IFPRI Project renewal: Erin Koos

1. State of the art

The structural properties of suspensions and other multiphase systems are vital to overall processability, functionality and acceptance among consumers. Therefore, it is crucial to understand the intrinsic connection between the microstructure of a material and the resulting rheological properties. In the previous portion of the project, we demonstrated how the transitions in the microstructural conformations can be quantified and correlated to rheological measurements. We found semi-local parameters from graph theory, the mathematical study of networks, to be useful in linking structure and rheology. Our results, using capillary suspensions as a model system, show that the use of the clustering coefficient, in combination with the coordination number, is able to capture not only the agglomeration of particles, but also measures the formation of groups [1]. A recent review paper outlines the various wetting-induced changes that occur in capillary suspensions [2].

1.1. Methodology

Capillary suspensions consisting of silica particles fluorescently labeled with rhodamine B isothiocyanate in a mixture of 1,2-cyclohexane dicarboxylic acid diisononyl ester (Hexamoll DINCH) and n-dodecane, with added aqueous glycerol. The three components are all index matched and the silica contact angle can be modified [3]. The attractive interaction strength can be modified by tuning the contact angle and fraction of secondary liquid. This lets us access both granular-like systems with weak interactions and strong attractive gels using the same model system. During the project, we switched from using porous silica particles to nonporous particles as there were problems noted with adsorption of the secondary liquid into the pores. This simplified the particle detection algorithm now includes a graphical user interface for both local detection and manual addition or removal of missing or misdetected particles improve the final detection efficiency.

Our initial goal of the project was to track microstructural changes in the network in response to external shear applied via a linear shear cell. These structural changes were correlated with the rheological response of the material. Application of external shear via the linear shear cell, however, was unsuitable. Due to the very low yield strain in capillary suspensions, the applied shear was often above the flow point and specific changes during yielding could not be adequately captured. Furthermore, the present setup only allowed for the deformation profile to be captured in one shear plane. While this has provided valuable information, proving that capillary suspensions tend to undergo solid-body movement, where the rotation of particles around their respective bridges is resisted through both the structure of the network and the extra torque provided by the contact angle pinning and/or the contact angle hysteresis, full 3D tracking is necessary. Therefore, a rheometer has now been mounted onto a high-speed confocal microscope. The improved setup will allow us to directly compare bulk, rheological changes with local, microscopic changes to the clusters and network.

1.2. Project results

Semi-local measurements capture rheological changes: Using both the coordination number and the clustering coefficient (Figure 1), we could rationalize the transitions in the structure and tie these changes to the rheological properties of the material. For instance, the transition from a pendular network, where particles are connected by binary bridges, to the funicular state, where larger clusters are formed, occurs at $\phi_{\mathrm{sec}}/\phi_{\mathrm{solid}} = 0.09$. This point corresponds to a peak in the coordination number and beginning of a plateau in clustering coefficient. While there is a slight shift in the distribution of coordination numbers, there is a large shift in the distribution of clustering. The number of particles with zero clustering drops significantly while there is an increase in intermediate and high clustering. These results are published in the journal Soft Matter [1].

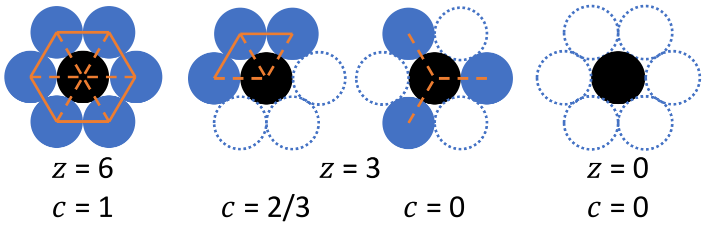

Figure 1: Difference between the coordination number z, the number of bonds per particle (dashed lines), and the clustering coefficient c. The clustering coefficient is defined as $c = \frac{2e}{z(z-1)}$, where the number of bonds between neighbors (solid lines) is e.

Particle volume fraction: Samples with particle volume fractions $\phi = 0.1 - 0.3$ were examined. Below $\phi = 0.15$, the flocs not fully percolated. The intracluster structure of all capillary suspensions was the same ($z \approx 5$ and $c = 0.33$), but the system becomes more dense with increasing particle volume fraction. This can be interpreted as a growing floc size with constant intrafloc structure. The microstructure after compression was examined for the higher particle volume fractions. The samples were compressed to a gap around 1 mm, equal to the measurement gap that was applied on the rheometer. The coordination number before and after compression remained constant, increasing at most by $z = 0.5$ for the $\phi = 0.3$ sample. The clustering coefficient was unchanged for all three samples.

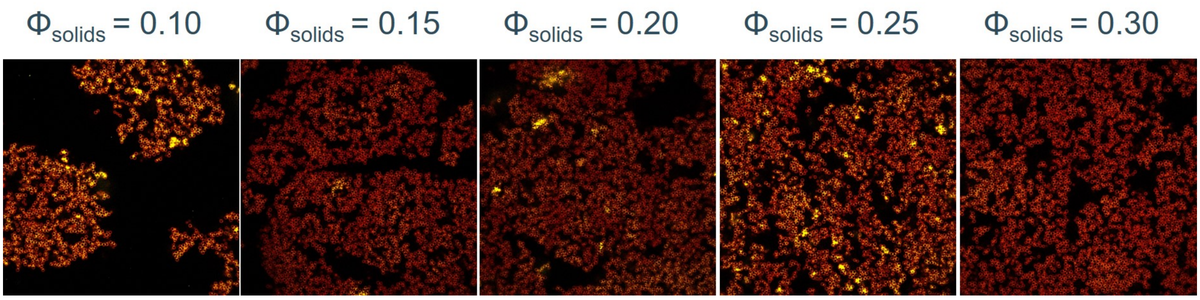

Figure 2: Confocal images of capillary suspensions with increasing particle volume fraction using non-porous particles.

Particle size: Samples with particles with sizes 3, 10 and 50 µm were prepared. The volume fractions are kept constant as is the contact angle and the mixing conditions. While it is expected that the particle size R should have an influence on the structure through the balance between the capillary and gravitational forces (Eötvös or Bond number),

$$\mathrm{E\ddot{o}} = \frac{\text{Capillary force}}{\text{Particle weight}} \approx \frac{2\pi R\Gamma\cos\theta}{\frac{4}{3}\pi R^3\rho} \sim \frac{1}{R^2}$$

no densification of the structure was observed. Changes to the bridge shape and distribution account for this relatively constant structure. In all three samples, a distribution of bridge sizes, ranging from large, coalesced bridges connecting three or more particles, binary bridges connecting two particles, and very small drops and bridges between particle asperities are observed. These small bridges or patches of secondary fluid appear as a "uniform" film on the small particles whereas they form patches (with an apparent contact angle near 90°) on the particle surface of the large particles. This implies an influence of the particle roughness. Comparing the yielding behavior, we see that the stress at the end of the linear viscoelastic region increases with decreasing particle size, as would be predicted from $\sigma_y \sim F_c/R^2 \sim 1/R$. The flow point, on the other hand, is nearly identical for the small 3 µm particles as the large 50 µm particles and highest for the 10 µm. This change may be due to the changes in the bridge volumes and network structure of this sample.

Particle polydispersity: Adding a small percentage of larger 10 µm particles to the small 3 µm particles shows some influence on the network strength. The storage modulus shows no change with 1% 10 µm particles but does increase slightly with the addition 5% 10 µm particles. This increases G' towards the value with 100% 10 µm particles. The loss modulus shows no clear trend and the data for 100% 10 µm remains higher. We do not see a dramatic in the meniscus size that would be expected from large-large interactions. Instead, the structure is dominated by the interactions between the small particles with some small-large interactions. Preliminary image detection shows that the average network structure is the same with only local changes around the large particles. The large particles have a larger coordination number, owing to their larger size. We also see region, particularly around the large particles, where there are dense flocs consisting of many coalesced bridges. This may imply some change in the mixing conditions caused by the large particles.

Particle roughness (raspberry particles): To directly test the influence of particle roughness on our system, silica nanoparticles are electrostatically adsorbed onto the surface of the larger microparticles and then smoothed with a Stöber silica layer [4]. By attaching differently sized NPs, we can form raspberry particles with tunable roughness. For samples with a constant secondary fluid volume, the increase in roughness results in several changes. First, for the attachment of 40 nm particles to the 3 µm primary particles, the storage modulus remains unchanged, but the loss modulus increases, shifting the yielding region and the flow point shifts to higher strain. With further increases in the roughness (attachment of 100 nm and 200 nm particles), a transition to asperity wetting – with corresponding decrease in the storage modulus – is observed. By adjusting the secondary fluid volume, the storage modulus in all samples can be matched. There remains, however, an increase in the yield strain and decreasing trend in z and c (Figure 3).

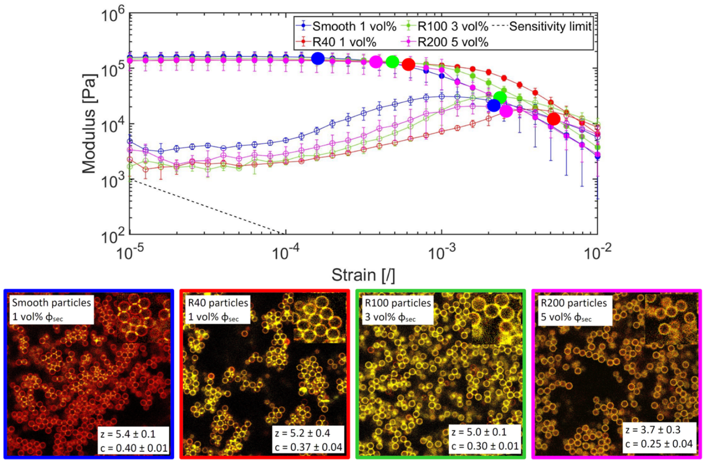

Figure 3: Influence of particle roughness for samples with secondary fluid volume adjusted to match the storage moduli. Increasing roughness increases the yield strain with very little effect on the flow point. The structure becomes less dense (decreasing both the coordination number and clustering coefficient) as the roughness increases.

The influence of particle roughness was further examined using information obtained from the medium amplitude (or asymptotically nonlinear) oscillatory shear regime. Previous research has shown that the third harmonic is non-integer and non-cubic [5] and the scaling of the third harmonic is sensitive to particle collisions [6]. The strength of the Hertzian contact is decreases with roughness as the samples transition from bridge to asperity wetting demonstrating the sensitivity of this rheological measure to the particle contact strength. The ratio of the elastic to viscous scaling is tied to the nature of the frictional contact and a transition from adhesion- to load-controlled friction may occur in these samples, but additional measurements must be conducted.

2. Proposed work

After discussion with project liaisons, we have decided to concentrate on the rheo-microscope in the project renewal. This will allow us to better connect the changes in the microstructure with the dynamics. The initial focus will be on the changes in the asymptotically nonlinear region to study both the bridging dynamics and yielding of the network. This will be supplemented by better detection of the bridge shape to determine changes to particle clustering and bridged contacts. A generalization of the particle detection algorithm will also allow us to investigate the influence of particle shape, integrating changes to the particle orientation and contact type (e.g. edge-edge or corner-edge).

While we will examine intermediate particle volume fraction in the renewal project up to $\phi_{solid} = 0.3$, the study of concentrated systems with $\phi_{solid} > 0.5$ is not envisaged. First, the strong attraction provided by the secondary fluid bridges means that the mixing becomes much more difficult at higher volume fractions leading to inhomogeneous samples. While we can use the squeeze flow caused by lowering the rheometer plates to expel some of the bulk fluid (thereby concentrating the particles and bridges), this is not a repeatable procedure. Second, concentrated systems, especially those exhibiting shear thickening, are also being investigated in the project of Jan Vermant. We are able to use similar particles (our rough particles follow the same procedure albeit usually with larger particle sizes) which should allow us to compare results.

2.1. Specific work packages

WP1: Yielding of capillary suspensions

We have now built a combined rheometer-confocal microscope setup that can be used to provide more accurate shear profiles while directly obtaining the resultant rheological properties. This new setup will allow us to better investigate the local, cluster-level changes to the structure and determine if yielding is the result of bond-breaking between a few, critical bridges or if general restructuring occurs. By tracking the individual particle deformation and that of the neighboring particles, we can correlate the motion of individual particles to the local clustering and local bridge strength. Of particular interest is the development of the coordination and clustering coefficient during shear.

To investigate the yielding dynamics, we will employ both oscillatory and step shear profiles. Our previous experiments showed how oscillatory shear in the asymptotically nonlinear regime is sensitive to particle collisions with little influence on the re-arrangement of the particles (resulting in network coarsening or compaction). Step shear profiles, however, can result in more pronounced re-arrangement and allow us to investigate the difference between inter- and intra-cluster bonds. We will also be able to directly track the different shear layers to investigate the influence of slip and shear banding. Such effects are expected to be more pronounced with the higher volume fraction samples.

WP2: Bridge sizes and asperity wetting

Previous experiments with both varying particle sizes and particle roughness have shown the importance of bridge size and size distribution on the structure and rheological properties. The transition between asperity wetting to particle bridging is associated with an increase in the storage modulus and decrease in the coordination number and clustering. This clustering can be highly inhomogeneous, however, as demonstrated for the mixtures of large and small particles. There, mixing conditions leads to a local change in the bridge size near the added large particles. Changes in the local displacement of particles both close to and far away from these inclusions should be further investigated. The previous experiments using large and small particle mixtures should further be expanded to investigate intermediate to high fractions and larger differences between the sizes. With the bimodal distributions, the mixing order (and particle wetting) is expected to play a larger role.

The experiments with rough particles also showed changes to the frictional contacts in the system with increased roughness. Despite matching the plateau storage modulus, the rougher particles had a lower clustering. There was scatter in the data between samples demonstrating adhesion- and load-controlled friction. This change should better be correlated to the local structure and the deformation of the particles. By modifying the particle hydrophobicity, we can include variations in the wetting to further investigate these changes.

WP3: Particle aspect ratio and cubic particles

The investigation of particles with a varying aspect ratio and/or angular shape is also viewed as of interest. Such particles can be printed using a Nanoscribe or particle stretcher. The strength of capillary suspensions varies with particle shape [7] and higher fractions of secondary fluid can induce changes from edge-edge contacts with high connectivity to hedgehog-like clusters formed through corner-corner contacts with low connectivity [8]. While these systems have been investigated rheologically, their structure remains largely unknown and of industrial interest. The local structure and aggregate behavior will be monitored as a function of the applied shear.

2.2. Gantt chart

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3. Leverage opportunities

I have already started to investigate the structure of capillary suspensions using these confocal microscopy techniques both within and outside of the present project. The project will also benefit from expertise added by a current doctoral student who is modeling capillary suspensions using the coarse-grained MD code ESPResSo. We recently improved the simulation methods so that pseudo-rheological experiments, mimicking the conditions present in the rheometer without the need for a biased shear, could be performed [9]. This can be further supplemented by the project "Computational Modeling of Particle Suspensions" currently in proposal stage.

I am also participating in a Marie Skłodowska-Curie Innovative Training Network "Dynamics of dense nanosuspensions: a pathway to novel functional materials" combining expertise from several European universities and companies to study the influence of combination of particles of different sizes and wettabilities as well as the properties of the liquid phases on the network structure and rheology of capillary nanosuspensions (capillary suspensions with nanoparticles both as the primary particles and with nanoparticles incorporated into the bridges). The aim of this project is to fabricate and characterize porous bodies from capillary suspensions containing particles of at least two different wettabilities and nanoparticles.

The industrial expertise of the IFPRI members has also been invaluable in identifying areas of specific interest for this project. This research should be a platform that we can use to gain a clear understand the dynamics on a limited scale. Thus, the problems and test methods should be used as a starting point in this project. We can then identify the specific microstructural changes occurring during these tests or under these specific conditions. By highlighting the microstructural changes, especially in relation to the particle interactions, we can have a positive feedback loop with industry to suggest minor changes and tackle increasingly more complex problems.

4. References

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