

**IFPRI BRIEF PROPOSAL:
SIMPLIFIED INDUSTRIAL FORMULATIONS
DESIGN CHALLENGES**

JAN VERMANT, DEPARTMENT OF MATERIALS, ETH ZURICH

1. INTRODUCTION

The International Fine Particle Research Institute (IFPRI) wishes to better understand the rheological properties of complex industrial colloidal formulations. To this end, a key question is if simplified industrial formulations (SIFs) can be designed which mimic the more complex industrial formulations. Even the simplest colloidal suspensions, consisting of spherical particles in a Newtonian matrix, display very rich and nonlinear rheological properties. For example the viscosity may vary over orders of magnitudes and in the same suspension shear thinning and shear thickening can occur. These phenomena arise because of a complex interplay between colloidal and hydrodynamic interactions. Much has been learned by looking at the simplest case of Brownian hard-sphere suspensions and by mapping the behaviour of other colloidal particles onto effective hard spheres as excellently reviewed in the book by Mewis and Wagner[1]. The number of parameters which govern such Brownian hard spheres are limited and include the *effective hard sphere* volume fraction (ϕ), the maximum packing (ϕ_m), the medium viscosity (η_m) and the particle size (a). This has been successfully applied to for example industrial latex dispersions [2]. But also for complex cementitious materials the expected shear stress-dependent effects of shear thickening and size scaling were used to distinguish between surface interactions, such as lubrication and volumetric contributions and also including the packing effects and admixtures could be defined by Lafarge guided by these principles [3]. However not everything could be predicted so far, and effects of colloidal interactions and surface topology of particles have been shown recently to play an important role as well, for example friction leading to discontinuous shear thickening in the same cementitious materials, to an extent not predicted for smooth Brownian hard spheres [4]. For stable suspensions there is a need to go beyond Brownian hard spheres, bringing the key aspects related to how particles pack (shape, softness) and interact in real systems (heterogeneity, roughness) to the forefront.

Attractive colloidal suspensions display far more complicated properties, often a solid-like behaviour at rest is observed due to their flocculated structure, and they liquefy (with non-Newtonian properties) when subjected to mechanical stress. In terms of material functions, the rheological properties of aggregated suspensions are described by an elasticity that depends on shear history, a yield stress, and a viscosity that not only changes reversibly with shear rate but also with time [5]. In addition to physicochemical

details (the volume fraction, the pair potential, the particle size and size polydispersity), the flow history plays an important part in the details of the microstructure, such as the local coordination number and the fractal dimensions, and the resulting mechanical properties [6, 7], which may reflect a strongly anisotropic microstructure in the mechanics [8]. Aggregated systems will need to be represented separately with some key effects (shape and percolation and noncentral forces) being investigated here.

As a final step, it could be investigated what the effects are of making a medium viscoelastic, due to polymeric additives. This would be a final step in complexity. Much progress has been made in understanding the changed hydrodynamics in viscoelastic suspensions (see e.g. [9] for a review) but translation of these results towards industrial systems seem to be lacking. This is however not incorporated into the scope of this proposal, but should be kept in mind as matrix formulations will be of importance as well in real formulations. However, we propose to focus on the inherent control of suspension rheology.

In this brief we propose to develop a number of simplified industrial formulations” building upon our understanding of model systems, characterising these suspensions by both integrative measurements (such as flow curves, LV properties) as well as potentially using some techniques which interrogate the physics more directly (High frequency rheology and orthogonal superposition rheometry).

2. CREATING A PARTICLE TOOLBOX

2.1. Stable dispersions. One way to produce simplified industrial formulations is to render the current model systems more complex. But in inducing complexity we can try to render model systems more realistic in such a way that they enable us to interrogate different effects of changes in either geometry, surface topography or interactions. A possible sequence of enhancing particle complexity is given in figure 1.

The ”fruitflies” of colloid science have been suspensions of systems such as poly-methyl methacrylate (PMMA) stabilized by grafted layers of poly-hydroxystearic acid (PHSA) (typically a few oligomers of the latter) and dispersed in an organic solvent, or similar systems based on silica particles. These sterically **stabilised suspensions** are models for Brownian hard sphere suspensions, when the particle size is in the order of microns and the stabiliser layer thin. Much has been learned by looking at this simplest case of Brownian hard-sphere suspensions and by mapping the behaviour of other colloidal particles onto effective hard spheres [1]. Some silica systems sterically stabilized by silane coupling agents (or using electrosterical stabilization) have also been discussed quite extensively as reference systems [10]. The data of these systems can be taken as benchmark or a relevant industrial mimic system should be identified.

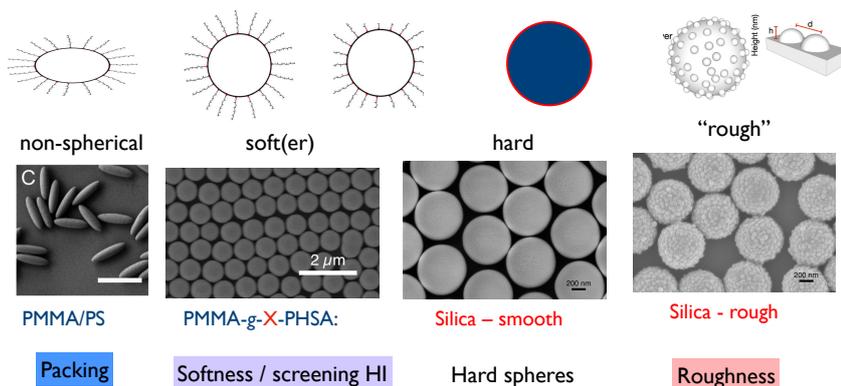


FIGURE 1. Recent trends in **bottom up** increase of complexity of colloidal building blocks: modulating the interactions (softness), the packing (shape) and the topography (roughness).

Softness is another aspect which has been imparted to particles and use as a form of "inherent" rheology control [11]. For example, recently our group has been able to increase the length of the brush in PM-PHSA systems so that by combining particle size control with brush control over the **softness** of the particles in the same model systems has been achieved. Similarly a lot of know-how has been obtained on microgel particles which have revealed how softness can be used as a design parameter in engineering the rheology of suspensions, typically by screening the hydrodynamic interactions[12] or improving the film forming properties of colloidal suspensions [13]. Finally, particle **shape** is an exciting aspect to tailor particle rheology, as both the maximum packing in the random jammed state and the orient-ability of the constituent particles, impart ways in which to separate control of shear and extensional properties. Methods for producing both oblate and prolate ellipsoids in sufficient quantities are now available (in part developed in our group) [14] and also model rod like particles can be readily produced [15]. Recently, the Isa group at ETH has developed particles with **controlled roughness**, which is obtained by employing charge-stabilised raspberry-like silica colloids with tuneable asperities [16]. The roughness (RB) can be characterised via the ratio of the height of over the distance between asperities, going from smooth to $RB.4 \rightarrow RB.5$. These model systems can be produced in sufficient quantities to measure the bulk rheology, while being well characterized and monodisperse, or controlled polydisperse. The different systems represented in figure 1 represent the archetypes of "inherent" rheology modification as they interrogate how the particle characteristics influence the a complex interplay between colloidal and hydrodynamic interactions. Softness of the interaction (or the particle) and effects of shape on packing and the effects of flow induced orientation are at least qualitatively understood. The influence of surface roughness and friction on discontinuous shear thickening has been the subject of several recent studies [17, 18]. Such non-central interactions were observed to be important for other phenomena as

well, such as for the rigidity of colloidal aggregates and gels [19, 20, 21] (see further).

Concluding, a toolbox of particles as shown in figure 1 could be viewed as to represent the essential methods in which to control (inherently) the rheology of colloidal systems consisting of a simple building block. The use of these particles has lead to relative good model predictions or at least scaling laws to predict the rheological properties, where both levels of viscosity, degree of shear thinning and shear thickening can be controlled¹. It should be noted that it is my personal opinion that further progress is only going to be achieved if there is also strong coupling with numerical simulations required, as some groups now can achieve both the scale relevant for predicting bulk properties in stable suspensions and gels and the feedback between simulations and experiments has proven extremely useful [22].

Building blocks for simplified industrial formulations: We propose to challenge the industrial partners to come up with less ideal particles which nevertheless capture the essential features of figure 1: changes in softness, shape and roughness or chemical heterogeneity.

Characterizing these or similar systems will require an important body of work, and prioritisation of the selected effects in light of the industrial realm will be required. Here Feedback of IFPRI members will be essential, as to highlight the most important characteristics, i.e. shape effects, roughness or chemical heterogeneity or deformability.

2.2. Flocculated dispersions. The rheological properties of aggregated suspensions are more complicated as their rheology depends on shear history, and typical rheological material functions are now a yield stress, and a viscosity that not only changes reversibly with shear rate but also with time. The difficulty with this kind of network structures is that they are inherently metastable. Hence, in addition to physicochemical details (the volume fraction, the pair potential), the flow history plays an important part in the details of the microstructure, such as the local coordination number and the fractal dimensions, and the resulting mechanical properties [5]. To investigate to what extent shape (orientability and change in percolation) and the occurrence of non-central forces on-central interactions are playing a role, the proposal is to investigate these properties in year 2 and 3 of the project for selected systems, for a limited range of volume fraction close to percolation. To this end it would be best if flocculation could be induced by screening the repulsive interactions (e.g; by influencing the solvent quality of a stabiliser layer or screening electrostatics).

Selected effects in thixotropic systems: We propose to focus on the role of shape effects and inducing non central interaction (roughness or heterogeneity) in flocculated suspensions .

¹Note that this represents probably more than 30 years of research in the whole field of rheology, including many IFPRI projects

3. BENCHMARK SYSTEMS AND PROPERTIES

I believe this project only will be meaningful if there is a closer than usual connection between the industrial and the academic partners with predefined feedback moments. The proposed research here would start by defining an **simplified particle toolbox** as in figure 1. Three to four particle types should be identified and it is important that they can be produced in sufficient quantities. Most likely the effects of softness are least relevant. As a fallback situations the model systems as in figure 1 could be scaled up to larger quantities, but then particles based on silica surface and having aqueous dispersion media seem warranted, as this will simplify the study of relevant flocculated dispersions. The first month of the project, an inventory should be obtained of possible particles, with some initial screening measurements.

It is also essential that an inventory is given of the benchmark properties desired, i.e. what flow profiles, thixotropic responses and possibly extensional properties are desired. The analysis of the desired properties should be carried out also at the start of the project.

It would be worthwhile to set, towards the end of the project, a design challenge where a certain rheological profile is set as a challenge. this could for example be a material with a specified yield stress, a predefined ratio between high and low shear viscosity, and a predefined recovery time (for example for applications in 3D printing).

4. ANALYSIS METHODOLOGY

The particles will be characterised by dynamic light scattering, SEM and TEM and their surface properties will be investigated using zeta potential measurements. For the rough Particles single particle AFM measurements can be performed if these are sufficiently large (several micron). Rheological measurements will be characterized by standard rotational rheometers (Anton Paar MCR 502, ARES-G2 and DHR-3), using different geometries to evaluate slip. Unless this would be desirable and come out of discussion with the IFPRI partners the elongational properties would be left aside.

To get insight in the local interactions high frequency rheology will be used. It as been established in earlier IFPRI projects that total deviatoric stress tensor in a suspension Σ can be written as [23]:

$$(1) \quad \Sigma = 2\eta\dot{\epsilon} + \Sigma_p = 2\eta\dot{\epsilon} + (\Sigma^H + \Sigma^B + \Sigma^P).$$

Here, $\dot{\epsilon}$ is the bulk strain-rate tensor so that $2\eta\dot{\epsilon}$ represents the stress in the suspending fluid. The particle contribution to the stress Σ_p can be further decomposed into direct hydrodynamic (Σ^H), Brownian (Σ^B) and interparticle (Σ^P) contributions. The hydrodynamic terms are responsible for a HF limiting viscosity η'_∞ . The linear viscoelastic response of the suspensions in the high-frequency regime can hence be used to interrogate

on the stresses at the particle level. This requires a limited number of measurements at relatively high volume fractions.

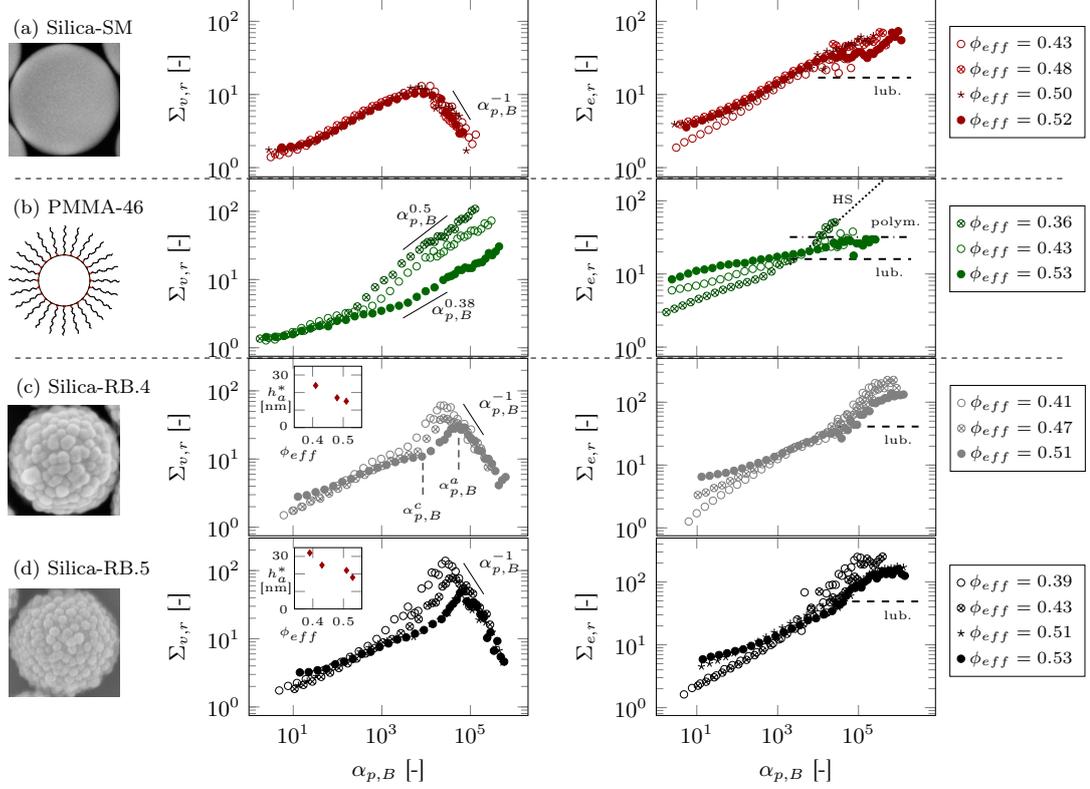


FIGURE 2. Reduced viscous (left) and elastic (right) stresses as a function of rescaled frequency for different volume fractions of (a) smooth, hard particles (Silica-SM), (b) particles with long polymeric brushes (soft) (PMMA-46) and (c,d) rough particles (Silica-RB.4, Silica-RB.5). (left) The solid lines indicate the experimentally observed scaling exponents in the HF regime. $\alpha_{p,B}^c$ and $\alpha_{p,B}^a$ (c) indicate the boundaries of the intermediate regime for RB suspensions at $\phi_{eff} = 0.51$. (right) Dashed, dotted and dashed-dotted lines present model predictions for $\Sigma_{e,r}$ based on lubrication [24], hard-sphere [25] and polymer-polymer interactions [26]. The inserts show estimates of the thickness of the rough layer thickness based on the interparticle distance at ϕ_{eff} and diffusive boundary layer thickness. Data from Schroyen et al. (submitted)

Scaling out the direct hydrodynamic (Σ^H) and Brownian (Σ^B) stresses and rescaling frequency by the characteristic Brownian frequency $\alpha_{p,B} = \frac{f}{f_{p,B}}$, data for hard silica-SM suspension in fig. 2 (a) $\Sigma_{v,r}$ decreases $\propto \alpha_{p,B}^{-1}$ and $\Sigma_{e,r}$ is constant within measurement accuracy, as a consequence of lubrication [27]. Soft PMMA suspensions (fig. fig:hf(b)) show a remarkably different asymptotic behaviour, depending on the thickness of the

stabilising layer. For longer grafted chain lengths, the exponent increases and varies as a function of frequency, reflecting a different degree of permeability of the layers [22]. Finally, in case of a suspension of rough silica particles (fig. 2 (a)) the behaviour is drastically different. At intermediate frequencies ($\alpha_{p,B} \sim 10^4$) both $\Sigma_{v,r}$ and $\Sigma_{e,r}$ strongly increase. A lubrication regime is found only at higher frequencies compared to the smooth particles. It is proposed to apply these high frequency rheology techniques to understand how the industry particle interact on a local scale. These local scale differences account for differences in shear thinning and shear thickening responses under steady state shearing flows. Having these local interactions quantified with a fairly simple screening tool will be an important step in understanding to control the rheology of colloidal systems consisting of a simple building block. Clearly this is only a stepping stone to more complex formulations.

In order to understand how the nonlinear rheological properties are linked to changes in the shear induced microstructure, studying the frequency dependent moduli, during flow seems worthwhile. Orthogonal Superposition Rheometry (OSR) can be used to study the flow behavior of colloidal gels and suspensions, allowing to probe how the different relaxation times of the material are affected by shear[8]. This will be done only on selected systems only, but having a technique which interrogates how the elastic and viscous properties of these systems evolve seems important for rational design of these systems (stress jumps would be an alternate, LAOS may also provide some insights).

5. WORK PLAN - EXPECTED OUTCOMES

We would propose a staged approach.

- (1) Inventory of potential particulate samples should be identified with IFPRI members (D.1, month 1).
- (2) Inventory of desired benchmark rheological properties and profiles, with request for feedback (D.2, month 1).
- (3) Report on the characterisation of the particle systems (D.3, month 6)
- (4) Basic rheological characterization of the linear viscoelastic behaviour and the flow curves of the stable suspensions (D.4, year 1)
- (5) Full rheological characterization including high Frequency rheological characterization to rationalize (D.5, month 18)
- (6) Rheological characterisation of selected thixotropic suspensions (D.6. month 30)
- (7) DESIGN challenge by IFPRI members (MO30-36)

REFERENCES

- [1] J. Mewis and Norman J Wagner. *Colloidal suspension rheology*. Cambridge University Press, 2012.
- [2] J. Mewis and J. Vermant. Rheology of sterically stabilized dispersions and latices. *Progress in organic coatings*, 40(1-4):111–117, 2000.

- [3] Fabrice Toussaint, Cédric Roy, and Pierre-Henri Jézéquel. Reducing shear thickening of cement-based suspensions. *Rheologica acta*, 48(8):883–895, 2009.
- [4] N. Fernandez, R. Mani, D. Rinaldi, D. Kadau, M. Mosquet, H. Lombois-Burger, J. Cayer-Barrioz, H. Herrmann, N. D. Spencer, and Lucio Isa. Microscopic mechanism for shear thickening of non-brownian suspensions. *Physical review letters*, 111(10):108301, 2013.
- [5] Jan Mewis and Norman J Wagner. Thixotropy. *Advances in Colloid and Interface Science*, 147:214–227, 2009.
- [6] Kasper Masschaele, Jan Fransaer, and Jan Vermant. Direct visualization of yielding in model two-dimensional colloidal gels subjected to shear flow. *Journal of rheology*, 53(6):1437–1460, 2009.
- [7] Jung Min Kim, Aaron PR Eberle, A Kate Gurnon, Lionel Porcar, and Norman J Wagner. The microstructure and rheology of a model, thixotropic nanoparticle gel under steady shear and large amplitude oscillatory shear (laos). *Journal of Rheology*, 58(5):1301–1328, 2014.
- [8] Gabriele Colombo, Sunhyung Kim, Thomas Schweizer, Bram Schroyen, Christian Clasen, Jan Mewis, and Jan Vermant. Superposition rheology and anisotropy in rheological properties of sheared colloidal gels. *Journal of Rheology*, 61(5):1035–1048, 2017.
- [9] Gaetano D’Avino and Pier Luca Maffettone. Particle dynamics in viscoelastic liquids. *Journal of Non-Newtonian Fluid Mechanics*, 215:80–104, 2015.
- [10] Brent J Maranzano and Norman J Wagner. The effects of particle size on reversible shear thickening of concentrated colloidal dispersions. *The Journal of chemical physics*, 114(23):10514–10527, 2001.
- [11] Dimitris Vlassopoulos and Michel Cloitre. Tunable rheology of dense soft deformable colloids. *Current opinion in colloid & interface science*, 19(6):561–574, 2014.
- [12] S. L. Elliott and W. B. Russel. High frequency shear modulus of polymerically stabilized colloids. *J. Rheol.*, 42:361–378, 1998.
- [13] Joseph Keddie and Alexander F Routh. *Fundamentals of latex film formation: processes and properties*. Springer Science & Business Media, 2010.
- [14] L. Palangetic, K. Feldman, R. Schaller, R. Kalt, W. R. Caseri, and J. Vermant. From near hard spheres to colloidal surfboards. *Faraday Discuss.*, 191:325–349, 2016.
- [15] Anke Kuijk, Alfons van Blaaderen, and Arnout Imhof. Synthesis of monodisperse, rodlike silica colloids with tunable aspect ratio. *Journal of the American Chemical Society*, 133(8):2346–2349, 2011.
- [16] M. Zanini, C.-P. Hsu, T. Magrini, E. Marini, and L. Isa. Fabrication of rough colloids by heteroaggregation. *Colloids Surf., A*, 532:116–124, 2017.
- [17] D. Lootens, H. van Damme, Y. Hémar, and P. Hébraud. Dilatant flow of concentrated suspensions of rough particles. *Phys. Rev. Lett.*, 95:268302, 2005.
- [18] C.-P. Hsu, S. N. Ramakrishna, M. Zanini, N. D. Spencer, and L. Isa. Roughness-dependent tribology effects on discontinuous shear thickening. *Proc. Natl. Acad. Sci. U.S.A.*, 115:5117–5122, 2018.
- [19] G. Bossis, A. Meunier, and J. F. Brady. Hydrodynamic stress on fractal aggregates of spheres. *J. Chem. Phys.*, 94:5064–5070, 1991.
- [20] V. Becker and H. Briesen. Tangential-force model for interactions between bonded colloidal particles. *Phys. Rev. E*, 78:061404, 2008.
- [21] J. Colombo and E. Del Gado. Self-assembly and cooperative dynamics of a model colloidal gel network. *Soft Matter*, 10:4003–4015, 2014.
- [22] Z. Varga and J. W. Swan. Linear viscoelasticity of attractive colloidal dispersions. *J. Rheol.*, 59:1271–1298, 2015.
- [23] J. F. Brady. The rheological behavior of concentrated colloidal dispersions. *J. Chem. Phys.*, 99:567–581, 1993.
- [24] R. A. Lionberger and W. B. Russel. Microscopic theories of the rheology of stable colloidal dispersions. *Adv. Chem. Phys.*, 111:399–474, 2000.
- [25] R. A. Lionberger and W. B. Russel. High frequency modulus of hard sphere colloids. *J. Rheol.*, 38:1885–1908, 1994.
- [26] S. T. Milner, T. A. Witten, and M. E. Cates. Theory of the grafted polymer brush. *Macromolecules*, 21:2610–2619, 1988.

- [27] T. Shikata and D. S. Pearson. Viscoelastic behavior of concentrated spherical suspensions. *J. Rheol.*, 38:601–616, 1994.