

12-01

**The Rheology of Anisometric Particle Dispersions and "Liquid Armor"**

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Novel ballistic resistant composite materials are formulated from colloidal dispersions of anisometric particles. Through ballistic testing, the mechanism of energy adsorption at ballistic rates is demonstrated to result from reversible shear thickening in the colloidal dispersion. As a basis for the rational design of ballistic resistant materials, we report a rheological and microstructural investigation of dispersions of stabilized, acicular precipitated calcium carbonate (PCC) particles of varying aspect ratio. The effects of particle shape on the low shear viscosity, shear thinning behavior, and onset of shear thickening is explored. Rheology-Small Angle Neutron Scattering studies (RHEO-SANS) demonstrate particle alignment with the flow and debunks previously hypothesized mechanisms for shear thickening in anisometric particles. The experimental results demonstrate that increasing particle aspect ratio leads to enhanced shear thickening at much lower particle concentrations than observed in comparable suspensions of spherical colloidal particles. These results are predicted by micromechanical models to elucidate the mechanism of shear thickening in suspensions of anisotropic particles. The application of these dispersions in formulating novel energy absorbing materials is discussed.

12-02

**Rheological Behavior of Bauxite Residue and Bauxite Residue Derivatives**

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Over 70 million metric tonnes of bauxite residue is produced annually as a by-product of aluminum production. Currently the residue is being landfilled and will continue to be stored in various locations requiring ongoing management because of the caustic nature of the residue. The objective of this research is to provide an understanding of the rheological behavior of bauxite residue and bauxite residue derivatives. Rheological measurements were carried out using a rotational rheometer for shear rates between 0 and 400 s<sup>-1</sup> in a range of pH values and various solid concentrations. Two dissimilar shear-thinning regimes are evident within each data set. As pH is reduced the corresponding viscosity curve is shifted to a lower viscosity. A practical rheological model for bauxite residue including the effect of change in pH (via CO<sub>2</sub> gas diffusion), solids concentration, while monitoring particle size distribution is described. The goal is to provide the aluminum industry with sufficient information to predict the flow behavior of bauxite residue and bauxite residue derivatives so that engineering processes for their disposal and/or conversion to commercial products can be designed.

12-03

**Active and Nonlinear Microrheology**

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Over the last decade a set of experimental techniques collectively known as ‘microrheology’ has emerged as an alternative to traditional ‘macrorheology’, with the ability to probe the

viscoelastic properties of soft heterogeneous materials (e.g. polymer solutions, colloidal dispersions, biomaterials, etc.) at the micrometer (and smaller) scale. In microrheology, elastic and viscous moduli are obtained from measurements of the fluctuating thermal motion of embedded colloidal probes. In such experiments, the probe motion is passive and reflects the near-equilibrium (linear response) properties of the surrounding medium. By actively pulling the probe through the material, further information about nonlinear material properties can be obtained, analogous to large amplitude measurements in macrorheology. We consider a simple model of such systems: a colloidal probe pulled through a suspension of neutrally buoyant bath colloids. The non-equilibrium spatio-temporal configuration or microstructure of particles induced by the motion of the probe is calculated analytically and via Brownian Dynamics simulations and used to infer the dispersion's 'effective microviscosity'. The computed effective viscosities compare well with analogous macrorheology studies of sheared colloidal dispersions, suggesting that active tracking microrheology can be a valuable tool with which to explore the rich nonlinear behavior of complex materials.

12-04

### **Microrheology of a Colloidal Suspension Using Laser Tweezers**

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The microrheology of a colloidal suspension is measured using laser tweezers and the structure is visualized with confocal microscopy. Suspensions of index-matched silica and fluorinated ethylene propylene (FEP) are seeded with index-mismatched melamine and polystyrene probe particles, respectively. The probes are trapped with laser tweezers and subjected to a uniform flow enabling measurements of the suspension microrheology. Good agreement is found between the microviscosities of FEP measured with laser tweezers and bulk viscosities using a couette cell. As the probe size approaches the suspension particle size, non-linear behavior similar to shear thinning is observed at higher suspension concentrations. This is consistent with the formation of a "wake" in the non-equilibrium pair distribution function between the probe and bath particles [Squires and Brady, 2005], which is demonstrated by confocal images of probe experiments in fluorescent silica suspensions.

12-05

**Rheological Behavior of Nano-Dendrimers / Silica Suspensions**

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The electrorheological behavior of dendrimers/silica/silicone oil suspensions has been investigated. A surprisingly strong correlation of the electrorheological response with the level of maximum shear stress during steady flow measurements has been noted. The experimental results may be explained by polar or polarizable particles lining up in an external electric field. The drive toward alignment must overpower the Brownian motion and/or mechanical perturbation. Dielectric properties of the suspended particles will favor alignment – but the resistivity of the suspended particles must be high enough to avoid excessive current flow.

12-06

**Melting in Temperature Sensitive Colloidal Suspensions**

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I will talk about recent experiments from my lab wherein we use temperature-sensitive NIPA polymer and NIPA microgel particles to drive melting transitions. In colloidal crystal experiments we observe premelting at grain boundaries and dislocations. In colloidal rod experiments we observe melting of lamellar phases into nematic phases.

12-07

**The Effect of Nanoparticles on the Structure and Rheology of Clay Suspensions**

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Suspensions of clay particles (kaolinite) combined with silica nanospheres undergo a dramatic stabilization process, which increases suspension viscosity as well as elasticity to the point where the suspensions can support their own mass as well as be sectioned. The suspensions develop a significant yield stress, which can be overcome by vigorous shaking, making the process completely reversible. These transitions are observed for kaolinite concentrations of 14 percent by volume (v/o), and nanosphere concentrations as small as 3 percent. Decreasing the nanosphere size at constant volume fraction results in higher yield stresses, significant elasticity, and shorter time scales for gel development. SEM micrographs obtained by cryogenic fracturing of the samples indicate that the added nanoparticles produce a more ordered, 'honeycomb-like' structure, possibly arising from a very localized phase separation. In some of the nanoparticle solutions, ordering of the clay platelets into dense stacks is also observed.

12-08

**Evaporation-Induced Particle Microseparations inside Freely Floating Droplets**

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We study colloid particle transport inside single microdroplets of water floating on the surface of inert fluorinated oil. This is done on a new type of microfluidic chips, where the droplets are manipulated with alternating electric fields applied to arrays of electrodes below the oil. The particles collect at the top region of the floating droplets and phase-separate in layers based on their size and density. These remarkable microseparation processes can be used for on-chip synthesis of advanced particles, microscale separations without other integrated components and innovative microbioassays. We report experimental results and theoretical simulations that explain the microseparation as a result of series of processes driven by mass and heat transfer. During the evaporation, a surface tension gradient on top of the droplet occurs as a result of a non-uniform temperature distribution. This interfacial tension gradient generates an internal convective Marangoni flow. The colloidal particles transported by the convective flow collect on the top of the droplets by the hydrodynamic flux compensating for the evaporation. The internal flow pattern and temperature distribution within the evaporating droplet were simulated using finite element calculations. The simulation was consistent with experiments using tracer particles.

12-09

### **Mobility and In-situ Aggregation of Charged Microparticles at Oil-Water Interfaces**

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Particle mobility, aggregate structure, and the mechanism of aggregate growth at the two-dimensional level have been of long-standing interest. Here we use Pickering emulsions as a model system to investigate the mobility of charged microparticles at polydimethylsiloxane (oil)-water interfaces using confocal laser scanning microscopy. Remarkably, the rate of diffusion of the charged colloidal-sized polystyrene particles at the oil (5 cSt)-water interface is only moderately slower than in the bulk water phase. The ambient diffusion constant of solid particles is significantly reduced from  $1.110^{-9}$  cm<sup>2</sup>/s to  $2.110^{-11}$  cm<sup>2</sup>/s when the viscosity of the oil phase increases from 5 cSt to 350 cSt. In addition, we have investigated the influences of interfacial curvature and successfully observed the in-situ structural formation of solid particles at the oil-water interface.

12-10

### **Crystalline Junctions in Associative Gels: PLA-PEO-PLA Triblocks with Tunable Rheology**

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Soft biomaterials derived from amphiphilic polymers have received considerable attention in the last decade. The ability to tune the modulus of implantable materials to match that of native tissue is crucial for scaffolding applications; unfortunately, a significant limitation of current polymeric biomaterials is a lack of mechanical robustness and a low elastic modulus. We address these issues using hydrogels of poly(lactic acid)-poly(ethylene oxide)-poly(lactic acid) (PLA-PEO-PLA) triblock copolymers, which form associative network gels with the PLA domains serving as network junctions. Our work distinguishes itself from previous studies

through controlled crystallinity of the junction points. We can create nanoscale crystalline junctions through use of copolymers in which the PLA block is poly(L-lactic acid) (PLLA), or amorphous junctions through copolymers in which the PLA blocks contain D-lactic acid and L-lactic acid (PDLLA). The crystalline junctions in the PLLA-based gels cause a significant increase in the elastic modulus over the PDLLA gels, allowing us to create biocompatible gels with elastic moduli that are an order of magnitude higher than previously reported with biocompatible associative gels. The modulus is also very sensitive to PLA block length and can be easily tuned through to match the moduli of native tissue for a variety of applications. These crystalline junction points may be considered a new mode of association in polymer gels and a novel method for tuning the rheological properties.

12-11

### **Microstructural and Microrheological Properties of Novel Self-assembled Hydrogels**

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Hydrogels are an important class of materials that have extensive uses in tissue engineering and drug delivery applications. Recently, a short 20 amino acid  $\beta$ -hairpin peptide has been designed for the preparation of novel hydrogels, that reversibly folds and gel by a process of hierarchical self-assembly. Little is known of the gelation kinetics and microstructure of these complex materials. A better understanding on a microscopic level is necessary because we expect that for these hydrogels the microscopic structure and heterogeneity will impact the cellular response to the material. In this study the gelation kinetics and microstructure of the self-assembled hydrogels was investigated with the use of multiple particle tracking. An increasing gelation time with decreasing peptide concentration was found. The self-part of the van Hove correlation function and a non-Gaussian parameter were used to obtain insight into the heterogeneity of the microenvironment of the hydrogel. Microrheological techniques enable us to understand the mechanical properties of hydrogels at a microscopic level, enabling the design of novel peptides that will lead to the ultimate microstructural and microrheological properties necessary for tissue engineering and drug delivery applications.

12-12

### **The Role of Bile Salt in Inducing Threadlike Reverse Micelles of Lecithin in Organic Solvents**

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Threadlike or wormlike micelles are formed by charged surfactants in water upon the addition of salt. Here, we report a similar phenomenon in organic solvents, i.e., the formation of reverse wormlike micelles by the phospholipid, lecithin upon the addition of a bile salt. Bile salts are biological amphiphiles having a planar, "facially-amphiphilic" structure. Adding a few mM of the bile salt, sodium deoxycholate (SDC) to a semidilute solution of lecithin in cyclohexane, is enough to induce the growth of reverse micelles from spheres to long, cylindrical threads. In the process, the sample is transformed from a low-viscosity fluid into a highly viscoelastic and flow-birefringent fluid. Similar results are observed in a range of nonpolar organic liquids. We will present data from rheology and small-angle neutron scattering (SANS) on these micellar fluids. A tentative model for the reverse micelle structure will be proposed in an attempt to clarify the role played by the bile salt in inducing micellar growth.

12-13

### **Dynamics of Brownian particles in Concentrated Wormlike Micelle Solutions**

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Brownian motion in complex fluids is of scientific interest as the particle motion couples to the underlying dynamics of the suspending media, as well of industrial interest in the consumer products, paints, detergents, and food industries for example, as such formulations often contain colloids and emulsions. Brownian particles are also used as probes of local linear viscoelasticity in complex fluids and biological materials, a technique known as micro-rheology. Here, we investigate the Brownian motion of model colloidal particles dispersed in an entangled wormlike micellar mesh and the associated mixture rheology and microstructure. This regime, where particle size and relaxation times are comparable to the length and relaxation time scales of the suspending medium, is poorly understood. Results of rheological investigations, small-angle neutron scattering, and dynamic and static light scattering are reported. The properties of the wormlike micellar solution and particles are systematically varied to explore the coupling between particle and self-assembled aggregate dynamics and microstructure. Significant effects are observed upon addition of Brownian particles on the relaxation spectra of the micellar fluid. Further, the self-assembled surfactant aggregates are observed to strongly influence the short-time particle dynamics. The results are interpreted with a microstructural model for particle self-assembled surfactant mixture.

12-14

#### **Interfacial Rheology of Globular and Flexible Proteins at the Hexadecane/Water Interface: Comparison of Shear and Dilatation Deformation**

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After long-time exposure, protein adsorption at fluid/fluid interfaces produces interfacial gel-like networks. We utilize interfacial shear and dilatational rheology to probe the structure of a globular protein, lysozyme, and a disordered protein,  $\beta$ -casein, at the hexadecane/water interface. For lysozyme, the shear moduli grow with interface age indicating a transition from fluid-like behavior at early times to solid-like network formation at later times. Conversely, the interfacial shear moduli of  $\beta$ -casein change very little with interface age. The strong protein intramolecular interactions that stabilize the native conformation of lysozyme act as kinetic barriers to conformational change and later become strong intermolecular interactions that result in aggregation at the interface. The interfacial dilatational storage modulus is comprised of a static response and a dynamic response. The dynamic contribution corresponds to rearrangement and reconfiguration of the protein molecules within the interface and gives a measure of the strength of interprotein linkages. Globular lysozyme, once adsorbed, resists compression giving a high dilatational storage modulus. Contrastingly,  $\beta$ -casein exhibits only a small interfacial dilatational storage modulus. For the first time, we establish that surface shear and dilatational moduli measure quite different but complementary molecular characteristics of adsorbed proteins at fluid/fluid interfaces.

12-15

#### **Influence of Non-Newtonian Behavior on the Dynamic Interface Shapes of Polymer Melts, Solutions and Boger Fluids**

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In this work, we characterize the liquid-vapor interface shape during forced wetting to quantify the effect of fluid elasticity on interface shape. The fluid mechanics near the three phase (solid-liquid-vapor) are complex and the impact of elasticity on this inherently confined geometry is poorly understood. We find that two polymer melts, polyisobutylene (PIB) and polystyrene (PS) exhibit dynamic wetting characteristics of a weakly elastic fluid. We study dynamic wetting by observing the liquid-vapor interface formed on the outside of a silica surface forced into a bath of the test fluid at controlled rates. The results show that the interface shapes of these fluids deviate from the prediction of models that include only Newtonian flow behavior. Using standard rotational rheometry, we examine the shear rates needed to cause non-Newtonian behavior in these fluids and ask where such shear rates arise near the contact line. Experiments on xanthan gum solutions have shown that an increase in shear thinning in the high shear region near the contact line decreases the curvature of the interface near a moving contact line. However, fluids with some level of elasticity and minimal shear thinning show an increase in curvature near the contact line. Differences in these fluid behaviors and ramifications on interface shape will be discussed.

12-16

#### **The Effect of Nonadsorbing Macromolecules on the Particle Dynamics Near an Interface**

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The optical technique of total internal reflection microscopy (TIRM) was used to study the normal Brownian motion of a single colloidal particle near an interface. Using our data analysis method, the particle's spatially-varying diffusion coefficient can be determined without any knowledge of the forces acting on the particle. Experiments were performed in solution containing small silica nanospheres, polyacrylic acid, and clay platelets to investigate the effect of nonadsorbing species on the dynamics of near-contact particle motion. This talk will focus on the dynamic particle behavior near a solid wall in dilute colloidal suspensions of synthetic clay particles (laponite) that are slowly thickening. Measurements of the equilibrium potential energy profile were also obtained which indicate the development of structures in the laponite solution over time.

12-17

#### **Dramatic Increase in Viscosity with Temperature as a Result of a Thermoreversible Vesicle-to-Micelle Transition**

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Complex fluids based on surfactants usually show a decrease in their viscosity upon heating. We report an example of the opposite effect, where the viscosity sharply rises upon heating as a result of a microstructural transformation. This phenomenon is observed in mixtures of the cationic surfactant, cetyl trimethylammonium bromide (CTAB) and a methyl-substituted

salicylic acid. Such mixtures self-assemble in aqueous solution to form unilamellar vesicles at room temperature. Upon heating, the vesicles are transformed into long, cylindrical micelles and consequently, the sample changes from a low-viscosity, Newtonian fluid to a viscoelastic, shear-thinning fluid. The zero-shear viscosity increases by a factor of 1000 or more with increasing temperature. The ensuing microstructural changes as a function of temperature are confirmed by small-angle neutron scattering (SANS) measurements. We will discuss and correlate the rheology and SANS data for various sample compositions.

12-18

### **Structure and Mechanical Properties of Nanocomposites: Proteins and Nanoparticles Templated in Self-Assembled PEO-PPO-PEO Mesophases**

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Highly ordered self-assembled block copolymer mesophases present an attractive way of transferring their structure to otherwise disorganized nanometer sols (proteins or inorganic nanoparticles). Unlike other “bottom-up” nanoparticle organization methods, the tunable structure of the ordered block-copolymer phase provides increased control over the structure of the templated nanoparticle arrays. This method allows us to organize large numbers of particles ( $10^{20}/L$ ) into controllable three-dimensional structures. Additionally, the use of thermoreversible polymer mesophases permits the stable dispersion of pre-made nanoparticles or globular proteins. In this study, we use rheology to thoroughly evaluate the mechanical properties of these nanocomposites and find that mechanical properties are strongly altered when the concentration of dispersed nanoparticles approaches and exceeds the number of available template sites. Small-angle neutron scattering (SANS) is used to evaluate the coupling between matrix and nanoparticle order. By using solvents containing isotope mixtures in SANS we are able to separately study the structure of the organic and inorganic phases through the variation of the neutron scattering contrast. It is found that the nanoparticles are templated by the polymer gel and that the level of organization is dependent on a number of controllable variables. We quantify the influence of relative concentration, relative dimensions and temperature on both the nanoscale structure and macroscopic composite properties.

12-19

### **Physical Gelation and Rheological Properties of Cationic Telechelic Polyelectrolytes**

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Telechelic polyelectrolytes (TP) are a novel class of Associative Polymers (AP) constituted from a long polyelectrolyte chain end-capped by hydrophobic short polymeric chains. The main feature that makes TP, distinguished from the conventional telechelic APs (non ionic hydrophylic part) is that the chain conformation of the soluble part can be controlled by external conditions such as pH and ionic strength. At a certain pH (depending of the polyelectrolyte nature) and at free salt conditions the central chain adopts a stretched conformation, which has fundamental consequences on the TP association and rheological properties. In this work cationic TP constituted of a long PDMAEMA end-capped by short PMMA blocks have been synthesized and explored in aqueous media. The motivation of this work was to combine the excellent properties of telechelic polyelectrolyte physical gels with the benefits of biocompatibility and capability of cationic macromolecules to be complexed with DNA. Above  $c_{gel}$  (0.1 wt%) a transient physical network is formed through an open association mechanism, macroscopically observed by a rapid increase of the solution viscosity. This pronounced concentration dependence is marked, up to a polymer concentration of about 1%wt. Above this critical polymer concentration, a stiff hydrogel is formed for which rheological properties are not significantly strengthened by polymer concentration enhancement. In this higher polymer concentration regime, the physical hydrogel exhibits a peculiar rheological behavior characterized by a Newtonian plateau at low shear stresses followed by a viscosity drop of about five decades, attributed to apparent yield stress behavior, a second Newtonian plateau at intermediate shear stresses and a shear thinning at high stresses.

12-20

### **Numerical Simulation of Methane Hydrate in Sandstone Cores**

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Production of methane gas from hydrate dissociation in a core is studied. It is assumed that the core is porous with the pores being partially saturated with hydrate. Using the Fluent™ code with appropriate user defined functions, an axisymmetric model of the core is developed and solved for multiphase fluid flow during the hydrate dissociation. The model contains three separate phases of hydrate (solid/heavily viscous fluid), methane (gas), and water (liquid). The hydrate zone is stationary but water and gas can move freely. For different core temperatures and various production valve pressures, time evolutions of gas and water during hydrate dissociation are evaluated and variations of temperature and pressure are simulated. Variations of relative permeability of the core are included using Corey's model for porous media. Porosity of the core also changes with saturation of hydrate. It is shown that to maintain a constant natural gas production rate, the production valve pressure must be decreased with time. The simulation

results show that the process of natural gas production is a sensitive function of reservoir temperature and hydrate zone permeability.

12-21

### **A Study of Three-Phase Liquid-Gas-Solid Flows in Microgravity**

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An Eulerian-Lagrangian computational model for simulations of gas-liquid-solid flows in microgravity was developed. In this study, the liquid phase was modeled by a volume-averaged system of Eulerian governing equations, whereas motions of particles and bubbles were evaluated using Lagrangian trajectory analysis approach. It was assumed that the bubbles remained spherical and their shape variations were neglected. The two-way interactions between particle-liquid and bubble-liquid were accounted for in the study. The discrete phase equations used included drag, lift, buoyancy, and virtual mass forces. Interactions between particle-particle and bubble-bubble were accounted for by the hard sphere model. The bubble coalescence was also included in the model. The predicted results under normal gravity condition were compared with the available experimental data in earlier simulations, and good agreement was obtained. The transient flow characteristics of the three-phase flow were studied and the effects of gravity, inlet bubble size, bubble number density and bubble superficial velocity on variation of flow characteristics were discussed. The simulations for low gravity showed that most bubbles are aggregated in the inlet region, and due to the longer residence time and bubble coalescence, and the Sauter mean bubble diameter becomes rather large which can be more than 10 mm.

12-22

### **A New Friction Factor Correlation for Laminar and Single-Phase Fluid Flow through Fractured Rocks**

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Single- and multi-phase flow through fractured media occurs in various situations, such as transport of dissolved contaminants through geological strata, sequestration of carbon dioxide in brine-saturated reservoirs, and in enhanced oil recovery from depleted field. In the present study fluid flows through individual fractures were simulated. A post-processing code was developed and used to generate the three-dimensional fracture inside AutoCAD package from the CT scan data. Several sections along the fracture were considered and Gambit<sup>TM</sup> code was used to generate unstructured grid for flow simulation. Single-phase flows through the fracture section with different flow rate were studied. It was shown that the pressure drop was dominated by the lowest height passages of the fracture. For geological reservoir simulations, the parallel plate model has often been used for estimating flows through fractures. It was shown that the parallel plate flow model with inclusion of the tortuosity effects was in reasonable agreement with the presented CFD simulation results. Based on the simulation data, a new expression for the friction factor for flows through fractures was developed and the model predictions were compared with the simulation results and favorable agreement was achieved.