Technical Summary

1993 Fall MRS Symposium O
"Complex Fluids"

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Please find enclosed a copy of the Technical Summary for Symposium O, "Complex Fluids", of the Fall 1993 Materials Research Society Meeting. This symposium was supported in part by the Office of Naval Research, ONR Grant Number N00014-94-1-0129, as well as by Exxon Research and Engineering and Exxon Chemical Company.

Sincerely,

Scott Milner

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Enc.

c. D. J. Gillespie
Introduction

The fall 1993 Symposium "O", Complex Fluids, consisted of 24 invited talks, 60 contributed papers, and over 40 contributed posters, covering the static and dynamic properties of complex fluids in bulk and at interfaces. The symposium received over 130 abstracts submitted, so we were able to be quite selective in preparing our program. Attendance was strong throughout the week, with a full conference room and lively discussion from Monday through Friday morning.

The subject matter of "complex fluids" comprises a wide variety of materials outside conventional condensed matter physics, including colloidal suspensions, gels, polymer melts or solutions, and surfactant-containing phases. These diverse systems have in common a number of features, including:

- **Self-assembly.** Many complex fluids contain mesoscopic structures that assemble spontaneously from constituent molecules, which are often specially designed to result in a particular self-assembled structure. Amphiphilic or surfactant molecules, with polar and non-polar regions on the same molecule, aggregate into a huge variety of structures, including micelles, monolayers, and bilayers. Block copolymers, consisting of chemically dissimilar polymer chains covalently joined together, behave in analogous ways. From the mesoscopic self-assembled building blocks, a wide variety of phases are formed, including many phases with crystalline or liquid-crystalline order.

- **Complex rheology.** The behavior of complex fluids under deformation and flow is typically complex, for several reasons. First, the presence of spatially extended structures in such systems leads to slow, nontrivial stress relaxation on the mesoscopic level, in contrast to simple fluids. Second, the thermodynamics of self-assembly can be affected by deformation and flow, as the self-assembled structures break, grow, or order under the influence of applied stresses.

- **Broad application.** Complex fluid systems are ubiquitous in chemical engineering, biology, and materials science; practical examples include paint, motor oil, slurry, ceramic precursors, cosmetics, blood, and disposable diapers.

The Fall 1993 symposium, as have previous MRS Complex Fluids symposia (held in alternate years), focused on several topics of current and growing interest in the academic and industrial research communities. These included self-assembly of surfactants into micelles, monolayers, and bilayers, and the resulting properties of phases containing these mesoscopic structures; the behavior of strongly interacting heterogeneous polymers, including polyelectrolytes, random copolymers, and proteins; the effect of flows on complex fluids; and wetting phenomena in complex fluids.

Self-Assembled Monolayers

The properties of self-assembled monolayers and bilayers were the focus of several invited talks. Tom Lubensky [Penn] described the theory of couplings between tilt order and bending in surfactant membranes; Jonathan Selinger [Naval Research Laboratory] spoke on monolayers of chiral molecules, and spontaneous chiral symmetry breaking in defect structures in monolayers with tilt order; he related these phenomena to the spontaneous formation of microtubules in certain lipid solutions. Dan Schwartz [UC Santa Barbara] presented atomic force-microscope studies of Langmuir-Blodgett films of simple alkanes, which exhibit characteristic line defects resulting from competition of molecular packing and head group area. Ray Goldstein [Princeton] described theory and simulations of the labyrinthine fingering instabilities of ferrofluid films in magnetic fields; this system is analogous to monolayers interacting through long-range dipolar interactions. Joe Zasadzinski [UC Santa Barbara] presented experimental studies of monolayers of natural
and synthetic lung surfactant; the surface-tension reducing properties of these materials make breathing possible, and synthetic replacements are needed in caring for premature infants.

**Surfactant Phases**

The static and dynamic properties of surfactant phases containing self-assembled structures was an area of focus for several speakers. Reinhard Strey [MPI, Göttingen] presented freeze-fracture, neutron-scattering, and interfacial tension studies of microemulsions and L₃ (sponge) phases, relating their phase behavior and geometry. Gregoire Porte [Montpellier] described temperature-jump experiments on sponge phases, in which he observed separate relaxation times for surfactant diffusion, leakage across bilayers, and changes in topology. Didier Roux [CRPP, Bordeaux] spoke on the striking effects of shear flow on lyotropic lamellar phases, including the production of monodisperse, metastable, multilamellar vesicles ("onions"). Such onions can be used to encapsulate drugs for delivery, or as microreactors for controlled chemistry. Jacob Israelachvili [UC Santa Barbara] described measurements using the surface forces apparatus to study the strength and range of two kinds of adhesive attractions between lipid bilayers; nonspecific adhesion, and site-specific "lock-and-key" binding of protein receptor and ligand molecules. Philippe Richetti [CRPP, Bordeaux] described surface forces apparatus measurements of fluctuation-induced interactions between the boundaries of a lyotropic liquid undergoing presmectic or prenematic fluctuations.

**Strongly-Interacting Heteropolymers**

Recent progress in understanding the behavior of strongly interacting heteropolymers in a variety of situations was the topic of several talks. Jean-Louis Barrat [IC3, Strasbourg] showed that the long-standing question of the persistence length of a single polyelectrolyte chain is strongly affected by taking into account bending fluctuations, resulting in a persistence length of the order of the Debye screening length. Mark Stevens [Exxon] presented molecular dynamics simulations of solutions of model polyelectrolyte chains, which gave good agreement with experimental osmotic pressure and scattering measurements, and was qualitatively consistent with the Barrat theory for single chains. Jean Candau [Univ. Louis Pasteur] spoke on the static and dynamic scattering of weak polyelectrolytes in a poor solvent, which show microphase separation as a result of competition between collapse due to poor solvent and the counterion entropy of mixing. Ken Dill [UC San Francisco] described a model of protein folding in which the driving force for folded conformations is the amphiphilic nature of amino acid groups; he showed with simulations that placing hydrophobic groups on the "inside" of folded configurations greatly reduces the number of candidate folded states, and speeds up the folding process. Eugene Shakhnovich [Harvard] presented models of protein folding using random heteropolymers, either with two or many different monomers and hence pairwise interactions. Using concepts from spin glasses, Shakhnovich showed that while random sequences of monomers would not find a folded configuration in a reasonable time, a small amount of "training", rearranging of the monomers to favor a given folded configuration, would greatly enhance the rapidity with which a chain could find its unique folded state.

**Complex Fluid Systems in Flow**

The behavior of complex fluid systems in the presence of flow was the topic of several presentations. Masao Doi [Nagoya Univ.] discussed the rheology of demixing fluids, and the mechanism by which flow determines the characteristic length scale in such fluids as a function of shear rate. Julia Kornfield [Caltech] presented experimental studies using
rheology and birefringence of the shear alignment of block copolymer lamellar phases, which align in shear flow either with the layer normal along the direction of the gradient or of the vorticity depending on conditions. Eric Herbolzheimer [Exxon] described the theory and experiment of a fluidized bed, in which a suspension of colloidal particles continually settles against an upward mean flow. Using light scattering and transmission measurements, the sedimentation velocity and its variance, diffusivity and shear modulus in the suspension was measured for a wide range of particle volume fraction and interaction strength. Charles Zukoski [Univ. of Illinois] spoke on rheological and scattering studies of colloidal suspensions under shear flow. As shear stress is applied to colloidal crystals, long-range orientational order is lost, regained, and lost again with shear rate; rheological anomalies such as shear thickening accompany these dynamical transitions.

Wetting Behavior of Complex Fluids

The wetting behavior of complex fluids, including binary fluid mixtures with complex substrates, and structured fluids such as microemulsions, were the subject of several presentations. Barbara Frisken [Simon Fraser Univ.] described light and neutron scattering studies of binary fluid mixtures imbibed into silica aerogels. Once proposed as an example of the random field Ising model, these systems appear to have behavior determined by the physics of wetting unrelated to the RFIM. In the aerogels, much of the phenomena is explained by growing wetting layers on the gel strands as the critical point is approached, which leads to large shifts in the average composition as a function of position. No unambiguous experimental signature of a surviving critical point has yet been observed. Jim Maher [Pittsburgh] presented experiments on the aggregation behavior of dilute polystyrene colloidal particles suspended in a binary fluid mixture (lutidine-water) near its critical point. Aggregation was observed by large increases in static light scattering and diffusion times for dynamic light scattering. Aggregation occurred sufficiently near the coexistence curve on the side of the phase diagram poor in the component wetting the spheres. This phenomenon is widely used in separation processes. Michael Schick [U. Washington] spoke on the striking wetting behavior of middle phase microemulsions in coexistence with oil-rich and water-rich phases. Using a Landau theory of a structured fluid (with an oscillatory correlation function for water/oil concentration), Schick showed that "good" amphiphiles give rise to strongly-structured microemulsions that do not wet the oil-water interface, which has been a long-standing puzzle.

--Scott Milner