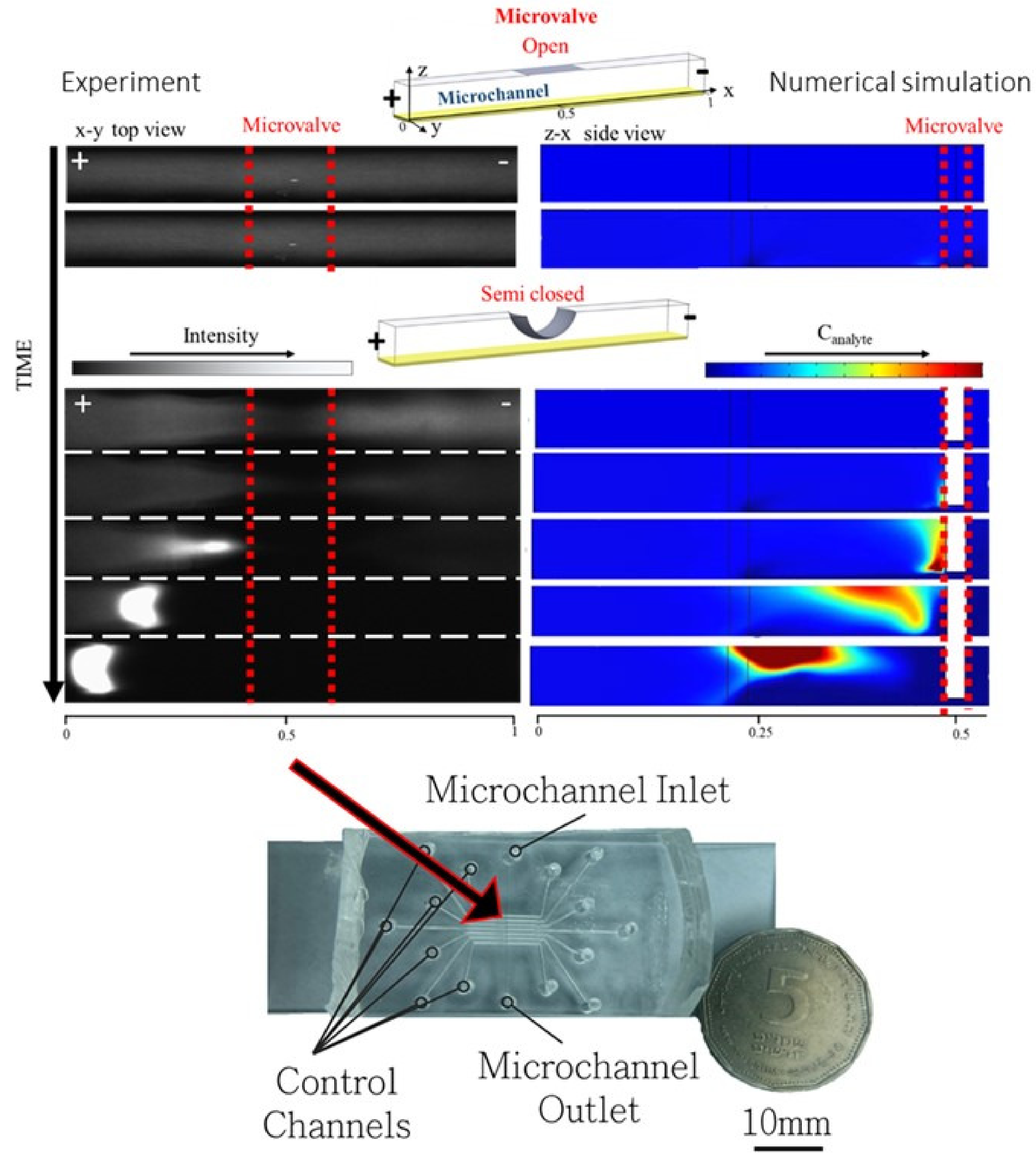

Figure 1: On-demand preconcentrated molecule plug generation by activating a microvalve. Experimental and numerical results (right and left columns, respectively). Bottom part: a picture of the microfluidic device.

[1] Park S., et al., Nanoscale. (2020): 23586-23595.

[2] Sabbagh B., et al., Nano Lett. (2020): 8524-8533

Wed-E7-06

Revisiting the electroacoustic phenomenon in the presence of surface acoustic waves

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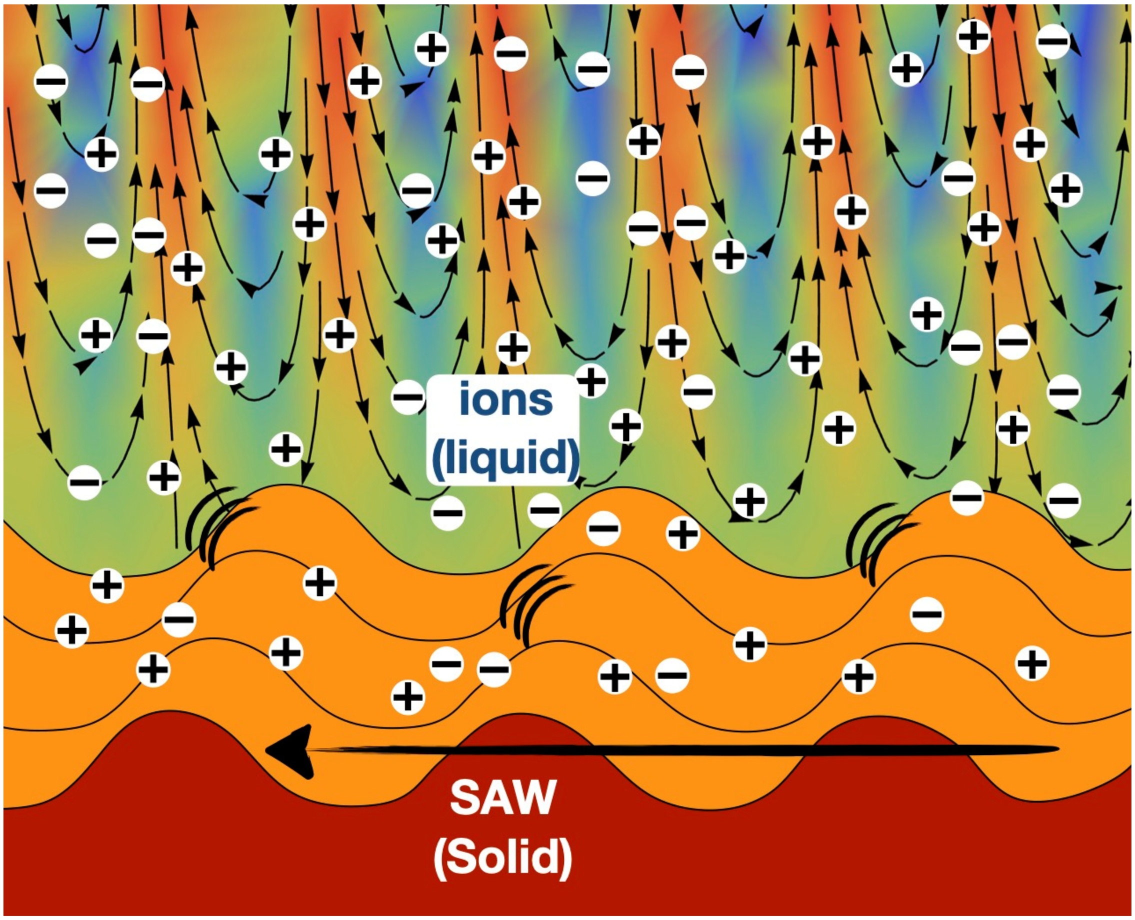
The electrical double layer of ions (EDL) to appear next to charged surfaces in electrolyte solutions is fundamental across countless natural and artificial systems and may considerably vary in properties between one system to another. Its applications range from supporting electrophoresis and electro-wetting to governing the kinetics of particulate coagulation, folding structures of proteins, surface properties of membranes, and particulate adsorption onto an underlying substrate. The generic nature of the EDL and the interplay between physical mechanisms therein alongside its short length scales of usually several nanometers and a relaxation time scale of nano- to micro-seconds render the EDL and the interplay between its different subcomponents an enigma, even now more than a century since it was discovered. We employ for the first time a MHz-frequency mechanical vibration, i.e., a Rayleigh type surface acoustic wave (SAW), in a solid substrate to dynamically excite the electrical double layer of ions (EDL) in the neighboring electrolyte solution. The excitation renders dynamic variations in the ion density and a partial electrical discharge in the EDL, which support the leakage of a measurable electrical signal off the EDL. The leakage possesses a frequency spectrum which appears to correspond to an array of mechanical-electrical responses therein. We show that the measurement agrees to leading order with a dedicated linear theory for the near equilibrium distortion of the EDL. The agreement facilitates a mean for deciphering the measured signal to potentially give new and direct insights about the EDL and its subcomponents. Moreover, we observe resonance and anti-resonance effects in the excited EDL which are akin to these phenomena in electrical circuits.


ions
(liquid)
SAW
(Solid)

Wednesday, July 13th | 09:30 - 11:10 | F7-Emulsions, Bubbles & Foams

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Wed-F7-01

LaMer Keynote: Predicting Aqueous Foam Stability Via Equilibrium Phase Behavior

Anirudha Banerjee, Yusen Qiao, Yihan Liu

The Dow Chemical Company

Foams are dynamic systems that undergo destabilization via liquid drainage, bubble coalescence and ripening. Several attempts have been made by foam formulators to visualize and analyze foam stability. These include highly sophisticated microscopy and macroscopic imaging techniques as well as surface characterization methods such as interfacial tension and interfacial rheology measurements to understand surfactant association at the air-water interface. However, most of these measurement techniques are either too cumbersome or deliver inconclusive results. Moreover, they lack the predictive ability that formulators desire when choosing a surfactant package for a specific foaming application. Here we re-introduce a classic colloidal science technique that has been successfully used in the past to predict and explain emulsion stability - equilibrium phase behavior. We map out the phase diagrams for three model surfactants (one fluorosurfactant and two silicone surfactants) in a surfactant-heptane-water ternary system and identify colloidal structures that govern the respective system's foam stability. We leverage the learnings from this phase behavior analysis to explain the stability and efficacy of foams that are used to extinguish hydrocarbon fuel fires.

Wed-F7-02

High Throughput Measurement of Droplet Surface Tension and Mechanics in Confined Flows

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[1] Chemical Engineering, Northeastern University[2] Mechanical & Industrial Engineering, Northeastern University[3] Chemistry & Chemical Biology, Northeastern University

We present a novel microfluidic device to collect high-throughput measurements of droplet surface tension in-line with a droplet generator, without requiring manual adjustment to input flow rates or driving pressures. Drops flow at a constant volume flow rate through increasingly narrower channels and thereby experience increasingly higher shear stress. Video analysis provides simultaneous measurements of drop velocity, v and deformability index, $D = (d_1 - d_2)/(d_1 + d_2)$, where d_1 and d_2 are the major and minor axes of the droplet, respectively. We calculate surface tension using its relationship to the viscous drag forces described in the capillary number, Ca, which is in turn related to deformability through $D = [(19\lambda + 16)/(16\lambda + 16)]\mathrm{Ca}$, where λ is the viscosity ratio between the droplet and continuous phases. We validate our tool using standard pendant drop measurements, in which one drop is measured at a time after reaching steady state, using a system of water drops in mineral oil stabilized by Span-80 over a range of concentrations. Our system has several key potential advantages over the pendant drop technique. Rather than measuring a single static image, as in pendant drop, we perform high-throughput, dynamic measurements to analyze thousands of individual drops flowing at linear velocities on the order of mm/s, with some closer to cm/s. By imaging at rates faster than 100 Hz, our results reveal oscillatory dynamics in the deformation of droplets subject to shear stress. These oscillations can be averaged to obtain surface tension measurements within 10% of those obtained via pendant drop. We also explore the mechanical response of droplets filled with non-Newtonian fluids.

Wed-F7-03

Coexisting phases as hidden destabilizers of self-assembled structures

Catherine G. Reyes [1], Joerg Baller [2], Takeaki Araki [3], Jan P.F. Lagerwall [2]

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Despite our understanding of liquid crystalline (LC) phases, non-trivial mixing phenomena remains ripe for exploration in LC-volatile solvent mixtures [1-4]. Here, we briefly demonstrate how unseen features in binary mixtures containing components capable of self-assembly can impact macroscale composite formation. Emulsions of 4-cyano-4′-pentylbiphenyl (5CB) and anhydrous ethanol have an unexpectedly broad miscibility gap, causing the formation of two distinct coexisting isotropic phases [1]. More surprisingly, if water is added to the ethanol-5CB mixtures as an impurity, the temperature range of the miscibility gap increases, allowing these previously unseen isotropic phases to persist even above 50°C while surpressing the formation of the ordered nematic phase. Thus, a cascade of destabilizing effects occurs at room temperature, in conditions where varying flow ratios of 5CB, ethanol, and water are induced; an example being electrified coaxial extrusions of 5CB within polymer-ethanol mixtures at elevated humidity used to form optically responsive membranes [2,5]. Phase diagrams, as well as real-time observations of their impact on fiber formation shown, highlight an example of how macroscale mixture processing for composite formation can exacerbate microscopic interfacial phenomena thought either be non-existant, or not applicable, at these scales. References: [1]. C. G. Reyes, J. Baller, et al. Soft Matter, 15, 6044-6054 (2019). [2]. C. G. Reyes, J. P. F. Lagerwall. ACS Appl. Mater. Interfaces, 12, 23, (2020). [3]. S. Vats, L. Honaker, et al. Macromol. Mater. Eng., In Press, (2021). [4]. S. Roh, M. Tsuei, et al. Langmuir, 38, 1 (2021). [5]. K. Schelski, C. G. Reyes, et al. Cell Rep. Phys. Sci., 2, 100661 (2021).

Wed-F7-04

Effects of gas type in foam in microfluidics porous media

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Foams are essential in applications ranging from enhanced oil recovery in production wells to carbon sequestration in hydraulic fracking sites. Therefore, there is great interest in understanding the fundamental physicochemical processes associated with foam to predict their flow in natural porous media environments. Microfluidics have been proved effective in visualizing small scale events and processes that would otherwise be difficult to observe in natural confined systems. In this study, a microfluidic device designed to mimic natural heterogenous sandstone porous media is employed to investigate the effects of gas types on gas trapping, foam generation, foam stability, and phase mobility in flowing foam. Carbon dioxide gas and nitrogen gas are evaluated in this work. Phenomena such as lamella division and foam coarsening are directly observed in microfluidic devices and compared between gases. We characterize pressure drops, apparent viscosities, and variations in foam texture across the model porous media. An in-depth picture of foam texture in relation to foam quality and flow rate is possible by combining real-time imaging and image processing.

Wed-F7-05

An Investigation of Formation and Separation Mechanics of Droplet Interface Bilayers by a Fluorescent Lipid Tension Reporter

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Droplet interface bilayers (DIBs) are artificial bilayers that are attractive for studies of the physicochemical features relating to the cell membrane. The mechanical response induced by mechanical stimuli is actively studied and has the applications to drug delivery. However, there is little knowledge concerning the tension distribution during such processes. Recent reports have identified a fluorescent lipid tension reporter (FliptR), a synthesized molecule that can monitor the changes in membrane tension. In this presentation, the FliptR probe was incorporated into lipid monolayers and bilayers and the orientation dynamics were measured using fluorescence lifetime image microscopy (FLIM). Monolayer tension measurements were first using FLIM on pendant drops of water immersed within lipid/hexadecane solutions. These measurements were then compared against the known tensions using pendant drop tensiometry for different cholesterol/lipid mixtures. Lifetime measurements were acquired during the DIB formation and separation and the data acquired from the monolayer measurements were used to infer tensions within the bilayers.

Wednesday, July 13th | 09:30 - 10:30 | H7-Geochemical and Environmental Systems

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Wed-H7-01

Solute-mediated transport of colloids in disordered media

Amir Pahlavan [1], Suin Shim [2], Niki Abbasi [2], Janine Nunes [2], Howard Stone [2]

[1] Yale University[2] Princeton University

Solutal gradients due to mixing and reactions in disordered media are ubiquitous. At the scale of a single pore (tens of microns), these gradients generate osmotic flows that can significantly enhance the rate of transport of colloids. Yet, it is not known how solutal gradients can influence the transport on macroscopic length scales. Here, using microfluidic experiments and numerical simulations, we show that solutal gradients can considerably hinder or enhance the transport of colloids through disordered media, and we develop a theoretical model that explains this coupling.

Wed-H7-02

Spray droplet size in liquid sheets containing surfactants and oil emulsions

Iaroslav Makhnenko [1], Cari Dutcher [1], Elizabeth Alonzi [2], Christine Colby [2], Steven Fredericks [2], Long Nguyen [1]

[1] University of Minnesota, Mechanical Engineering Department[2] Winfield United

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 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 break-up and droplet size distributions are discussed. Herein we experimentally measure the droplet size distribution of sprays from agricultural spray nozzles using a wind tunnel, and the oil emulsion size distribution in the sprayed liquid using Optical Particle Analyzer. The sprays were either homogeneous or contained an emulsion, and the dynamic surface and interfacial tensions were varied. We identified the influence on spray volume fraction below 150 µm and on the volume median diameter, which are correlated with the spray drift risk and deposition, respectively. 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.

Wed-H7-03

Effect of nanoparticles on oil spill bioremediation by oil-degrading bacteria

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Prompt and thorough remediation of marine-based oil spills is a necessity. Bioremediation is an oil spill remediation method where naturally occurring microbial species metabolize hydrocarbons, removing oil from the environment. Unfortunately, complete biodegradation 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. This study investigates the effect of three model nanoparticles, namely silica, silver, and lignin, on the hydrocarbon-degrading properties of a model marine 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. However, the addition of chitosan-coated silver nanoparticles resulted in a more than threefold 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 the presence of nanoparticles with the interfacial tension measurements, suggesting that chitosan-coated lignin nanoparticles facilitate the proliferation of A. borkumensis and likely assist in the increase of biosurfactant production by the bacterium. These findings indicate that naturally, derived nanoparticles can enhance the bioremediation of spilled oil, thus providing a new sustainable alternative to large-scale oil spill remediation.

Wednesday, July 13th | 09:30 - 11:50 | I7-General aspects of Colloids and Interface

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Wed-I7-01 Withdrawn

Polymer-Based Functional Composite Particles via Microfluidics for Fluorescence Labeling and SERS Sensing

Nikunjkumar Visaveliya

The City College of New York

Labeling through fluorescent materials are increasingly advantageous for in vivo and in vitro imaging applications for diagnostic and theranostic purposes. A wide range of various fluorescent organic dyes is routinely utilizing for various labeling purposes due to their easy use, low cost, availability of full emission wavelength range. However, organic dyes are very sensitive to their surrounding in which they rapidly degrade either via chemical degradation or photodegradation. In order to avoid the concern of degradability, inorganic nanoparticles, in particular, quantum dots are highly versatile and photostable. However, quantum dots are relatively toxic to biological systems, and hence their widespread and safe uses are a concern. Alternatively, dye-doped polymer particles are promising for labeling and imaging due to their properties that overcome limitations of photodegradation as well as toxicity. In this work, various experimental strategies for the nanoscale and microscale fluorescent polymer particles have been developed to bind the fluorophores inside the matrix covalently or non-covalently, as well as at the surface through direct adsorption or based on bio-conjugation. On the other hand, surface-enhanced Raman scattering (SERS) spectroscopy is one of the most powerful analytical techniques in which significant field enhancement can be realized upon adsorption of molecules (analytes) on the surface of metal nanostructure that allow detection (sensing) of analytes at a very lower concentration. A key element for the better outcome through this method is the SERS substrate that needs to be equipped with plenty of hotspots as well as metallic rich and relatively roughened surface. Despite a large number of SERS substrates are routinely utilizing, there is still room and hence search is continuing for the dynamic substrates that reveal the extraordinary signal outcome. Polymers can provide the platform to meet such requirements by systematically depositing metal nanostructures at the surface. Here, the development of the polymer-metal composite particles at nanometer and micrometer length scales, and their applications as sensor particles for SERS sensing are presented.

Wed-I7-02

Gold Nanoparticle-Shelled Nanocapsules as Mechanochromic Sensors

Jae-Hyun Kim [1], Joseph Rosenfeld [1], Ye-Chan Kim [1], Emanuele Marino [2], Sean Choe [3], Russell.J Composto [1], Daeyeon Lee [1], Rémi Dreyfus [3, 4]

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Colloidal mechanochromic microsensors have been shown to enable the in-situ detection of mechanical loads within materials[1]. Enhancing the sensitivity of these sensors to small scale loads and deformation while enabling reversibility of the sensing capability would expand their utility in various applications including in biosensing and chemical sensing. In this presentation, we introduce the synthesis of nano-sized multifunctional colloidal sensors using a simple and versatile fabrication method. Multifunctional colloidal nano-sensors are prepared by emulsion-templated assembly of polymer grafted gold nanoparticles. To induce the adsorption of gold nanoparticles at the oil-water interface of the emulsion droplets, citrated gold nanoparticles (~11nm) are functionalized with thiol terminated polystyrene (PS, MW = 12000). These PS-grafted gold nanoparticles are suspended in toluene and subsequently emulsified to form droplets with a diameter of ~30µm. By evaporating the solvent of the oil-in-water emulsion, we form nanocapsules decorated by PS-grafted gold nanoparticles (diameter <1µm). We have explored two different potential applications of these nanocapsules as chemical and mechanical sensors. (i) First, upon exposure to an organic solvent, the grafted polystyrene brush layer undergo swelling, increasing the particle-to-particle separation and shifting the absorbance peak towards lower wavelengths. The absorbance peak returns to the initial position upon removal of solvent, demonstrating reversibility. (ii) Second, as a strain sensor, gold nanoparticle-based nanocapsules are embedded in an elastomer matrix. The addition of a plasticizer reduces the glass transition temperature of the PS brushes, imparting flexibility to the nanocapsules. The plasmonic peak of the nanocapsules shifts towards lower wavelengths upon application of uniaxial tension on the gold nanocapsule/PDMS composite, indicating increased particle-to-particle distance. The composite recovers its original plasmonic peak upon the release of the strain, demonstrating reversibility. This study provides a robust and easily scalable method of producing nanocapsule based sensors that can potentially detect the presence of chemicals or small stress/strain present at the nanoscale in biological cells.

1 Burel, C. A. S.; Alsayed, A.; Malassis, L.; Murray, C. B.; Donnio, B.; Dreyfus, R. Plasmonic-based Mechanochromic Microcapsules as Strain Sensors. Small 2017, 13, 1701925.

Wed-I7-03

Surface Micropatterning of Colloids

Gary Zabow

National Institute of Standards and Technology (NIST)

Size and shape play key roles in determining colloidal properties and utility. Being easiest to synthesize, spherical colloids are most common, but their high symmetry can limit their functionality. Considerable work is therefore also directed towards less symmetric / more anisotropic particles, including microcubes, rods, ellipsoids and other non-spherical microstructures whose anisotropic natures add, among others, new rotational and directional differentiation and control. Here, a different approach towards increasing particle functionalization is introduced that reverts back to more widely available spherical particles but that instead breaks symmetry via tailored micropatterning of these microparticle surfaces. Several routes to increasing functionality by patterning the surfaces of colloids do already exist, notably including hemispherical Janus-like particle coatings, which add bi-directional properties to colloids, or those based on colloidal clusterings, which can add multiple "patches" to colloid surfaces useful in, for example, directed self-assembly. While their capabilities differ, each existing surface functionalization approach is, however, limited in scope to only a small subset of all possible surface patternings that might be imagined; arbitrary surface micropatterning, similar to that achievable in the semiconductor microchip industry for example, has thus far remained challenging. Specifically, the highly curved surfaces of colloidal microparticles precludes their patterning with conventional microlithographic tools because such equipment requires ultra-flat, planar 2-dimensional substrates to ensure accurate focusing of the employed patterning light across the surface. Here, however, more arbitrary colloid surface patternings are enabled via a newly developed transfer microprinting approach which uses ultra-flexible materials to transport pre-fabricated micropattern designs. This allows for conventionally microfabricated, initially planar designs to be transferred over to, and directly wrapped onto, the microparticle surfaces. By thus leveraging the power and precision accrued from decades of investment in planar semiconductor lithographic tools, the approach allows for arbitrary, high-resolution surface micropatternings, extending design and control options beyond those of more common homogeneous, two-sided, or colloidal cluster patternings. As will be explained, the process also allows for parallel patterning of many microparticles simultaneously. The new functionalities enabled by these new patternings may then in turn contribute across multiple colloidal science fields, from new magnetic/optical control schemes to microrobotics to new

colloidal clusterings and crystallizations through directed self-assemblies employing new “patchy” particles with more arbitrarily designable directional interactions.

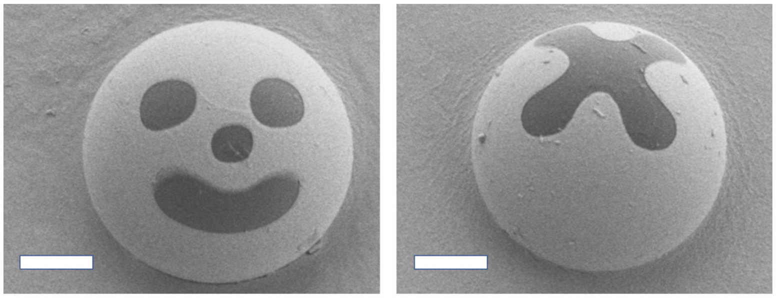

Figure: Top-down and angled scanning electron micrographs (SEM) of arbitrarily patterned microspheres. Scale bars in both images ~ 2 microns.

Wed-I7-04

Multivariate Analysis of Peptide-Driven Nucleation and Growth of Au Nanoparticles

Kacper Lachowski [1], Kiran Vaddi [1], Lilo Pozzo [1, 2]

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Sequence defined molecules such as peptides and peptoids enable significant control over the formation of inorganic nano-structured materials. The bio-inspired use of sequence defined molecules to synthesize inorganic nanoscale materials is motivated by the ability to form complex structures at mild reaction conditions. The sensitivity of syntheses to small changes in a molecule's sequence makes these approaches both potent and difficult to leverage. Additionally, one needs to consider experimental parameters like solution conditions (pH, ionic concentration etc.) and reagent concentrations because these can significantly change how sequence defined molecules interact with inorganic precursors and nanoparticles. We posit that the design of sequence defined molecules for inorganic nanomaterial synthesis will be accelerated by integration of experimental automation and new data analysis methods. We believe that extended sampling will provide insights into the connection between molecular design and synthesis outcomes which would be missed or misinterpreted in experiments with limited sampling of experimental parameters. Therefore, we developed a model system in which Au nanoparticles are synthesized in the presence of Au binding peptides using a liquid handling robot. Our objective was to study the effects of targeted sequence changes and lipid tail conjugation in 5 variants of a Au binding peptide (Z2) across 64 different reagent combinations (concentration of precursor, reducing agent, and peptide). Each sample was characterized by UV-Vis spectroscopy which serves as a proxy for the structure of plasmonic nanoparticles. Functional principal component analysis and a graph Fourier transform were applied to the spectra to make quantitative comparisons between each of the peptides (7 in total) in the large experimental design space (448 samples). Finally, we validate this approach by analyzing key features of UV-Vis data, ultra-small-angle X-ray scattering (USAXS), and electron microscopy. Both of our approaches were in agreement that key changes to a peptide sequence have a more significant impact on synthesis outcomes than conjugation of a lipid tail. We also report on formation of fused anisotropic particles in the presence of one variant.

Wed-I7-05

Stability of Uncapped Gold Nanoparticles Produced Via Laser Synthesis

Kaitlin Kay [1], Laysa Frias Batista [2], Katharine Tibbetts [2], James Ferri [1]

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Nanoparticles are excellent catalysts due to their high surface area to volume ratio that results in an increased number of catalytically active sites per unit mass. This plethora of highly reactive sites is often in contrast with the catalyst stability. Capping agents are used to maintain stability against aggregation; they can however have adverse effects on the catalytic activity of the nanoparticles by obstructing reactant access to active sites. Capping agents and other surface chemistry is typically a function of the synthesis method used. A unique set of synthesis methods that leverage lasers are capable of producing catalytic nanoparticles that remain stable despite their lack of capping agent. One such method, Laser Reduction in Liquid (LRL), is capable of producing a colloid dispersion of catalytic metal nanoparticles. The mode of stabilization for uncapped laser nanoparticles is unknown. Given their lack of capping agent, the stabilization against aggregation must arise from electrostatic repulsion. There are three main hypotheses that seek to describe the source of this electrostatic repulsion: oxidized species at the particle surface, adsorbed ions at the particle surface, or trapped electrons within the particle. Understanding the mode of stabilization is key in the effective design and scale-up of LRL particle synthesis. We investigated the stability of LRL nanoparticles using both zeta potential and time resolved dynamic light scattering (TR-DLS). Two types of LRL particles were analyzed: particles produced using a long laser pulse duration on the order of ns, and particles produced using a short laser pulse duration on the order of fs. The primary difference between these two synthesis conditions arose from the presence (fs) or absence (ns) of an electron rich plasma during nanoparticle synthesis. Further, in the case of fs particles altering the laser focal area produces a plasma of variable electron density. Zeta potentials were measured for both ns and fs particles and it was determined the ns particles were significantly less stable than their fs counterparts. Aggregation kinetics measurements were taken for the fs nanoparticles at two laser focus levels using TR-DLS. The TR-DLS data produced a critical coagulation concentration (CCC). By using DLVO theory and Au-H_2O-Au Hamaker constants, the surface potential of the fs nanoparticles were determined. The surface potential allowed us to calculate the theoretical electron density of the fs particles as a function of synthesis condition. The electron density for a tight focus setting was found to be 2.83×10^{19} cm^{-3} and the electron density for a loose focus setting was found to be 5.13×10^{18} cm^{-3}. These electron densities are similar to the

electron density of the plasma in which they were synthesized. This corroborates the trapped electron hypothesis as being a key mode of stabilization for LRL nanoparticles.

Wed-I7-06

Nanoimaging in real-time

Christopher Bolton, Ray Dagastine

Department of Chemical Engineering, University of Melbourne

Imaging small or transparent particulate samples is a challenge central to many research areas and critical to many industrial processes for tuning product fabrication, formulation and quality control. Existing microscopy tools trade-off spatial resolution against slow and complicated workflows, blunting both the cutting edge of research and modern manufacturing. For example, electron and super-resolution microscopies require extensive and often very harsh sample preparation (extreme temperatures/vacuum, sputter coating, chemical labelling, *etc.*), while nanometrology tools provide indirect measures of size and often assume particulates are spherical (or some other convenient shape). In many fields of discovery these limitations restrict the pace and scope of inquiry, with researchers forced to balance the time and expense of measurement(s) against the level of distortion considered acceptable for an application. In this talk we present an elastic evanescent field scattering technique employing multiple light sources to enable high-speed, non-destructive, label and stain-free imaging of the boundaries of particulates with nearly any composition or shape, ranging in size from hundreds of microns to tens of nanometres. We describe various simple approaches for implementation, and demonstrate nanoscale imaging fidelity by accurately measuring the size of a large selection of spherical calibration particles and nanotubes/rods. We also demonstrate *ad hoc* sub-wavelength imaging and measurement of a diverse range of anisotropic and biological samples with dimensions as small as 24nm. Finally, we present a miniaturised device that can be attached to any brightfield microscope and used in conjunction with our software to provide nanoimaging capabilities in real-time (up to hundreds of FPS). In addition to routine metrology applications, because the technique requires no sample preparation it should be especially useful in the life sciences for *in situ* studies of delicate or transient biological systems under ambient conditions.

Wednesday, July 13th | 09:30 - 11:10 | K7- Rheology and Dynamics

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Wed-K7-01

Deformation Dynamics of Semiflexible Chains

Sibani Lisa Biswal

Rice University

Elastic filaments exhibit rich rheological responses when subjected to external stresses like fluid flow and external fields. Such configurational dynamics have inspired the design of artificial filaments that can be manipulated by external stimuli. Semiflexible chains assembled from DNA-linked paramagnetic particles are suitable candidates for such applications due to their fast response to changes in external magnetic fields. The combination of induced dipolar interactions, elastic resistance, thermal motion, and viscous drag acting on the colloidal chains leads to a plethora of novel and unexpected deformation dynamics. We will examine distinct forcing scenarios and identify the nondimensional scaling groups that capture the dynamics.

Wed-K7-02

Rheology of collagen-based hydrogels tailored by tannic acid particles

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Hydrogels are porous three-dimensional structures with polymeric cross-linked networks that allow sufficient water and nutrient flow for cell proliferation and stimulate the regeneration of defective tissues. Compared to surgical scaffold implantation, injectable hydrogels can be easily applied by minimal invasive techniques to form a self-standing hydrogel. As a naturally derived polymer, collagen has been widely employed as injectable hydrogel since it inherits the structural and functional cursors to accelerate tissue formation. However, it shows poor mechanical strength. The use of biodegradable tannic acid particles provides a useful approach to improve the rheology of these systems while its inherent antibacterial and anticarcinogenic nature adds to the gel functionality. Polyphenolic tannic acid particles could potentially interact with collagen through multiple hydroxyl groups allowing the modulation of the rheology. In this study we examine how tannic acids impact the rheological properties of collagen-based hydrogels. Synthesized needle-shaped tannic acid particles and colloidal tannic acid are incorporated into collagen. While samples exhibit solution-like features at storage conditions (4 ℃), they transform into gels at physiological temperatures (37 ℃). The temperature- and time- dependent sol-gel transition are monitored as a function of tannic acid particle concentration. Interestingly, particulate tannic acid incorporation produces the largest increase in elastic modulus compared to tannic acid solution at similar concentration. The yield stress determined from the elastic stress method also reveals a similar trend. These results are interpreted in terms of the underlying interactions of the tannic acid with collagen, as examined using other analytic approaches. The results from the live dead assay of the composite hydrogels with tannic acid particles shows significantly higher cell viability.

Wed-K7-03

Tuning the Linear and Nonlinear Rheology of Polymer-Linked Emulsions

Daniel Keane, Ryan Poling-Skutvik

University of Rhode Island

The ability to tune the rheology of materials is vital to numerous soft matter processing applications ranging from spray coating to 3D printing. Here, we use a telechelic block copolymer polystyrene-b-poly(ethylene oxide)-b-polystyrene (PS-PEO-PS) to physically crosslink cyclohexane-in-water emulsions, greatly enhancing their stiffness and elasticity. The hydrophobic PS endblocks and hydrophilic PEO midblock drive the polymer chains to take one of two conformations—bridging in which the chain's endblocks imbed in different droplets or looping in which both endblocks partition into the same droplet. With a sufficient density of bridging chains, a percolated network of droplets is formed. We use oscillatory rheology to probe the effect of each block's molecular weight (Mw) on the polymer's ability to develop a robust, elastic network in the emulsion, finding that the size of each block size plays an important role. First, longer endblocks promote stronger thermodynamic interactions with the dispersed phase, and second, longer midblocks increase the fraction of chains in the bridging conformation—both of which contribute to the formation of a stronger, more elastic network. Furthermore, nonlinear rheology of the system indicates that end- and midblock Mw affects the yield transition of the network and its ability to recover. The results presented here provide insight into how to tune the rheological properties of complex fluids and colloids.

Wed-K7-04

Elastic turbulence in structurally-heterogeneous porous media: Linking pore-scale flow behavior to macroscopic flow resistance

Christopher Browne, Sujit Datta

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 (often termed 'elastic turbulence') in which the flow exhibits strong spatio-temporal fluctuations reminiscent of inertial turbulence, despite the vanishingly small Reynolds number. We quantitatively establish that the energy dissipated by unstable pore-scale fluctuations generates the anomalous increase in flow resistance through the entire medium. Moreover, we show that this finding applies across porous media with different mean grain sizes and generalize it to the case of flow in media with different degrees of structural heterogeneity. Finally, we show how elastic turbulence can be used to homogenize flow in structurally-heterogeneous porous media, and develop quantitative principles to predict and control this flow homogenization for a given 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 polymer solution flows in a variety of porous media.

Wed-L7-01

Ternary Noble Metal Nanoparticle Catalysts

Simon Humphrey

University of Texas at Austin

Microwave-assisted heating in the polyol synthesis of noble metal nanostructures provides access to randomly alloyed structures of binary and ternary phases that cannot be obtained using conventional heating methods. The resulting nanostructures are solid-solution structures that are metastable and resist segregation upon heating above 300 °C. Model heterogeneous catalysis studies reveal order-or-magnitude increases in hydrogenation reactivity, based on synergistic (ensemble and electronic) effects. In the case of ternary systems, it is possible to create random alloys that consist primarily of two earler noble metals from Groups 8-11along with a minority of a third, more oxophilic metal, such as Cu, to generate highly reactive catalyst species for applciations in HER and OER aplications. High-resolution electron microscopy, EXAFS and PDF coupled with experiment and theory allow a deeper understanding of reactivity benefits due to nanoscale alloying. Fine control over alloy compositionallows for optimization of reactivity for targeted applications, including in electrochemistry and in catalytic nitrate reduction and sulfide fouling resistance in water treatment.

Wed-L7-02

Shape matters, nanostructured materials with unique properties in carbon capture and catalysis

Ryan Richards

Colorado School of Mines Department of ChemistryNational Renewable Energy Laboratory

The Richards' group is working on new synthetic methods to control the size, shape and composition of nanoscale materials and applying them in systems integral to alternative energy technologies and carbon capture. In particular, the ability to manipulate earth abundant metal oxides presents an important potential technology to develop sustainable materials with novel properties. These materials are of interest due to the coordination environments that can be achieved and to the high degree of control over properties that can result from tailoring the exposed facets and from mixing metal oxides including the formation of high entropy systems. The initial synthesis of MgO and NiO with (111) facets as the primary surface (Angew., Adv. Mater.) has been followed by recent work utilizing a multiscale characterization platform to discover the underlying phenomena associated with the electrolytic properties of NiO(111) for Li ion batteries (Nature Comm., Nano Letters) and electrochromics. In a joint experimental-theoretical work with international collaborators, we unravelled the potential of (111) polar surfaces for carbon capture (JACS). Most recently, in-situ microscopy studies have revealed insights into the NiO active sites for electrolysis (PNAS) and the underlying dynamics of doping with iron (JACS).

Wed-L7-03

Establishing half- and single- cell baselines for the oxygen evolution reaction (OER) on non- platinum group metal (PGM) oxide electrocatalysts in alkaline media

Emily Volk [1], Stephanie Kwon [1, 2], Shaun Alia [1, 3]

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Background and Motivation. Electrochemical H_2 production is a promising strategy to provide clean energy and drive industrial decarbonization. However, this process is currently limited by high overpotentials of OER at the anode and a harsh near-surface environment (low pH, high voltage) in acidic media which necessitates the use of costly and rare platinum group metal (PGM) materials. As electricity costs have dropped, system/materials costs have become major inhibitors to the scalability of this technology; reducing dependence on PGMs is essential. Earth-abundant and cost-effective non-PGM transition metals, which corrode in acidic media, present as their solid oxide or hydroxide forms in alkaline media [1]; recent advances in anion exchange membrane (AEM) technology [2] have opened doors for catalyst development and integration research in alkaline electrolysis systems such as AEM electrolyzers. However, while OER has been studied extensively on IrO_2 in acidic media [3], not much is understood about i) the mechanism or ii) what the optimal catalyst candidates are in alkaline media. To address these gaps, a comprehensive catalyst screen for non-PGM metal oxides in both half-cell, rotating disc electrode (RDE) setups and single-cell, membrane electrode assembly (MEA) setups was performed. ***Results.*** 1st row transition-metal oxides were first tested using an RDE setup and compared to IrO_2. The electrochemically active surface area (ECSA) was determined by the double layer capacitance method [4], and specific capacitance (C_s) was determined at the same conditions as RDE experiments. Results in Fig. 1 indicate that i) Co_3O_4 may be a better catalyst than conventional IrO_2 or $NiFe_2O_4$ catalysts (low overpotential, low Tafel slope); ii) there may be a possible potential dependence of the mechanism for IrO_2 versus non-PGM metal oxides (as shown by the change in Tafel slope occurring at η = 400-500mV); iii) the notable performance differences among the catalysts provided from different suppliers, suggesting OER kinetics may be sensitive to subtle structural or compositional changes. A selection of catalysts was further tested in MEA setups to assess how RDE performance translates to AEM devices. Voltage breakdown analyses were performed to evaluate the contributions of ohmic losses, kinetic losses, and transport/other losses to the overpotential. Preliminary MEA results show performance trends of $IrO_2 \approx Co_3O_4 >> NiFe_2O_4$, which is comparable to RDE results. The Tafel slopes for the same catalysts determined from RDE vs MEA data increased (Fig. 1b); next steps will look to isolate kinetic differences from those arising due to differences in how catalysts integrate into MEAs. ***Impact and Future Work.*** This work establishes baselines for non-PGM metal oxide catalysts at relevant conditions for AEM systems and guides future work to elucidate possible differences in the OER mechanism between IrO_2 and non-PGM transition-metal oxide catalysts. The work ultimately aims to inform the optimized design of OER electrocatalysts for AEM devices and facilitate the deployment of H_2 at scale.

References. [1] Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston (1974). [2] Lindquist, *ACS Applied Materials & Interfaces* (**2021**). [3] Naito, *Inorganic Chemistry Frontiers* (**2021**). [4] Trasatti, *Pure and Applied Chemistry* (**1991**).

Wed-L7-04

A Kinetic Analysis of the CO Electro-Oxidation Reaction on Bimetallics: Understanding the Interplay of Bifunctional and Electronic Effects

Adam Holewinski

University of Colorado Boulder

CO electro-oxidation is one of the most widely studied reactions in electrocatalysis for both fundamental and technological reasons. CO* is a strongly-binding intermediate which poisons the most active oxidation catalysts (Pt,Pd) during conversion of many organic molecules (e.g. methanol, formic acid, and larger oxygenates such as molecules derived from biomass). For this reason, there is much interest in developing CO-tolerant materials to mitigate this poisoning effect and improve electro-oxidation activity, in turn improving the efficiency of direct-organic fuel cells and/or oxidative electrosyntheses. A number of bimetallics, (e.g. PtxRu1-x, AgxPd1-x) show improved CO-oxidation activity, and the effects are often interpreted in terms of “bifunctional” mechanisms, in which the added element serves to introduce OH* (from water) to the surface at lower potentials to form CO2. In this talk we will discuss kinetic signatures of bifunctional mechanisms in contrast to the alternative in which one element mainly electronically modifies the other. We then experimentally investigate a series of AgxPd1-x/C alloy catalysts and compare their activities in both CO and methanol electro-oxidation under a range of conditions to assess the extent to which enhancements may be attributed to bifunctional vs. electronic effects.

Wed-L7-05

Roles of Cu in coke oxidation during regeneration of spent Cu/BEA catalyst from renewable high octane hydrocarbon synthesis

Anh To, Qiyuan Wu, Daniel Ruddy, Susan Habas

National Renewable Energy Laboratory

Cu-modified BEA zeolite catalyst (Cu/BEA) has demonstrated advantage over HBEA zeolite in the conversion of methanol and dimethyl ether to high-octane gasoline by shifting the hydrocarbon pool chemistry toward olefin pool instead of aromatic pool. Identity and relative composition of surface carbon species, which are often linked to deactivation, are also affected by addition of Cu to BEA zeolite. Complementary ex situ and in situ characterization techniques were utilized to understand the structures of surface carbon species on post-reaction Cu/BEA and unmodified BEA catalysts and the removal of these surface species under thermal oxidation. It was found that the presence of Cu promoted carbon removal at lower temperatures than for unmodified BEA through activation of O2 by Cu oxide. The roles of Cu speciation to O2 activation and oxidation of surface species were also clarified by the model Cu/BEA catalysts containing either ion exchange Cu or Cu metal oxide cluster. The fundamental insights into the composition of surface carbon species enabled the design of an effective and efficient regeneration strategy for the DME homologation reaction over Cu/BEA, resulting in full recovery of the catalyst activity.

Wednesday, July 13th | 13:00 - 14:20 | C8-Colloids, Macromolecules, and Surfaces in Life Science

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Wed-C8-01

Evaluating asymmetrical flow field-flow fractionation-multiangle light scattering for determining size heterogeneity and numbering of outer membrane vesicles

Christine L Plavchak [1], Allison Z. Werner [2], Gregg T. Beckham [2], S. Kim R. Williams [1]

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Outer membrane vesicles (OMVs) are nanometer sized lipid particles (25-500 nm) that are produced from the outer membrane of gram-negative bacteria. Their importance includes their diverse roles in cell signaling and potential for lignin depolymerization. Analytical challenges associated with OMVs, and other extracellular vesicles (EVs) are centered around determining size distributions, particle counts, particle proteins and lipids identities and loads, and correlating these parameters to EV function. Current methods for sizing and determining particles counts such as flow cytometry, Coulter counter, and nanoparticle tracking analysis (NTA) are limited in their sensitivity to size (> 50 nm) and results are often biased by polydispersity in size. These techniques except for the latter are done with a bulk sample and biases due to polydispersity can be mitigated if a separation technique is utilized prior to these counting techniques. Asymmetrical flow field-flow fractionation coupled to multiangle light scattering (AF4-MALS) has recently been used to separate and quantify a variety of EVs. While the separation mechanism eliminates the influence of polydispersity in OMV samples, particle counting by MALS remains challenging. The uncertainty in OMV refractive indices (RI) raises questions about the accuracy of MALS counts over visual counting methods such as NTA, which does not depend on the analyte RI value for determining particle counts. This work evaluates the impact of OMV RIs on MALS particles counts. RI values obtained from published literature and estimates based on a hard sphere or core-shell structure of two different OMV samples ranged between 1.35 and 1.65. The impacts of core and shell RI as well as the physical model, e.g., hard sphere versus coated sphere, on the particle counts of separated OMVs were evaluated. The coated sphere model appears to be more sensitive to noise in the measured signal intensity and gives rise to erroneous counts (> 10^{20} particles/mL). Samples with larger signal-to-noise ratios (S/N >800) returned reasonable particle counts (10^{8}-10^{11} particles/mL) but are influenced more by the inner sphere RI than the shell RI. The sphere model is less sensitive to signal-to-noise, but this RI range still yielded as much as a 200% difference in particle counts. Overall, this work demonstrates that MALS is useful for particle counting and errors can be mitigated when using the correct model and refractive index values.

Wed-C8-02

Effect of Tear Film Lipid Layer on Water Evaporation

Xiaojie Xu, Yi Zuo

Department of Mechanical Engineering, University of Hawaii at Manoa

Tear film is a multilayered biological barrier that protects, lubricates, and provides a smooth optical surface for proper vision. Being the outermost layer of the tear film, the tear film lipid layer (TFLL), has long been regarded as the major chemical component responsible for retarding water evaporation and thus maintaining stability of the tear film. Frequently broken TFLL contributes to the pathophysiology of the dry eye disease. However, in vitro experiments have showed controversial results on whether or not the TFLL is able to retard water evaporation. Most existing in vitro experiments were performed with the classical Langmuir film balance, and the effects of spread TFLL on the water evaporation rate were examined gravimetrically for hours, due to the low sensitivity and lack of rigorous environmental control in these experiments. We have developed a novel experimental model based on constrained drop surfactometry (CDS), recently developed in our laboratory. CDS allows a rigorous control of the mass transfer area by maintaining a droplet with a constant surface area. The rate of water evaporation is inversely calculated from the water replenished into the droplet to maintain the constant surface area over a 30 min period. Using this new method, we have studied the effect of TFLL on water evaporation, as a function of surface tension of the TFLL. Our experimental results may provide novel implications into better understanding the physiological function of the TFLL in health and in dye eye.

Wed-C8-03

Numerical Simulations, Scaling Analysis, Surrogate Experiments, and Analytic Model of Microbial Growth in a Rotating Bioreactor

Joshua A. Adeniran [1], Mingyang Tan [2], Travis Walker [1, 3, 4]

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Microbial growth in space has been reported to be enhanced over growth in stagnant tanks under gravity. The increases in size and in population are believed to be caused by a reduction of settlement under microgravity in space, resulting in a more spatially homogeneous distribution of microorganisms. Earth-based counterparts have been developed to provide a possible alternative to in-space experiments. For example, rotating wall vessels (RWV) can generate forces that counteract the gravitational force by rotating the wall of a horizontal vessel. Studies of RWV's have been conducted both theoretically and experimentally; however, most investigations neglect the particle-wall and the particle-particle interactions. Thus, a predictive model needs to be developed to determine the distribution of microbial particles, which can be utilized to optimize microbial growth. In our work, parameters for efficient operation of RWVs, such as aspect ratio, rotation velocity of the reactor, Pe´clet number, Rayleigh number, etc., are investigated via a scaling analysis. An analytical solution was derived to predict the location of spherical surrogates of microbes in the absence of the wall. To include the presence of the wall, we utilize Stokesian dynamics to accurately describe the motions of the simulated microbes (spherical and aspherical) in a RWV in the presence, for example, of gravitational, centrifugal, drag, and Brownian forces. To build aspherical particles and the rotating wall, we use a collection of spheres so that the hydrodynamic interactions can be accurately calculated. Finally, we present simplified experimental results of spheres in a RWV to verify our results.

Wed-C8-04

Solubilization of aqueous-insoluble phenothiazine drug in TX-100 micellar solution and interactions of cationic/anionic surfactants with phenothiazine–TX-100 system

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This work discusses the interaction of surfactants such as tetradecyltrimethylammonium bromide (TTAB), hexadecyltrimethylammonium bromide (CTAB), cetylpyridinium chloride (CPC), cetylpyridinium bromide (CPB) and sodium dodecylsulphate (SDS) in presence of poorly soluble drug phenothiazine (PTZ) in triton X-100 (TX-100) micellar aqueous media through the investigation of different physicochemical parameters. The interaction of surfactants in PTZ–TX-100 media has been studied using conductometric technique at pH 7.4 (SP buffer) and at three temperatures. The conductometric results reveal the sequence of critical micelle concentration (CMC) values of surfactants as SDS > TTAB > CPC > CPB > CTAB. UV–vis spectroscopy studies were used to learn the interactions of surfactants with the drug PTZ in TX-100 aqueous media (at 303.15 K and pH 7.4) which suggest the interactions are highly feasible (change of Gibbs energy; < 0) and greatly improve beyond the CMC values of corresponding surfactants. The estimated parameters using the Benesi–Hildebrand equation indicate higher binding constant for cetylpyridinium surfactants and least for SDS and the drug–surfactant complex formations are found to be in 1:2 stoichiometric ratios. Fluorescence technique has also been employed to study the aggregation number (Nagg), Stern-Volmer constant (KSV) and micro-polarity of TTAB/CTAB/SDS in PTZ–TX-100 systems at 303.15 K. The evaluated thermodynamic parameters such as change in Gibbs energy, enthalpy and entropy of micellization show the process of micellization of all studied surfactants in PTZ–TX-100 aqueous media are spontaneous and exothermic.

Wednesday, July 13th | 13:00 - 14:40 | D10-Self and Directed Assembly

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Wed-D10-01

Preparation of structured biomimetic composite materials through magnetic control of sol-gel phase transitions

Marco Lattuada

University of Fribourg Department of Chemistry

Nanocomposites are an important class of materials, with unique properties resulting from the unique combination of the matrix and the dispersed phase. Here we present a new strategy for the preparation of bioinspired composite materials, by using magnetic colloids to control the structure of a silica gel phase by magnetically manipulate the sol-gel phase transition. The gel phase has then be used as a skeleton for the preparation of a polymer-inorganic hybrid material. Magnetic colloids were added to the silica sol precursor solution, and a magnetic field was applied during the sol−gel transition. A static field led to a fiber-like structure, with silica fibers aligned in the direction of a field. Conversely, when exposed to a rotating magnetic field, magnetic colloids organized in layers parallel to the plane of rotation of the field and template the growing silica phase, resulting in a layered anisotropic silica, reminiscent of the inorganic structure of nacre. The final nanocomposite materials have been created by filling the porous structure with a monomer, leading to an elastomer upon polymerization. Compression tests of the structured composite show that their mechanical properties far exceed those of non-structured composite materials with an identical chemical composition. Furthermore, more complex silica structures have been obtained by first creating a structured silica gel, and then impregnating it with a second sol solution containing magnetic colloids, and applying a magnetic field in a different direction. In this case, silica gels with a fiber structure connected by perpendicular rods connecting them, or layered silica gels with rods perpendicular to the layer and connecting them were obtained, eventually leading to even stronger composite materials, with defined anisotropy and with a complex architecture could be prepared. Some of these architecture are shown in the Figure below. References [1] J. Medinger, M. Nedyalkova, M. Furlan, T. Lüthi, J. Hofmann, A. Neels, M. Lattuada, ACS Applied Materials & Interfaces, 13, 8040-48052 (2021)

Wed-D10-02

Understanding Sub-Nano Surface Structure Variations in Self-Assembled Monolayers

Martin Thuo, Chuanshen Du, Jiahao Chen, Zhenjiang Wang

Materials Science & Engineering Iowa State University

Ability to organize molecules on coinage metal into ordered Self-Assembled Monolayers (SAMs), presents a simple way to engineer surfaces at the sub-nanometer level – one chemical bond at a time. The odd-even parity effect is a simple (chemically), yet not so obvious, manifestation of the structure and equilibration process during the formation of SAMs. Our ability to observe this property has, however, been riddled by uncertainty starting with the Porter-Whitesides discrepancy. Resolution of this disparity is essential if this technology is to be fully understood. Felicitous choice of surfaces (identity and roughness) has recently allowed us to confirm limitations to the observation of this phenomenon by using wetting and spectroscopic measurements. This talk explores the role of roughness, probe liquid and defects in the quantitative observation of the odd-even parity effect. We demonstrate that advances in preparation of quality metal surfaces coupled to advances in surface characterization has allowed for sub-nanometer resolution in characterization of SAMs.

Wed-D10-03

Role of particle shape and surface chemistry on flow-induced microstructural changes in wormlike micellar solutions

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Wormlike micelles (WLMs) are long, threadlike aggregates of surfactant molecules, an example of a class of association colloids that form under appropriate solution conditions. WLMs are found in a wide variety of consumer products such as cleaners, soaps, and cosmetics. The design, development, and efficacy of formulations containing WLM solutions demand investigation of their rheology and microstructure. In this study, we explore the possibility of tuning the rheology and microstructure of WLM solutions of cationic surfactant CTAB via the addition of charged nanoparticles of well-defined size, shape, and surface chemistry. A significant change in zero shear viscosity and viscoelasticity of solutions has been observed on increasing the particle concentration. The addition of like-charged particles significantly increased the WLM solution's zero shear rate viscosity and relaxation time, whereas the addition of oppositely charged particles showed a decrease in both. The changes are hypothesized to originate from the incorporation of the charged particles into the micellar networks. The Dynamic light scattering measurements confirmed the tail on adsorption of surfactant molecules onto charged particles. Thus, the addition of nanoparticles can impart additional functionality to the resulting material leading to new or superior applications in personal and housecare formulations

Wed-D10-04

Evaporative assembly of spheres and rods on hydrophilic and superhydrophobic substrates

Ahmed Al Harraq, Bhuvnesh Bharti

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

Drying droplets of colloidal suspensions is a useful assembly mechanism to obtain microstructured materials. We consider two paradigms of assembly based on the wettability of substrates with respect to aqueous drying droplets. On wettable substrates, where the water-solid contact line is pinned, drying droplets can provide two-dimensional assembly as a tool to pattern the microstructure of surfaces. On non-wettable substrates, where the contact line is unpinned, drying droplets are templates for assembly of 3D structures. We display results obtained by drying droplets containing silica nanoparticles of spherical and rod-like shapes with a focus on the morphological role of rods. In the 2D setup, we introduce small amounts of rod-like nanoparticles to act as impurity in colloidal crystals formed by evaporative assembly of nanospheres. We analyze the effect of the rod-like shape in reducing order in the final microstructure, by tracking the reduction in hexatic crystallinity and its replacement with a glassy phase. In the 3D setup, we study the role of rod aspect ratio in offsetting the traditional buckling dynamics observed when drying spherical nanoparticles. We find that higher aspect ratio rods form shells that sustain drying and do not buckle. Packing arguments suggest that the permeability of shells formed by longer rods promotes mechanical stability. Our findings are of interest in the application of drying droplets for surface patterning structural color, and in the suppression of buckling for microencapsulation and spray drying processes.

Wed-D10-05 Withdrawn

Assembly Architectures of Functional Polymer Particle in Hierarchical Orders via Controlled interfacial Interactions

Nikunjkumar Visaveliya

The City College of New York

Polymers are soft materials and hence useful in biological and biomedical applications. The engineering of polymer nanoparticles with controlled properties is very promising. 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.

Wed-D11-01

Emulsion imaging of DNA-liquid phase diagram reveals valence and electrostatic effect

Nathaniel Conrad [1], Grace Chang [1], Deborah Fygenson* [1, 2], Omar Saleh* [2, 3]

[1] UCSB Physics[2] UCSB Biomolecular Science and Engineering[3] UCSB Materials

Liquid-liquid phase separation (LLPS) in polymer solutions is the result of many confounding factors, such as polymer structure, the nature of polymer-polymer interactions, and solution conditions (notably, for charged macromolecules, salt concentration). Here, we explore how the LLPS phase diagram of a programmable, cross-linking DNA nanostructure, known as a DNA Nanostar (NS), is affected by NS valence and solution salt. Experimentally, it can be difficult to quantify the high-density, 'liquidus' binodal in LLPS phase diagrams, due to complications in handling and assaying the dense macromolecular phase. Here we develop a novel method that accurately quantifies the NS liquidus binodal: From low NA pictures of micron-sized, water-in-oil droplets containing a mixture of fluorescently-tagged NSs and similarly-tagged, non-interacting DNA hairpins, we measure the volume fraction of the dense liquid phase, φ, as a function of the total NS concentration, c. As per the "lever rule", $\varphi(c)$ should be linear, with a slope related to the concentration of the dense and dilute phase and an x-intercept equal to the concentration of the dilute phase. We demonstrate experimentally that the lever rule indeed applies to NS solutions, and extract from the analysis the dilute and dense-phase concentrations. We utilize this technique to measure the temperature-concentration phase diagram of DNA Nanostars as a function of NS valence and solution salt (NaCl) concentration. We find the results are in good agreement with recent theoretical and computational work. Our results on NS behavior give fundamental insight into limited-valence phase self-assembly, while the method we have developed will likely be useful in the study of other LLPS systems.

Wed-D11-02

Stability and Self-Assembly of Cylindrical Coiled-Coil Domain into Discrete Nanoparticles and Soluble Aggregates

Kenneth Crane-Moscowitz [1], Eric Furst [1], Chris Kloxin [1, 2], Darrin Pochan [2]

[1] Department of Chemical and Biomolecular Engineering, University of Delaware[2] Department of Material Science and Engineering, University of Delaware

Peptide bundlemers are a new class of nanoparticle that offer exquisite control of structure and chemistry. These synthetic peptide sequences self-assemble in aqueous solutions into 4 nm long, 2 nm diameter cylindrical coiled-coil domains and can be functionalized to undergo polymerization into micrometer-length rigid rods. However, little is known about their solution stability as proteins; peptides are known to aggregate or disperse depending on their sequence and formulation conditions. In the present work, the self-assembly behavior of an exemplary peptide bundle nanoparticle is examined in solutions at pH 2, 6, and 10 and in low and high ionic strength aqueous suspensions via dynamic light scattering. The intensity autocorrelation function data is fit using the CONTIN algorithm. The peptide bundles form into two distinct size populations with hydrodynamic radii of 1.7 nm and the other at 60 nm. These populations are assessed to be individual coiled-coil peptide bundles and collections of bundles forming soluble aggregates. The solution conditions also dictate which of the two populations will become the dominant species as the sample ages. This investigation demonstrates the solution stability of such peptide-based bundles and their potential as a new class of stable highly engineered colloidal nanoparticles in solution.

Wed-D11-03

Peptide Mediated Assembly of Putrescine Oxidase

Cindy Berrie

Department of Chemistry, University of Kansas

The control of binding and orientation of enzymes at interfaces is critical for a number of applications include biosensing and biofuel cell devices and yet such control remains a significant challenge. In this work, we have investigated the use of a genetically engineered peptide (AuBP) coupled to the enzyme PutOx as a model system for the investigation of the peptide mediated assembly as one potential approach for controlling the binding and orientation of biomolecules. Through investigations of both the native enzyme (PutOx) and the peptide labeled enzyme (PutOx-AuPB) we have been able to demonstrate definitively both the selectivity and specificity of the peptide for the Au(111) surface as well as changes in molecular shape upon adsorption. Other surfaces were investigated as well, and revealed no difference in binding between the PutOx and the PutOx-AuBP. Preliminary data suggest that the peptide mediated assembly of the PutOx may lead to enhanced thermal and temporal stability of the enzyme. Use of such peptides will require the detailed understanding of the role of the sequence, linker, and location of the peptide tag in order to optimize assembly and activity and investigations are currently underway in this direction.

Wed-D11-04

Diverse morphologies of oppositely charged homochiral peptide mixtures

Nairiti Sinha [1, 2], Craig Hawker [1], Matthew Helgeson [2]

[1] Materials Research Laboratory, UC Santa Barbara[2] Chemical Engineering, UC Santa Barbara

The delicate balance of electrostatic and hydrophobic interactions are critical during protein folding events and misfolding has been linked to many diseases. An important example is that of Alzheimer’s disease involving formation of pathological amyloid fibers of misfolded tau proteins that are intrinsically disordered proteins. Similarly, previous studies of aqueous mixtures of poly-L-lysine and poly-L-glutamic acid have shown that solid precipitates form instead of liquid-like coacervate droplets that has been linked to hydrogen bonding driven beta-sheet formation and aggregation. Our investigation into similar peptide mixtures have revealed that a previously unreported dependence of this phase behavior on peptide concentration via the delicate balance of intra- and intermolecular interactions. Specifically, at low ionic strengths, whereas mixtures above the overlap concentration C* of peptides form solid-like precipitates consistent with published literature, mixtures form liquid-like coacervate droplets to dense networks of partially coalesced droplets at concentrations below C*. Molecular dynamics simulations suggest that this difference can be traced to extended peptide complexes with higher beta-sheet content that form at elevated concentration, which are prone to non-equilibrium self-assembly into bulk precipitates. Furthermore, we show that the pathway of precipitate formation is different below and above C* in the presence of added salt, resulting in distinct precpitate morphologies that are sensitive to thermal history and mixing pathways. Finally, at high ionic strengths (2-5 M NaCl), we observe a re-entrant transition to coacervate droplets, indicating that release of counter-ions and low beta sheet content can facilitate liquid-liquid phase instability under these conditions. This complex phase behavior suggests a subtle balance between non-equilibrium hydrogen bonding-driven beta-sheet assembly and electrostatically-driven coacervate formation results in a diversity of morphologies; the new results and its implications for protein folding and assembly will be discussed in this talk.

Wednesday, July 13th | 13:00 - 14:40 | E8-Electrokinetics and Microfluidics

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Wed-E8-01

High Throughput Screening of Crystallization Condition for Protein using X-ray Transparent Microfluidics

Sarah Perry [1], Sarthak Saha [1], Can Özden [2], Margaret Stratton [2]

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The determination of a protein structure begins with expressing and purifying the protein, followed by high-throughput screening to identify possible crystallization conditions. Once optimized conditions are achieved, the crystals are harvested and analysed by X-ray diffraction to resolve the final 3D structure. Finding the right crystallization condition is the major bottle neck in this process. We have developed a microfluidic device for counter diffusive protein crystallization, which allows screening of large number of conditions from a single experiment. Apart from the advantage of high throughput screening, the use of microfluidics allow scaling out for large numbers of highly-reproducible parallel experiments while maintaining exquisite control over local conditions and concentration gradients. Traditionally, silicone based elastomer alongside thermoplastic and paper are the most widely used materials for microfluidics. However they do not allow in situ analysis of protein crystals, due to their low X-ray transparency. We take the advantage of UV curable polymers, which has high level of X-ray transparency required for structural biology studies. Finally we have incorporate a sophisticated fluid handling system in our devices that takes advantage of the surface forces that controls the mixing of liquids in the device. The developed device provides an one step solution for structural biologist from screening crystallization conditions to determining the protein structure.

Wed-E8-02

Digital Microfluidics-Like Manipulation of Electrokinetically Preconcentrated Biomolecules using Ion Concentration/Polarization (CP) in 1D/2D Microfluidic Networks

Sinwook Park [1, 2], Barak Sabbagh [2], Ramadan Abu-Rjal [1], Gilad Yossifon [1, 2]

[1] School of Mechanical Engineering, Tel Aviv University[2] Faculty of Mechanical Engineering, Technion I.I.T

Herein, we demonstrate digital microfluidics-like manipulations of preconcentrated biomolecule plugs within a continuous flow that is different from the commonly known digital microfluidics involving discrete (i.e. droplets) media. This is realized using one- and two-dimensional arrays of individually addressable ion-permselective membranes with interconnecting microfluidic channels. The location of powered electrodes, dictates which of the membranes are active and generates either enrichment/depletion diffusion layers, which, in turn, control the location of the preconcentrated plug.[1] An array of such powered membranes enables formation of multiple preconcentrated plugs of the same biosample as well as of preconcentrated plugs of multiple biosample types introduced via different inlets in a selective manner. Moreover, digital-microfluidics operations [2] such as up-down and left-right translation, merging, and splitting, can be realized, but on preconcentrated biomolecule plugs instead of on discrete droplets. In a one-dimensional microfluidic network with individually addressable membranes, the conceptual digital-like operations of translation, splitting and merging can be realized by manipulating a single preconcentrated plug under continuous flow. In addition, simultaneous formation of multiple plugs and digital control of multiple preconcentrated plugs were examined which is of importance for increasing the parallelization of the system and to enable multiplex sensing. These experimental observations performed in 1D channel networks were complemented by numerical simulations for a qualitive comparison which used a fully coupled, two-dimensional (2D) time dependent model with Poisson–Nernst–Planck–Stokes (PNPS) equations [3]. The two-dimensional array of membranes and microfluidic network enabled introduction of several samples and hence, formation of plugs of different biosample sources, and control of their interaction. Specifically, multiple samples were introduced and manipulated within the main microchannel, to form different combinations in a selective and controlled manner by connecting separate inlets to the main microchannel with an array of individually addressable embedded membrane pairs acting as valves. Such capability enabled not only control of the location of single and multiple plugs, but also their composition in terms of the preconcentrated molecules. Adding an upstream sorting membrane pair also enabled valving of the introduced analyte that was being preconcentrated downstream, without any limitation on the amount of sorted sample. This technology, based on nanoscale electrokinetics of ion transport through permselective medium, opens future opportunities for smart and programmable digital-like manipulations of preconcentrated biological particle plugs for various on-chip biological applications. [1] R. Kwak, J. Y. Kang and T. S. Kim, Anal. Chem., 2016, 88, 988–996. [2] H. Moon, A. R. Wheeler, R. L. Garrell, J. A. Loo and C. J. Kim, Lab Chip, 2006, 6, 1213–1219. [3] S. Park and G. Yossifon, Anal. Chem., 2020, 92, 2476–2482.

Wed-E8-03

“Remote wetting”: reversible droplet modulation in a contactless world

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Electrowetting (EW)-based technologies inform state-of-the-art platforms for droplet wetting state modulation on surfaces. However, the requirement of direct droplet-electrode contact may pose scalability challenges as droplet sizes become smaller and the number of droplets to be actuated increases. Here we present a contactless method that is capable of modulating droplet wetting states reversibly on non-wetting substrates. The method, dubbed dielectric charge injection (DCI), involves corona discharge-based charge injection – above a critical voltage, electric field concentration around a sharp, conductive probe exceeding the surrounding medium’s dielectric strength leads to ionization of the dielectric medium. The generated ions then accelerate away from the probe due to like-polarity repulsion, leading to charge injection onto any target surface containing a reference electrode and overlaying dielectric layer. Voltage plays a central role in this multiscale transport phenomena, manifesting as discrete ions and electric fields toward manipulation of macroscopic contact angles. Using DCI, we demonstrate wetting of a pure water droplet on a polydimethylsiloxane (PDMS) surface immersed in hexadecane, a low dielectric liquid. Starting from a completely non-wetting state, DCI is able to facilitate wetting of the droplet, with tunable wide-range resultant contact angles. By simple removal of the stimulus, the droplet is able to dewet fully back to the non-wetted state. The nonwetting-wetting state reversible transition is capitalized in an application towards droplet-surface material interchange, which possesses utility in integrating droplet encapsulation-based technologies (e.g. microfluidics) to surface-based analytical technologies (e.g. MALDI-MS). DCI presents a contactless, reversible droplet wetting state modulation platform that builds upon the inspiring successes of EW-based technologies – simple yet powerful, with vast application potentials in fluidics, lenses/displays, and beyond.

Wed-E8-04

Inkjet printing low aspect ratio microfluidic devices through tunable sacrificial layers

Pooria Pirdavari, Huy Tran, Min Y. Pack

Department of Mechanical Engineering, Baylor University

There has been an increasing interest in passive microfluidic mixers due to their various applications in different fields and their lower cost compared to the active mixers. Among the numerous passive micromixers, low aspect ratio curved microchannels are widely used due to their high efficiency. The curvature in these micromixers results in the development of secondary flow which generates Dean flows that can highly affect the mixing performance. This project aims to provide an alternative to manufacturing microfluidic devices at a low expenditure using inkjet printing through tunable sacrificial layers to understand the mixing mechanism at the low aspect ratios of microfluidic devices. By studying fluid dynamics at different aspect ratios smaller than 1:10 and different Dean numbers, this project enables us to better perceive the relation between the Dean number and the mixing performance of the low aspect ratio curved microchannels.

Wed-E8-05

Don’t go breaking my charge: induced charge electrophoresis of surface-modified Janus particles

Cooper Thome, Julia Bendorf, Jin Gyun Lee, Ankur Gupta, C. Wyatt Shields IV

Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, 80303, USA

Since the first experimental demonstration of induced charge electrophoresis (ICEP) of metallodielectric Janus particles nearly 15 years ago,[1] numerous groups have studied the ICEP of particles with different shapes[2] and patch geometries.[3] However, few groups have studied the effects of surface modifications on ICEP. Here, we examine the ICEP of metallodielectric Janus particles modified by antifouling polymer brushes, antigens, and/or antibodies. ICEP stems from an asymmetry in polarizability of each hemisphere of the Janus particle: one metallic and highly polarizable, and one polymeric and weakly polarizable (or dielectric). When a uniform AC electric field is applied to a spherical Janus particle, it reorients such that the interface between the hemispheres aligns parallel with the field. The field initially intersects perpendicular to the particle surface and ions in solution accumulate preferentially at the metallic hemisphere, yielding an induced charge cloud. At steady state, the induced charge cloud leads to expulsion of the field lines parallel to the surface, and fluid is drawn to the particle parallel to the field and ejected perpendicular to the field, away from the metallic hemisphere.[4] This asymmetric ejection of fluid leads to particle propulsion in the direction of the dielectric hemisphere. It has been shown that analogous induced flows at a flat metal surface can be affected by contamination with a dielectric film due to the potential drop being split between the dielectric coating and the charge cloud, as well as the film “buffering” ions through surface reactions.[5] In the present study, we examine the effects of more complex “contaminants” (i.e., polymer brushes, proteins) on metallodielectric Janus particle ICEP for the first time to study their potential as particle-based biosensors. To fabricate Janus particles, we coated monolayers of carboxylated polystyrene particles with chromium and gold via electron-beam evaporation. Polymers, proteins, and small molecules were either adsorbed or bound to the surfaces of the particles via carbodiimide chemistry (on the polystyrene hemisphere) or gold-thiol chemistry (on the gold hemisphere). Particle ICEP was driven by the application of a 10 kHz AC electric field (with field strengths spanning 200-300 V cm^{-1}) in coplanar electrode chamber, positioned on an inverted microscope. Particle speeds were extracted via analysis of captured videos and typically ranged from 0 to 10 µm sec^{-1}. We show that protein accumulation on the surfaces of the Janus particles suppresses ICEP through reducing asymmetry in the induced flows around the particle, but that antifouling coatings can predictably control this decrease in particle speed. We further show that particle speed can be increased proportionally with direct conjugation of antibodies to the metallic hemispheres of the particles. Our study reveals a rich design space largely unexplored in the field of electrokinetics, and we offer potential mechanisms for the yet unexplained phenomena we have observed.

(1) Gangwal et al. *Phys. Rev. Lett*. **2008** (2) Brooks et al. *Proc. Natl. Acad. Sci.* **2018** (3) Lee et al. *Nat. Commun.* **2019** (4) Bazant and Squires. *Phys. Rev. Lett.* **2004** (5) Pascall and Squires. *Phys. Rev. Lett.* **2010**

Wednesday, July 13th | 13:00 - 14:00 | F8-Emulsions, Bubbles & Foams

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Wed-F8-01

Bijel Disordered Bicontinuous Aperiodic Networks (DBANs) for Advanced Materials

Tiancheng Wang, Daeyeon Lee, Kathleen Stebe

Chemical and Biomolecular engineering department, University of Pennsylvania

The extensive studies of highly ordered porous structures (e.g. inverse opal and gyroid) reveals very well their processing-structure-property relationship. However, there is a lack of effort on developing this relationship for disordered materials. Our work explores disordered bicontinuous aperiodic networks (DBANs) for materials innovation. DBANs feature at least two distinct disordered, bicontinuous phases which provide numerous modalities for interaction with fluids, electric charge, and electromagnetic waves. DBAN formation by kinetic arrest allows components with distinct functionalities to be assembled via scalable methods. Bicontinuous interfacially jammed emulsion gels (bijels), a unique class of particle-stabilized fluid-bicontinuous DBANs structures, are formed by arresting the spinodal decomposition process of two liquid phases via jamming of nanoparticles at interface. Its fast kinetics, high tunability and self-assembled nature makes it an ideal path for DBANs fabrication. However, existing methods of bijels fabrication faces the challenges of limitations on feature size, materials selection and fabrication environment. We have developed a pathway for triggering spinodal decomposition, vaporization induced phase separation (VIPs), that enables scalable fabrication of bijels under ambient condition. Furthermore, bijels with uniform submicron domain sizes are generated by combination of VIPs and STRIPs (solvent transfer induced phase separation) methods that greatly extended the potential of bijels-DBANs in various applications. Passive day time radiative cooling (PDRC) based on bijel is demonstrated as an example to show the structure-optical property of bijel DBANs. By carefully tunning the feature size and material selections of bijel, >95% reflectance in the solar spectrum and >95% emittance in the LWIR window is realized and Its cooling performance is proved in outdoor tests. Except optical properties, we have also transferred bijels geometry to carbon material by doing carbonization of the polymer phase. The resulting carbon bijels are tested as cathode material for air/metal battery.

Wed-F8-02 Withdrawn

Microscopic and Macroscopic Dynamics of Thin Liquid Films during Bubbles' Impact on Inclined Surfaces for Fruit Cleaning using Air Bubbles

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Fruit cleaning with air bubbles is demonstrated as an effective method in removing bacteria and biofilms on fruit surfaces, but the mechanism at a microscopic scale is still elusive. The hypothesis is that the shear force generated during bubble sliding on surfaces overcomes the adhesion force, resulting in the removal of contaminations from the surface. In this work, both the experimental study and numerical modelling of bubble bouncing and sliding on inclined surfaces were performed. A free air bubble rose and impacted an inclined surface. Macroscopic dynamics, e.g. bouncing and sliding, of air bubbles on the surfaces were monitored by a side-view camera, while microscopic dynamics, such as film drainages and bubble sliding, were examined using the Synchronized Multi-Wavelength Reflection Interferometry Microscopy (RIM). Spatial and temporal evolution of the film thickness of the thin liquid films was determined from the recorded interference fringes. From both the sliding velocity and film thicknesses, the shear stress was determined. The experimental results were compared with those obtained in numerical simulations. Effects of impact velocity, bubble size, and inclination angles on the film thickness and consequently the shear stress were evaluated. Results showed that the impact velocity impacted bubbles' bouncing on solid surface, but had minor impacts on both sliding velocity and film thickness during the bubble sliding. At low inclination angles, i.e. 2.5 – 7.5 degrees, the shear stress was in the range of 22-28 Pa, and it increased with increasing the inclination angle. Surface cleaning by air bubbles was demonstrated in the laboratory. This work provides fundamental knowledge on fluid mechanics at the interface, and the result can be used in guiding future development of cleaning technology using air bubbles.

Wed-F8-03

Optical Methods to improve the accuracy of Diffusing Wave Spectroscopy investigations of emulsions, with relevance to experiments in microgravity

Valentina Lorusso [1], Davide Orsi [1], Marco Vaccari [1], Robert McMillin [2], Libero Liggieri [3], Luigi Cristofolini [1], James Ferri [2]

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Diffusing Wave Spectroscopy (DWS) [1,2] is a powerful tool to investigate structure and dynamics in turbid samples, such as foams and emulsions. However, decoupling structural and dynamical information relies on the knowledge of the distribution P(s) of the length s of the paths followed by photons before reaching the detector. While the classical analysis for DWS is based on analytical forms for P(s) which are only valid for idealized geometries, we recently showed that in realistic conditions this assumption might lead to drastically unreliable estimates for the time-dependent mean square displacement. This can lead incorrect assumptions regarding models of droplet dynamics and limitations on the use of DWS to study the kinetics of emulsions destabilization. We will present results from DWS experiments when P(s) is obtained by Monte Carlo simulations accounting for the experimental geometry, namely shape and dimensions of the sample cell and the scattering geometries. This is applied to experiments on emulsions performed in a setup built for investigations in microgravity on the "Soft Matter Dynamics" facility aboard the International Space Station, where some of the parameters of the scattering geometry might not be directly measurable with the required accuracy [3,4]. Preliminary results relating to the microgravity experiment on water/oil emulsions will be presented. Aknowledgements: European Space Agency (ESA) MAP project "Emulsion Dynamics and Droplet Interface - EDDI" (Contract n. 4000128643/19); National Aeronautics and Space Administration (NASA) project "Particle Stabilized Emulsions and Foams – PASTA (Grant 80NSSC21K2080) [1] D.J. Pine, D.A. Weitz, P.M. Chaikin, E. Herbolzheimer, Diffusing wave spectroscopy, Phys. Rev. Lett. 60 (1988) 1134–1137. doi:10.1103/PhysRevLett.60.1134. [2] D.J. Durian, Accuracy of diffusing-wave spectroscopy theories, Phys. Rev. E. 51 (1995) 3350–3358. doi:10.1103/PhysRevE.51.3350. [3] V. Lorusso, D. Orsi, F. Salerni, L. Liggieri, F. Ravera, R. McMillin, J. Ferri, L. Cristofolini, Recent developments in emulsion characterization: Diffusing Wave Spectroscopy beyond average values, Adv. Colloid Interface Sci. 288 (2021). doi:10.1016/j.cis.2020.102341. [4] Lorusso et al., Optical Methods to improve the accuracy of Diffusing Wave Spectroscopy investigations of emulsions, with relevance to experiments in microgravity, submitted on Colloids and Surfaces A: Physicochemical and Engineering Aspects.

Wednesday, July 13th | 13:00 - 14:20 | H8-Geochemical and Environmental Systems

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Wed-H8-01

ADSORPTION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) ON MICROPLASTICS

Philip Brahana, Bhuvnesh Bharti

LSU: Cain Department of Engineering

Per- and polyfluoroalkyl substances (PFASs) were commercially used as surfactants for decades, but have since been phased out. Today, PFASs are one of the most prominent pollutants in the environment and the human body, while being linked to various environmental catastrophes and severe human illnesses. PFASs are known as “forever chemicals” due to their inability to degrade, and this characteristic makes them particularly dangerous. Like PFASs, microplastics (MPs) are ubiquitous in the environment, and the adsorbate-adsorbent relationship of these two pollutants may magnify their negative consequences. Here, we compared the adsorption capability of Perfluorooctanoic Acid (PFOA) onto weathered and unweathered microplastics. Results indicate that the PFOA molecules have an increased binding affinity for unweathered MPs. This can be attributed to the hydrophobic interactions between the unweathered MPs and the fluorocarbon tails of the PFOA molecules. As MPs are weathered, they undergo a hydrophobic-to-hydrophilic shift, as well as developing a negative charge. These chemical changes decrease the hydrophobic interactions, while simultaneously increasing electrostatic repulsion. This ultimately leads to less adsorption of PFOA onto weathered MP particles. Highlighting the adsorption mechanism of PFASs onto a microplastic substrate is necessary when assessing the growing threat of microplastics to both the environment and human health.

Wed-H8-02

Characterizing solvency effects and the connection to interfacial properties on model asphaltene systems

Olivia M. Haider, Junchi Ma, Lynn M. Walker

Department of Chemical Engineering, Carnegie Mellon University

The degree of aggregation and overall stability of asphaltene dispersions is highly dependent on molecular characteristics, bulk concentration, and solvent composition. These conditions vary widely between individual asphaltene studies. It has been determined that complex interfacial behavior of asphaltenes, connected 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 has been studied to predict compositional gradients of asphaltenes in crude oil systems. However, a systematic, detailed characterization of bulk solvency effects is still needed to fully understand the impact on mechanical behaviors associated with interfacial stability. The goal of this work is to study the effects of solvent quality on the stability of bulk asphaltene dispersions, demonstrate a powerful technique to efficiently analyze bulk stability in opaque colloidal systems, and connect solvent conditions to complex mechanical behaviors in asphaltene 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 both demonstrate fluid-like behavior under small-amplitude compression and expansion, while showing solid-like behavior at larger compression strains in the poor solvent. 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 water emulsions in crude oil systems.

Wed-H8-03

Quantification of the effect of nanoplastic on the hatching process of a zooplankton in a milifluidic platform

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Anthropogenic activities produce a wide range of pollutants in the marine environment. And plastics are the most prevalent of these contaminants, owing to their extensive use in everyday products. These plastics range in size from mega to nano. Due to the mechanical degradation, photo-degradation, hydrolysis, etc. larger size plastic debris in the aquatic environment can be fragmented into nanoplastics. These nanoplastics exhibit colloidal behavior, contain toxic elements, and hence have the potential to be extremely damaging to marine lives due to their physicochemical features. Zooplankton make up a substantial component of the marine food chain and are therefore critical to the marine ecology. *Artemia*, or brine shrimp, is a significant zooplankton species that is abundant in the world's hypersaline marine environments. Being a primary zooplankton and a popular live feed in the commercial aquaculture, they have both ecological and commercial importance. Under adverse conditions (extreme or very low salinity, temperature, etc.), this microcrustacean creates a dormant cyst. Once the conditions are favorable, these cysts begin their metabolism and hatch. With the increasing marine nanoplastic pollution and possible interaction with these cysts, the effect of these nanosized plastics on the hatchability of *Artemia* is crucial to know, but not well studied. In this study, a milifluidic platform was developed to investigate the effect of the nanoplastic pollutant on the hatching process of *Artemia* cysts. The effect of the nanoplastic on the various stages of hatching was quantified in real-time automatically using changes in their physiological processes and visual information. Correlating this data to the end-point hatching rate gave insight into the surrounding nanoplastic environment and its effect on the underlying biological processes involved in *Artemia* hatching. The findings from this study can be used to quantify the influence of nanoplastic pollution on the marine ecosystem via population changes in a major zooplankton.

Wed-H8-04

Transport of Polymer Stabilized Colloidal Activated Carbon in Saturated Porous Media: Implications for In-situ Remediation of Groundwater

Xun Guan, Xitong Liu

Department of Civil & Environmental Engineering, George Washington University

Colloidal activated carbon (CAC) is widely used for in-situ remediation of coastal groundwater sites contaminated by PFAS. However, after the CAC particles are emplaced, the remobilization of the CAC particles from the aquifer materials reduces the long-term effectiveness of the remediation and may also result in colloidal facilitated PFAS migration downgradient. Some polymers are used as stabilizers to enhance the dispersion and colloidal stability of CAC particles in the remediation processes. To date, the influence of different polymer modifications on CAC transport and retention behaviors remains unclear. In this study, we examine the effect of two polymer modifications, carboxymethyl cellulose (CMC) and polydiallyldimethylammonium chloride (PolyDADMAC), on CAC transport in saturated porous media under different ionic strengths. We find that both CMC and PolyDADMAC increase the colloidal stability of the CAC particles. As a result, the CMC- and PolyDADMAC-coated CAC have higher mobility than bare CAC at low ionic strength (0.1 mM NaCl). We also find that significant release of CAC particles occurs upon the introduction of solution with low ionic strength following deposition at high ionic strength (100 mM NaCl), thus highlighting the potential of secondary contamination caused by the released CAC particles during in situ remediation.

Wednesday, July 13th | 13:00 - 14:20 | I8-General aspects of Colloids and Interface

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Wed-I8-01

Structural and Non-Coulombic Effects on the Properties of Electric Double Layers

Dimiter Petsev, Frank van Swol, Laura Frink

Chemical and Biological Engineering, University of New Mexico

We examine an electric double layer (EDL) with surface charge regulation, which results from the thermodynamic equilibrium between the reactive interface and the potential determining ions (PDIs) in the fluid. The focus of our analysis is on the effect of the precise solution structure near the surface and its coupling to the surface chemical equilibrium. This structure is strongly affected by the explicit presence of the solvent molecules, because of their overwhelmingly large numbers in comparison with that of the dissolved ionic species (see the Figure). The solvent molecules are involved in various non-Coulombic interactions with the surface as well as in the fluid, away from the charged interface. Our analysis is based on the classical density functional theory (cDFT), which allows for taking both Coulombic and non-Coulombic interactions into account. cDFT offers precise molecular-level detail in the description of EDLs, while being very computationally efficient. The latter feature is particularly important when there is a great disparity in the number of the different components. An important example is the case where the PDIs are the hydronium ions and the surface charge is a function of the solution pH. For typical pH values, the difference between the hydronium ions concentration and the solvent molarity may be about 4 – 5 orders of magnitude. We present results on the solvent effect on the overall properties of EDLs and demonstrate that the solution structure couples to the surface charge regulation equilibrium. We argue that an explicit account for the structural contribution of the solvent molecules in the EDL is necessary to attain a realistic description of charged interfaces that involve electrolyte solutions. Our approach allows assessing the effects of ionic and surface solvation, size variations, and ionic valency.

Wed-I8-02

Effect of confinement on adsorption, assembly, and catalytic activity of gold nanoparticles in mesoporous silica

Yingzhen Ma, Bhuvnesh Bharti

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

The assembled state of nanoparticles (NPs) within porous matrices plays a governing role in directing their biological, electronic, and catalytic properties. However, the effects of the spatial confinement and environmental factors, such as salinity, on the NP assemblies within the pores are poorly understood. In this study, we use adsorption isotherms, spectrophotometry, and small- angle neutron scattering to develop a better understanding of the effect of spatial confinement on the assembled state and catalytic performance of gold (Au) NPs in propylamine-functionalized SBA-15 and MCM-41 mesoporous silica materials (mSiO2). We carry out a detailed investigation of the effect of pore diameter and ionic strength on the packing and spatial distribution of AuNPs within mSiO2 to get a comprehensive insight into the structure, functioning, and activity of these NPs. We demonstrate the ability of the adsorbed AuNPs to withstand aggregation under high salinity conditions. We attribute the observed preservation of the adsorbed state of AuNPs to the strong electrostatic attraction between oppositely charged pore walls and AuNPs. The preservation of the structure allows the AuNPs to retain their catalytic activity for a model reaction in high salinity aqueous solution, here, the reduction of p-nitrophenol to p-aminophenol, which otherwise is significantly diminished due to bulk aggregation of the AuNPs. This fundamental study demonstrates the critical role of confinement and dispersion salinity on the adsorption and catalytic performance of NPs.

Wed-I8-03

Rheo-dielectric Characterization of Oxidized Carbon Nanoparticles for use as Conductive Additives in Flow-electrodes

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Carbon black nanoparticles are ubiquitously utilized as a conductive additive in flow-electrode capacitive deionization (fCDI) to facilitate charge transport and enhance charge efficiency. Though low-cost and highly conductive, these nanoparticles agglomerate, transforming flow electrodes to a viscous gel with unacceptable pumping costs. Previous work has demonstrated that surface functionalization of carbonaceous nanomaterials can mitigate high viscosities but can also lower the suspension conductivity. A quantitative explanation to the microstructural origin of this tradeoff is inherently missing. We believe that tuning the nanoscale forces between carbon black particles is key to predicting and designing flow electrodes with optimal performance. Therefore, in this work we oxidized Vulcan XC72R carbon black particles to increase their surface charge density and found an enhancement in their colloidal stability. We further investigated the change in the macroscopic behavior by measuring the mechanical and electrical properties of suspensions formulated across the fluid to solid transition. For the more stable oxidized suspensions, we observed a shift in the onset of solidification to higher particle loadings without sacrificing electronic charge transport. Through small-angle X-ray scattering and dynamic light scattering, we discovered that the formation of the fractal agglomerates was inhibited. We conclude that lower viscosities are achievable by preventing carbon black agglomeration, and that the agglomerates are not necessary for forming a charge-carrying network.

Wed-I8-04

Influencing the colloidal interactions in ionic liquid-based dispersions by altering the water and salt content

Dóra Takács, István Szilágyi

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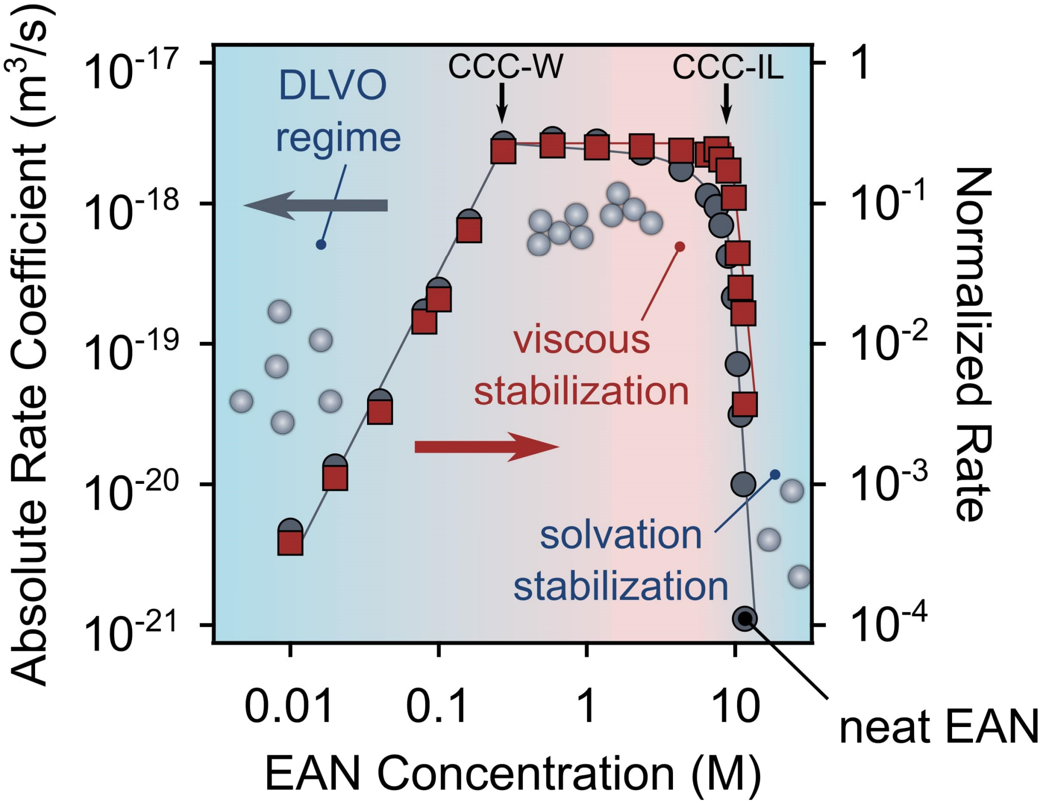
Ionic liquids (ILs) have attracted considerable interest in many fields of chemistry due to their unique physicochemical properties. Among their application, particle suspensions in ILs represent an important class of media, as they are relevant in synthesis and catalysis. Once nanoparticles are dispersed in ILs the interfacial assembly of the IL constituents and the resulting solvation of the surfaces play crucial roles in the colloidal stability of the particle dispersions [1,2]. This is a key point, as the colloidal stability greatly influences the success of the application.



The scope of this work is to contribute to the fundamental understanding of the structuring features of solid–IL interface by focusing on its response to external influences, such as the addition of water and Na+ salt to the colloidal system. Therefore, the aggregation kinetics and charging characteristics of polymer-based particles were studied in ethylammonium nitrate and its water mixtures by electrophoretic and dynamic light scattering techniques [3]. Aggregation rates were found to vary systematically as a function of the IL-to-water ratio (Scheme). Repulsive electrostatic interactions between particles dominated at low IL concentrations, while they were significantly screened at intermediate IL concentrations, leading to destabilization of the dispersions. When the IL concentration was further increased, the aggregation of latex particles slowed down due to the increased viscosity and finally, a striking stabilization was observed in the IL-rich regime close to the neat EAN. The latter stabilization is due to the formation of IL layers at the interface between particles and IL, which induce repulsive forces. The presence of the added salt in the system affected the structure of the interfaces around the particles. The sign of the charge and the composition of the particle surfaces were found to be the most important parameters affecting colloidal stability. The results indicate that the presence of even low concentrations of water and salt in the system (as undesirable impurities) can strongly alter the interfacial structure and thus, the aggregation mechanism in particle IL dispersions.

Acknowledgment: Supported by the ÚNKP-21-3-SZTE-413 New National Excellence Program of the Ministry for Innovation and Technology from source of National Research, Development and Innovation Fund.

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Wednesday, July 13th | 13:00 - 14:40 | K8-Rheology and Dynamics

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Wed-K8-01

Evolution of shear banding instabilities in high elasticity polymeric wormlike micelles (WLMs)

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Similar to small molecule surfactant wormlike micelles (WLMs), nonionic polymer WLMs exhibit elastic flow instabilities including shear banding, where the flow separates into bands of distinct structure and viscosity. Here, the formation and evolution of shear banding and related instabilities are examined in a highly-elastic, model polymeric WLM solution composed of 15% wt aqueous triblock poloxamer P234 (P234) in 2M NaCl. In addition to the high elasticity which drives unique flow behaviors, the slow dynamics and long relaxation times of these WLM solutions versus traditional surfactant WLMs enable clear identification of both transient and steady state flow phenomena with high resolution. Using a combination of linear and nonlinear shear rheology and rheo-particle tracking velocimetry (rheo-PTV), we find that the P234 WLMs exhibit temperature-dependent signatures of both shear banding and fracture, due to the gel-like nature of the WLMs. Shear startup experiments at shear rates immediately following the onset of shear banding reveal significant flow reversal due to elastic recoil after the stress overshoot, the degree to which decreases with increasing shear rate. These experiments are only the second time flow reversal has been documented in WLMs via PTV, and the first time that negative velocities which exceed the magnitude of the inner wall velocity are observed. Additionally, flow reversal begins near the stationary interface, and the duration of flow reversal scales weakly with shear rate. Following this period of flow reversal, the fluid in the high shear rate band continues flowing while that in the low shear rate band becomes nearly immobilized, showing similarities to both shear banding and fracture. Interestingly, flow reversal is not associated with significant wall slip; however, significant fluctuations in the band interface position are observed at longer times when slip becomes more pronounced. Finally, fracture is shown to preclude shear banding with minor changes to the thermal history, suggesting close competition between these mechanisms. These experiments lend insight into elastic instability formation and propagation in gel-like wormlike micelles, providing a data set that can be used to improve or develop models of shear banding in highly entangled, elastic WLMs.

Wed-K8-02

Microrollers make voids: generating wake fields in Stokes flow via hydrodynamics

Shih-Yuan Chen, Michelle Driscoll

Northwestern University

A common application of colloidal materials is to use these small particles as local probes to characterize their surroundings, e.g., colloidal suspensions, polymer solutions, gels, and biomaterials. This measurement technique, called microrheology, allows one to measure the material properties from the microscopic point of view using these colloidal probes - the thermal fluctuation of the probes tells us information about the effective viscosity in a non-Newtonian fluid. Recently, this technique has been expanded using active probes, i.e., driving the embedded colloidal particles with an external field. By deliberately driving the probes, one goes beyond the passive, thermal fluctuation range to active, controllable movement, which then allows for a measurement of the complex modulus in a viscoelastic network gel or the elastic pulling force from a cell. In this talk, we demonstrate a new method to actively probe a complex fluid through hydrodynamic means by using colloidal particles embedded with hematite cubes. We use Helmholtz coils to control magnetic fields and rotate the magnetic dipoles of the particles. The rotating particles drag the fluid around their surfaces and generate flows. When the particles sediment to the bottom of the container, the flow above the particles (to free space) and the flow below the particles (to the bottom of the container) are asymmetric, resulting in a hydrodynamic coupling that can be used to move the particles in a designable direction. Here, we explore how these driven particles can be used to restructure a matrix of passive colloids: the microrollers interact with surrounding passive colloids mainly through hydrodynamic interactions. We find that the microrollers push the passive colloids away and generate depletion zones downstream of their motion, known as wakes. We characterize these wakes by changing the frequency of driving, the size and the volume fraction of the passive particles, and the viscosity of the solution.

Wed-K8-03 Withdrawn

Re-entrant Dynamics and Anomalous Fluctuations in Strongly Confined Liquids

Jeremy Palmer

University of Houston

The dynamics of liquids become increasingly heterogeneous in space and time as their glass transition is approached. These spatial heterogeneities are thought to be connected to a growing length scale over which dynamics are correlated. Confining liquids inside a thin geometry modifies the dynamics and introduces a competing length scale characterizing the extent of confinement. Here, we investigate the consequences of confinement on the dynamics on polydisperse hard-sphere liquids confined in small slit pores using simulation. We show that these systems exhibit re-entrant dynamics resulting from a growing static length scale associated with local structural ordering in the liquid. Our simulations also reveal that these confined liquids exhibit long-wavelength fluctuations that decay in magnitude as the extent of confinement in decreased. We discuss the broader implications of these two unusual behaviors and their connections with those observed in two- and three-dimensional bulk systems.

Wed-K8-04

Coexistence of liquid and solid phases in impacting colloidal drops

Phalguni Shah, Srishti Arora, Michelle Driscoll

Department of Physics and Astronomy, Northwestern University

Understanding the rich and nuanced physics of drop impact is crucial in many processes: for example, geological erosion, industrial coating, forensics, and agrochemical delivery, and the drop impact of Newtonian fluids has been a studied extensively for over a century. However, literature on the impact dynamics of complex fluids is relatively sparse, despite the ubiquity of complex fluids in many natural and industrial impact processes. Here, we present a systematic study of colloidal drop impact over a large range of volume fractions and impact velocities, allowing us to explore the full range of non-Newtonian flow behaviors. We observe impact behaviors ranging from liquid-like spreading to solid-like jamming and connect them to the bulk rheological behavior of our colloidal system. These experiments allow for an exploration of the rich flow behaviors that are only apparent in the absence of confinement, and they provide a window into high-stress suspension dynamics, inaccessible by other means.

Wed-K8-05

Viscoelasticity and Rheological Hysteresis

Shweta Sharma, V Shankar, Yogesh M Joshi

Indian Institute of Technology Kanpur

Rheological characterization of complex fluids subjected to cyclic shear-rate sweep often exhibits hysteresis. Since both viscoelastic and thixotropic materials show hysteresis loops, it is important to understand distinguishing features (if any) in the same shown by either. Lately, there has been substantial work that attempts to relate the area enclosed by the hysteresis loop with the manner in which shear rate is varied in the cycle, in order to infer thixotropic parameters of a material. In this work, we study the Giesekus model, which is a standard non-linear viscoelastic model, under application of cyclic shear-rate sweep. We find that this model produces each type of hysteresis loop that has hitherto been ascribed to thixotropic materials. We also show that the area of the hysteresis loop for a viscoelastic material as a function of sweep rate shows bell-shaped/bi-modal curves as also observed for the thixotropic materials. This study illustrates that caution needs to be exercised before attributing hysteresis loops and associated features observed in a material exclusively to thixotropy. Another feature related to the hysteresis loop is the occurrence of shear banding instability. We find that viscoelastic hysteresis may not have any connection to shear banding instability.

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