PRF #59208-DNI9
Project title: Combining experiments and simulations to understand the glassy rotations of frictional particles in slurry flow
PI: Lilian Hsiao
Affiliation: North Carolina State University, Chemical & Biomolecular Engineering
Narrative Report for Project period 2018-2019 (Year 1)

Summary of scientific aims and project work plan
Topological anisotropic colloids have garnered interest due to the importance of surface topography on slurry flow and processing. Here we investigate how topological anisotropies affect the glassy dynamics and flow properties in highly concentrated colloidal suspensions. We synthesize smooth and rough colloidal particles and suspend them in a specific solvent. We measure the viscoelastic rheological signatures from linear experiments like dynamic frequency sweep and non-linear experiments like large amplitude oscillatory shear, steady shear and creep. To facilitate the connection of macroscopic features to microscopic properties of the colloidal suspensions under flow, a 3-stage coupling device is built to connect confocal microscope with the rheometer. A review article in *Current Opinion in Colloid and Interface Science* was published (Hsiao & Pradeep, COCIS 43, 94, 2019) while other manuscripts are in preparation.

Research activities and findings in the past year
Year 1 of the proposal focused on the synthesis of poly(12-hydroxystearic acid) (PHSA)-stabilized smooth and rough colloids by free radical dispersion polymerization reaction. The thickness of the PHSA layer grafted on PMMA microspheres is estimated to be 10 nm. Briefly, the comb copolymer was added to a thermally activated initiator (2-azobisisobutyronitrile, AIBN) in a mixture of dodecane and hexane. The reaction vessel was connected to an Alihn condenser with cooling water and purged with nitrogen gas. Once heated to 80 ^{o}C, the fluorescent dye Nile Red and the monomer methyl methacrylate (MMA) were added. For smooth colloids, no further addition was needed and the reaction was allowed to proceed for 2 hours. To synthesize rough colloids, we added a crosslinking agent ethylene glycol dimethacrylate (EGDM) at a rate of 500 mL min^{-1} and at a concentration of 1.3 wt% with respect to the monomer. The crosslinker is thought to induce the microphase separation of co-polymerized oligomers that precipitate out of the mixed solvent to form nucleation sites for further growth into primary PHSA-stabilized PMMA particles. Once the reaction cooled to room temperature, particles were cleaned by multiple washes with hexane and stored dry until further use. Using this method, we synthesized a number of batches of stable PMMA colloids with different surface morphologies. Fig. 1(a) & (b) show monodisperse PHSA-stabilized PMMA spheres of two different topological features, with diameters $2a$ = 700nm ± 5% and 500nm ± 4% respectively.

After the synthesis of rough and smooth colloidal suspensions, research was focused on the rheology of very high volume fraction ($\phi > 0.50$) colloidal suspensions to investigate the effect of topological features. Sterically-stabilized PMMA colloid were suspended in two different solvents: 1) squalene, which is refractive index matched and density mismatched with PMMA; 2) bromocyclohexane (CHB) and decalin at a 66:34 percentage such that both refractive index and density are matched. In the CHB and decalin mixture, tetrabutylammonium chloride (TBAC) at a concentration of 5mM was added to screen out electrostatic interactions.

All rheological experiments were done on a TA DHR-2 rheometer using a cone and plate geometry with a 1^{o} angle 27 µm truncation gap and 50 mm diameter. We performed linear oscillatory measurements and measured the storage and loss moduli of smooth and rough colloidal suspensions suspended in squalene (Fig. 1(c)) and CHB/decalin (Fig. 1(d)). At high volume fractions, the topological differences between smooth and rough in not manifested in the linear viscoelastic responses specifically when the colloids is suspended in squalene. Colloids were also suspended in CHB/decalin mixture solvent in order to investigate if electrostatic charges amplify the topological features in concentrated colloidal suspensions. Initial results show that irrespective of the solvent, the smooth and rough colloidal suspensions show similar linear viscoelastic behavior. The mismatch between the moduli in Fig. 1(d) is due to the volume fraction difference. The effect of the charge in the CHB/decalin mixture suspended colloidal particles can be clearly visualized as the increase in the viscoelastic moduli in Fig. 1(d) compared to those suspended in squalene Fig. 1(c). Moreover, the elastic modulus in greater than the viscous modulus in the whole linear viscoelastic frequency range probed for both rough and smooth suspensions in CHB/decalin mixture solvent unlike the colloidal suspended in squalene. Generally, we find that the particle morphology strongly affects non-linear flow behavior (Fig. 2) while having minimal impact on linear viscoelasticity (Fig. 1).

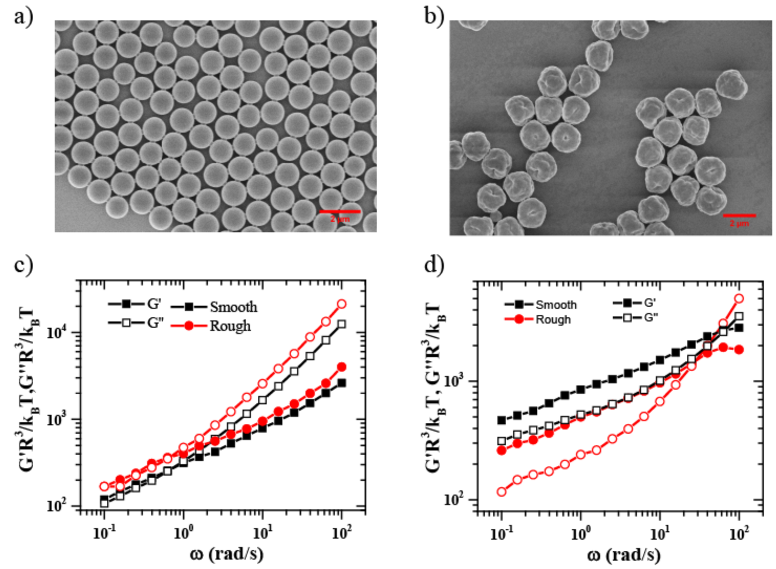

Figure 1: Scanning electron micrographs of (a) smooth and (b) rough colloidal particles. The storage modulus and loss modulus scaled with thermal energy as function of frequency for ϕ = 0.57 for colloidal particles suspended in (c) squalene and (d) CHB/decalin. In (d) ϕ = 0.60 for smooth suspenisons and ϕ = 0.59 for rough suspenions.

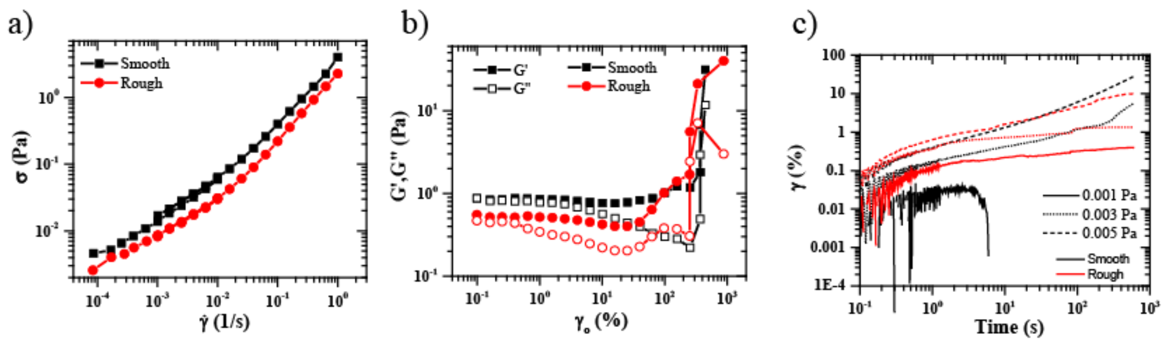

Figure 2: Rough and smooth colloidal suspensions suspended in squalene for the linear viscoelasticity shown in Fig. 1(c) at ϕ = 0.61. (a) The flow curve showing the stress as a function of shear rate. (b) The elastic and viscous modulus as function of oscillatory strain amplitude during large amplitude oscillatory shear. The sudden upturn in the viscoelastic moduli is due to the shear thickening phenomenon prevalent at these volume fractions. (c) Creep or constant stress experiments where the strain of deformation is plotted against time.

Impact on PI and student career

This grant was instrumental in getting the PI off startup funds and supporting a graduate student trained in the area of the PI's fundamental research focus. Because fundamental work can often take more effort in fund-raising and is generally less available for young investigators, the PRF DNI grant was extremely useful in efforts to collect preliminary data such that full grants can be secured from the National Science Foundation.

The PRF has also partly funded a PhD student who is in his 3rd year of training. The student has learned a number of microscopy and rheometry techniques required to generate fundamental understanding of particle dynamics in shear flow. This student has also been working on a manuscript that discusses the nature of measuring contacts between particles that have surfaces deviating from a smooth sphere - a key criterion for connection with mechanical properties like the shear modulus and viscosity in particulate suspensions. This work was presented by the student in national meetings (American Physical Society March Meeting and the Society of Rheology Annual Meeting).