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Author(s):
Zhao, Yaqi; Hlobil, Michal; Kammer, David S.

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Modelling of the Flocculated Polydisperse Microstructure of Fresh Cement Paste

Y.Q, Zhao[1*], M. Hlobil[2], and D.S. Kammer[3]

[1] *ETH Zürich, Zürich, Switzerland*
Email: zhaoya@student.ethz.ch
[2] *ETH Zürich, Zürich, Switzerland*
Email: michal.hlobil@ifb.baug.ethz.ch
[3] *ETH Zürich, Zürich, Switzerland*
Email: dkammer@ethz.ch

ABSTRACT

Granular materials present in nature are commonly polydisperse, featuring an inconsistent grain size distribution. This characteristic directly affects particle packing, and consequently influences attributes such as maximal packing fraction, bulk density, rheology, and derived properties. For cement, this has direct consequences as polydispersity, among other factors, influences considerably the rheology and concurrent microstructural build-up in the fresh paste. Previous studies on polydispersity in granular systems considered only mechanical contact forces among particles, but omitted non-contact colloidal interactions, which dominate the microstructure in cement paste. Therein, the flocculation of particles, caused by these interactions, creates a percolated network, which is strongly affected by the polydispersity, but is not fully understood yet. In this paper, we show how flocculation affects the microstructural build-up and the resulting rheological and mechanical properties of fresh cement paste. By accounting for flocculation in our numerical modelling, we can produce statistically representative microstructures, which maintain physically consistent rheological properties. We observed that the mechanical properties of percolated particle networks due to flocculation depend on their packing fraction and size distribution. A higher packing ratio offers a higher shear resistance of the fresh paste. Accounting for polydispersity in flocculated build-up does influence the shear resistance, as opposed to a granular system with only contact forces, where the shear strength is independent of grain size span. Our model provides insight into the micro-mechanical origin of the rheology of fresh cement paste, contributing to a better balance between workability and buildability in early stage, and to a better understanding reignited for the design of new concrete mixtures for digital fabrication.

KEYWORDS: *Polydispersity, flocculation, fresh cement paste, colloidal interaction, granular system.*

1. Introduction

Printable concrete shows its strong potential in construction with two main advantages: free-form architecture and precision material placement, see Wangler et al (2019). As cement is the governing material of concrete in the hardening process, optimization between workability and early shear strength of cement paste is of great interest. It was observed in experiments that the particle size distribution of cement grains and water-to-cement ratio are the two major factors influencing the rheological properties of cement paste, but the underlying mechanisms have not been fully understood yet.

In industry, raw cement has a very broad particle size span, usually from sub-micron to 100 microns, with different particle size distributions depending on their producers. As the size of cement particle is on a scale of microns, there are not only contact forces but also non-contact colloidal interactions between cement particles to be considered. In close vicinity, cement particles interact via van der Waals forces, see Flatt (2004), and electrostatic forces that result from the presence of adsorbed ions at the surface of the particles, see Flatt and Bowen (2003). Due to these colloidal interactions, a phenomenon called flocculation will happen. It is a physical process of agglomerating fine particles to form large flocs. For dense highly-polydispersed colloidal suspensions such as cement slurry, the flocculation process will finally build up a percolated microstructure that can resist external forces.

2. Numerical Model

We consider an equilibrium state of a particle-based microstructure. The system of interest is built by means of the molecular statics methods. We use a particle size distribution (PSD) obtained from the measurement of a real ordinary Portland cement (OPC) powder. The PSD is re-discretized into 8 size bins, trimming off the particle sizes that are smaller than 1 microns, which occupies a small volume fraction but a giant number of particles, and those larger than 50 microns, which can lead to high inhomogeneity in force transmissions in a small simulation box, see Cantor et al (2018). Particles are assumed to be spherical. Simulations are conducted with solid volume fractions (p) 0.45, 0.55, and 0.65. For the given solid volume fraction and PSD, the number of particles for each size is calculated.

For OPC, like other colloidal particles, the main interaction forces between particles consists of van-der-Waal force and electrostatic force, see Flatt and Bowen (2006):

$$\mathrm{F_{vdw}} \approx \frac{1}{12}\mathrm{A_h}\frac{\bar{r}}{h^2}, \tag{1}$$

$$\mathrm{F_{es}} \approx -2\pi\epsilon\epsilon_0\psi^2\frac{\kappa e^{-\kappa(h-2L_e)}}{(1+e^{-\kappa(h-2L_e)})}\bar{r}, \tag{2}$$

where h is the separation distance between particles, $\bar{r}$ is the harmonic average of the radii $\bar{r} = 2r_1r_2/(r_1+r_2)$ of the two particles of size $\mathrm{r_1}$ and $\mathrm{r_2}$. According to DLVO theory, the equilibrium position of each particle pair varies with particle sizes and their electrostatic properties. To simplify the interaction potential function in our simulations, we use the shifted Lennard-Jones (LJ) potential for the OPC interaction. The well of the LJ potential is set at a center-to-center distance equal to the sum of the radii of the two particles and a constant tiny separation distance. The depth of the potential well is also scaled proportional to the harmonic mean of the radii of the pair of particles $\bar{r}$. The potential function has the following form:

$$\mathrm{U} = 4\epsilon\left[\left(\frac{\sigma}{r-\Delta}\right)^{12} - \left(\frac{\sigma}{r-\Delta}\right)^{6}\right] \tag{3}$$

where Δ is the shift distance, namely the sum of the radii of the particle pair and the separation distance at equilibrium.

We randomly distribute particles into a cubic simulation box with length 200 microns. The potential energy of samples is minimized to eliminate the overlapping of particles. This process is further repeated under a given tiny random displacement, until the potential energy of the system remains constant. This approach leads to an initial configuration with a stable particle network.

Based on this energy-minimized microstructure, simple shear tests are applied on the samples. The simulation box has periodic boundary conditions in *x,y,z* directions. The cubic simulation box is tilted in *xz* plane with a constant increment of 0.005% of the length of the simulation box. Each time the box shape is changed, particle positions are remapped to the new box via an affine transformation to match the box deformation. The remapped particle positions are generally out of balance. Thus, each box deformation and its resulting remapping require an energy minimization. With the energy-minimized stable configuration, we can measure the shear force that is needed to remain this deformation.

To study the effect of solid volume fraction on the mechanical behavior of the flocculated particle network, we conduct a parameter. To investigate the effect of solid volume fraction, we study the development of the initial-stage shear modulus with respect to the increasing solid volume fraction. The analysis is further extended to the relationship between the shear modulus and the connectivity of particle network.

3. Results and discussion

In all our simulations, the flocculation process eliminates the floating particles, and turns the random packed configuration into a percolated microstructure, as shown in Fig 1.

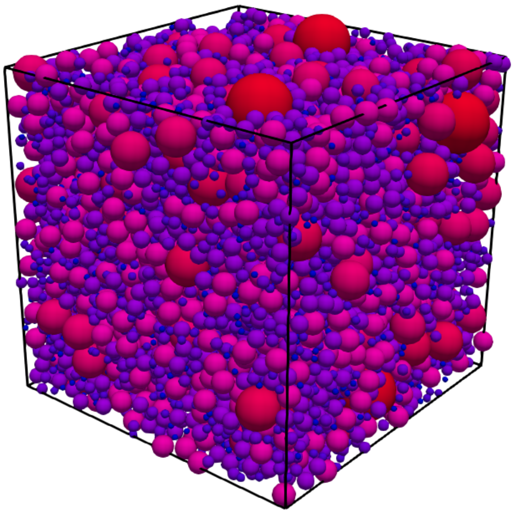

Figure 1 Flocculated microstructure of cement suspension with p = 0.55. The color indicates the size of particles: smaller particles tend to blue colors while larger particles tend to red colors.

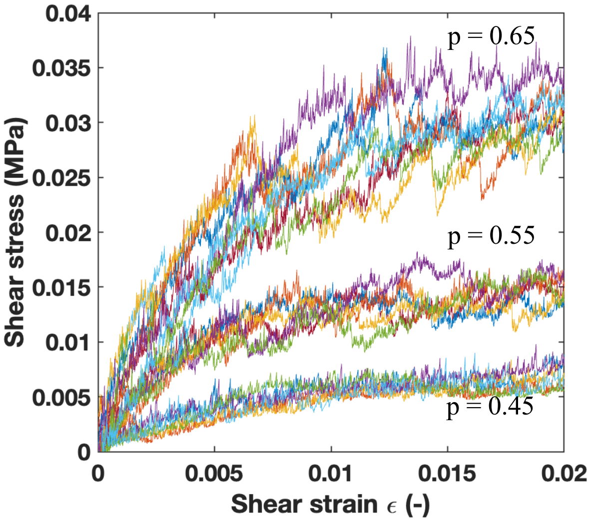

Figure 2 Shear stress- strain curves for 3 simulation groups of 6 runs, each with p = 0.45, 0.55, 0.65.

The static stress-strain curves are directly affected by their solid volume fractions (see Fig 2). We directly observe the stress/strain slope, the shear modulus, increases with the solid volume fraction. In other words, a denser particle microstructure has a better resistance against external forces, which is a behaviour we expected.

The curves in Fig 3(a) are simulation results with p = 0.55 taken from Fig 2. We observe that, in the very first stages of the shearing test, the shear stress increases very rapidly with the shear strain. Then, at a critical shear strain, the curve slope drops abruptly, keeping an increasing tendency with the shear strain. This curve qualitatively corresponds to the reference experimental results of a Vane test on a cement paste with a water to cement ratio of 0.4 (see Fig 3(b)), that the shear stress-strain curve also consists of two regimes: the first is with a steep slope while the second is flatter, see Roussel et al (2012).

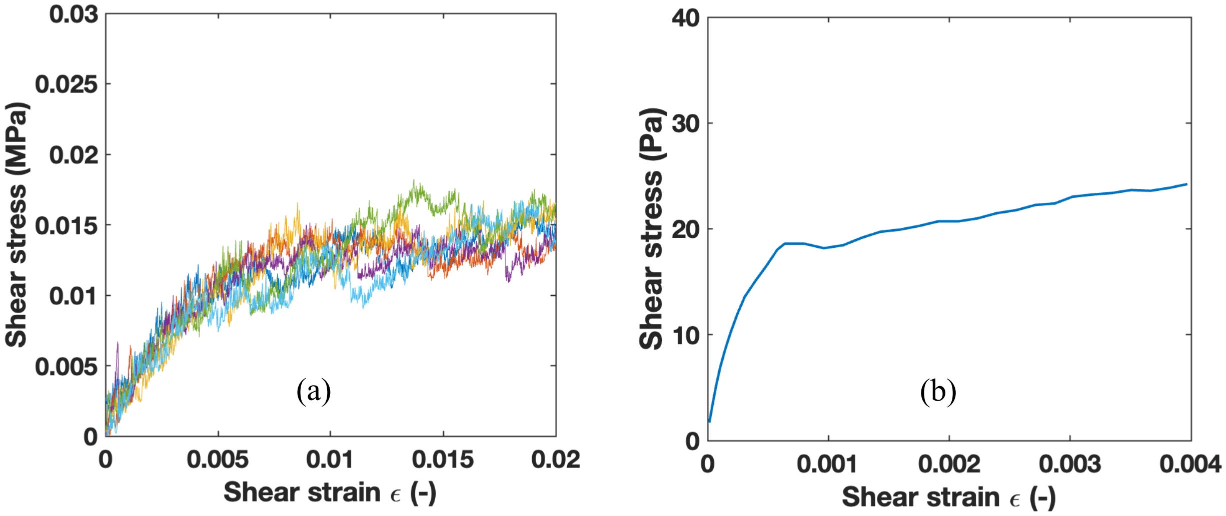

Figure 2 Evolution of shear stress σ as a function of the shear strain γ. (a) Shear stress-strain curves from simulations with 6 runs of $p = 0.55$. (b) Shear stress-strain curves from experiment during a Vane test on a cement paste with a water to cement ratio of 0.4, extracted from (Roussel, N., Ovarlez, G., Garrault, S., & Brumaud, C. (2012)) Fig. 2(b).

4. Conclusions

In this paper, we simulated the shear loading process on the flocculated microstructural build-up of fresh cement paste, to investigate its rheological and mechanical properties. We presented a systematic analysis of the influence of solid volume fraction on the shear modulus of the fresh cement paste that is composed of spherical particles. It is shown that the shear modulus increases with increasing solid volume fraction, which agrees with our common sense. Our analysis also remarks that in the very first stages of the shearing test, the stress/strain curves clearly have two regimes: initially, it increases steeply, then it flattens. This behavior qualitatively agrees with a reference experimental result of fresh cement paste.

Acknowledgements

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