1. PRF#: 57452-DNI9
2. Project Title: Realizing an Electric Ferrofluid through Rational Nanoparticle Design
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NARRATIVE PROGRESS REPORT
9/1/2018 to 8/31/2019

OVERVIEW

The goal of this project is the incorporation of rationally designed nanoparticle constructs into fluids in a manner that endows the fluid with emergent properties. In order to achieve this, there are three facets that must be addressed: (1) Bulk properties of colloidal suspensions must be interrogated in a robust fashion. (2) An understanding of how nanoparticle properties lead to emergent properties of a fluid must be realized. (3) New methods must be developed for fabricating or synthesizing nanoparticles with controlled properties. In the past year, we have advanced all three of these facets. Building on our progress last year, we proved our previous hypothesis that emergent mechanical properties of interfaces can be tied to the interparticle interactions by conducting a series of macroscopic experiments. Secondly, we invented a new method of studying the polarizability of nanoparticles and used it to, for the first time, quantify the polarizability of sparse nanoparticles in solution. Finally, we have developed a new class of magnetorheological fluids that are rationally designed to exhibit improved yield stress. In the subsequent sections, we detail our specific achievements in these areas.

EMERGENT MECHANICAL PROPERTIS FROM PARTICLES ON INTERFACES

In the prior year, we reported experiments exploring the mechanics of particle-coated liquid-air interfaces. In particular, we studied 'liquid marbles' which constitute millimeter-scale drops of fluid coated with non-wetting particles. A key result was that marbles composed of particles with weak interparticle interactions exhibited more ductile behavior and we hypothesized that this could be in analogy with failure performance in metals. In order to explore this hypothesis in the present year, we conducted a series of experiments studying the biaxial expansion of rafts of millimeter scale particles on water-air interfaces using a newly-developed funnel method. In particular, we discovered that interparticle interaction can be tuned through the particle mass and used this fact to compare the failure of weakly- and strongly-interacting particles (Figure 1). Interestingly, while strongly interacting particles exhibited failure at larger values of strain, more weakly interacting particles were able to rearrange to heal fractures, preventing the long-range propagation of cracks. This observation bears a strong analogy to failure performance in metals and ceramics where the ductility of metals arises from their ability to halt the propagation of cracks through local plastic deformation. In addition to providing useful fundamental insight while introducing a new handle for the design of materials, this result underscores the importance of connecting the properties of particles to the emergent properties of fluid systems.

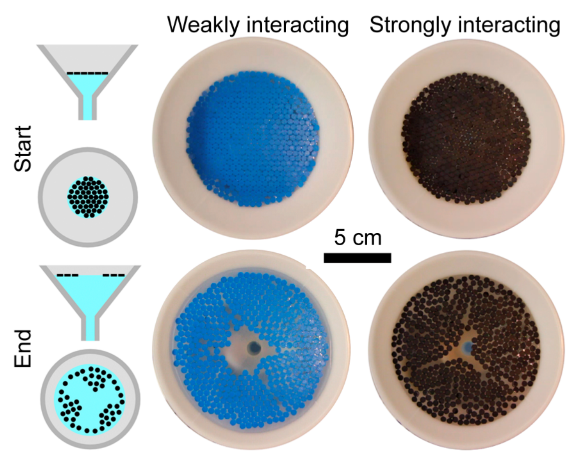

Figure 1. Emergent mechanical behavior of particle rafts observed using the newly developed funnel method. A funnel is lowered to apply a biaxial stress to a particle raft. Weakly interacting particles (left) exhibit circular ductile failures while strongly interacting particles (right) exhibit cracks that propagate throughout the raft. These results highlight the analogy between particle films and solid mechanics.

ELECTROHYDRODYNAMIC PROPERTIES OF COLLOIDAL SUSPENSIONS

In the development of advanced particle suspensions for their responsiveness to electric fields, it is critical that we have a deep understanding of how individual particles react to electric fields. The fundamental way this occurs, through the polarization of the particle, is poorly understood as experiments to quantify the polarizability of nanoparticles have only explored a narrow range in properties and have been previously limited to extremely dense suspensions. We invented a new method for quantifying nanoparticle polarizability based upon a microfluidic chamber with integrated microelectrodes. In particular, we apply a modest electric field and detect the concentration enhancement of the particles using fluorescence microscopy. Importantly, through this experimental study, we observed that nanoparticles exhibit polarizability values up to 30 times larger than would be predicted using conventional models (Figure 2). We present a model to explain this effect based upon the space charge effect of the Debye layer. In fact, we report the general result that particle polarizability is consistent with a perfectly polarizable sphere that has a radius equal to the nominal hydrodynamic radius plus twice the Debye length. This result has important implications for the development of field-responsive fluids such as electric ferrofluids.

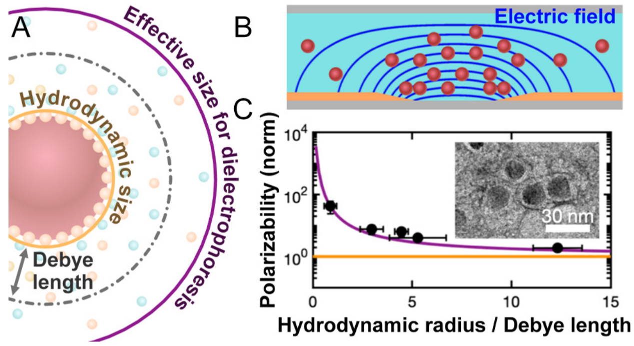

Figure 2. (A) Schematic of the effective dielectrophoresis size of nanoparticles. (B) Experimental system to measure nanoparticle polarizability. (C) Experimentally measured polarizability enhancement of nanoparticles as the hydrodynamic radius approaches the Debye length.

MAGNETORHEOLOGICAL FLUIDS

A recent area that we have begun to explore is the utilization of magnetorheology to understand and optimize the interaction between magnetic fields, particles, and fluid stresses. In particular, we are studying magnetorheological (MR) fluids, or suspensions of magnetic particles that solidify upon the application of a magnetic field. Upon constructing a simplified model of this solidification using magnetostatics, we find that conventional MR fluids have a much lower yield stress than predicted. We hypothesized that this non-ideality was due to the particle chains shearing prematurely owing to the shear-thinning nature of the solutions conventionally used to stabilize MR fluids. To test this hypothesis, we synthesized a shear-thickening MR fluid that, when compared with a conventional MR fluid with the same functional loading of particles, exhibited nearly twice the yield stress (Figure 3). These initial results lead us to believe that further engineering of the complex rheology of the MR fluid will both allow us to drastically improve the performance of MR fluids and provide a new fundamental understanding of their behavior.

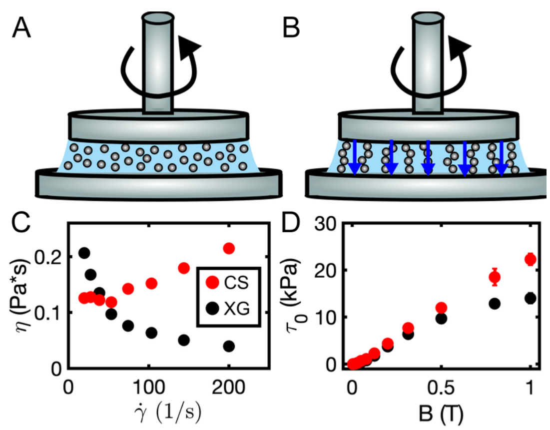

Figure 3. Rheology of magnetorheological (MR) fluid (A) without and (B) with a magnetic field $\boldsymbol{B}$ applied. (C) Tuning the viscosity $\boldsymbol{\eta}$ such that it increases (red) or decreases (black) with increasing shear strain rate $\dot{\boldsymbol{\gamma}}$ leads to (D) an increase in yield stress $\boldsymbol{\tau_0}$ for the shear-thickening MR fluid.

CAREER IMPACT

This support has provided an empowering series of career opportunities for the PI, a graduate student, an undergraduate (who is now a graduate student at Caltech), and a high school student. In particular, this support has provided the resources for the PI to embark on a new research direction which has led to three published papers, one additional paper in review, and two more in preparation. Additionally, in the last year, this work has resulted in the PI being invited for an invited talk at Harvard, being invited to give a talk at a local conference, and given the PhD student the results needed to win a prestigious BUnano interdisciplinary graduate fellowship.