IFPRI research proposal: Converging the suspension rheology of academic and industrial particulates

Lilian C. Hsiao, Dept. of Chemical & Biomolecular Engineering, North Carolina State University
E-mail: lilian_hsiao@ncsu.edu; Website: www.hsiaolab.com; Tel: (919) 515-8057

1. Summary: Although particulate suspensions have been ubiquitous in many applications for decades, there is still an unmet need to connect the rheology of academic systems with their industrial counterparts. Most IFPRI projects tend to focus on the science of model colloids before translation to industrial systems. Unsurprisingly, the knowledge gap persists because the field of suspension rheology was built on a foundation of well-characterized colloids, while industrial formulations typically include mixtures of additives and particle shapes that are challenging to quantify. **The overarching goal of this research is to create a paradigm shift in bridging academic and industrial suspensions, while developing contact interactions as a new scientific concept to unify attractive and repulsive systems (FIG. 1).**

To accomplish this goal, we will work closely with IFPRI member companies from the start to obtain simplified industrial formulations (SIFs). Examples include organic crystals, milled active pharmaceutical ingredients, and calcite powders. These non-spherical and rough particulates are readily found in the coatings, chemicals, and consumer sectors. It is also known that surfactants, stabilizers, and thickeners are important additives in these SIFs. **An outstanding question in colloidal suspension rheology – one that has never been fully addressed – is whether there are any common structural frameworks applicable to suspensions with different interparticle interactions.** Based on our earlier insight gained from colloidal gels [1] (under the IFPRI project for Solomon/Furst) and from dense suspensions of rough colloids [2], in which we drew heavily from the disparate fields of granular systems and tribology, I hypothesize that the *contact interactions* between particles can be used to predict the rheology of a broad class of particulate suspensions. **Industrial collaboration goes hand-in-hand with new scientific understanding here**, because the hypothesis is best tested with model colloids and SIFs where differences in the particle morphology, microstructure, rheology, and handling techniques can be immediately quantified and refined.

For the 3-year period of this proposal, we focus on the creep and recovery of dense colloidal suspensions (diameters 500 nm ≤ $2a$ ≤ 10 μm) in which the particle asphericity, sizes, and interactions are adjustable. Creep has important applications for dense suspensions driven by stresses below the macroscopic yield stress ($\sigma \leq \sigma_y$), for example in times when paints or coatings dry on a vertical surface. Particle asperity and roughness may impart surprising advantages, as demonstrated by preliminary studies in which dense suspensions of bumpy colloids exhibit longer relaxation times and remnant elasticity that were not seen with smooth spheres. Creep flow is also compatible with particle-level imaging due to the slow velocity profiles. Our research objectives and work program are as follows:
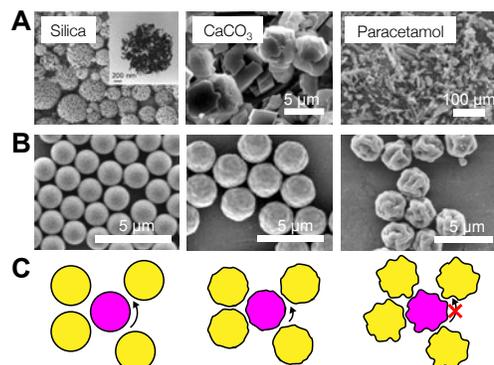

FIG. 1. How do we bridge ideal model particles to industrial systems? Particle geometry, pairwise interactions, and rheology of IFPRI SIFs will be used to tune the properties of our model colloidal suspensions. A unified structural framework based on particle contacts could generate a fresh perspective on suspension rheology.

<u>Objective 1: Match particle-level morphology, pairwise interactions, and suspension microstructure for SIFs and model colloids.</u> Together with IFPRI members such as Syngenta and Chemours, we will use a combination of atomic force microscopy (AFM), scanning electron microscopy (SEM), and confocal laser scanning microscopy (CLSM) to characterize SIFs and

model colloids in parallel. Our model colloids are poly(methyl methacrylate) (PMMA) stabilized by a grafted layer of poly(12-hydroxystearic acid) (PHSA), where we have control over their surface morphologies and shapes [2, 3]. Tunabe particle-level morphologies include asphericity and roughness parameters [2, 4]. Pairwise interactions for SIFs containing a limited number of additives will be matched to the pairwise interactions of model colloidal suspensions. These interactions will be tuned using depletion agents, salts, and surfactants [1, 5]. Microstructural details include particle positions and contact distributions in quiescent suspensions at volume fractions below jamming ($\phi \leq \phi_J$).

Objective 2: Characterize particle contacts in creeping suspensions. Our group has a fully operational confocal rheometer that is capable of simultaneous imaging and stress measurements at high resolutions. We plan on imaging and analyzing creeping flows containing fluorescent PMMA colloids that have been matched to the conditions of SIFs, as described in Objective 1. Local clusters with correlated mobilities are expected to result in avalanche-like deformations, which we have observed in our bulk rheometry experiments. Other microstructural parameters such as the radial distribution function and number density fluctuations will also be obtained for colloids with different surface geometries. The microstructural parameters will be directly connected to rheological measurements of creep and flow cessation (**FIG. 2**).

Objective 3: Simulate suspension rheology using microtribology models. The whole point of characterizing contact microstructure is to estimate the tribological variation at the particle level for densely packed suspensions. Our preliminary studies on lubricated microtextured elastomers show that the friction coefficient is a strongly nonlinear function of sliding speed, normal forces, and solvent viscosity. The strategy here is to measure and model the tribological behavior of textured surfaces, then use computational fluid dynamics (CFD) simulations of particulate systems in which the friction coefficient depends on the local velocity and contact microenvironment of each particle. Data from SIFs and model colloids will be used as inputs.

2. IFPRI member involvement: The creeping flow and recovery of dense particulate suspensions are important across a broad range of industries. However, the presence of surfactants and additives often dramatically alters processing conditions in a difficult-to-predict way. **We invite IFPRI members to provide us with a few sets of SIFs with known additive interactions and particle size/shape distributions, even if the exact values are not known.** The SIFs will enable us to perform benchmarking and validation of our model system. Regularly planned meetings with SIF providers to discuss differences in observations between the SIFs and model systems will be helpful in fine-tuning our experimental measurements.

3. PI's other projects of interest to this proposal
- Synthesis of monodisperse non-Brownian smooth and rough PMMA colloids ($2a \geq 8$ µm) that are stable in aqueous media;
- Calibration and build of a customized confocal tribometer;
- Modeling the micro-elastohydrodynamic lubrication behavior of a broad class of microtextured substrates, ranging from steel to poly(dimethyl siloxane) (PDMS).

4. Background
    Colloids are micron-sized particles that exhibit thermal fluctuations when suspended in a fluid. These materials are exploited to maintain consistency and stability across a range of pharmaceuticals, foods, and consumer products. The flow properties of colloidal suspension are classically known to depend on ϕ and interparticle forces [6], but there is **increasing evidence that the dissipative forces should scale universally as the number and area of**

microscopic contacts that form between particles [7, 8]. The exact nature of the contact is certainly important, but these contacts would form whether the suspensions are attractive or repulsive. This is because *the dynamical arrest brought on by bond formation in attractive systems is also brought on by cage formation in dense repulsive systems [9].* This begs the question: is there a single microstructural parameter that links attractive and repulsive systems? **Addressing this question is important industrially, because the predictions could potentially work for many SIFs regardless of their additives, flow conditions, and particles shapes.**

New answers to this old problem must build upon parallel advances in the colloidal and granular literature. It is now accepted that the overall stress of a flowing suspension is a combination of the ensemble-averaged hydrodynamic and contact stresses (if present) from each particle [10, 11]. Multiple studies collectively suggest that the *number and distribution of particle-level contacts are key parameters that control the elastic response of particulate suspensions*. This statement has been supported for both dilute attractive systems and shear thickening suspensions. Our group, along with others, have discovered that localized dense clusters serve as load-bearing structures that contribute to elasticity in sheared depletion gels [1]. For discontinuously shear thickening dense suspensions, particles tend to overlap with one another because of an added push from flow; the contacts give rise to a frictional interaction that drastically increases suspension stresses and manifests as force chains in simulations [8]. Separately, the granular literature has focused on the connection between the shear modulus and the friction coefficient of particles in contact [12]. Although this is typically discussed within the context of packings above ϕ_J, such concepts could be equally valid for flowing particulate suspensions below ϕ_J in the dense regime. The instabilities generated by flow, along with random Brownian motion of individual colloids, are likely contributing to the presence of transient clusters that support stress-bearing networks.

An insight that we gain from these disparate fields is that **the solid-like stresses borne by densely packed particles depend on their microscopic contact distributions, which in turn depend on material and processing conditions**. The contact distribution is important because it is a measure of the friction coefficient experienced by particles in the suspension. Yet, there are *no known experimental studies that have directly probed the connection between contact distributions and mechanical properties for colloidal suspensions*. In addition, experiments are prone to uncertainties from instrumental and material fluctuations; the effect of these uncertainties on the precise definition of contact have not been studied *in situ*. What exactly is the role of interparticle separation in defining whether two particles are in contact? How does the nature of this contact vary if particles are aspherical and surfaces are uneven? Can we predict suspension rheology based on a statistical analysis of different contact parameters?

The interparticle separation distance (h) during flow is particularly important, because it dictates the particle friction coefficient, μ [13]. The value of μ is the ratio of the shear (F_s) and normal forces (F_n) on a particle, both of which
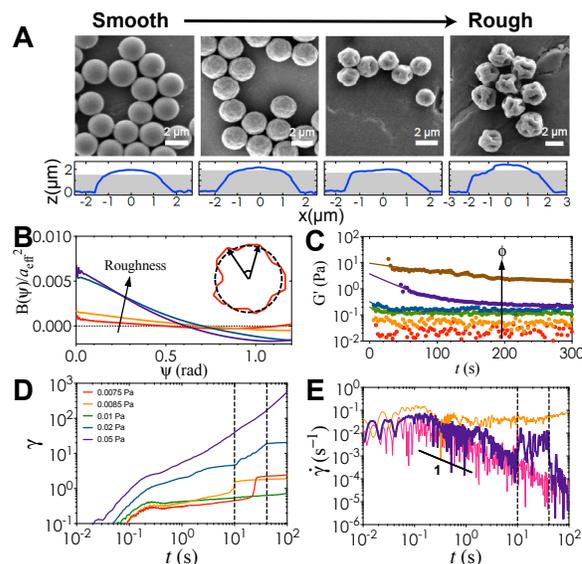

FIG. 2. Influence of particle surface morphology on suspension rheology. Details of the surface morphology and asphericity directly impact contact distributions and friction. This manifests as an unexpected remnant elasticity after cessation of flow, random strain jumps in creeping flow, and avalanche-like behavior which could impact the conformation of industrial coatings.

diverge as h decreases in lubrication flow ($F_s \sim 1/h$ and $F_n \sim 1/h^2$) [14]. Even for a perfectly smooth and flat surface, **the value of μ is a non-trivial function of the sliding speed and solvent viscosity**, as captured in the so-called Stribeck curve in tribology. Our group has shown that **this dependence of μ is even more complex when surfaces are roughened**, due to geometry-dependent transitions in the elastohydrodynamic lubrication (EHL) regime. This understanding motivates us to apply microtribological frameworks to understand the suspension rheology of smooth and rough particles. Because the sliding speed, viscosity, and contact distances are measurable for each particle, we will be able to extract the local value of μ and use it as an input to CFD simulations in which the particle geometry, interparticle interactions, and flow conditions are experimentally defined. The end goal for this proposal is to use microtribology principles to obtain rheological predictions for both SIFs and model colloids.

5. Research plan
The deliverables of this project include **generalized parameters that are translatable between model colloids and SIFs in terms of morphology, microstructure, and rheology**. It will also introduce a **new microscopic structure-property framework based on contact interactions between particles**. Our group has significant expertise in confocal microscopy and rheometry techniques for colloidal suspensions. We will combine experiments and simulations to connect particle-level contact information to the microtribology and rheology of particles in creep flows.

5.1 Methodology
Materials. We will synthesize fluorescent PHSA-PMMA colloids with diameters ranging from 500 nm $\leq 2a \leq 5$ μm. The surface morphology is tunable from smooth to bumpy to mimic industrial particulates (**FIG. 2A**). The colloids are stable in a variety of organic media, ranging from cyclohexyl decalin blends to squalene, depending on whether density/refractive index matching is needed. Hard sphere behavior to charged interactions are possible through the addition of salts such as tetrabutylammonium chloride. Attractive interactions can be generated by deliberating changing the refractive index of the solvent, by addition of depletion agents such as polystyrene, or by switching to an aqueous solvent which introduces van der Waals interactions. The switching to aqueous systems is possible because we have synthesized poly(vinylpyrrolidone) (PVP)-stabilized PMMA particles with diameters up to 10 μm.

Roughness and asphericity characterization. AFM measurements in tapping mode will be used to obtain the 3D surface morphology of our model colloids and SIFs (**FIG. 2B**). The topography measurements will be fitted to an effective sphere and deviations from the spherical geometry will be characterized. Measures like the autocovariance, root-mean-squared roughness, and slopes of asperities will be obtained.
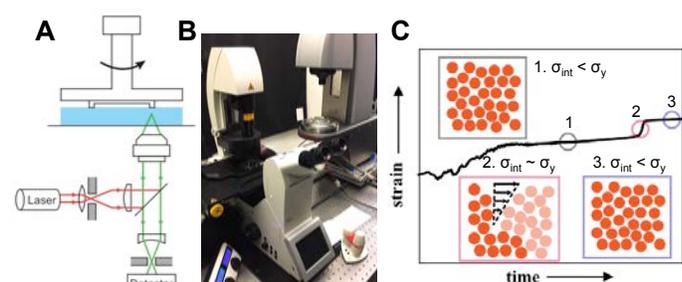

FIG. 3. Simultaneous imaging and stress measurements on a confocal rheometer allow us to probe local changes in contact distribution, velocity correlations, and other microstructural changes for dense creeping flows.

Bulk rheometry. Preliminary studies on a stress-controlled rheometer have shown that rough colloids exhibit reduced values of ϕ_J, likely because frictional interactions increase excluded volumes in flow [2]. We also found that the suspension elasticity relaxes much more slowly in dense suspensions rough colloids after shear ceases (**FIG. 2C**). Furthermore, the suspensions undergo stochastic strain jumps when creep flows are applied at $\sigma < \sigma_y$ (**FIG. 2D**). Between intermittent strain jump events,

suspensions exhibit strain rates that scale inversely with time (**FIG. 2E**). This so-called Andrade-like creep behavior has been observed in protein gels and granular solids [15]. Our results provide early evidence that it is also found in dense colloidal suspensions. Collectively, these data suggest that particle geometry strongly affects the structural relaxation of aspherical particles.

<u>Confocal rheometry and microstructural analysis.</u> Our group has completed the build of a confocal rheometer that is capable of imaging particulate suspensions and measuring bulk stresses during shear flow (**FIG. 3A, B**). This technique allows us to pinpoint the microstructural origin of strain jumps in creeping flow, perhaps due to collective rearrangements and avalanche-like behavior (**FIG. 3C**). The CLSM images rapidly in 3D and standard image processing algorithms are used to identify particle centroids during flow, as we have shown earlier for colloidal gels [1]. Imaging can be done at very high speeds (f = 24kHz, meaning 1-µm particles diffuse no more than 1% of their radius per frame even with water as a solvent) and high resolution (down to 120 nm in the xy-plane). We expect to identify cluster correlation lengths such as that shown in **FIG. 4A**. These clusters could be quite important in connecting microstructure to rheology, such as the type described by nonlocal models for sheared granular systems [12]. Within each correlated cluster, the number of contacts for smooth and rough colloids is expected to be different due to frictional interactions (**FIG. 4B**). The microstructure and pairwise interaction potential will be quantified using the radial distribution function (**FIG. 4C**), the contact number distribution and mean contact number $<z>$ (**FIG. 4D**), as well as the measured maximum packing of smooth ahd rough colloids under sedimentation (**FIG. 4E**).

<u>Tribology measurements and modeling.</u> The contact information and local velocity of particles obtained from confocal rheometry allows us to estimate the friction coefficient at the particle surfaces based on the Derjaguin approximation (**FIG. 5A**). This approximation states that at small enough length scales, circular bodies can be conceptualized as flat surfaces. We have conducted preliminary measurements of microtextured soft surfaces using a ball-on-three-plate tribology accessory on our stress-controlled rheometer (**FIG. 5B, C**). These textured surfaces are made out of PDMS, which is an elastomer with well-characterized mechanical and surface properties. Our data demonstrates that friction is highly complex with textured surfaces, even in the completely lubricated regime. The Stribeck curves for various surface geometries show an intermediate friction peak as a function of the non-dimensional Sommerfeld number, which embodies the sliding velocity and solvent viscosity (**FIG. 5D**). We have made significant strides in developing a scaling theory to predict these Stribeck curves (**FIG. 5E**), which has never been successfully done in the tribology literature. We plan to develop these frameworks for more complex surface geometries and to use them as input to simulations of particulate suspensions.
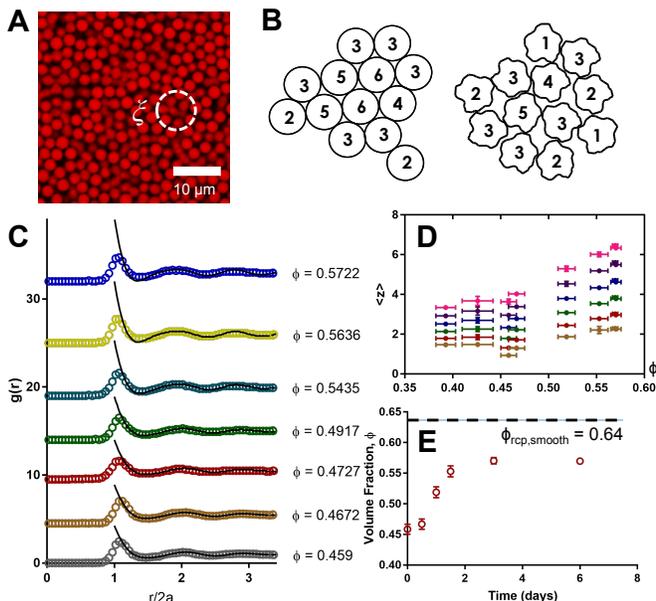

FIG. 4. The nature of particle contacts dictates local friction, which dramatically alters bulk rheology. Contact distributions and microstructure will be quantified with high speed imaging during creep flow on our confocal rheometer platform, using model systems and SIFs.

CFD simulations of particulate suspensions. We will use COMSOL Multiphysics as a first step to simulate the behavior of particulate suspensions in unconfined creep flow. The geometry of the particles will be defined with the AFM experimental data. If particles come into contact, we will impose additional frictional forces depending on the local velocity and geometry of the particles. The form of the friction will be estimated from the Stribeck behavior for microtextured surfaces. Simulation results will be validated against macroscopic rheology and microscopic structural signatures obtained from experiments.
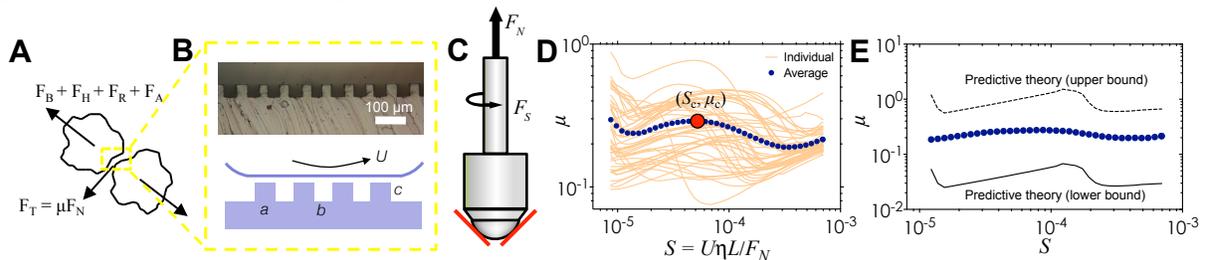

FIG. 5. The friction between rough particles may be estimated from the tribology of microtextured surfaces. We have developed a scaling model that predicts the elastohydrodynamic lubrication transitions for a very broad class of textured materials, including soft elastomers, metals, and high molecular weight polymers. This model will be used as input to CFD simulations of particulate flows in which the friction force at contact can be defined as a function of particle geometry and local flow velocities.

5.2. Project timeline

Year 1
- Characterize the 3D surface profiles for SIFs and model colloids with AFM;
- Extract estimates of pairwise interactions for SIFs with different additives and particle shapes, either by light scattering or microstructural characterization;
- Match experimental conditions of model colloidal suspensions to SIFs.

Year 2
- Image and quantify the particle-level contact microstructure of model systems with various particle geometries and additives;
- Quantify cluster correlation lengths in model suspensions during creep and recovery;
- Measure macroscopic rheology of SIFs as a third benchmarking tool.

Year 3
- Set up CFD simulations with particle geometry, local velocities, and Stribeck curves for various contact configurations as obtained from experiments;
- Establish general frameworks for how particle asphericity, pairwise interactions, and surface morphology impact contact microstructure in SIFs and model systems.

5.3 Budget: We request $38,000 per year for 3 years to partially fund a Ph.D. student to work on this project. The remainder of the student's stipend and tuition will come from a federally funded project with complementary objectives. The tentative allocation of this annual budget is as follows: $29,000 will be assigned to student support, $3,000 for faculty salary support, $3,000 for travel, and $3,000 for materials and consumables.

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