

Effects of Particle Hardness on Shear Thickening Colloidal Suspension Rheology

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Abstract. Concentrated suspensions that reversibly shear thicken have also been reported to show a second shear-thinning regime at high shear rates and stresses beyond shear-thickening. We hypothesize that this behavior is due to the elastic particle deformation driven by the high lubrication forces acting between the particles in the hydroclusters. This limiting behavior is described here by an elastohydrodynamic model which predicts a limiting viscosity, $\eta \propto \dot{\gamma}^{-1/2}$.

Semi-quantitative agreement is found by assuming Hertzian contact between the particles and estimating the particle shear modulus. High strain rate compression-shear split Hopkinson pressure bar (CS-SHPB) experiments are performed on shear thickening silica dispersions to test for this limiting behavior.

Keywords: Suspension rheology, elastohydrodynamics, shear thickening

INTRODUCTION

Concentrated suspensions undergo a wide range of varied flow behavior including shear-thinning and shear-thickening; example rheology is seen as Fig. 1. These concentrated suspensions typically undergo shear thinning at lower shear rates or stresses and shear thickening at higher shear rates or stresses, marked by a critical shear rate or stress for shear thickening[1, 2]. One interesting phenomenon occasionally reported in the literature [3] but not often investigated is that of a second shear-thinning regime measured at stresses above the shear thickened state. This second shear-thinning regime has sometimes been attributed to wall slip. However, we propose that this limiting behavior is a real suspension property dictated by the particle's mechanical properties. This hypothesis is tested by combining models for the hydrocluster theory of shear thickening with an elastohydrodynamic model for the lubrication forces acting between particles in the hydrocluster to develop a model for this limiting behavior, which is compared to data.

ELASTOHYDRODYNAMIC MODEL

We propose that at high stresses, two particles will elastically deform when they come into close contact, with a thin fluid layer between them. We treat this phenomenon as an elastohydrodynamic deformation with Hertzian contact, similar to previous models of pastes that treat the deformation of a single particle near a wall[4, 5]. Meeker et al.[4] argues that the stress resulting from the lubrication forces acting between elastically deformable particles (with Hertzian contacts) scales as:

$$\sigma \sim \left(\frac{\eta_s V G_0}{R} \right)^{1/2} \left(\frac{G_0}{G_p} \right)^{1/6}, \quad (1)$$

where σ is the stress, η_s is the solvent viscosity, V is the plate velocity, R is the plate radius, G_0 is the particle shear modulus, and G_p is the particle elastic modulus. If we assume the $(G_0/G_p)^{1/6} \propto O(1)$, the limiting scaling of the stress as a function of shear rate becomes:

$$\sigma \sim (V/R)^{1/2} (\eta_s G_0)^{1/2} = \dot{\gamma}^{1/2} (\eta_s G_0)^{1/2}, \quad (2)$$

which can also be written in terms of a limiting suspension viscosity, η , being power-law shear-thinning,

$$\eta \sim \dot{\gamma}^{-1/2} (\eta_s G_0)^{1/2}. \quad (3)$$

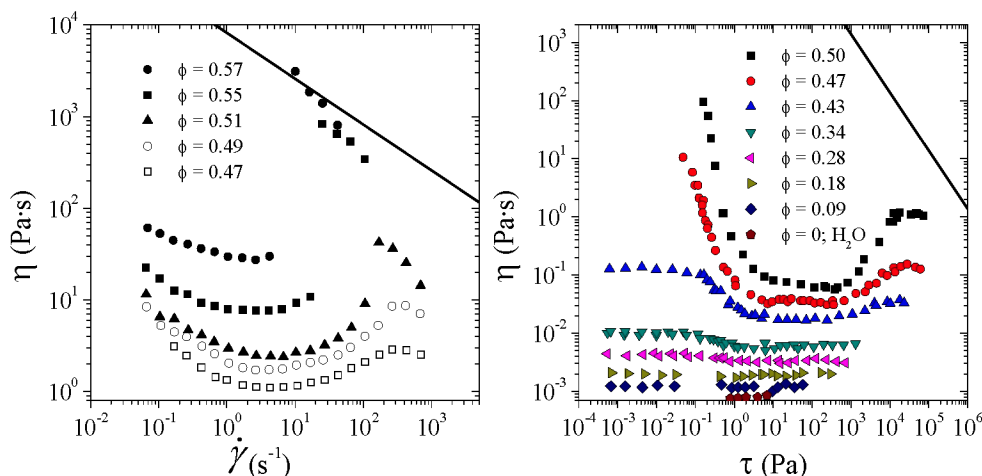


FIGURE 1. *Left*) Steady shear viscosity of 1.25 μm PVC particles in dioctyl phthalate (DOP) from Figure 4 of [3]. Line is Eq. 3 with $\eta_s=0.042$ Pa-s and $G_s=1.59$ GPa. *Right*) Steady shear rheology of poly(styrene/ethyl acrylate) spheres in water from [6]. Line is Eq. 3 with $\eta_s=1\times 10^{-3}$ Pa-s and $G_s=1.39$ GPa.

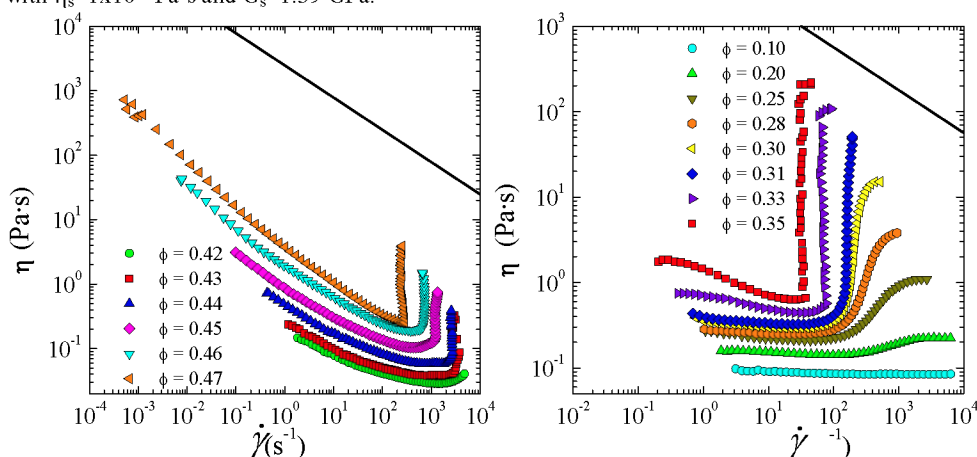


FIGURE 2. Concentrated suspensions of mineral particles. *Left*) Steady shear rheology of kaolin in water from [7]. Line is Eq. 3 with $\eta_s=1\times 10^{-3}$ Pa-s and $G_s=6$ GPa. *Right*) Steady shear rheology of precipitated calcium carbonate (CaCO_3) (PCC) in water from [8]. Line is Eq. 3 with $\eta_s=1\times 10^{-3}$ Pa-s and $G_s=32$ GPa. SEM micrographs of the particles can be seen in Figure 3.

SUPPORTING DATA

In Fig. 1, we compare the scaling theory derived above to a range of published data for poly(vinyl chloride) and poly(styrene/ethyl acrylate) polymer lattices [3, 6], which are normally treated as effective “hard spheres” in shear rheology. These systems both show a limiting behavior that is not a measurement artifact and is bounded by the elastohydrodynamic limiting theory presented above. It is important to note that the bulk shear moduli of the respective polymers are used in the calculation, which likely overestimates the actual particle shear moduli due to plasticization of the polymers as well as nanoscale surface effects.

Figure 2 shows the steady-shear rheology of two suspensions of harder mineral particles: a disc-like kaolin clay and a rod-like precipitated calcium carbonate (PCC)[7, 8]. The measured rheology for both dispersions does not exhibit the limiting behavior seen in the polymer particles (Fig. 1) within the range of rheometrically accessible stresses. The model predictions indicate that significantly higher stresses would be needed to probe this limiting behavior for the kaolin dispersion, whereas it is nearly achieved for the softer PCC dispersions, which is seen as a slight bend over at high stresses.

To test this theory further, we prepared model dispersions of relatively soft PMMA particles (diameter 1.05 μm , synthesis of [9]) particles in polyethylene glycol as well as harder silica nanoparticles[7]. Measurements for the polymer particles were performed on a TA Instruments AR-G2 with a 40mm 4 $^\circ$ Aluminum cone and Peltier plate at 25 $^\circ\text{C}$. Figure 3 shows the shear thickening rheology for these dispersions along with the predictions of the

elastohydrodynamic model. The shear-thickening and subsequent shear-thinning behavior is reversible, seen from the similar behavior of ascending and descending stress sweeps. The softer PMMA particles show evidence of a second shear thinning regime within the stresses attained. Tests with roughened plates and different geometries showed that the second shear thinning behavior for the PMMA dispersion is not wall slip and is indeed a property of the dispersion. The result is again bounded by the elastohydrodynamic model, which is expected to be an overestimate of the limiting viscosity due to the use of the bulk shear modulus of the PMMA particles which are likely plasticized due to the synthesis method. For the silica dispersions, however, the model predicts that the stresses attained are significantly lower than those required for significant particle elastic deformation. As seen, the data do not show any evidence of reaching this elastohydrodynamic limit. Further experiments are being performed to test this hypothesis further by both reaching higher stresses for the harder mineral and oxide particle dispersions, as well as attempting to measure the shear modulus of the particles.

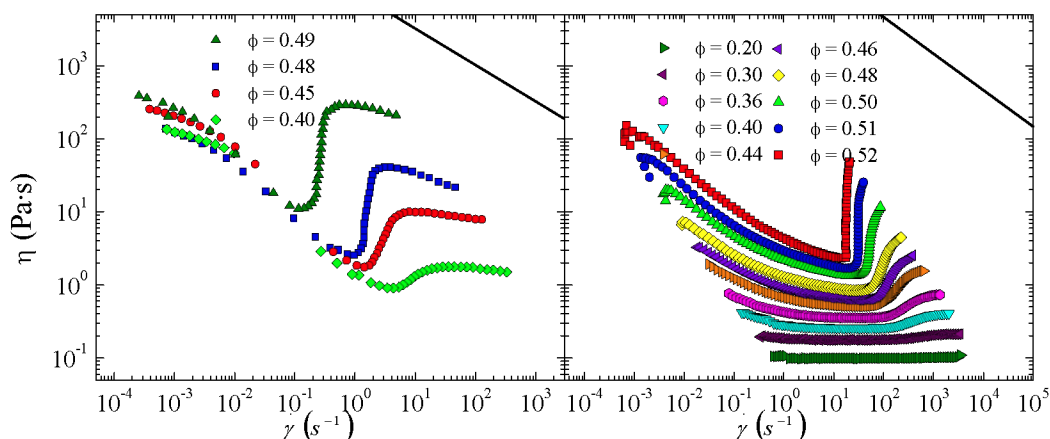


FIGURE 3. *Top Left)* Steady shear rheology of PMMA particles in PEG-200. Line is Eq. 3 with $\eta_s=0.049$ Pa-s and $G_s=2.14$ GPa. These particles were produced via the synthesis of [10], to a particle size of $1.05\mu\text{m}$. *Top Right)* Steady shear rheology of 450nm commercial SiO_2 in PEG-200 from [7]. Line is Eq. 3 with $\eta_s=0.049$ Pa-s and $G_s=44$ GPa.

CONCLUSIONS

The limiting behavior of shear thickening colloidal suspensions is proposed to be governed by elastohydrodynamic forces acting between particles comprising the stress-bearing hydroclusters. A simple model based on Hertzian contact forces and lubrication theory is adapted to estimate the limiting viscosity at high shear rates and stresses in the shear thickening regime. Shear thinning is predicted after shear thickening, and the effect is governed by the shear modulus of the particles. The model semi-quantitatively explains literature data for the high shear limiting viscosity of shear thickening dispersions of relatively soft, polymer lattices, as well as indicating that sufficient stresses are not achieved to observe this behavior in harder mineral dispersions. Experiments on model dispersions synthesized for testing the hypothesis show the same behavior and support the conclusion. Quantitative discrepancies are, in part, due to overestimation of the actual particle shear moduli by using the known, bulk properties of the materials.

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