

American Conference on Neutron Scattering

Soft Matter

* Invited Paper

SESSION C02.01: Structure and Dynamics in Biological Materials

C02.01.01*

Measuring the Elastic and Viscous Properties of Soft Lipid Membranes with Neutron Scattering
Elizabeth Kelley; National Institute of Standards and Technology, United States

The elastic and viscous properties of biomembranes influence biological processing ranging from protein conformation changes on the nanoscale, to the energetics of membrane remodeling on the macroscale. Yet quantifying these properties in a soft material that is only 5 nm thick can be experimentally challenging. Neutron spin echo spectroscopy (NSE) is uniquely suited to measuring the collective dynamics on the nanoscale that are dictated by the same elastic and viscous properties of membranes that are crucial to cell function. Here we use NSE to measure the collective bending and thickness fluctuations in model lipid membranes and use these measurements to extract the membrane bending rigidity, compressibility modulus and viscosity. These measurements provide a direct link between the membrane structure and dynamics and reveal how subtle changes in lipid chemistry and composition can significantly affect the membrane properties.

C02.01.03

Plasmalogens, an Overlooked Lipid Class, Influence Lateral and Transverse Organization in Model Lipid Bilayers

Haden L. Scott^{1,1}, Alison Leonard², Edward Lyman² and Frederick Heberle¹; ¹The University of Tennessee, Knoxville, United States; ²University of Delaware, United States

Plasmalogens are a class of glycerophospholipids found in a wide variety of organisms including bacteria and animals. In mammalian plasma membranes, they are located almost exclusively in

the cytosolic (inner) leaflet, where they comprise as much as 20 mol% of the total phospholipids. While most biologically relevant phospholipids are diacylglycerols that possess ester linkages between the glycerol backbone and the two hydrocarbon chains, plasmalogens are distinguished by a cis-vinyl ether linked fatty alcohol at the *sn*-1 position. Most naturally occurring plasmalogens possess either a phosphatidylcholine (PC) or phosphatidylethanolamine (PE) headgroup and an ester linked polyunsaturated fatty acid (either 20:4 or 22:6) at the *sn*-2 position. Intriguingly, some evidence indicates that plasmalogens contribute to increased chain order and decreased fluidity in bilayers despite their polyunsaturated *sn*-2 chain, leading to speculation that plasmalogens may be enriched in—and an important driver of—lipid rafts. Aside from their structural effects on lipid bilayers, plasmalogens also may play other critical roles in the cell such as antioxidants, helping to preserve other lipids in the membrane that are in danger of oxidation. Despite the clear importance of plasmalogens to biological processes, structural studies of these lipids are lacking. Additionally, their influence on domain formation in model membranes under physiologically relevant conditions, let alone in living systems, has not been systematically investigated. Here, we take two approaches to investigate this void in the literature. First, we assessed how six different plasmalogen variants influence the bilayer thickness and average area per lipid in PC and PE bilayers with an ester linked *sn*-1 chain. We also investigated their influence on lateral lipid organization using canonical domain forming mixtures composed of a high melting lipid, low melting lipid, and cholesterol. We find that both PC and PE plasmalogens with an 18:1 ester linked fatty acid at the *sn*-2 position have a strong ordering effect on the membrane that is evident from an increase in bilayer thickness and a decrease in the area per lipid compared to the plasmalogen-free bilayer. Additional PC and PE plasmalogens displayed decreased order compared to the PC or PE background, however, they order the membrane once

compared to the appropriate diacylglycerol phospholipid. Both PC and PE plasmalogens also lead to a decrease in domain stability when substituted for the low-melting lipid of a canonical raft mixture, a finding that also suggests that plasmalogens are more ordered than their corresponding diacylglycerol phospholipids. Taken together, these results have important implications for biological phenomena mediated by the plasma membrane.

C02.01.04

Biomolecules for Non-Biological Things— Materials Construction through Peptide Design and Solution Assembly

Darrin Pochan; University of Delaware, United States

Self-assembly of molecules is an attractive materials construction strategy due to its simplicity in application. By considering peptidic molecules in the bottom-up materials self-assembly design process, one can take advantage of inherently biomolecular attributes; intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicity, to define hierarchical material structure and consequent properties. A new solution assembled system comprised of theoretically designed coiled coil bundle motifs, or ‘bundlemers’, will be introduced. The molecules and nanostructures are not natural sequences and provide opportunity for arbitrary nanostructure creation with peptides. With control of the display of all amino acid side chains (both natural and non-natural) throughout the peptide bundles, desired physical and covalent (through appropriate ‘click’ chemistry) interactions have been designed to produce one and two-dimensional nanostructures as well as networks. One-dimensional nanostructures span exotically rigid rod molecules that produce a wide variety of liquid crystal phases to semi-flexible chains, the flexibility of which are controlled by the interbundle linking chemistry. The two dimensional nanostructure is formed by physical interactions and are nanostructures not observed in nature. All of the assemblies are responsive to temperature since the individual bundle building blocks are physically stabilized coiled coil bundles that can be melted and reformed with temperature. Additional, novel nanostructures to be discussed include uniform nanotubes and molecular networks with stiffness, temperature responsiveness, and nanostructure/morphology all controlled by the use of bundlemers in the network design. Included in the discussion will be molecule design, hierarchical assembly pathway design and control, click chemistry reactions, and the characterization of nanostructure via microscopy, small-angle neutron scattering, and rheological measurements, as well as inherent material properties (e.g. extreme stiffness,

responsiveness to temperature and pH, stability in aqueous and organic solvents).

C02.01.05

Aggregation Behavior in Injectable Pharmaceutical Formulations

Peter Gilbert¹, Norman Wagner¹, Yun Liu^{2,1}, Ken Qian³ and Zhenhuan Zhang^{2,1}; ¹University of Delaware, United States; ²National Institute of Standards and Technology, United States; ³Eli Lilly, United States

Injectable pharmaceuticals require the therapeutic protein to be uniformly suspended in solution over long periods of time. Amphiphilic surfactants, like polysorbate 80 (PS80), stabilize proteins and prevent protein association with air and solid interfaces. Preservatives that inhibit bacterial growth are also a necessary component of pharmaceutical formulation. Alone in solution, PS80 molecules assemble into stable ellipsoidal core-shell micelles, where the core of hydrophobic tails is protected by a shell of hydrophilic head groups. Addition of small polar organic preservatives, like m-cresol or phenol, disrupts PS80 self-assembly causing micelle aggregation and changes in micelle morphology. This results in increased solution turbidity and often a decrease in therapeutic effectiveness. Other formulation components, including salts and sugars, can mitigate micelle solution instability caused by preservative addition. We create solutions containing PS80, preservatives and various salt and sugar additives to determine the impact of each component on solution stability. Using neutron and x-ray small-angle scattering techniques, we examine PS80 micelle morphology and determine the mechanism by which additives induce aggregation and morphological changes. We find that preservative-induced micelle morphological changes are caused by inclusion of large amounts of preservative molecules in the micelle as evidenced by our contrast matching measurements. Specifically, increasing preservative concentration causes PS80 micelles to become longer and swell in volume. Additionally, aggregate size reversibly increases with temperature in solutions containing both surfactant and preservative. However, solutions of PS80 only or preservative only have little to no temperature dependence in their aggregation behavior. We map the temperature- and concentration-dependence of these surfactant solutions to inform pharmaceutical formulation.

SESSION C02.02: Self-Assembled Materials and Networks

C02.02.01* Anomalous Dynamics in Associative Polymer Networks

Bradley Olsen, Helen Yao and Ameya Rao;
Massachusetts Institute of Technology, United States

Associative polymer networks are everywhere: they are used to modify the texture of our food, the rheology of our consumer products, and to develop biomedical materials. They are used in enhanced oil recovery, and they also form the basis for many natural systems in our own bodies. While existing theories of these materials have been widely successful in explaining rheological behaviour, recent experiments from our group suggest that something fundamental is missing. In particular, measurements of diffusivity show a non-Fickian superdiffusive regime at length scales much larger than any structural scale in the gel. This behaviour is common across several chemically different polymer systems, suggesting it is a widespread phenomenon in associative polymers. The diffusion results can be empirically captured by a simple two-state reaction/diffusion model, but the connection to molecular properties is unclear. Recently, we have developed a coarse-grained model for Brownian dynamics simulation that captures molecular diffusion, qualitatively reproducing the experimental behaviour and providing insight into the molecular origins of anomalous diffusion in associative polymers. The new results originate from the fact that molecules may both hop and walk through the gel, with the difference being the number of sticky feet attached to the network. In the regime where skipping (a combination of hopping and walking) is dominant, superdiffusive scaling is observed. However, prior experiments explored a limited range of length and timescales, making a full test of the predictions of the theory difficult. Here, we have constructed an extended range Forced Rayleigh scattering instrument and combined this with neutron spin echo (NSE) measurements of dynamics in polymer gels in order to enable probing of molecular diffusivity across many decades of length and timescales. The combination of these techniques clearly illustrates predicted submolecular, caging, superdiffusive, and Fickian regimes predicted by the theory. Measurements on tracer probes also suggest that collective molecular motion plays a key role in material dynamics.

C02.02.02 The Role of Backbone Rigidity on Entanglement Behavior and Mechanical Property for Conjugated Polymers

Xiaodan Gu¹, Luke Galuska¹, William McNutt², Jianguo Mei² and Zhiyuan Qian¹; ¹University of Southern Mississippi, United States; ²Purdue University, United States

Incorporation of the conjugation break spacers (CBS) to the rigid conjugated polymers (CP) has been shown to greatly impact the backbone rigidity of the conjugated polymer and result in a drastic change in modulus and ductility. In the current work, we investigate the influence of CBS length on the backbone rigidity for an n-type NDI-based conjugated polymer PNDI-Cx using neutron scattering. We systematically varied the CBS length x varied from 4 to 7 and engineered into each repeat unit. The rigid backbone was found to drop by up to 100%. The stretchability in terms of crack onset strain (COS) was probed by measuring the ultra-thin film mechanics with pseudo-free-standing thin film tensile tester. Oscillatory shear rheometry was utilized to determine the entanglement molecular weight (Me), which is found to be approximately 15 kDa and relatively insensitive to the length of CBS. A direct correlation between the degree of entanglements and COS is observed, i.e., more entanglements lead to higher COS. This work shows how neutron can guide the design of the conjugated polymer through tuning of backbone flexibility.

C02.02.03 Phase Behavior of Diblock Copolymer-Homopolymer Ternary Blends Near the Putative Lifshitz Point

Bo Zhang, Shuyi Xie, Frank S. Bates and Timothy P. Lodge; University of Minnesota Twin Cities, United States

A Lifshitz point (LP), a unique tricritical point where disordered, uniformly ordered, and periodically ordered phases meet, is predicted by mean-field theory to exist in symmetric A/B/A-B ternary blends, where A and B are homopolymers and A-B is the corresponding diblock copolymer. At finite molecular weights, the LP is superseded by a channel of bicontinuous microemulsion (B μ E) due to fluctuation effects. A recent study of symmetric ternary blends, where A is poly(cyclohexylethylene) (PCHE) and B is poly(ethylene) (PE), demonstrated that the B μ E is bracketed by a line of congruent lamellar-disorder (LAM-DIS) transitions on the copolymer-rich side, and a Scott line of critical points on the homopolymer-rich side, at homopolymer contents near the predicted LP value. We investigated the phase behavior of a similar PCHE/PE/PCHE-PE ternary blend but with a compositionally asymmetric

diblock copolymer by a combination of optical transmittance measurements, small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS). The ordered phase morphologies were determined by SAXS, while the congruent LAM-DIS transition was identified by a step change in optical transmittance. The location of the Scott line was determined by SANS, as indicated by the nearly divergent coherent scattering intensity at low q of each sample at the binodal temperature. The main finding was that the line of congruent transitions is decoupled in composition from the Scott line of critical points. We also found that a wide range of phase space between the compositions associated with the congruent condition and Scott line contains the B μ E morphology. The SANS profiles for such B μ E specimens were fitted with the Teubner-Strey model to evaluate domain spacing, correlation length, and amphiphilicity factor, which provide essential structural information about the B μ E.

C02.02.04

Elasticity and Phase-Separation in Amphiphiles Self-Assemblies—From Biology to Nanotechnology

Rana Ashkar; Virginia Tech, United States

Amphiphiles self-assembly is a ubiquitous process which not only underpins the origin of life itself but also constitutes a facile approach to a wide range of bottom-up nanomaterials. Given their diverse portfolio, the self-assembly of amphiphiles has justifiably taken center stage in the last few decades, with research interests ranging from natural self-assemblies in biosystems to engineered amphiphiles with extensive applications in material science, drug delivery, and nanoscale transport. A prime example of functional amphiphile self-assembly can be found in cell membranes, where the dynamic assembly of lipids and proteins enable highly specific cellular functions and lend inspiration to new nanotechnologies. Whether natural or engineered, the function and performance of such assembled structures is governed by universal physical properties which closely depend on molecular geometry, energetics, and thermodynamics. This talk will focus on recent directions in the synergistic integration of neutron scattering/spectroscopy and molecular dynamics simulations to explore structure-property relations in lipid self-assemblies as a model system for amphiphile bilayers. Specific emphasis will be given to mesoscale mechanical properties and lateral phase separation – key features in the stability and function of lipid membranes and similar amphiphilic assemblies in biological settings or technological applications.

SESSION C03.01: Student Research Spotlight

C03.01.01

Decouple Conjugated Polymer's Backbone and Sidechain Conformation by Selective Deuteration and Neutron Scattering

Zhiqiang Cao^{1,2}; ¹University of Southern Mississippi, United States; ²Oak Ridge National Laboratory, United States

Although considerable progress has been made to optimize the optical and electronic properties of conjugated polymers (CPs), it's still challenging to rationally design CPs. It remains underexplored to experimentally characterize conjugated backbone conformation and relate it to material's macroscopic properties. Here, small angle neutron scattering (SANS) with contrast variation (CV) experiments on poly(3-alkylthiophenes) (P3ATs) with both deuterated and protonated sidechains were performed to decouple the backbone and sidechain scattering signal. We obtained the form factor of P3ATs' backbone, sidechains, and cross scattering term by deconvoluting their respective scattering signal. Strong scattering signal from side chains and cross term between backbone and sidechains makes the conjugated polymer appears more rigid. This work provides a way to decouple the scattering function from the CPs' backbone and sidechains and allows one to focus the study on the electronically functional conjugated polymeric backbone without being obscured by scattering signal of long alkyl sidechains, and provide a unique perspective on the structure-property relationship for semiconducting polymers. Poly(3-decylthiophene) (P3DT) showed a Kuhn length of 2 nm for the backbone while the overall chain would show 4 nm.

C03.01.02

Structural Analysis of Polythiophene-Polystyrene Blends via Small-Angle Neutron Scattering

Caitlyn Wolf, Lorenzo Guio and Lilo D. Pozzo; University of Washington, United States

Organic electronics, such as photovoltaics, wearable electronics, and chemosensors, rely on the properties and performance of conjugated (semiconducting) polymers (CPs) within their active layers. These materials are light-weight, flexible and have facilitated processing when compared to their inorganic equivalents. However, they are also more expensive than commodity polymers (e.g. polystyrene, polyethylene), prone to cracking, and have low environmental stability. In response to these disadvantages, researchers have explored the use of

blends of conjugated and commodity polymers. Environmental stability and mechanical robustness can be improved by the choice of commodity polymer, while comparable device performance is maintained at conjugated polymer concentrations as low as 1 to 10 wt%. In this work, we explore the molecular conformation and self-assembly of conjugated polymers inside these blends to further understand structure-function relationships. Polymer blends are comprised of a polythiophene conjugated polymer, including regio-regular (semi-crystalline) and regio-random (amorphous) poly(3-hexyl thiophene) (RRe-P3HT and RRa-P3HT), poly(3-dodecyl thiophene) (P3DDT), and poly(3-(3''didodecyl quarter thiophene) (PQT-12) dispersed at concentrations ranging from 0.1 to 50 wt% in a matrix of atactic deuterated polystyrene. With the use of contrast-variation small-angle neutron scattering (CV-SANS and USANS), we find that RRe-P3HT readily self-assembles into nanofibers, a favorable structure for charge transport mechanisms. Meanwhile, blends with RRa-P3HT, PQT-12 and P3DDT form globular regimes or fractal networks of the conjugated polymer phase. We also investigate the effect of solvent quality (for P3HT) during the processing stage on the final, solid blend conformation. Interestingly, nanofiber formation can be encouraged at lower concentrations of RRe-P3HT with use of a moderate solvent (toluene) rather than a good solvent (chloroform, bromobenzene). Through model fitting and power-law analysis of the SANS data, and supplemental wide-angle x-ray scattering (WAXS) measurements, we provide a rich analysis of the molecular conformations in these conjugated and commodity polymer blends. With a deeper understanding of these behaviors, we can enable control over the performance of these blends and improved organic electronic technology in the future.

C03.01.03

Exotic Hybrid Polymers of Computationally Designed Coiled Coil Bundlomers—A Structure and Dynamics Study Using Neutrons

Nairiti J. Sinha^{1,2}, Grethe V. Jensen² and Darrin Pochan¹; ¹University of Delaware, United States; ²National Institute of Standards and Technology, United States

Coiled coils are oligomers of alpha-helical peptides that are emerging as promising candidates for building new materials via self-assembly and bioconjugation techniques. We demonstrate the utility of computationally designed coiled coils, i.e. bundlomers as modular protein-mimicking systems that can also be used to assemble 1D polymers using a hybrid physical-covalent assembly pathway. Small angle-neutron scattering (SANS) along with Transmission Electron Microscope (TEM) have been utilized to characterize the solution behavior of the

novel bundlomers and their assemblies. Specifically, SANS has shown that the bundlomers are 2 nm x 4 nm nanocylinders that display short-range attraction and long-range repulsion (SALR) interactions in solution. The exact inter-bundlomer interaction landscape depends on the sequence of bundlomers and solution conditions such as pH and ionic strength. Exotic polymers were built by end-to-end reaction of the bundlomers via Thiol-Michael *click* reaction. Interestingly, we have found that the type of linker between bundlomers greatly impacts the persistence length of the polymers, resulting in extremely stiff rigid rod-like polymers with short-linkers and semi-flexible chains with longer tetrafunctional linkers. These differences are clearly visible in TEM micrographs of the exotic polymers, as well as in their solution structure probed using SANS. Neutron Spin Echo (NSE) has further confirmed that the linker-type impacts the dynamics of the polymers at the nanoscale; the semi-flexible chains showed bending dynamics that were fit using Zilman-Granek theory, whereas the rigid rods did not show any bending fluctuations at corresponding length scales.

C03.01.04

Investigating Interfacial Monolayers and Their Path Dependent Isotherms via Combined Neutron Reflectivity and Interfacial Rheology Technique

Ying-Heng S. Tein¹, Charles F. Majkrzak², Brian Maranville², Jan Vermant³ and Norman Wagner¹; ¹University of Delaware, United States; ²National Institute of Standards and Technology, United States; ³ETH Zürich, Switzerland

Interfacial structure and rheological properties are critically important in biological (e.g. membranes) as well as many synthetic systems (e.g. emulsions); a better understanding how these are correlated can guide the formulation of systems with targeted interfacial properties. The early works of interfacial studies were investigating the thermodynamic state behaviors of interfacial systems through surface pressure versus molecular area isotherms, or π -A. These diagrams have long been considered the two-dimensional analogues to three-dimensional p-V isotherms. For example, stearic acid on air-water interface has a well-defined isotherm with distinct liquid-condensed and solid-like regions due to the existence of a discontinuous change in slope; however, phase and structural determinations of complex fluid interfaces are not rigorous or trivial, as they are often determined through slope changes and indirect viscosity measurements. In this presentation we investigate stearic acid above an aqueous salt subphase, a gel-like interface, with an ill-defined isotherm and discuss how processing conditions can affect the structure and interpreted rheological

behavior. Combining trough studies with both Brewster angle microscopy and neutron reflectivity provides detailed structural measurements of the interface at the microscale and nanoscale that elucidates the source of this path dependence.

C03.01.06

Anomalous Fast Dynamics of Water-in-Oil Microemulsions Probed *via* Neutron Spin Echo

Tanvi Sheth and Matthew E. Helgeson; University of California, Santa Barbara, United States

Understanding the dynamic and elastic properties of surfactant-laden fluid interfaces is increasingly critical for engineering the behavior of conventional emulsions and, more recently, multi-phase nanoemulsions that take advantage of combinations of high interfacial curvature and low interfacial tension in mixed surfactant systems. Although neutron spin echo (NSE) has become an important tool for quantifying such properties from microemulsion systems, its application has primarily been limited to water-continuous structures. It remains unclear whether the models and assumptions used for these systems can be translated to the inverse (water-in-oil) situation. Here, we use NSE to investigate the equilibrium dynamics of oil-continuous droplet microemulsions formed by asymmetric pairs of ethoxylated surfactants. We find that the probed droplet microemulsions exhibit anomalous dynamical behavior, and their dynamics are not adequately captured by the conventional Milner-Safran theory for floppy droplet microemulsions. Using additional contrast variation NSE and small-angle neutron scattering experiments, we eliminate potential dynamic contributions from internal surfactant dynamics and non-spherical shape fluctuations. Instead, we hypothesize that the observed stretched relaxation profiles arise from strong interactions of one surfactant's head group with the dispersed aqueous phase, preventing large-amplitude shape fluctuations into the bulk and increasing high-order spherical mode contributions to the measured droplet deformation. We show that the apparent dynamical behavior is similar to that observed in rigid vesicles and bicontinuous structures and can be modeled by the Zilman-Granek theory for undulating membranes to determine reasonable values for the surfactants' effective elastic constants. Our results demonstrate a potentially new understanding of surfactant film behavior in oil-continuous emulsion structures.

C03.01.07

Real Space Study of Liquid Dynamics Using Neutron Scattering

Yadu Krishnan Sarathchandran¹, Wojciech Dmowski², Eugene Mamontov³ and Takeshi Egami^{2,1}; ¹University of Tennessee, Knoxville, United States; ²The University of Tennessee, Knoxville, United States; ³Oak Ridge National Laboratory, United States

The dynamics of liquids are characterized by local atomic/molecular correlations in real-space and time. The traditional approach of using spectroscopic techniques to measure dynamic properties cannot fully describe them due to the lack of spatial information. We present an alternative method to study the real-space correlated dynamics using a time-dependent atomic pair-correlation function, the Van Hove function, $G(r, t)$, obtained from inelastic neutron scattering measurements. This is possible due to the recent advances in the instrumentation of neutron scattering facilities. In this work, we use the Van Hove function to study two different liquid systems. 1) Water exhibits an anomalously high dielectric constant, $\epsilon=78$, at ambient temperature. This is caused by a Debye peak in the dielectric spectrum with a maximum at ~ 20 GHz. It is reported that this Debye peak reflects some hydrogen bond mediated, collective dipolar dynamics in water. However, a clear microscopic description of this phenomenon is lacking. We report our results on the microscopic picture of water's dielectric relaxation using the Van Hove function over a time range of 20 picoseconds. 2) Liquid gallium is of strong theoretical interest due to the reported asymmetry of its prominent peak in the snapshot structure factor and the shoulder at the high-Q side of the peak close to the melting point, which indicates the peculiar nature of its atomic bonding. The dynamic structure factor, $S(Q, E)$, from inelastic neutron measurements are double Fourier transformed to obtain $G(r, t)$ to investigate the temporal evolution of atomic/molecular correlations in real-space in liquid gallium at several temperatures.

SESSION C04.01: Emulsions, Suspensions and Micellar Systems

C04.01.01*

Using Neutrons to Probe the Formation and Structure of Multi-Phase Nanoemulsions

Tanvi Sheth, Mengwen Zhang, Paula Malo de Molina and Matthew E. Helgeson; University of California, Santa Barbara, United States

Multi-phase emulsion droplets have opened up a vast new design space for particle technologies and formulated chemical products. However, scaling the droplet size of such “multiple emulsions” to the nanoscale has been a considerable challenge due to lack of capabilities for both the production and characterization of complex nanodroplets. Here, we show how both elastic and quasi-elastic neutron scattering are critical in developing, understanding and designing new processes for producing multi-phase nanoemulsions. These processes rely on the use of co-surfactants that simultaneously produce ultra-low interfacial tension to facilitate the formation of nanoscale droplets, as well as frustrated spontaneous interfacial curvature to thermodynamically promote and stabilize internal droplet interfaces. Combined cryo-TEM and contrast variation SANS provide a unique means of quantifying nanodroplet morphology and internal speciation. These methods show how droplet morphology is effectively selected through fluid and surfactant composition, suggesting that – despite the highly non-equilibrium nature of multiple nanoemulsions – their structure can be predicted solely through considerations of their near-equilibrium interfacial energy. We leverage this finding to develop a new interfacial thermodynamic model that incorporates curvature-induced surfactant demixing to design co-surfactant systems and compositions that achieve multi-phase nanodroplets with well-specified morphology. Because of the ultra-low interfacial energies of the surfactant systems involved, SANS and neutron spin echo provide an essential means of characterizing the interfacial mechanical properties that are used as inputs to the model, and enable comparisons between experiments and model predictions of preferred droplet morphologies. Ultimately, we show how these new insights into the structure and dynamics of surfactant mixtures at high interfacial curvatures facilitates the design, production and stability of multi-phase nanodroplets.

C04.01.02 **Assessing Shear-Induced Scission of Wormlike Micelles Using Flow-SANS**

Jiamin Zhang, Patrick T. Corona, L. G. Leal and Matthew E. Helgeson; University of California, Santa Barbara, United States

Wormlike micelles (WLMs), long thread-like surfactant aggregates, remain an important class of surfactant-based materials for both consumer applications and as model viscoelastic fluids for rheological studies. Although it is widely accepted that equilibrium micelle scission dynamics greatly influences the rheology of WLMs, there is still considerable theoretical debate regarding whether

scission dynamics is affected by flow under nonlinear deformations. This is because there are still few if any experiments to test how flow potentially affects the scission and recombination process and the resulting length distribution of the micelles. Although flow-small angle neutron scattering (flow-SANS) is suitable for characterizing the effects of flow on micelle length distributions, such experiments are complicated by challenges in the analysis of scattering from anisotropic, polydisperse, semi-flexible and entangled objects, as well as flow instabilities such as shear banding and elastic instabilities. To circumvent these issues, we report new flow-SANS experiments on a carefully designed series of linear, weakly entangled WLMs, which provide access to stable flows to relatively large shear rates. These measurements are used to distinguish the relative contributions of changes in segmental alignment and changes in micelle length distribution in shear flow. In particular, we find that the low- q intensity monotonically decreases with increasing shear rate, which is consistent with the net breakage of the WLMs. We use model calculations of scattering from deformable objects in shear flow in order to deconvolute the contributions to the scattering from potential changes in micelle orientation, stretching, and interactions from effects due to changes in micelle length in flow. We find that without including micelle breakage, none of the other factors is able to explain the qualitative trends we observe in experiments. This suggests that the length distribution of wormlike micelles is significantly affected by shear and opens up new possibilities for measuring and modeling the effects of flow on the reversible scission of WLMs.

C04.01.03 **Kinetic Analysis of Oil Exchange between Surfactant-Stabilized Emulsions Using Time-Resolved Small Angle Neutron Scattering** Yi-Ting Lee and Lilo D. Pozzo; University of Washington, United States

Emulsion systems are dynamic and several physical mechanisms can lead to mass transport between droplets (e.g. coalescence, diffusion, micelle-driven). Understanding how oil exchanges between emulsions is also critical to developing applications such as new drug-delivery vehicles and emulsion polymerization processes. Researchers have aimed to fundamentally examine mass transport between stabilized emulsions using characterization techniques such as differential scanning calorimetry, microscopy, pulse gradient NMR, and turbidity measurements. However, all of these require the use of dissimilar oils and/or labeling droplets with fluorescent molecules. Here, we take advantage of large differences in neutron scattering length density between hydrogenated and deuterated versions of alkane oils

to use time-resolved small angle neutron scattering to directly examine mass transport between emulsions with identical chemical compositions. We specifically examined mixing between alkanes in oil-in-water emulsions stabilized by anionic (i.e. sodium dodecyl sulfate) and non-ionic surfactants. Fully deuterated and partially hydrogenated hexadecane emulsions with equal contrast relative to the solvent were prepared identically (e.g. sonication) and subsequently mixed to monitor oil exchange kinetics. As oil exchanges between droplets over time, a decrease is observed in scattering intensity due to contrast-matching conditions between the solvent and the fully-mixed oil phases. When emulsions are ideally mixed, minimal scattering is detected. This talk will summarize findings of measurements of mass-transport for emulsion systems with a large number of variable parameters including surfactant concentration, surfactant type, temperature and oil-type. Multiple physical mechanisms are suggested to play important roles in controlling transport in emulsion systems.

C04.01.04 Structural Characterization of Polysorbate-20 Microemulsions Using Small Angle Neutron Scattering

Adam Imel¹, Brian Barth¹, K. McKensie Nelms¹, Douglas Hayes¹ and Thomas Zawodzinski^{1,2}; ¹The University of Tennessee, Knoxville, United States; ²Oak Ridge National Laboratory, United States

Research and discovery of new electrolytes is crucial for advancing the fundamental understanding and development of new opportunities in electrochemical systems. Through an Energy Frontier Research Center (EFRC) for Breakthrough Electrolytes for Energy Storage (BEES), the approach we are taking is to establish a system for decoupling the nature and solubility of electroactive material from the conductivity and transport of ions in the surrounding solution. We accomplish this with microemulsions as a pathway to solubilize hydrophobic redox active materials in an aqueous solvent. Microemulsions are isotropic, nanoscale dispersions of two immiscible liquids, stabilized by a surfactant, and cosurfactant. Microemulsions are an interesting electrolyte because they possess several properties that make them useful as an energy storage medium – they are thermodynamically stable, have fast dynamics, possess large interfacial areas, and can solubilize large concentrations of hydrophobic redox-active compounds in an aqueous electrolyte solution. Cyclic voltammetry experiments have shown reversible behavior in microemulsions up to 22 V/s with a double layer capacitance less than expected with such high scan rates. In order to understand the electrochemical behavior, we have begun with

understanding the nanoscale structure of the microemulsion. Presented here are the small angle neutron scattering results on polysorbate-20 microemulsion systems. The microemulsion has a tunable nanoscale structure as it transitions from spherical droplets of oil-in-water to bicontinuous by only increasing surfactant loading.

C04.01.06 Microstructure and Rheology of Thixotropic Carbon Black Suspensions by Rheo-SANS and Rheo-USANS

Julie Hipp¹, Jeffrey J. Richards² and Norman Wagner¹; ¹University of Delaware, United States; ²Northwestern University, United States

Carbon black suspensions are critically important in many technological applications ranging from inks and paints to tires and electrochemical energy storage devices. In these applications, key design parameters such as viscosity, electrical conductivity, and stability are dictated by the suspension microstructure, which varies depending on the various shear conditions applied during mixing, processing, and application steps. These shear-dependent changes in microstructure occur at the agglomerate length scale and take place over a finite period of time, which is observed in the macroscopic properties as a time-dependent, or thixotropic, response to a change in applied shear. To understand this shear-dependent behavior, the steady state microstructure of carbon black suspensions is directly measured by performing Rheo-USANS (Ultra-Small Angle Neutron Scattering) experiments at a range of applied shear rates in a stable flow regime (Hipp *et al.* J. Rheology, 2019). The suspensions studied consist of two commonly used conductive carbon blacks, Vulcan XC-72 and KetjenBlack EC-600JD, suspended in two Newtonian fluids, propylene carbonate and light mineral oil, at a range of volume fractions above the mechanical percolation threshold (Richards *et al.* Langmuir, 2017). The effects of interaction strength, particle loading, and carbon characteristics on the shear-dependent size and fractal dimension of carbon black agglomerates are measured. An unstable regime is identified for $Bi^{-1} < 1$, where shear-flocculation and sedimentation lead to macroscale heterogeneities and rheological anomalies. A shear stable regime is identified for $Bi^{-1} > 1$, carbon black agglomerates decrease in size with increasing shear intensity while maintaining a constant fractal dimension. This self-similar breakdown is shown to be dependent on the Mason number, which compares shear forces to interparticle attractions. This attractive force is estimated using the yield stress of the network formed by the agglomerates, which is determined by measuring self-similar structure flow curves and fitting to the Herschel-Bulkley model. A universal description relating the microstructure and

shear rheology to the Mason number is demonstrated that has value for the formulation and processing of products using carbon black.

SESSION C04.02: Structure and Dynamics of Polymers and Composites

C04.02.01*

Enabling SANS on Disperse, Non-Uniformly Labeled Polymers

Brian Habersberger; Dow Inc, United States

Commercially relevant polymer resins such as polyolefins are often disperse by design, with component chain populations playing important roles in controlling the rheological, mechanical, and other physical properties of the material. Neutron scattering studies of such resins often substitute well-labeled and structurally uniform model polymers, which, while convenient to prepare and analyze, lack the critical features and properties of the true materials of interest. Performing isotopic exchange chemistry on polyolefins is an attractive means of enabling neutron studies, but because the exchange is potentially non-uniform, it introduces a new dimension of dispersity to an already complex system. Allowing all of this dispersity of chain species and scattering contrast raises concerns about the ability to analyze and extract meaningful understanding from SANS measurements. This presentation will review the use of highly dispersity, non-uniformly labeled polyolefins in SANS studies, as well as discuss the capabilities and limitations of scattering models extended to incorporate these complexities.

C04.02.02

Structure and Dynamics of Polysaccharides

Howard Wang^{1,2}, Xin Zhang¹, Yimin Mao^{1,3}, Madhusudan Tyagi³, Markus Bleuel³ and Robert Briber¹; ¹University of Maryland, United States; ²Songshan Lake Materials Laboratory, China; ³National Institute of Standards and Technology, United States

We have applied neutron scattering to understanding the structure and dynamics of polysaccharides in solutions and composites. Because of difficulties in dissolving cellulose in aqueous or organic solvents, ternary solutions of microcrystalline cellulose (MC) in mixtures of an ionic liquid (IL) and a polar organic solvent dimethylformamide (DMF) have been studied. The dissolution phase diagram of ternary cellulose mixtures of MC/IL/DMF at room

temperature has been determined. Data show the molecular partitioning of IL into coexisting states. The structure partitioning is manifested as IL adsorbed to cellulose molecules with additional IL self-assembled to form clusters in solution, while the dynamics partitioning shows dynamical heterogeneities of the IL with slow dynamics resembling neat IL and fast dynamics being coupled with the solvent. Molecular solutions of cellulose have been used to produce cellulose thin films with thicknesses of 8 - 100 nm and sub-nanometer roughness by spin-casting. Cellulose films are fully amorphous, and their mass densities are comparable to that of the bulk amorphous cellulose. Furthermore, oligomeric cellulose has been produced to understand the chain dimensions and conformation. Using low polydispersity oligocellulose as a model system, small angle scattering shows that short cellulose chains can be described as rigid slabs. When oligocellulose is dispersed in corn starch as individual molecules, the gelatinization behavior of the starch is drastically altered.

C04.02.04

QENS Insights on the Nanoscopic Origin of Rheological Properties in Polyethylene Oxide Based Polymer Nanocomposites

Antonio Faraone¹, Erkan Senses² and Madhusudan Tyagi¹; ¹National Institute of Standards and Technology, United States; ²Koç University, Turkey

Polymer nanocomposites (PNCs) with attractive polymer–nanoparticle (NP) interactions, are often reported to disperse individually, enabling the investigation of interfacial effects on the rheological properties without contribution from particle percolation. By taking advantage of selective isotope labeling of the chains, neutron scattering techniques uniquely allow the possibility of investigating the structural and dynamical properties of the polymers in the matrix. We employed high-resolution QuasiElastic Neutron Scattering (QENS) techniques, such as backscattering and Neutron Spin Echo, to directly observe the chain motions at the nanoscale in composites of PolyEthylene Oxide (PEO) with well dispersed silica nanoparticles. Thus, we studied both the segmental dynamics at the monomer level and the entangled/collective dynamics at larger scales. The effect of the presence of the NPS on the polymer matrix Rouse dynamics and entanglements explains how both a reinforcing and an unusual softening can be induced in the same material. The results also provide insights on the dynamics of the interphase layer and its persistent mobility even at high nanoparticle loadings.

C04.02.05

Neutron Reflectivity Studies of Soft Nanoparticle Tracer Diffusion Coefficients in All Polymer Nanocomposites

Sahar Rostom¹, Umesh Shrestha¹, Tomonori Saito², Ken Schweizer³ and Mark Dadmun^{1,2}; ¹The University of Tennessee, United States; ²Oak Ridge National Laboratory, United States; ³University of Illinois at Urbana-Champaign, United States

Understanding the diffusion of nanoparticles in a polymer matrix is lacking as it is often difficult to quantify the motion of slow-moving nanoparticles in a polymer matrix. Tuning contrast between the nanoparticle and the matrix can also be difficult. To overcome these hurdles, a neutron reflectivity protocol to measure the tracer diffusion coefficient of soft nanoparticles in a linear polymer matrix has been developed. Combining this protocol with recently developed synthetic control over soft nanoparticle structure provides a method to independently elucidate the effects of the molecular weight and nanoparticle softness on its diffusive behavior. These studies revealed unexpected results where the molecular weight dependence of the nanoparticle diffusion is very weak, $ca. D \sim M^{-1}$. A simple and predictive statistical mechanical model captures this behavior by invoking the threading of linear polymer chains with the loops that exist in the crosslinked soft nanoparticle as constraints that inhibit nanoparticle motion. This theory predicts that the diffusion coefficient of the soft nanoparticle will scale as inversely proportional to the product of the nanoparticle molecular weight and nanoparticle crosslink density; $D_{SNP} \sim (MW_{SNP} * \% \text{ xlink})^{-1}$. Our current results of the tracer diffusion of soft nanoparticles agree with this prediction over three orders of magnitude, strongly suggesting the validity of this new model. It is important to emphasize that these results also provide a foundation for understanding the motion of other soft materials such as dense microgel and nanogel suspensions, and linear/ring polymer melts.

SESSION C05.01: Heterogeneous Structures in Solution

AM C05.01.01*

Color, Structure and Rheology of a Diblock Bottlebrush Copolymer Solution

Matthew Wade¹, Johnny C. Lee¹, Kathleen M. Weigandt², Elizabeth Kelley², Dylan Walsh¹, Damien Guironnet¹ and Simon Rogers¹; ¹University of Illinois at Urbana-Champaign, United States; ²National

Institute of Standards and Technology, United States

A structure-property-process relation is established for a diblock bottlebrush copolymer solution, through a combination of neutron scattering, imaging, and rheological measurements. Polylactic acid-b-polystyrene diblock bottlebrush copolymers are dispersed at 5 deg C in toluene with a concentration of 175 mg/ml, making a lamellar phase. The reflected solution color is shown to be a function of the shear rate. Under equilibrium and near-equilibrium conditions, the solution has a green color. At low shear rates the solution remains green, while at rates around 100 s^{-1} it is blue, and at rates around 300 s^{-1} the solution is purple. The lamellar spacing is shown to be a decreasing function of shear rate, partially accounting for the color change. The lamellae are oriented 'face-on' with the wall under quiescence and low shear rates, while a switch to 'edge-on' is observed at rates around 1000 s^{-1} , where the reflected color disappears. The intermolecular distance between bottlebrush polymers does not change with shear rate, although at high shear rates, the bottlebrush polymers are preferentially aligned in the vorticity direction within the lamellae. We therefore form a consistent relation between structure and function, spanning a wide range of length scales and shear rates.

C05.01.02

Capturing the Elusive Butterfly—Quantification of Large Concentration Fluctuations of Polymeric Liquids under Deformation

Yangyang Wang¹, Weiyu Wang¹, Kunlun Hong¹ and Yun Liu²; ¹Oak Ridge National Laboratory, United States; ²National Institute of Standards and Technology, United States

We demonstrate how the large concentration fluctuations of polymeric liquids under deformation and flow can be quantitatively studied by applying the spherical harmonic expansion technique to small-angle neutron scattering. Using binary polymer blends, we show that the emergence of the so-called butterfly patterns is caused by the change of sign in the leading anisotropic component of the small-angle spectrum, when the scattering is dominated by intermolecular correlation associated with viscoelastic phase separation. Additionally, the increasing spatial fluctuation of concentration is evidenced by the enhancement of the isotropic component of the scattering spectrum in the zero-angle limit and peak shift of the anisotropic spherical harmonic expansion coefficients towards low q . The methodology described in this work provides a concrete venue for quantitative studies of phase transitions of fluids under deformation and flow via small-angle scattering techniques, where mainly

qualitative approaches have been previously employed.

C05.01.03

Model-Free Estimation of Nanoparticle Orientation Distributions from SANS in Applied Fields

Patrick T. Corona¹, Kevin S. Silmore², Christian Lang³, Lionel Porcar⁴, Joachim Kohlbrecher⁵, Pavlik Lettinga^{6,7}, James W. Swan², L. G. Leal¹ and Matthew E. Helgeson¹; ¹University of California, Santa Barbara, United States; ²Massachusetts Institute of Technology, United States; ³Jülich Centre for Neutron Science, Germany; ⁴Institut Laue-Langevin, France; ⁵Paul Scherrer Institute, Switzerland; ⁶Forschungszentrum Jülich GmbH, Germany; ⁷KU Leuven, Belgium

The nonlinear coupling of nonspherical particle orientations with applied external fields (i.e., flow, electric, magnetic fields) is critical in determining mechanical and transport properties of anisotropic materials. For the case of soft materials, rheo-small-angle neutron scattering (rheo-SANS) is a powerful technique to probe this coupling through measurement of microstructure under well-defined flow fields *in situ*. However, there is currently no general framework to solve the ‘inverse problem’ of using measurements of reciprocal-space anisotropic scattering to extract ‘real-space’ orientation probability distribution function (OPDF) of material constituents. Here, we propose and validate a general method, called maximum *a posteriori* scattering inference (MAPSI), by which one may extract OPDFs from experimental scattering measurements and a model of the constituent particles without any assumptions of the underlying physical or mathematical form of the OPDF. We test MAPSI using the case of dilute, nonspherical, axisymmetric cylindrical particles in Stokes flow for which the orientation probability distribution functions (OPDFs) may be predicted from theory. Analytical solutions for the scattering from arbitrarily oriented particles are derived and combined with numerical solutions for the OPDF to yield theoretical predictions for the scattering patterns under flow. We compare the predicted scattering patterns to rheo-SANS experiments on dilute rod-shaped particle dispersions, where the model predictions with zero adjustable parameters show excellent agreement with experiments, validating the framework for connecting OPDFs to SANS. We then use MAPSI to extract OPDFs from rheo-SANS experiments on dilute and semi-dilute rod-shaped particle dispersions. We show that MAPSI enables – for the first time – direct, accurate experimental estimation of higher-order moments of the OPDF that are used in the determination of mechanical and transport properties. These new tools provide an unprecedented path

toward experimental validation of dynamical theories of complex fluids and soft materials, and measurement of their non-equilibrium materials properties with SANS.

C05.01.04

A Generic Method to Form Thermo-Reversible Bicontinuous Colloidal Gel Using a Binary Solvent

Yuyin Xi^{1,2} and Yun Liu^{1,2}; ¹National Institute of Standards and Technology, United States; ²University of Delaware, United States

Colloidal assembly into bicontinuous structure has been demonstrated useful for many industrial applications. Here, we show a novel generic method that can drive colloidal assembly to form gel with bicontinuous structures driven by the binary solvent phase separation. It is termed as the solvent segregation driven gel (SeedGel). Different from the neutrally wetted nanoparticles used in bicontinuous interfacially jammed emulsion gel (Bijel), SeedGel utilizes nanoparticles that favor one of the solvent components. By performing contrast variation experiments with small angle neutron scattering (SANS), we conclusively demonstrate that the particles in favor of one component of the solvent stay within one of the bicontinuous liquid domains. The solvent in this domain is rich with the component that preferentially adsorbs on the particle surface. Using silica colloidal particles in the lutidine-water binary solvent as a model system, we show that the local particle concentration is about 40 % volume fraction inside the particle domain. The domain size of the bicontinuous structure is found thermally reversible and is determined to be a few micrometers. Temperature-dependent SANS and USANS studies are carried out to understand the gelation process. With quasi-static ramping (0.02C/min), SeedGel greatly reduces the fast quenching rate required by Bijel (17C/min). The particle packing distance are reversible in response to temperature change. We further show that SeedGel is a general method readily applicable to different particle size and solvent pairs. SeedGel allows the formation of bicontinuous structure with particles as small as 7 nm, which is challenging to achieve with Bijel. The gelation temperature can be altered at will by adjusting the interactions between solvent molecules. SeedGel provides a new mechanism for arresting bicontinuous structures and renders excellent versatility for tuning the corresponding properties.

Poster Session: Soft Matter

PC.01.02

Influence of Added Salt on the Chain Conformation of poly(ethylene oxide) Melts—A Small-Angle Neutron Scattering Study

Shuyi Xie¹, Bo Zhang¹, Yimin Mao^{2,3}, Kunlun Hong⁴, Lilin He⁴, Frank S. Bates¹ and Timothy P. Lodge^{1,1}; ¹University of Minnesota Twin Cities, United States; ²University of Maryland, United States; ³National Institute of Standards and Technology, United States; ⁴Oak Ridge National Laboratory, United States

Poly(ethylene oxide) (PEO)-based electrolytes have gained increasing attention in both industry and fundamental research, but any influence of the ions on the structure of the polymer is not fully understood. Small-angle neutron scattering (SANS) is a powerful means to determine single polymer chain conformations. We conducted SANS experiments on 50:50 blends of hPEO and dPEO of two different molecular weights (20 kDa and 40 kDa) doped with two different salts (LiTFSI and LiClO₄) at various concentrations. Scattering profiles of salt-doped hPEO/dPEO blends were measured, and the incoherent scattering from hPEO and deuterated dPEO doped with salt was measured separately. A strong low-*q* upturn was observed in some of the blends and dPEO homopolymers. The statistical segment lengths of PEO-salt mixtures were derived from a Kratky analysis. The scattering profiles were then compared with those calculated by the random phase approximation (RPA). The segment length decreases modestly with increasing amounts of LiTFSI, but first increases then decreases with increasing amounts of LiClO₄. At the highest salt concentration ($r = [\text{Li}^+]/[\text{EO}] = 0.125$), a roughly 10% decrease in statistical segment length was observed in both LiTFSI and LiClO₄ doped PEOs, for both molecular weights. This work confirms that added salt causes a contraction of the PEO chain dimensions, but the effect appears slightly weaker than reported recently (W. S. Loo, et al., *Macromolecules*, **2019**, 52, 8724-8732). Difficulties in data analysis will also be described.

PC.01.03

High Throughput Experimentation with Small Angle Scattering

Kacper J. Lachowski and Lilo D. Pozzo; University of Washington, United States

High throughput experimentation (HTE) approaches have been embraced by biological subfields and have been integrated into biology focused beamlines. However, these techniques have not yet been embraced to solve materials problems where achieving desired features or performance metrics requires empirically optimizing a large number of experimental parameters. To address this, our group is using HTE to better develop colloidal systems with controlled properties and function. Two of these areas of research include: 1) spontaneously formed perfluorocarbon emulsions for ultrasound imaging and therapy, and 2) the analysis of controlled mineralization of nanoparticles over stabilized emulsion interfaces. Spontaneous emulsification, or the ‘ouzo effect’, takes advantage of rapid solubility changes to generate monodisperse nanoemulsions. In these systems, emulsification is triggered by addition of a ‘poor’ solvent (e.g. water) to a hydrophobe (e.g. alkanes, perfluoroalkanes) that is dissolved in a miscible ‘good’ solvent (e.g. ethanol). Unfortunately, the effects of co-dissolved colloidal stabilizers like lipids, surfactants, and polymers on emulsification are still poorly understood. Thus, HTE with pipetting robots and x-ray (USAXS) analyses have been used to develop complex correlations and to map the structure-composition phase diagram. In a second system, molecular stabilizers that are adsorbed to a dispersed emulsion interface are systematically altered to evaluate their effect(s) on the controlled mineralization of inorganic particles. We report on how small angle scattering can be used to study complex relationships in these two experimental systems. Samples are prepared in HT using a liquid handling robot and loaded into custom-designed well plates for HT x-ray scattering experiments. We also demonstrate how HT model fits of large datasets are implemented and used to map formulation parameters (e.g. component concentrations) to the size and structure of both experimental systems. Finally, we provide guidelines for performing successful HT scattering experiments.

PC.01.04

The Impact of Concentration and Salt on the Structure of Nanoscale Organic Hybrid Materials (NOHMs) from Small Angle Neutron Scattering

Md Ashraf Haque¹, Sara Triana Hamilton², Tony Gordon Feric², Ah-Hyung A. Park² and Mark Dadmun^{1,3}; ¹University of Tennessee, United States; ²Columbia University, United States; ³Oak Ridge National Laboratory, United States

We are interested in developing novel soft electrolytes for use in redox flow batteries, including

nanoscale organic hybrid materials (NOHMs), which are promising solvent-free electrolytes. However, the structure of the NOHM, including the impact of concentration and added salt on the grafted polymer layer and free polymer is not well understood. In this presentation, we describe small angle neutron scattering (SANS) results that document the change in NOHM nanoscale structure to changes in packing and the presence of salt. SANS provides the opportunity to incorporate contrast variation in the sample which is essential in our analysis. Our recent experiments performed at the National Institute of Standards and Technology included varying concentrations of NOHMs dissolved in D₂O. The data is modeled with SasView using a core-shell model. Analysis of the 10% NOHM sample finds that ~1 nm long polymer chains are grafted successfully on ~8 nm SiO₂ nanoparticles. Further analysis of the 15%, 20%, 25%, 30%, and 40% samples, shows that the extension of the grafted polymer decreases with the increasing concentration of NOHMs. Furthermore, the high q-region of the SANS curve provides evidence of the presence of free polymer in all solutions. We have also measured the SANS curves of the same samples that include KNO₃ salt. This data is still being analyzed. Our future plans include Neutron Reflectivity measurements on NOHMs in order to understand their ordering near a solid surface that will provide insight into their behavior near an electrode.

PC.01.05

Towards Enhanced Neutron Scattering from Spin-Hyperpolarized Substrate Molecules—Calculations and Simulations

George M. Thurston and Michael Kotlarchyk;
Rochester Institute of Technology, United States

We calculate and simulate absolute polarized neutron scattering cross sections from prototypical substrate molecules, such as pyridine, that have been proven to acquire nuclear spin hyperpolarization via *Signal Amplification by Reversible Exchange* (SABRE). Because of the pronounced spin-dependence of polarized neutron scattering, combined with degrees of hyperpolarization that can be orders of magnitude in excess of thermal polarizations, such molecules will exhibit scattering cross sections that provide for potentially useful probes of molecular conformation and solution structure. We examine cross-sections for the neutron spin-flip and no-spin-flip cases. Experiments that combine these cross-sections can yield useful partial structure factors, including direct measurements of distances between selected nuclei.

We explore protocols that yield potentially useful signals that are proportional both to the first and second powers of the degree of nuclear spin hyperpolarization, and address considerations needed for practical implementation.

PC.01.06

Morphological Transitions in Surface Active Ionic Liquid-Bile Salt Mixed System—A SANS Study

Vijaykumar I. Patel; JNM Patel Science College,
Bharthana Vesu, India

Due to the potential use and widespread applications of mixed micelles, herein we report the formation of rod-like micelles from the mixtures of a surface active ionic liquid and bile salt. Mixed micelles of sodium deoxycholate and sodium cholate with 1-decyl-3-methylimidazolium chloride have been assessed by spectral and scattering techniques. These bile salts display electrostatic and hydrophobic interactions with the IL. The incorporation of bile salts in IL micelles leadsto an increase in solution viscosity suggesting micellar growth and transitions. These observations are confirmed by dynamic light scattering and further supported by small angle neutron scattering. The unusual viscosity behaviour is observed by altering the solution pH. NMR provided information on deeper penetration of sodium deoxycholate molecules in IL micelles. Such a bile salt induced sphere-to rod micellar transition further modulated by pH is of its first kind in an IL–bile salt mixed system.

PC.01.07

Temperature Dependent Single-Chain Structure and Solution Behavior of Polyzwitterions via SANS

Phillip Pickett, Michael Lueckheide, Yuanchi Ma and Vivek Prabhu; National Institute of Standards and Technology, United States

Responsive polyzwitterionic materials have become important for a range of applications such as environmental remediation and targeted drug delivery. Much is known about the macroscopic phase-behaviors of such materials. But how the smaller scale single-chain structure of polyzwitterions respond to external stimuli is not well understood. These single-chain dynamics are important in commanding their respective larger scale responsive properties. Here, we study the temperature dependent single-chain structure of a model zwitterionic homopolymer using small angle

neutron scattering (SANS) with and without added electrolytes. Zimm plot analysis reveals values for the radius of gyration (R_g) and the second virial osmotic coefficient (A_2) of single chains. We also probe the smaller-scale intra-chain correlations using Kratky plots. Our findings provide further insight into the single-chain structure and dynamics of polyzwitterions which can be used to guide structure-property models of responsive zwitterionic-based assemblies.

PC.01.08

Polymer-Coupled Local Dynamics Enhances Conductivity of Ionic Liquids

Siqi Liu¹, Madhusudan Tyagi² and Pinar Akcora¹; ¹Stevens Institute of Technology, United States; ²National Institute of Standards and Technology, United States

Solvent and polymer-grafted nanoparticle addition to the 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-TFSI) was investigated by measuring the translational diffusion of cationic species in quasi-elastic neutron scattering (QENS) experiments, and ionic conductivity using electrochemical impedance spectroscopy. Adding polymers or nanoparticles to neat ionic liquids generally increases their viscosity and lowers the ionic diffusivity. In this work, we added two different solvents (acetonitrile and methanol) to HMIM-TFSI-grafted particle mixtures to understand the interplay between polymer-ionic liquid interactions and conformational state of brushes, which governs the transport properties (diffusivity and conductivity) of ionic liquids. Our results showed that with grafted chains swollen in acetonitrile, the cationic mobility and ionic conductivity were improved with the number of grafted chains on particles. The unusual high conductivity attained with the addition of PMMA-grafted magnetic nanoparticles suggests that polymer coupled ionic liquid dynamics can be effective in increasing the free cation amount and, therefore, ionic conductivity in particle-based electrolytes.

PC.01.09

Free-Standing Ultrathin Film Mechanics—The Role of Mobile Interfaces

Luke Galuska¹, Eric Muckley^{2,3}, Zhiqiang Cao¹, song zhang¹, Ilia Ivanov² and Xiaodan Gu¹; ¹University of Southern Mississippi, United States; ²Oak Ridge National Laboratory, United States; ³The University of Tennessee, Knoxville, United States

Although the glass transition phenomena of ultrathin

confined polymer films have been heavily investigated for the last two decades, the mechanical properties of such sub-100 nm thin films have remained elusive until much more recently. Our previous work utilized a pseudo-free-standing tensile test which relies on water as a support and has successfully been employed throughout many systems. However, the effect of water on the mechanics of nanoconfined films is unclear. Here, we developed a novel truly free-standing (in air) tensile platform to study sub-100 nm thick films and compare the mechanical properties obtained to that of the film on water technique thereby elucidating the influence of the interface on the mechanics of these thin films. Tensile characterization of stiff glassy polystyrene and soft semicrystalline poly(3-hexylthiophene-2,5-diyl) films has been achieved down to 19 nm and 80 nm respectively. We observed minimal difference in moduli obtained from on water and in air measurements, while yield stress and crack-onset-strain were greater for films supported on water. Neutron reflectometry was then employed to quantify the uptake of water within these films, matching the environment of our pseudo-free-standing tensile test (air-polymer and polymer-water interfaces), and justify our mechanical results. These measurements support that water is penetrating these hydrophobic films, concentrated near the water-film interface, and mitigate crack propagation with minimal influence towards modulus.

PC.01.10

Organosilica Nanoparticles with Continuously Tunable Scattering Length Density for the Analysis of Ligand-Driven Phase Separation in Mixed Colloidal Systems

Yue Zhai and Michael Bockstaller; Carnegie Mellon University, United States

Over the past decades, silica nanoparticles have received much attention in diverse areas, such as catalysis, adsorption, separation and chromatography. Due to the high level of biocompatibility and the well-established surface chemistry of silica that enables versatile functionalization of particle surfaces, more recent applications of silica nanoparticles also include nanotechnology and nanomedicine. However, although small particle sizes are preferable in these applications, there are only few reports concerning the use of sub-10 nm particles, as their synthesis has remained a challenge. Recently, we developed a one-step process (based on the condensation of brominated organosilane precursors) to prepare ATRP initiator-modified

organo-silica hybrid particles with diameter that is tunable within the range 3-30 nm and narrow size dispersity. The hybrid particles could readily be polymer-modified via surface-initiated atom transfer radical polymerization (SI-ATRP) without further surface modification. The accessibility of the surface -Br initiating sites was evaluated by the polymerization of poly(methyl methacrylate) (PMMA) ligands from the surface of the oSiO_2 nanoparticles. The ultra-small size, tunable composition and ease of surface modification may render these nanoparticles an interesting alternative to conventional silica nanoparticles for functional material design. We demonstrate the ability to tune scattering length density of organosilica nanoparticle by replacing allyl alcohol with deuterated d8 allyl alcohol in the synthesis process of precursor and then blending it with hydrogenated organosilica precursor. We demonstrate that the deuterated and hydrogenated organosilica precursor have same condensation mechanism and chemical properties except for scattering length. They can be cross linked to form deuterated organo-silica particles with built-in ATRP-functionality without affecting particle size. The scattering length density of both hydrogenated and deuterated organosilica nanoparticle is determined to be 1.23×10^{10} and $3.11 \times 10^{10} \text{ cm}^{-2}$ by contrast matching with partially deuterated PMMA polymer brushes using small angle neutron scattering (SANS). The potential of tuning scattering length density is especially useful for research field using neutron scattering experiments. For example, we can study the phase separation behavior of polymer tethered particles blend in bulk film using SANS by contrast matching polymer tethers and nanoparticle cores. This synthetic innovation provides new opportunities to elucidate the anomalous domain growth kinetics in particle brush blend and the effect of polymer interactions on assembly behavior of colloidal systems.

PC.01.11

Morphology of Nanocrystalline Domain Reinforced Polyisobutylene (PIB) Rubber Revealed Using SANS

Aarushi Srivastava, Yihong Zhao, John Meyerhofer, Li Jia and Mark D. Foster; The University of Akron, United States

Controlling dynamic mechanical properties and the energy dissipation process is a key for elastomer applications, particularly for tires. Energy dissipation is beneficial for achieving fracture resistance, but disadvantageous for fuel efficiency. This tradeoff is a

perennial dilemma for the development of tire materials. In the ideal situation, one would like to have an elastomer that does not dissipate energy at low strains and strongly dissipates energy at high strains, because such characteristics minimize energy waste under normal tire-running conditions ($< 50\%$ strain) and prevent catastrophic failure under severe stress and strain (for example, at crack tips). Such properties can be attained in a polyisobutylene (PIB) rubber which is reinforced by hard domains of nanoscale size self-assembled from grafted side chains consisting of a few units of β -alanine. Various studies have led to the hypothesis that the reinforcement ability of the crystalline nanodomains formed should vary markedly with the size of the domains. Domains that are truly nanoscale in three dimensions provide better reinforcement than those that are fibrillar in morphology. Nanodomain size has been tailored here by designing the grafted side chain chemistry in order to alter the grafting density of portions of the PIB backbone at the nanocrystal interfaces. β -alanine trimer grafted polyisobutylene chains were designed to present a layer of brush-like hydrocarbon chains on the surface of the β -sheet crystals. Morphological control of the β -sheet crystals has been achieved by varying the surface chain density. A combination of TEM and SANS has confirmed the formation of fibrous and particulate crystals in the continuous polyisobutylene phase. Both particulate and fibrous β -sheet crystals are highly effective in reinforcing the elastomer, producing high modulus and high extensibility at the same time. Since the β -alanine volume fraction in the PIB rubber is only about 4 vol%, these materials not only provide mechanical properties similar to those of conventional (~ 50 vol% silica or carbon black filled) rubbers, but are also more sustainable, with a much lower carbon footprint. Results from TEM, SAXS and SANS characterizations of the reinforced rubber morphology are consistent with the contention that increasing the density of chain grafting at the crystalline nanodomain surface can sharply limit the growth of the nanodomains in the direction of hydrogen-bonding in the crystals. The surface chain density, gradient in chain stretching, and volume fraction of unperturbed chains differ with nanocrystal size. The SANS data provide direct evidence for the existence of a layer of brush-like chains at two surfaces of the β -alanine crystals. The brush layer resists penetration by organic deuterated solvents and therefore is visible in SANS. The structure can be modelled using a parallelepiped core-shell model.

PC.01.12

Solution Structure of Lipophilic-Charged Block Cooligomers and Complexes for Delivering Therapeutic Nucleic Acids

Michael J. Lueckheide¹, Timothy Blake², David Walton², Robert M. Waymouth², Yuanchi Ma¹, Yimin Mao¹ and Vivek Prabhu¹; ¹National Institute of Standards and Technology, United States; ²Stanford University, United States

Charge-altering releasable transporters, or CARTs, are block cooligomers with a lipophilic block and a cationic block. They are synthesized via organocatalytic ring-opening polymerization with controlled numbers of cationic monomer units that rearrange and degrade at physiological pH to form neutral products. Their structure and degradation profile make CARTs effective at complexing and transfecting therapeutic anionic nucleic acids like messenger RNA (mRNA), and releasing them inside the cell to be translated into proteins. They are also relatively unique from a fundamental standpoint because they are lipophilic-cationic block cooligomers instead of the hydrophilic-cationic block copolymers that are commonly used, and the presence of the lipophilic block is required for successful delivery. CART/mRNA complexes were previously shown to efficiently induce expression of different mRNAs in both cultured cells and animals, but their fundamental physical structure has yet to be determined. Small-angle neutron scattering, light scattering, and cryogenic transmission electron microscopy results will be shown that characterize the solution structure of the CART molecules and CART/nucleic acid complexes. As a comparison, nondegradable CART analogues are also studied and serve as model systems without the added complexity of pH sensitivity.

PC.01.13

Structure and Dynamics of Oil-Swollen Surfactant Membrane Including Hydrophobically Modified Gold Nanoparticles

Michihiro Nagao^{1,2,3}, Robert Bradbury^{1,2}, Siyam M. Ansar⁴ and Christopher Kitchens⁴; ¹National Institute of Standards and Technology, United States; ²Indiana University, United States; ³University of Delaware, United States; ⁴Clemson University, United States

Nanoparticles (NPs) exhibit distinct physical and chemical properties from the bulk materials, and applications of NPs span broad range of science and engineering fields, such as new nanoscale devices in biological, pharmaceutical and even physical biomedical applications. Especially in these

applications, potential toxicity of NPs is a problem, therefore, understanding effects of NPs to a membrane has gained attention. An oil-swollen surfactant lamellar membrane is a unique environment to study properties of membranes, as we can create such systems without charge in the system and can change the bilayer thickness easily so that hydrophobic mismatch to be investigated when inclusions are embedded. In the present study, hydrophobically modified gold nanoparticles (AuNPs) were incorporated into such membranes to measure structure and dynamics of the membranes. Small-angle neutron scattering (SANS) and neutron spin echo (NSE) spectroscopy were employed, and the scattering contrasts of the membrane were tuned by employing either protiated or deuterated oil. As increasing the membrane thickness by increasing the amount of oil in the membrane, membrane became softer, which is interpreted as an increasing membrane compressibility with adding oil. Although the bulk modulus of oil is relatively high, the compressibility of the membrane becomes higher originated from the lateral mobility of oil molecules in the membrane. This leads to an increase of the thickness fluctuation wavelengths in the lateral direction and the thickness fluctuation relaxation time gets slower. The incorporated hydrophobic AuNPs were synthesized to be about 5 nm in diameter, which were embedded into the membrane with the thickness ranged from 4 nm to 8 nm. Addition of AuNP in the membrane induced thinning and softening of the membrane. Increased membrane compressibility by addition of AuNPs was confirmed by thickness fluctuation measurements as well. We estimated the membrane viscosity both from the NSE and solution rheology measurements, which showed the same orders of magnitude. However, the increasing trend observed by NSE contradicted to the rheology measurements which were almost constant with the amount of oil. The result suggests that the diffusion of AuNPs in the membrane may affect the dynamics of the host membrane.

PC.01.14

Towards Realistic Tribological Models: Experimental Structural Studies of Confined Lubricating Surfaces

Robert Barker¹, Hannah Boyd^{2,1}, Chloe Skingle¹, Juan Francisco Gonzalez² and Javier Sotres²; ¹University of Kent, United Kingdom; ²Malmö University, Sweden

Surfaces in tribological contact and relative motion are common occurrences in nature as well as in man-made device such as motorised engines. In all cases

they need to be lubricated in order to achieve an optimal and long-lasting performance as well as reduce wear. However, the underlying molecular mechanisms of lubricating action at such interfaces when they are in tribological contact and undergoing shear remains largely unknown. A variety of experimental techniques have been developed to study forces experienced at confined and sheared interfaces directly, including the pioneering work using surface force apparatus and AFM. However, while these give insight into the forces, no techniques existed to study effectively the structural and mechanistic view of these films, particularly when doing their job under confined and lubricating conditions. Recently, harnessing the strengths of neutron scattering combined with the design of novel new sample environment, we have made a number of innovations in this field. These have enabled the study of structural changes at these interfaces with sub-nanometer resolution when under direct confinement and and/or hydro-dynamic shear. Three specific cases will be discussed:

1. Directly Confined Interfaces

We have developed a unique surface force type apparatus that allows direct measurements using neutrons of the structure of interfaces under a confining pressure.¹ We have shown that inflation of a flexible membrane against the bio-interface of interest provides close and even contact between the interfaces over a large surface area. This has recently been used to study the structure & mechanical properties of a number of systems, including: (a) polymer brushes;² (b) oil-based lubricants; (c) cartilage lubrication mechanisms in joints³ and (d) salivary lubrication,⁴ a key factor in oral health and food consumption.

2. Sheared Interfaces in Contact

Building on this direct confinement work, we have recently shown two new approaches to study interfaces in contact under shear in both a rolling and sliding motion. Revealing structural changes in thin films at the interface between two solid materials in motion relative to each other. Particular applications in oil-based and biological lubrication will be discussed.

3. Hydro-Dynamic Shear at Interfaces

We have designed a number of microfluidic flow cells to enable the control and manipulation of fluids at interfaces. These have been particularly designed for controlled shear across interfaces, allowing high resolution mechanistic studies using neutron scattering to be carried out in-situ. Specifically, the ongoing application of this approach for studying the interfacial interaction of blood under shear will be discussed.⁵

¹ de Vos, W.M., et al., *Revi. Sci. Instrum.*, 2012. 83: p. 113903.

² Abbott, S.B., et al., *Macromolecules*, 2015. 48: p. 2224-2234.

³ Mears, L.M., et al., In Preparation.

⁴ Boyd, H., et al., Submitted.

⁵ Skingle, C.M., et al., Submitted.

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Effect of Chain Adsorption on the Diffusion of Star Polymer Chains

Ayse Caglayan¹, Sumeyye Ozer¹, Guangcui Yuan², Sushil K Satija², David Uhrig³, Kunlun Hong³ and Bulent Akgun¹; ¹Bogazici University, Turkey; ²National Institute of Standards and Technology, United States; ³Oak Ridge National Laboratory, United States

Irreversible adsorption of polymer chains on solid substrates have a huge impact on the wetting, glass transition, aging, and polymer chain mobility in thin films. Recently, the existence or absence of segmental mobility for the adsorbed polymer chains is under discussion. We have investigated the effect of polymer chain adsorption on the mobility of polymer chains in thin films for linear and star polymers. The vertical mobility of polystyrene (PS) chains was determined by probing interdiffusion between protonated PS (hPS) and deuterated PS (dPS) layers using neutron reflectivity. By carefully controlling the amount of deuterated adsorbed chains in the bottom layer for linear dPS, 4-arm star dPS and 8-arm star dPS, we have determined that these layers are not dynamically dead. The apparent diffusion coefficient for adsorbed 8-arm star PS chains was the largest even though X-ray reflectivity measurements showed that 8-arm star PS chains form adsorbed layers with the highest normalized thickness among these three polymers.