

IFPRI Brief

Simplified industrial formulations - part 2

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1 Goals & Results so far

The goals within the IFPRI project for the first period have been threefold

1. To explore how, moving away from model systems containing spherical colloids with near hard interactions, we can widen the range of rheological responses by changing the properties of the building blocks of the suspensions, so that even in simple formulations a wide range of behaviors can be "built in", i.e. obtaining formulation guidelines to do "more with less" or simplifying formulations from within.
2. To further develop a limited number of rheological and structural tools to interrogate the rheological response of the such dispersions, focusing on
 - Advanced rheological methods which allow for stress deconvolution;
 - High resolution confocal microscopy to probe structural development in-situ during flow (4D imaging);
 - Local scale tribological measurements using AFM.
3. Apply these methods to simplified industrial dispersion by industrial partners and compare with the formulation guidelines obtained from (1).

Of these goals several aspects have now been - at least partially - achieved, some remain in the full focus of the ongoing research. Experimental methods and model systems are now available and being explored. We also developed a constitutive model for industrial suspensions, based on insights from the advanced rheological methods (stress de-convolution) and using models taking into account plastic flow behaviour using an Eyring like approach and a viscoelastic upper convected Maxwell model. This should be a generic and simple modelling approach for dense suspensions, which will be further evaluated.

2 Goals for the next period

For the next period we now propose :

1. Particle roughness has been identified to generate surprising effects in colloidal gels and could both be tool to engineer materials from within for rheology or gravitational stability. For now the focus has been on systems which show maximal interlocking The effect of roughness will now be explored more systematically. For gravitational stability, we will also study combined effects of roughness and shape.
2. A full study of the structural evolution of systems in (1) will be investigated by 4D confocal rheology, with an emphasis on understanding the yielding transition and the deformations gel strands are subjected to.
3. To understand the role of non-central forces we would intensify the measurements of local scale mechanics using AFM (to characterize rolling and sliding friction) and micro mechanics of model aggregates.
4. we propose to also study these systems in 2D as this also has application to engineer strong interfaces or understand what happens in protein solutions, as a model system for lock and key interactions. The 2D nature of these systems makes them also a stepping stone for doing the micromechanics not immediately on the 3D systems.
5. we propose to continue the investigation of simplified industrial dispersion by industrial partners especially in light of systems with roughness and shape variations (e.g. a Paracetamol dispersion)

3 Simplified industrial systems : bottom-up

3.1 How can roughness be used?

As reported in IFPRI ARR-46-10 a model thermoreversible gel system has been developed, consisting of a thermoreversible silica system (building on the building blocks of Zanini et al. [1], with a polymer layer now grafted to the surface) which allows to exclusively compare the influence of primary particle surface roughness on the macroscopic gel properties at rest and under shear. The novel rough particle gels enable engineering of gel elasticity, but the materials will yield only at order of magnitude larger strains or stresses, have flow independent porosity and are essentially non thixotropic, with fast and full recovery, as demonstrated using 2 applications. The volume fraction range explored by us was in the range of industrial dispersions, i.e. going from 0.05 to highly concentrations. Literature studies which so far have thought about the role of bending and interlocking were more often than not, limited to dilute fractal regimes [2]. Most studied on gels have been performed on depletion systems, and the subtleties of the interactions potentials in systems with e.g. DLVO or sticky polymer brush interactions may well be quite different and can not necessarily be represented as a network of particles connected by linear springs [3]. By having particle topography as a new parameter to interrogate mechanics of elasticity and plasticity in gels, we shed new light on a long standing question, as the changes we see are quite dramatic.

In our work, however, we only compared smooth particles with those interlocking. We propose to further explore the effects of roughness by varying the number of asperities per particles, as well as the height of the asperities relative to the particle size, as shown schematically in figure 1.a. We now control the synthesis quite well, have also produced novel rod-like suspensions (more bullet-like) starting from the work of Kuijk et al. [4], then using hetero-coagulation and additional silica coating using Stöber chemistry (TEOS/Ammonia), shown very schematically in

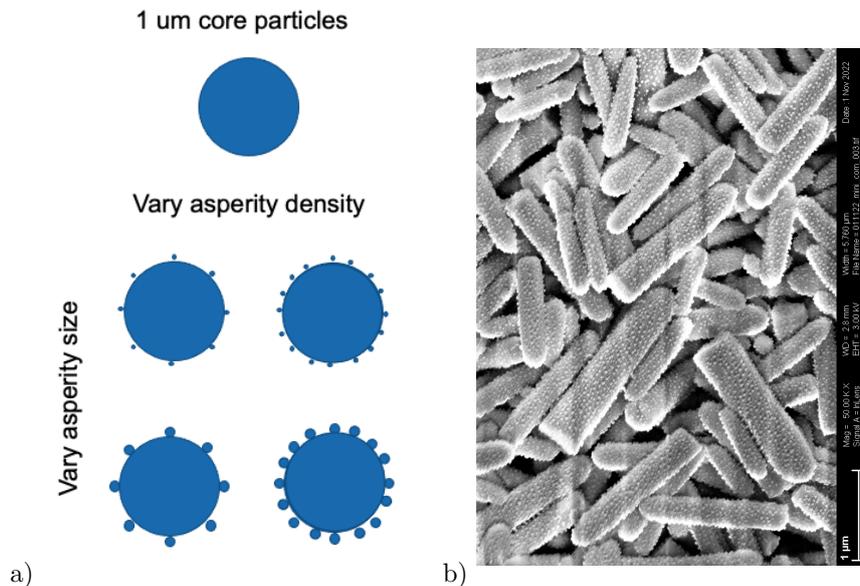


Figure 1: a) Sketch of the rough particle parameter space to be explored. b) Rough colloidal rods recently synthesized as a proof of concept.

fig. 1.b. We propose to study these systems in particular for their effects on gravitational stability.

The goal is to have a benchmark data set which capture the effects of roughness and shape on the elastic to plastic transition, which governs the yielding and gravitational stability. For roughness we intend to investigate 4 asperity densities and one variation of asperity size at the highest density. This constitutes 5 systems which would need to be studied at a few volume fractions in the range of 0.05-0.15. Concerning rheological data we look to the work of R. Zia for comparison with simulations, for the gravitational stability, the effects of roughness of the particles and gel "toughness", as controlled by roughness will be compared to the scaling analysis from Varga and Swan [5] for the hydrodynamic instability in freely settling colloidal gels. This will force us to look into the effects of bending stiffness of the colloidal strands [2] (which we will try to measure as indicated below).

3.2 4D imaging

As reported in IFPRI ARR-46-10, the experimental setups are now fully functional and the experimental protocols have been established for efficient 4D imaging of colloidal gels. Triangular wave experiments under controlled rate and creep-recovery experiments explore plasticity and elasticity in a different manner. First time resolved 3D data sets were obtained on depletion gels. But the goal is to interrogate the mechanics - by measuring the mechanisms of elastic deformation (and identifying the different deformation modes in the elastic regime), and then to identify the phenomena which underpin the yielding transition from elastic to plastic deformations. The fundamental aspect of plasticity is that it represents an unloading of an elastic stress, very locally. In colloidal glasses (or glassy materials in general) these rearrangements occur over a few particle diameters [6], and for densely packed amorphous solids much progress has been made linking

these processes to macroscopic properties [7]. However, the open, porous nature of gels entails two differences. On the one hand there is more space to re-arrange as the structure can even be locally fractal and gel strand plasticity comes into play [8,9]. On the other hand, the strain field resulting from a plastic event will also propagate differently. Finally the long range hydrodynamics plays an important role into how floccs reorganize [10]. Evidently we aim to understand specifically how particle topography (roughness), through the bending/twisting stiffness, influence structure development. The goal is to provide insights into the role of structural heterogeneity and rigidity percolation and their interplay between the local gel strand deformation modes and the nature of the stress bearing structures in these systems. This should provide a good mental framework to analyze industrial systems and guide the design beyond the design rules currently known.

3.3 Single particle level tribological measurements using AFM and optical tweezers

As reported in IFPRI ARR-46-10 we have been developing a colloidal probe for lateral force microscopy (LFM) that allows free rotation of an encapsulated particle and simultaneous imaging of the contact via fluorescence microscopy. A friction coefficient of the investigated colloid-substrate system can be determined. The three-dimensional rotation of the particle during the LFM scans is confirmed by tracking fluorescent markers on the colloid. Direct comparison to a fixed colloidal probe is possible, enabling the observation of sliding and rolling friction. We intend to study the properties of a same roughness range as studied in the macroscopic measurements to provide an insight on the role of adhesive forces, sliding friction and rolling friction.

To further study the behaviour of this effect of interlocking on gel mechanics, an optical trap is being built up with the help of Prof. E. Furst (Ifpri, consultant). An optical tweezer (OT) can probe forces ranging from 0.1 pN up to several hundred pN, making it a valuable tool for investigating interparticle forces which can then be related to bulk systems. The goal is to make model colloidal aggregates and investigate it is possible to measure the forces of the bending rigidity of an array of particles, as well as gain insights on the anisotropy of the interparticle forces, as was first demonstrated by Pantina and Furst [11,12] and more recently Bonacci et al. [13]. We also intend to print cantilever structures (using a Nanoscribe) to grab onto the colloidal strands which should extend the range of deformation modes to excite the model colloidal strands (twisting, bending and shearing) An OT with multiple trapping capabilities will be used to measure the micromechanical response of interparticle interactions. The aggregation force, the bending and twisting mechanics as well as the rupture force of particles, can be measured. The OT allows the study of the micromechanical properties of the colloidal interactions. Over the course of the last year, we conceived and built an OT setup and the goal is to extend this to the particles from section 2. The goal of this section is to answer minimally the question "when" and preferably "how" do the local scale effects influence the rheology and gravitational stability.

3.4 Gelation in 2D : interfaces with rough particles

Heterogeneity of the particle surface, plays an essential role in the self-assembly behavior and their interfacial mechanical properties. They can either be driven through alternating chemical or topographic features. In particular, for particles at fluid-fluid interfaces, lateral capillary forces can be altered by undulations of the contact lines, which then govern the self-assembly and the interfacial mechanical properties of the resulting particle-laden interface. There was an interest of IFPRI members in these systems, as models for proteins. In our work we propose to study, the macroscopic interfacial mechanical properties with topographical matching convex and concave

surface features confined at a water-air interface were measured in a double-wall ring (DWR) setup. 2D systems have the advantage that all microstructural information is contained in single plane and that less material is needed.

We have described the raspberry particles in previous IFPRI reports. But we can also make golfballs to have a lock and key behaviour. Liang et al. [14] recently reported a novel one-pot synthesis approach for thiol-functionalized Golf-ball like particles (GbPs) through a one-step sol-gel reaction using 3-mercaptopropyl trimethoxysilane (MPTMs) and TEOS in a 4:1 molar ratio. Depending on the reaction conditions, the resulting particles have shallow concave dents over them. The formation mechanism depends on stress build-up during the co-condensation reaction of the two precursors, which results in buckling of the particles.

Preliminary results showed how it possible to make a mixture of particles with the capability of interlocking when sheared, resulting in a strong mechanical response.

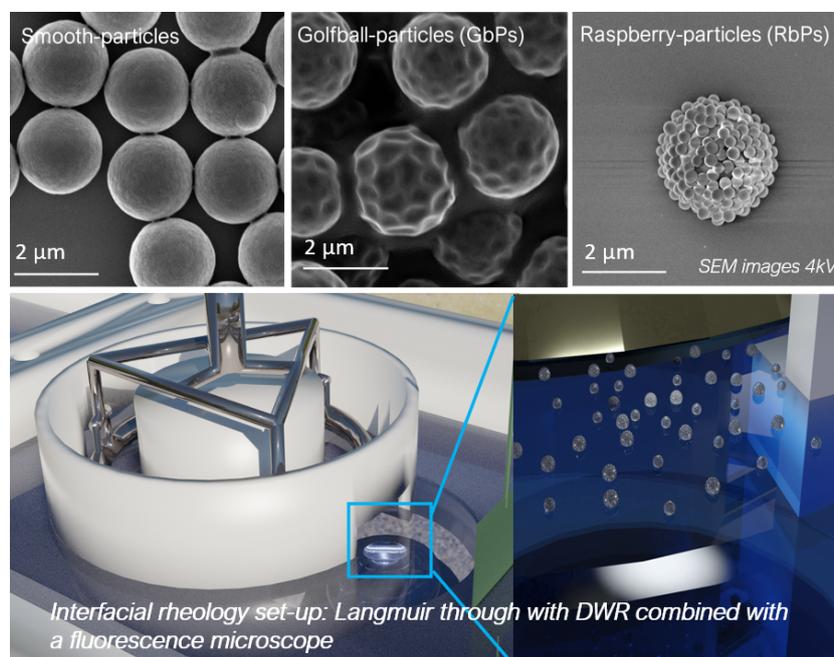


Figure 2: Upper images respond to smooth particles, Golfball-like particles, and raspberry-like particles, the image below is a rendering of the DWR setup.

At simple liquid-liquid interfaces, the surface tension σ as a scalar and thermodynamic quantity can be sufficient to describe the system accurately. However, structured or so-called complex interfaces usually have a significant interfacial extra stress tensor τ_s contribution to the interfacial stress tensor.

$$\sigma = \sigma I_s + \tau_s \quad .$$

The double-wall ring (DWR) experiment is a method to probe at least the shear components of the interfacial stress tensor τ_s and link the interfacial shear rheological properties with appropri-

ate constitutive equations. In this setup, a Langmuir trough with an adapted double-wall ring attached to a stress-controlled rheometer was used to measure the mechanical properties [15]. Additionally, a microscope was used to measure the surface coverage during the experiments. With these matching features, the particles should be able to interlock, therefore, have a more robust response for shear deformation at a lower surface coverage. Small amplitude oscillatory shear measurements with the DWR allow measuring a complex interfacial shear modulus (or viscosity) using a generalized form of the Boussinesq-Scriven constitutive model in the linear visco-elastic regime.

Figure 3 shows preliminary results on these systems, starting with an amplitude sweep for

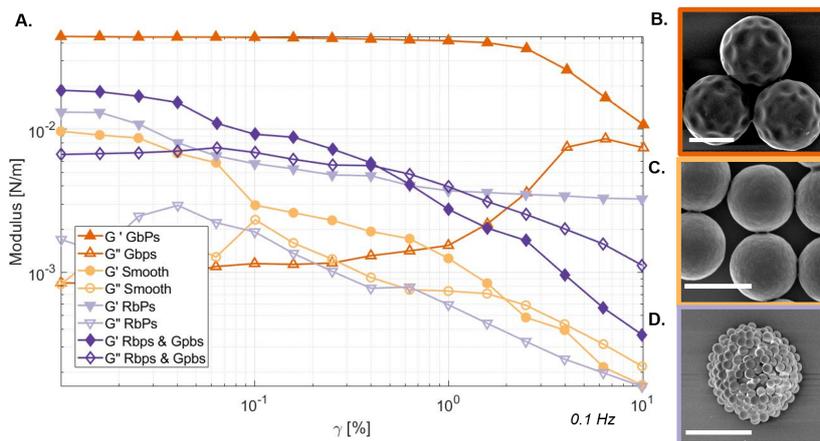


Figure 3: A. Amplitude sweep of smooth, GbPs, RbPs, and a mixture of GbPs and RbPs, B-D show GbPs, smooth and RbPs particle, the graph is color-coded

GbPs, smooth particles, RbPs as well as a mixture of GbPs and RbPs. Elastic interfaces are obtained with the moduli changing orders of magnitude by just varying the particle topography. The GbPs show the highest modulus and most extended linear viscoelastic region - nearly 2 orders of magnitude higher storage modulus compared to the smooth silica particles at similar surface coverage and surface chemistry. In a mixture of RbPs & GbPs, the viscous contribution (G'') is increased compared to the other measurements.

The self-assembly behavior of the particles is determined by the interplay between the different interparticle forces, where the roughness of particles plays a crucial role in the interfacial mechanical properties [16]. Gaining more insight on the interparticle forces and their relation to the interfacial rheological properties of particle assembly at a liquid-liquid interface will provide us with a toolbox to engineer desired interfacial properties to stabilize many industry-relevant multiphase-systems [17].

Observing the particle-particle interactions to the 2D network formation at the interface of non-spherical particles and studying as well as relating the interlocking of the bending modulus of an array of RPs and GBs with an optical tweezer, similar to the experiments of Bonacci et al. [13] is what we propose to carry out, in 2D as well (the analysis will be easier). There will be advantages of doing this in 2D as a stepping stone for the systems mentioned above in 3D.

4 Industrial systems

- The possibility to obtain different structures by milling (with different roughness) and subsequent recrystallization and having a system which displays many of the features experienced in our model systems of section 2, make the Paracetamol dispersions an interesting industrial model system to study further using rheology, high frequency rheometry and superposition rheology. We intend to continue discussions with the IFPRI members to further identify suitable systems or conditions.
- We also propose to look at interfaces of relevant pharmaceutical dispersions, using the interfacial rheology techniques mentioned above

5 Concluding remarks

1. The goal of this work is to show how - bottom up - roughness of particles can be used as an additional functionality to engineer the gravitational stability and rheology of colloidal gels. Scaling rules should provide insights into how these phenomena can be used.
2. The confocal and micro-mechanical studies will provide clear insights in the structure property relations.
3. We also propose to study some of these phenomena at liquid-liquid interfaces, to rationalize problems in formulations in pharmaceutical dispersions.

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