

Origins of Shear Thinning to Shear Thickening Transition in Cement Pastes

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Introduction

Cement is the most abundantly used man made material on the planet, accounting for a 40 Billion USD market in the US alone [1]. Widespread use of cement includes applications in oil well casings, roadways, buildings, and even as a bone graft technology for the treatment of osteoporosis[2,3]. As cements role as the foundation of our infrastructure broadens, demand for higher strength and increased longevity will become more important.

The strength of concretes made from cement is directly related to the amount of water present in cement slurries. While, low water content leads to stronger concretes, these concretes may not be flowable or easily formed. Over the past several decades the advent of super plasticizers has greatly enhanced the flowability of cements with low water content. Despite such advances, the rheology of cement slurries is still poorly understood[3]. In this work we will bring to light some of the origins of the non-Newtonian behavior of cement pastes through molecular dynamics simulations.

Model

Cement slurries, like granular materials, are high in solids volume fraction (0.3-0.5). Yet, the particles are small enough (1-100 μ m) to experience interparticle potentials characteristic of colloids. Peclet numbers in these flows are also large, O(10⁵), i.e. no Brownian motion. Extension of relatively well-studied granular systems looks to be a natural starting point for research. Granules are often modeled as spherical particles with a linear spring-

dashpot contact law in the normal direction, which allows a constant coefficient of restitution, e_{LSD} [4].

As a model system we first considered a binary system of two colliding inelastic particles including a van der Waals adhesion interaction [5]. All results for the kinetic behavior of the system can be collapsed using the nondimensional parameter $Ha = 4AR / \pi\rho D^3 d_0 v_i^2$, where A , ρ , D , d_0 and v_i are the Hamaker constant, particle density, diameter, interatomic distance, and relative velocity, respectively. The system exhibits a critical value of Ha , under which no particles can escape the adhesive potential well and become stuck together.

$$Ha_{crit} = \frac{e_{LSD}^2}{1 - e_{LSD}^2} \quad (1.1)$$

Previously, Campbell et al. and many others have studied the homogeneous shear of inelastic in great detail and produced regime maps for typical systems[6]. For the different regimes present in these flows the shear stress σ_{xy} scales differently with shear rate $\dot{\gamma}$; quasi-static regime $\sigma_{xy} \neq f(\dot{\gamma})$, inertial regime $\sigma_{xy} = f(\dot{\gamma}^2)$, and an intermediate regime $\sigma_{xy} = f(\dot{\gamma}^{(0,2)})$. Regime transitions are particularly sensitive to changes in particle friction and solid volume fraction, ϕ_s . However, regime boundaries are insensitive to changes in shear rate over many magnitudes of variation. Cement slurries and colloids behave in a markedly different manner, exhibiting shear rate dependent rheology[3].

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Results

Using our modified version of the molecular dynamics code LAMMPS, homogeneous shear flow of dry adhesive particles was simulated. We should note that the normal velocity component between collisions in shear flow can be approximated by for non-flocculated cases as $v_i = \dot{\gamma}D$, i.e. all kinetic fluctuations arise from shear.

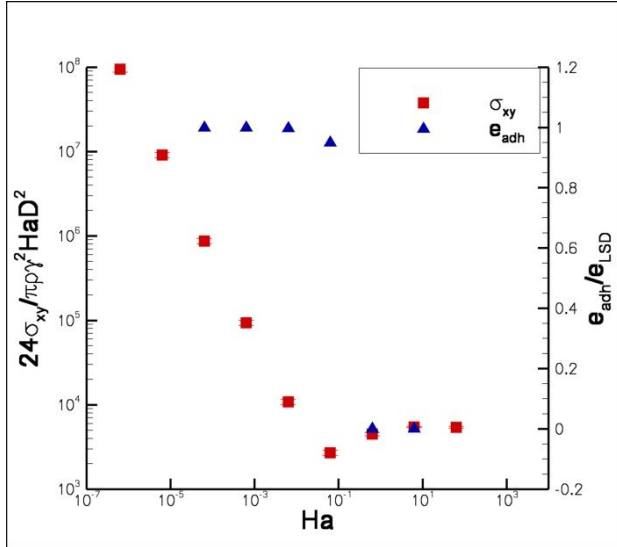


Figure 1: Comparison of shear results displayed alongside binary predictions, $\phi_s = 0.55$ and $e_{LSD} = 0.875$.

Fig. 1 displays several interesting behaviors of the rheology of adhesive particles, namely that the rheology is rate dependent and the transition between inertial scaling and quasi-static-like scaling occurs at the critical value of Ha . Below the critical value of Ha , agglomeration can greatly affect particle microstructure forming in this case a gel-like state. In fact, we have observed larger values for the pair correlation function at contact in the sub-critical regime implying agglomeration. Agglomeration in this system is analogous to a solid-liquid phase transition, in which particles no longer have enough energy to remain free to move and instead settle into the primary minimum at contact.

In Fig. 2, the nondimensional viscosity is plotted as a function of nondimensional shear rate. Included in the plot is the behavior of a suspension of Portland cement in a rotating vane viscometer, material properties were obtained via atomic force microscopy[7,8]. Note that in general one should not expect a quantitative comparison; the simple model is meant to display qualitatively similar behavior.

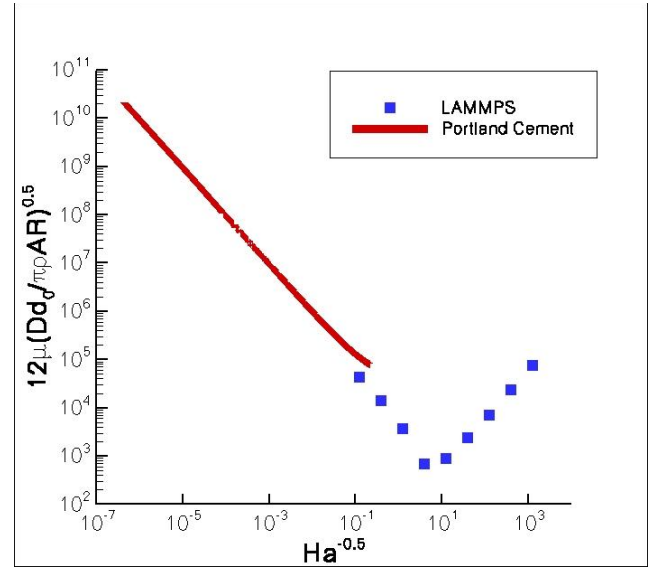


Figure 2: The nondimensional viscosity is plotted against nondimensional shear rate for the same system as in Fig. 1. Viscometer data for a Portland cement slurry sheared up to 100 s^{-1} is plotted as well.

These results can tell us a great deal about the behavior of aqueous slurries. Firstly, there are many reasons this transition would be of interest in practical applications: it serves as to identify the optimal flow rate in pumping applications and in many cases it is desirable to have a dispersed solid phase. We have shown that in order to understand this transition, a good understanding of the interaction between the attractive and repulsive potentials and energy dissipation is necessary. Furthermore, a better understanding is needed to extend results from the simple homogeneous shear problem to non-viscometric flows.

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