Flocculated suspensions
from microstructure to macroscopic behavior

A workshop organised by
The Lafarge-École des Ponts ParisTech Chair “Material Science for Construction”

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Ecole des Ponts ParisTech (Champs sur Marne)

Topics

Colloidal suspensions such as cementitious suspensions, sewage, muds, paints, ... are yield stress fluids which display a time-dependent behavior. Their peculiar behavior comes from the ability of the particles to flocculate at rest and under shear. The flocculated particles can also be redispersed, at least partly, by shearing or by agitation. Knowledge of the structure of flocculated materials and of the physical processes which govern this structure is necessary for understanding their flow behavior. Such knowledge is also a key for developing models and for industrial applications.

Objectives

The aim of the workshop is to present recent advances in the field of flocculated suspensions obtained with complementary advanced tools (direct visualization of 2D model systems; confocal microscopy; neutron scattering; microrheology; numerical simulation; homogenization approaches...). Studying the mechanical behavior of individual flocs and measuring the structural properties of sheared flocculated suspensions are indeed key elements that should be used to validate numerical approaches and to predict their rheological behavior in micromechanical approaches.
Applications and open questions in the field of fresh cementitious materials, for which admixtures, mixing process and shearing history among others influence the flocculation level and thus the material workability, will also be presented.
The workshop offers the opportunity to bring researchers and engineers together so as to combine the skills of both fundamental research and technical matters solving.

Invited speakers

- Emmanuela Del Gado (ETH Zürich)
- Robert Flatt (ETH Zürich)
- Eric Furst (University of Delaware)
- Akira Furukawa (University of Tokyo)
- Hélène Lombois (Lafarge Centre de Recherche)
- Viktor Mechtcherine (Technische Universität Dresden)
- Frédéric Pignon (Université de Grenoble)
- Stéphane Rodts (Université Paris-Est, Navier)
- Jean-Noël Roux (Université Paris-Est, Navier)
- Peter Schall (Amsterdam University)
- Fabrice Toussaint (Lafarge Centre de Recherche)
- Jan Vermant (Katholieke Universiteit Leuven)

Organizing committee

- Paul Acker (Lafarge Centre de Recherche)
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- Fabrice Toussaint (Lafarge Centre de Recherche).

Abstracts

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Gelation of Brownian and non-Brownian suspensions

Modeling and numerical simulations gain significant insight into local processes and physical mechanisms underlying the interplay of gelation and flocculation in colloidal suspensions. We study local rearrangements, structure and dynamical heterogeneities in colloidal gels and discuss their relevance to the rheological behavior. Starting from this, we analyze similarities and differences in structure and rheological behavior of non-Brownian suspensions of flocculated grains. Modeling and numerical simulations offers significant insight into local processes and physical mechanisms underlying the interplay of gelation and flocculation in colloidal suspensions.

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Yodel: A first principle model of Yield stress

A model for the yield stress of particulate suspensions is presented which incorporates microstructural parameters taking into account, volume fraction of solids, particle size, particle size distribution, maximum packing, percolation threshold and interparticle forces [1]. It relates the interparticle forces between particles of dissimilar size and the statistical distribution of particle pairs expected for a log-normal size distribution. The model is tested on published data of sub-micron ceramic suspensions [2]. It represents those data very well, over a wide range of volume fractions of solids. It also correctly predicts the multimodal mixtures with 10% of experimental accuracy [3].

In addition to capturing well the main dependence of yield stress of suspension, this model presents the advantage of incorporating physical parameters that can largely be assessed by separate experiments. This makes it particularly interesting for comparative studies, assessing for example the role of dispersants. To this end, an example will be given in which the YODEL is successfully use to analyse the impact that polymeric dispersants of controlled molecular structure have on yield stress [4].

[1] Flatt R.J., Bowen P., "YODEL: A Yield stress mODEL for suspensions", *J. Am. Ceram*. Soc. **89**(4), 1244-1256, 2006.
[2] Zhou Z., Solomon M. J., Scales P., Boger D. V., "The yield stress of concentrated flocculated suspensions of size distributed particles", *J. Rheol.* **43**(3), 651-671, 1999.
[3] Flatt R.J., Bowen P., "Yield stress of multimodel powder suspensions: an extension of the YODEL (yield stress model)", *J. Am. Ceram. Soc.* **90**(4), 1038-1044, 2008.
[4] Kjeldsen A. M., Flatt R. J., Bergström L., "Relating the molecular structure of comb-type superplasticizers to the compression rheology of MgO suspensions", *Cem. Concr. Res.* **36**, 1231-1239, 2006.

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Colloidal gel micromechanics and microrheology

The micromanipulation and dynametrical capabilities of laser tweezers provide an ability to probe the mechanics, interactions and microrheology of colloidal materials on nanometer to micrometer lengthscales. I will present our work to study the mechanical properties and microrheology of particulate gels. Our approach focuses on the micromechanics of aggregates that mimic the stress-bearing backbone in gels. Using time-shared optical traps, backbone mimics are directly assembled in salt solutions into precisely-controlled geometries. The aggregate bending rigidity is then measured. Aggregates behave elastically up to a critical bending moment, after which they exhibit small stick-slip rearrangements. The bending rigidity is found to be sensitive to the particle surface chemistry, ionic species and ionic strength. The bending rigidity between individual particles agrees with the JKR model of particle adhesion, providing a direct link between the micromechanics and the interfacial adhesion energy of the particles. Overall, these experiments enable us to bridge macroscopic rheology of colloidal gels to the underlying microstructural response. Furthermore, the new insight we have gained provides useful strategies for controlling gel behavior by manipulating the nanoscale near-contact interactions between Brownian particles.

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Key roles of hydrodynamic interactions in colloidal gelation

Colloidal gelation is caused by the formation of a percolated network of colloidal particles suspended in a liquid. Thus far the major transport process leading to gelation has been believed to be the Brownian diffusion of particles. Contrary to this common belief, we reveal by numerical simulations that many-body hydrodynamic interactions between colloidal particles also play an essential role in gelation: They significantly promote gelation, or lower the colloid volume fraction threshold for percolation, as compared to their absence. We find that the incompressible nature of a liquid component and the resulting self-organization of hydrodynamic flow with a transverse (rotational) character are responsible for this enhancement of network-forming ability. Our simulation method of colloidal suspensions will be explained in detail. This method enables us to fully take the interparticle hydrodynamic interactions into account.

[1] A.Furukawa and H.Tanaka, *Phys. Rev. Lett.* 104, 245702 (2010).

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The stakes of flocculation / deflocculation in the industry of building materials.

Mortars and concretes are typically non colloidal partially flocculated media. Admixtures are usually used to counteract the agglomeration. Now, (de)flocculation may be a key lever for several operations in this industry. 3 of them will be considered here.

The 1st one is the initial mixing stage. Both the extent of the deflocculation and its kinetics have to be controlled then. Indeed, the deflocculation extent will pilot the end user properties: the fluidity of the mix at short term and the mechanical strength at longer age. The kinetics of this deflocculation must also be optimized to increase the productivity. All of this is the result of a complex interplay between the deflocculating admixture, the process and the mix design.

The 2nd operation is the placing of these materials in low shear conditions. The yield stress is then the relevant parameter, and it varies with time because of the hydraulic reactivity. Deflocculation extent is thus a key lever (even though not the only one) to increase the fluidity and ease the placing. Self-Consolidating Concretes are the leading products in this respect. With these optimally deflocculated mixes, segregation becomes nevertheless an issue to address.

The 3rd operation is the placing at higher shear rates. The viscosity is then concerned. The way to account for a partial flocculation at this stage is then less clear. This is still more true when complex phenomena as shear-thickening come into play.

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Simulating the behaviour of fresh concrete using Distinct Element Method

This contribution describes a numerical approach based on the Distinct Element Method (DEM) as a means of fresh concrete simulation during its different working processes. First, a rheological model for concrete in a fresh state as well as its implementation into a DEM code are presented. An extensive study follows to investigate the effect of various model parameters on the results of the numerical simulation of the slump test. The calculation results are discussed with regard to the correct choice of values for the model parameters as required for a realistic simulation of specific material behaviour. In order to verify the model, subsequently, the J-Ring and the L-Box tests are simulated using the same set of model parameters as derived from the simulation of slump tests. The numerical results agree well with the experimental findings. Finally, an algorithm to derive the model parameters connected to yield stress according to the Bingham model is presented.

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Structure and flow properties of colloidal suspensions: Combination of *in-situ* scattering and rheometric techniques

Establishment of relationships between the rheological behavior and the microstructure of colloidal suspensions is of vital importance for controlling the industrial processes in which they are involved. Under the effect of shear flow, extensional flow or pressure conditions, the colloidal suspensions can exhibit several complex structural organizations (aggregations, orientations, flocculation, phase changes) which have a strong influence on their time-dependent rheological properties (yield stress, viscosity, viscoelastic moduli). The small-angle neutron or x-ray scattering (SANS, SAXS) as well as static light scattering (SLS) are well established techniques to probe these structural organizations and interactions from the length scales of the elementary particles (a few nanometer) to the lengths scales of the complex organizations (several micrometers). Simultaneous rheological and scattering measurements have been performed, thanks to the development of various specific shear-flow cells or filtration cells. The structure at mesoscopic length scale has been linked to the macroscopic mechanical behavior on several colloidal systems composed of aqueous anisotropic colloidal clays, stearyl grafted silica suspended in n-dodecane or casein micelles suspensions. The deduced aggregation, concentration and orientation mechanisms of these systems are presented under several controlled physicochemical conditions (pH, ionic strength, peptizer content).

[1] Pignon, F., Magnin, A., Piau, J.M., Cabane, B., Lindner, P. and Diat, O., "A yield stress thixotropic clay suspension: investigations of structure by light, neutron and x-ray scattering", Physical Review E, **56**, 3281-3289, 1997.
[2] Pignon, F., Magnin, A. and Piau, J.M., "Thixotropic behavior of clay dispersions: combinations of scattering and rheometric techniques", J. Rheol., **42**, 1349-1373, 1998.
[3] Narayanan T., Sztucki M., Belina G. and Pignon F., "Microstructure and rheology near an attractive colloidal glass transition", *Phys. Rev. Lett*, **96**, 258301, 2006.
[4] Pignon F., Belina G., Narayanan T., Paubel X., Magnin A. and Gésan-Guiziou G.," Structure and rheological behavior of casein micelle suspensions during ultrafiltration process", *The Journal of Chemical Physics*, **121**(16) 8138-8146, 2004.
[5] David C., Pignon F., Narayanan T., Sztucki M., Gésan-Guiziou G. and Magnin A., "Spatial and temporal in-situ evolution of concentration profile during casein micelle ultrafiltration probed by SAXS", *Langmuir*, **24**, 4523-4529, 2008.

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Characterization of dilute flocculated suspensions by means of MR-relaxation

Magnetic Resonance relaxation is a common technique to characterize saturated porous systems, or particle concentrations at the local scale in homogeneous suspensions. It relies on the measurement of MR relaxation times of the embedded fluid. The usual interpretation frame is that of Brownstein and Tarr. It relies either on a closed porosity and/or isolated pore assumption for porous systems, or on an assumption of fast diffusion of the suspending fluid between particles in the case of a suspension.

The use of MR relaxation for the characterization of dilute flocculated water suspensions raises new issues :

- Signal detection: signal originating from the inside of flocs represents only a minor fraction of the overall water signal.
- Data interpretation: flocs have an open, fractal-like porosity, compromising a straightforward use of Brownstein & Tarr results. Their self-organized structure nearly spans up to the length scale of 100 micrometer, and the fast diffusion assumption breaks down.

In this talk, we first tackle the problem of MR relaxation in open fractal systems by means of numerical simulation in 2D model structures. This study suggests an adaptation of Brownstein & Tarr results to such systems. It is shown that in some circumstances, a power-law decay may be observed in the time domain, directly connected to some fractal floc dimension. We also present a newly developed methodology to separate the tiny MR-signal of flocs, and that of the suspending fluid. Examples will be taken from a recent study on flocculated TiO_2 suspensions.

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Numerical simulations of adhesive, non-Brownian particles

Some recent numerical simulation results on assemblies of adhesive non-Brownian particles, both in quasistatic conditions and in steady shear flow, are reviewed, with special emphasis on the differences with cohesionless systems and on the influence of the micromechanical model ingredients on the macroscopic behaviour (e.g., plasticity index in static compression, effective friction in steady shear flow). Control parameters are identified in dimensionless form, among which the reduced pressure, assessing the relative importance of confining and adhesive forces, and sliding and rolling friction coefficients, the effects of which are enhanced in cohesive assemblies, are especially important. The relevance of a fractal blob model is discussed, for elastic or plastic response of aggregates, as well as other simple prediction schemes (e.g., the Rumpf formula for tensile strength of cohesive powders). Some comparisons are given with laboratory measurements on cohesive powders. Perpectives in future numerical works are suggested.

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Confocal microscopy: 3D Real-space observation of colloidal flocculation

Confocal microscopy is an invaluable tool in soft matter and material science to image the structure and dynamics of matter at the (sub-) micron scale. In this talk, I will show how the three-dimensional imaging capability of confocal microscopy can be applied to study colloidal flocculation at the single-particle scale. Using new temperature-sensitive systems, we quench the colloidal system into states of increasing particle attraction, and we investigate the aggregation of particles directly in real-space. Our observations show the formation of fractal aggregates with fractal dimension that varies continuously with attractive strength.

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Flocculation of cementitious materials: modelling and mix design rules

Concrete is a multiscale material with particle size ranging from centimeters down to hundreds of nanometers. The stability and self placing properties of modern concretes are strongly linked with the yield stress and the viscosity of the paste. The flocculation level of the paste affects directly these parameters. It can be monitored by using admixtures, but it is also sensitive to the shear stress applied on the suspension, and its history. Therefore mixing and pouring conditions must be considered. The prediction of yield stress and viscosity remains very difficult with industrial material and processes. Understanding better the structure of the flocs is a necessary step to improve modeling and therefore the way to optimize concrete mix design at the end. A characterization of the size of the flocs in dynamics conditions would be of great interest. The optimization of the packing density of the particles is a key rule to optimize the mix design of a concrete. We investigated the critical conditions under which the packing effect becomes not effective, in static and dynamic conditions. It gives some indirect information on the size of the flocs under shearing. Taking into account chemical and mechanical deflocculation, a first attempt to predict the yield stress and viscosity of industrial mixes is proposed.

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Flow induced changes in the microstructure of flocculated suspensions: comparing 2D with 3D

The flow-induced changes in the microstructure of flocculated suspensions are to a large extent responsible for the complex rheological properties and the thixotropic nature of these systems. Experiments on model two-dimensional suspensions enable us to explore the changes in the microstructure with excellent spatial and temporal resolution, for a wide range of concentrations and for different flow types. However, it is not clear to what extent the results for 2D systems can be carried over to their 3D counterparts. In the present work, we will compare the results obtained by video microscopy on 2D systems to both literature results and high resolution flow SAXS studies of flocculated suspensions in 3D.