

**IFPRI UPDATE:
SIMPLIFIED INDUSTRIAL FORMULATIONS
DESIGN CHALLENGES**

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1. GOALS

The goal of our work at ETH Zürich represents a combined effort of the labs of Profs. Lucio Isa and Jan Vermant. Our goals within the IFPRI project and more globally within our groups are 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 tools to interrogate the rheological response of the such dispersions by advanced rheological methods and methods to probe structural development in situ during flow using high resolution confocal microscopy.
- (3) Apply these methods to simplified industrial dispersion by industrial partners and compare with the formulation guidelines obtained from (1).

2. PRACTICAL

Three PhD students were working in this general area and graduated in the course of the last 12 months. Gabriele Colombo (Vermant group) group defended his thesis 12.2019, and Chiao-Peng Hsu (Isa group) defended 05.2020 and R. Massaro (a long term visiting student from KU Leuven) defended 05.2020. The theses can be obtained on request. We obtained additional funding through a Swiss national foundation grant and the ETH Zurich for 3 new PhD students, Vincent Nigel (started 05.2019, Isa group) will work on imaging the relative motion of rough and non-spherical particles in suspensions in relation to their rheology, Florence Müller (03.2020, Vermant group) will work on gels made with rough and non-spherical particles, and Pierre Lehericey (08.2020, Vermant group) will focus on the elastic properties and yielding events. Additionally a postdoc will work (as of 06.2020) on the image processing routines. The Corona virus crisis had severe impact on the momentum of the group and transfer of know how between students. Due to the Corona virus crisis Activities were completely suspended as of 15.03 and partially restarted as of 27.04 with a full restart of experimental work 08.06.

We had also foreseen to have a visit of one of Prof. Lilian C. Hsiao students (Shravan Pradeep), but this exchange is postponed (The plan was to perform shear reversal with the ultra fast confocal, along with fast crystallization kinetics of rough PMMA particles)

We had some exchanges with IFPRI partners to identify suitable industrial systems to be studied, but discussions were not yet finalized and now would be a good time to do so. The new students are around and trained to run the experiments and protocols are in place.

3. RESULTS

The focus of this work is on rheological phenomena which arise because of particles being in close contact, i.e. continuous and discontinuous shear thickening in stable dispersions, and thixotropic effects in colloidal gels.

3.1. Stable dispersions. The effect of **nanoscale surface roughness** on the dilatant discontinuous shear thickening of dense silica suspensions was investigated, to establish a link between the single particle properties and the bulk rheology. Nanotribological measurements of the interparticle contacts of model rough colloids were carried out along with macroscopic rheological studies. Rough particles exhibit discontinuous shear thickening over a broader range of shear rates and for volume fractions much lower than smooth colloids, possibly due to interlocking of surface asperities. One can increase the solid loading to postpone undesired shear thickening by mixing a small amount of low-friction particles into the system, and we suggest an engineering-tribology approach to control the macroscopic rheology of shear-thickening suspensions. Second the **role of reversible, short-range chemical bonds** in determining the frictional and adhesive interactions between particles was studied. Urea molecules were used as a tool to partially or fully screen hydrogen bonding between particles and therefore influence their contact properties. Time-dependent urea sorption reduces friction and adhesion, inducing a reduction in the high-shear viscosity of dense suspensions. Finally, we use **stimuli-responsive polymer brushes**, synthesized to a precise length by controlled radical polymerization, for the in situ, selective tuning of interparticle friction and adhesion, and for the modulation of surface roughness.

N. M. James*, C. P. Hsu*, N. D. Spencer, H. M. Jaeger, L. Isa, Tuning Interparticle Hydrogen Bonding in Shear-Jamming Suspensions: Kinetic Effects and Consequences for Tribology and Rheology. *J Phys Chem Lett* 10, 1663-1668 (2019)

B. Schroyen, C. P. Hsu, L. Isa, P. Van Puyvelde, J. Vermant, Stress Contributions in Colloidal Suspensions: The Smooth, the Rough, and the Hairy. *Phys Rev Lett* 122, 218002 (2019)

C. P. Hsu, J. Mandel, S. N. Ramakrishna, N. D. Spencer, L. Isa, Disentangling the roles of roughness, friction and adhesion in discontinuous shear thickening by means of thermo-responsive particles. Submitted, arXiv preprint: arXiv:2004.05970

<p>Exploiting roughness and adhesion: Further work will focus on visualizing relative particle motions using the high speed confocal rheometer to understand what happens when particles are in 'contact' and how this should be engineered. High frequency rheology or superposition rheology may be exploited to interrogate this link further.</p>
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3.2. Flocculated dispersions. Here the main focus was on establishing the link between the microstructure and flow properties of colloidal gels. First, we systematically investigated the effects of interparticle attraction strength and steady shear deformations on the microstructure of a model depletion gel of PMMA spheres in CHB/Decalin at intermediate volume fraction $\phi = 0.2$. Particular care was taken to ensure reproducible initial structures, by using either a diffusion step of screening salt into a charge stabilized colloid-polymer mixture, or well-defined pre-shear protocols. By applying these procedures, we could observe the initial stages of gel formation across a wide range of depletant concentrations (polystyrene), ranging from shallow quenches close to the spinodal to high attraction strengths, where early arrest and fine particle strands were observed. Using a recently developed rheoconfocal setup, we investigated the shear-induced rearrangements occurring in the gels, by live imaging of the microstructure under steady flow at a stagnation plane. Dramatic variations in **gel heterogeneity** were observed as a function of the shear rate, far outweighing the influence of the depletant concentration and we obtained good scaling relations for the evolution of the microstructure. This work is being prepared for publication, pending comparison with simulations by the group of Jim Swan at MIT. However, the rheological signatures of these weak depletion gels were too small to warrant further detailed rheological studies.

To compare rheological with structural data, matrices with higher viscosities were used and model flocculated suspension in both a Newtonian and a also viscoelastic medium was studied by combined rheological and rheo-confocal methods. To this extent model micrometer sized fluorescent PMMA particles were dispersed in polymeric matrices (PDMS). The effect of fluid viscoelasticity is studied by comparing the results for a linear and a branched polymer. Stress jump experiments on the suspensions were used to de-convolute the rate dependence of the viscous and elastic stress contributions in both systems. These results were compared to a qualitative and quantitative analysis of the microstructure during flow as studied by fast structured illumination confocal microscopy, using a counter-rotating rheometer. At equal viscous strength (comparable Pe numbers) but different stress ratios, the microstructural analysis showed that **denser clusters are developed in a viscoelastic matrix**. Furthermore, from the evolution of the viscous stresses at high shear rates, cluster densification in a viscoelastic matrix could be inferred from a lowered effective volume fraction.

R Massaro, G Colombo, P Van Puyvelde, J Vermant Viscoelastic cluster densification in sheared colloidal gels *Soft Matter* 16 (10), 2437-2447

Thixotropic systems: We now propose to focus on the role of roughness and shape effects in flocculated suspensions and elucidate how yield stresses and thixotropy can be better controlled.

4. ANALYSIS METHODOLOGY

- A stress-controlled rheometer was coupled to a fast scanning, instant structured illumination confocal microscope and a focus-tunable lens was incorporated in the setup to acquire 3D image volumes at video rates. The work was published:
G Colombo, R Massaro, S Coleman, J Lauger, P Van Puyvelde, J. Vermant, Ultrafast imaging of soft materials during shear flow, *Korea-Australia Rheology Journal* 31 (4), 229-240 (2019).
- A high frequency rheometer setup is available and is being modified for combined steady shear and HF rheometry studied. A review on the use of high frequency rheology was published:

B Schroyen, D Vlassopoulos, P Van Puyvelde, J Vermant Bulk rheometry at high frequencies: a review of experimental approaches *Rheologica Acta* 59, 1-22 (2020)

- New setup for superposition rheometry, as a prime method to interrogate how rheology emerges from the contributions to viscous and elastic stress contributions for the different formulations strategies has been developed.
- Particles down to 500nm characterized at the single particle level using colloidal probe AFM (friction and adhesion)

5. WORK PLAN - EXPECTED OUTCOMES

We proposed a staged approach.

- (1) Inventory of potential particulate samples should be identified with IFPRI members (D.1). A discussion has been started but not been finalized. It would be good to have this overview after the virtual AGM - to be ready by September 2020
- (2) Inventory of desired benchmark rheological properties and profiles, with request for feedback (D.2). Feedback from IFPRI members is urgently requested. It would be good to have this overview ready by September 2020
- (3) Report on the characterization of the particle systems (size, stability and initial rheological results) (D.3, month 6) This report is available, particles have been characterized using electron microscopies, AFM nanotribology and initial rheological results.
- (4) Basic rheological characterization of the linear viscoelastic behaviour and the flow curves of the stable suspensions (D.4, year 1) This report will be delivered with the annual report.
- (5) Full rheological characterization including high Frequency rheological characterization to rationalize the behaviour (D.5, month 18) Most likely this will be delayed by 8-12 months. A setup is being developed to do high frequency rheology with pre-shear or during flow.
- (6) Rheological characterisation of selected thixotropic suspensions, combined with some rheo-confocal studies (D.6. month 30) This has been partially achieved.
- (7) Responding DESIGN challenge by IFPRI members (MO30-36)

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