4bj Engineering Colloids – from Interparticle Interactions to Advanced Materials Assembly
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Colloidal materials appear in a wide host of natural phenomena and fundamental problems in soft matter physics. Examples are diverse and include the origins of glass transition in dense suspensions, blood clotting, and self assembly in interacting, Brownian systems. Technologically, colloidal assembly serves as a route to manufacturing functional materials with applications in photonic devices, sensors, ceramics, inks, and pharmaceuticals. The physical properties of these microstructured materials, which mediate their functionality, are themselves regulated by the complex interactions between the colloidal particles. Therefore, understanding and controlling these interactions is essential to efficient process design and the functionality of the end product.

During my graduate work at The University of Michigan I have investigated the role of the geometry of interparticle interactions in the physical properties of colloidal materials. Anisotropic excluded volume interactions are shown to have a profound effect on the structure, dynamics, and non-linear rheology of colloidal materials. This work is presented in three parts:

1.1. Effect of monomer geometry on the structure and dynamics of colloidal aggregates and gels (with David B. Moler, Prof. Robert M. Ziff, and Prof. Michael J. Solomon). The fractal structure of clusters formed in the diffusion-limited cluster aggregation of colloidal rods is quantified by laser light scattering over three decades of the scattering vector, and displays an unexpected dependence on the geometry of the primary particles. Monte Carlo simulations of Brownian rod aggregation corroborate the experimental finding that the measured fractal dimension is an increasing function of the particle aspect ratio, r. For rods with $r > 30$, the structural distinction between clusters formed in the diffusion- and reaction- limited cluster aggregation is diminished. Moreover, increasing r results in arrested dynamics at lower colloid volume fractions. The internal dynamics of colloidal rod aggregates is fundamentally different from that of colloidal spheres, and is consistent with clusters formed by angularly rigid bonds between the particles.

1.2. Orientation and rupture of weak colloidal gels during start-up of steady shear flow (with Prof. Michael J. Solomon). The transient structural evolution of fractal colloidal gels during start-up of steady shear flow is quantified by time-resolved flow light scattering and rheometry. For colloidal spheres, three distinct regimes are identified in the velocity-gradient plane: near-affine deformation, rupture, and cluster densification. In the first regime, the normalized structural anisotropy displays universal scaling with the applied strain, and flow cessation experiments show no structural relaxation. In the second regime, the anisotropy attains a maximum, which is identified as the gel rupture point. Rheological measurements demonstrate that this point coincides with a sharp maximum in the shear stress. The volume fraction dependence of the critical rupture strain displays the scaling $1+0.6\gamma_c \sim \varphi^{(1-x)/(3-D)}$, where x and D are the backbone and cluster fractal dimensions, respectively. Qualitative differences between the transient anisotropy of colloidal gels comprised of colloidal spheres and rods are observed. The findings suggest that the microstructural origin of the large anisotropy in colloidal sphere gels upon non-linear deformation is the relative angular displacements of singly connected particles that interact via a spherosymmetric potential.

1.3. Self-assembly of anisometric colloidal particles via sedimentation (with Prof. Michael J. Solomon). Colloidal self-assembly is a commonly used method for building ordered structures. In analogy with molecular systems, particle shape anisotropy may offer new possibilities for ordered colloidal assembly. In this section the orientational ordering of colloidal rods of variable aspect ratio is

quantified in 3-D by means of confocal laser scanning microscopy (CLSM) and digital image processing. The particles are prepared by the extension of literature methods. The procedure consists of the deformation of fluorescent poly(methylmethacrylate) (PMMA) microspheres by the uniaxial extensional flow of a composite matrix. The sterically-stabilized particles are dislodged from the matrix and dispersed in index-matching solvents for 3-D visualization. Distributions of rod centroid positions and orientation angles are extracted from 3-D image volumes by image processing. The measured distributions are consistent with aspect-ratio dependent jamming and orientational order/disorder transition in the rod sediments.

My postdoctoral research at the University of Illinois has involved manipulating colloidal interactions and phase behavior to facilitate their assembly into useful materials. This work is presented in two parts:

2.1. Structure and dynamics of biphasic colloidal inks (with Summer K. Rhodes, Prof. Eric R. Weeks, and Prof. Jennifer A. Lewis). Biphasic colloidal mixtures, in which a population of individually dispersed particles and a non-equilibrium colloidal gel phase coexist, display unusual rheological properties and find applications in the direct-write assembly of complex 3-D structures from colloidal and nanoparticle inks. Here the structure and dynamics of these biphasic mixtures are investigated by means of CLSM and quantitative image processing. The biphasic behavior is achieved in a controlled manner by carefully tailoring the surface chemistry of the colloids. Particle cores of the two phases are labeled with different fluorescent dyes to allow their differentiation during CLSM. The structural and dynamical parameters relevant to the mixture's rheology are quantified, and implications of the biphasic nature of the system on these quantities are discussed.

2.2. Light-regulated electrostatic interactions in colloidal suspensions (with Kyle Plunkett, Prof. Jeffery Moore, and Prof. Jennifer A. Lewis). The spontaneous assembly of colloidal particles into functional structures is strongly regulated by the nature of interparticle interactions. The ability to locally regulate and manipulate these interactions in a non-invasive manner may offer new possibilities for the assembly of novel materials. Here, colloidal particles that display photo-responsive surface chemistry are developed, and the light-regulated interparticle interactions are utilized to both study fundamental problems in colloid science and to explore novel routes to constructing functional materials.

My future research plan is to expand both on the use of colloidal systems as precursors for building advanced materials, and on the fundamental understanding of the physics of soft condensed matter. The approach will be primarily experimental. Some specific topics of interest will be discussed in the poster.