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MICRORHEOLOGICAL OBSERVATIONS ON THE ONSET OF NON-NEWTONIAN BEHAVIOR IN SUSPENSIONS

KEYWORDS: falling-ball viscometry, concentrated suspensions, geometry effects, continuum behavior, microstructure

ABSTRACT: As the volume fraction of solids increases above about 0.30, suspensions of non-Brownian, uniform spheres in Newtonian liquids begin to exhibit shear-thinning, normal stresses, and other non-Newtonian behavior. Here, we report on observations obtained from falling-ball and capillary rheometry at these high volume fractions. Specifically, we find that measured viscosity values are dependent on the size-scale of the viscometer (cylinder diameter, D, and falling-ball diameter, d) relative to the diameter of the suspended spheres, d_s. We report the dependence of the measured viscosity on the ratios d/d_s, D/d, and D/d_s, as well as critical values of these ratios above which the apparent viscosity is constant.

REFERENCE: MONDY, L. A., GRAHAM, A. L., AND GOTTLIEB, M., Microrheological observations on the onset of non-Newtonian behavior in suspensions.
Proc. Xth Internat. Congr. Rheol., 1988, Sydney, Aug. 14-19.

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INTRODUCTION

Dilute and moderately concentrated suspensions in Newtonian fluids have been observed to behave as Newtonian continua [1,2]. However, as the concentration of solids increases, the rheological behavior of suspensions becomes more complex. Eventually, at the extreme of high concentration, a suspension will not flow at all. Our intent in this paper is to report on a variety of physical phenomena which occur in model suspensions of large, uniform spheres in the transition region between concentrations exhibiting simple Newtonian behavior and those at which a solid, packed bed is formed.

It is in this transition region that macroscopic measurements of normal stresses, elastic modulus, and other non-Newtonian behavior have been reported. These non-Newtonian modes of behavior first appear at moderate concentrations of particles and increase rapidly as the concentration of particles approach maximum packing [3]. An additional feature of data reported in the literature is the enormous scatter in viscosity measurements in the transition region, even in carefully designed, well characterized experiments [4,5,6]. This scatter is largely attributable to induced microstructure in the suspensions, and it occurs even in the absence of colloidal (nonhydrodynamic) forces, such as Brownian, electrical, and London-van der Waals forces [3].

In this paper we focus on the microstructure of the suspensions, formed at high concentrations, and show that it can be dictated by the relative dimensions of the suspended spheres and the measuring apparatus, as well as the flow field. Specifically, we find that falling-ball and capillary experiments lead to measured viscosity values in the transition region that are dependent on the size-scale of the viscometer (cylinder diameter, D, and falling-ball diameter, d) relative to the diameter of the suspended spheres, d_s. We investigate three regimes determined by the ratios d/d_s, D/d, and D/d_s. We will report the dependence of the measured viscosity on these geometric ratios, as well as critical values of these ratios, above which the apparent viscosity is constant.

EXPERIMENTAL

Falling-ball and capillary viscometry were used to measure the viscosity of suspensions of solids volume fractions (ϕ) ranging from 0.05 to 0.55. The table summarizes the experiments performed. Details of the falling-ball experimental technique and error analyses can be found elsewhere [2,7]; therefore, we will only briefly summarize the suspensions and procedure here.

The suspensions were of uniform polymethyl methacrylate spheres in one of two Newtonian oil mixtures, with viscosity of 12 Pa·s or 28 Pa·s, respectively. The suspended spheres were chosen to be one of three sizes: diameters equal to 0.32, 0.64, or 1.27 cm. The particles and liquid had the same density (1.1818 g/cm^3) at 20.0 °C. Any settling or rising of the suspended particles, due to slight variations in density, occurred over a time scale several orders of magnitude smaller than the time scale of the experiments. The suspensions were tested in a variety of containing cylinders, ranging from 3.8 to 14.6 cm in diameter. All cylinders were 50 cm high. Also, a variety of falling balls were used, ranging in diameter from 0.06 to 3.81 cm. Reynolds numbers, based on the diameter of the ball, ranged from 1.5×10^{-4} to 1.5×10^{-1}.

The suspensions and balls were placed in an insulated water tank, controlled by a constant temperature circulator to ±0.5°C. A guide tube at the top of the cylinder was used to ensure that the balls were dropped along the centerline of the cylinder. Before each ball was dropped, the suspension was stirred so that a new configuration of suspended spheres was tested. This mixing was accomplished by briskly raising, lowering, and randomly twisting a long brass rod with a handle on the top and eight short prongs on the bottom.

The trajectory of each ball was recorded on video tape. With opaque suspensions, the ball was imaged using real-time radiography. Generally, 10 to 20 balls of each diameter were used. The number of balls to drop was determined as that number which would give an average value of viscosity that was statistically indistinguishable from a second set of data taken with an equal number of balls.

In capillary experiments, a suspension was placed in a large, straight cylinder with a removable bottom. The bottom would be removed abruptly, and the time for the liquid level to fall between two lines, etched at a known interval, would be measured. This time was then compared to that of the Newtonian suspending liquid. The straight tube design allowed us to know exactly the volume fraction of solids of the suspension and to avoid changes in concentration induced by the contractions present in standard capillary viscometers [8,9].

RESULTS

Dilute and moderately concentrated (ϕ <0.30) suspensions may be characterized in falling-ball experiments, on average, as Newtonian continua. Not only do they exhibit wall effects predicted for Newtonian liquids, they also exhibit the same relative viscosity as measured in viscometric flows (Figure 1). Furthermore, falling balls the same size or smaller than the suspended spheres experienced the same effective continuum, in the absence of wall effects, as the larger balls [2].

For $\phi \geq 0.30$, a change in mechanism is observed, and the measured viscosity depends on the scale of the falling-ball viscometer relative to the size of the suspended spheres. For example, in highly concentrated suspensions, the measured viscosity decreases rapidly and linearly as the ratio d/d_s goes below 0.75. Above that ratio, the relative viscosity is constant; we will call this the "plateau viscosity" $\mu_{plateau}$. When plotted in Figure 2 as the measured specific viscosity of the suspension ($\mu_r - 1$) normalized by the specific viscosity seen with the larger-sized balls ($\mu_{plateau} - 1$), the data for three suspensions, with different concentrations and suspended sphere sizes, superimpose. This shows that a similar critical ball size exists, at approximately $d/d_s = 0.7$. As will be discussed in another paper [10], there exist some question as to whether the relative viscosity limits to one or $1 + 5/2\phi$ as d/d_s approaches zero.

Another effect seen at higher concentrations is an increase in wall effects over those predicted for a pure, Newtonian liquid [2]. These additional wall effects are not seen for the suspensions of ϕ=0.20. At ϕ=0.30, we measured slight increases in the relative viscosity for the largest falling balls. At higher solids volume fraction, ϕ equal to 0.45, 0.50, and 0.55, we measured a marked increase in the magnitude of the wall effects as the ratio D/d becomes less than 10. These data do not appear to correlate with d/d_s.

The measured viscosity of a highly concentrated suspension ($\phi > 0.45$) also exhibits a dramatic dependence on the ratio D/d_s, as is shown in Figure 3. As D/d_s becomes less than four, the measured viscosity of the suspension increases towards infinity (if a ball on the order of the same size as the suspended particles would not settle through the suspension, we defined the falling-ball viscosity to be "infinity"). On the other hand, when D/d_s is above about 46, the measured viscosity is independent of the cylinder size and appears to be that measured in shear flows [5]. However, between these critical values ($4 < D/d_s < 46$), the apparent viscosity actually decreases. A similar viscosity minimization is seen in capillary measurements on suspensions of $\phi = 0.55$, also plotted in Figure 3. Viscosity minimization in capillary flow has been reported in suspensions of lower concentrations, as well [8,9,11,12].

Finally, a dramatic effect is seen when the microstructure is rearranged by changing the stirring technique, especially at higher concentrations. In Figure 1, all data represented by solid triangles (▲) were taken with similar stirring procedures. It was felt that this stirring, outlined in the previous section, produced a homogeneous suspension. However, if the suspension was stirred so as to scrape the walls of the cylinder with a long, flat straightedge, the measured viscosity increased dramatically. This alternative stirring technique did not lead to inhomogeneities in the suspension which could be detected visually, directly or with radiographs. The dramatic dependence on the stirring technique is shown with the open triangles (△) in Figure 1. Note, however, that with consistent stirring, the viscosity measured using smaller values of D/d_s remained lower than that at $D/d_s = 46$. This is shown for $D/d_s = 12$ with the inverted triangles in Figure 1.

DISCUSSION

We have observed that falling ball viscometry can give a measurement of the viscosity of suspensions which agree with that measured in shear flows, subject to several geometric constraints. At high concentrations (generally $0.55 \geq \phi \geq 0.45$), d/d_s must be greater than about 0.7, D/d must be greater than about 10, and D/d_s must be greater than about 46. When above these critical ratios, the falling-ball viscometer gives results consistent with other measurements in the literature (Figure 1). Due to the dramatic increase in resistance as maximum packing is approached, extrapolation of these critical values to concentrations above those tested is of questionable validity. At lower concentrations (generally $\phi < 0.30$), such critical ratios, if they exist, are below the range of our experimental parameters.

Intuitively, we expect that as the falling ball becomes much larger than the suspended particles ($d \gg d_s$), the velocity of the ball would reflect a continuum-like behavior of the suspension. It seems remarkable that this behavior is seen with d approximately equal to d_s, even at high volume fractions of solids. However, as the concentration increases to about $\phi = 0.50$, very small balls ($d/d_s < 0.7$) feel less resistance from the suspension, as if they were slipping through the interstices without causing bulk deformation of the suspension. This decrease in apparent viscosity seen with very small balls is discussed in detail in another paper [10].

The next observation is the increased resistance to the fall of larger balls ($d/D > 0.1$). The magnitude and reproducibility of this increase cannot be explained by considering inertial effects or the possibility that the balls move off the centerline of the cylinder. One possible mechanism could be a local increase in concentration and "jamming" of the suspended particles resulting from the squeezing flow between the falling sphere and the containing walls. (In converging flow the particles will also "bridge" across the opening.) This effect does not seem to be a strong function of the size of the suspended spheres.

The changes in the measured viscosity, as the containing cylinder becomes smaller, provide additional insight into the microstructure of concentrated suspensions. It is not surprising that the falling-ball viscosity approaches infinity as the cylinder size approaches the suspended particle size. Particle packing in the constrained geometry simply prevents the downward motion of the ball. The viscosity minimization, that occurs when $4 < D/d_s < 46$, also may be the result of bridging or locked-in packing, which in turn causes an apparent slip condition at the ball boundary due to increased resistance to bulk deformation of the suspension.

The capillary viscosity reaches a local minimum and then increases with decreasing D/d_s, similar to the falling ball viscosity; however, further decreases in D/d_s lead to lower viscosities. This dependence is qualitatively similar, and quite possibly attributable, to the dependence of the maximum packing fraction of spheres in a cylinder on the same ratio D/d_s [13]. One can intuitively see that, near maximum packing, the suspension would not be free to deform as a homogeneous, one-phase fluid, but would form a structure which slips along the walls. Karnis, Goldsmith, and Mason have reported plug flow and apparent slip at the capillary wall boundaries developing in the same experiments in which they measured dramatic decreases in viscosity [12]. In our experiments, we observe a similar plug-like flow in the viscosity-minimization region, with suspended particles near the walls moving with approximately the centerline velocity.

That induced structure can affect the measured viscosity is dramatically demonstrated by the dependence of the measurements on the type of stirring. Stirring the suspension by scraping the walls of the container influences the local packing and/or the ordering of the suspended particles. By "local packing" we mean the volume fraction of solids in the vicinity of the path of the falling ball. At lower volume fractions, one could conceivably put a large fraction of the suspended particles in the path of the falling ball, dramatically increasing the local ϕ above the overall ϕ. However, at high concentrations there simply is not enough room to make such major changes. Nevertheless, at high ϕ, the viscosity changes rapidly with small changes in ϕ (Figure 1). It is likely that the ordering of the suspended spheres could be changed through stirring. This conjecture is supported by theoretical studies demonstrating that ordering affects the viscosity [14].

Our observations of highly concentrated suspensions of large spherical particles in Newtonian liquids lead to arguments that structure/ordering effects can be induced by the apparatus geometry or by stirring. Comparing our measurements with measurements of dynamic and shear viscosity, we see that at very high solids volume fraction, the measured viscosity can vary by almost an order of magnitude, depending on the microstructure imposed by the measuring apparatus (Figure 1). These observations provide additional evidence that it is not possible to characterize a highly concentrated suspension with a scalar viscosity, even if that suspension is of large uniform spheres so that only hydrodynamic interparticle forces are appreciable. Indeed, due to the microstructure and flow field dependence of measurements in these systems, the usefulness of material properties and viscometric functions, dependent only on the properties of the constituents and on the shear rate, for predicting arbitrary flows is questionable. The results of this study, combined with other recent studies [3,6] involving well characterized, monomodal suspensions with no appreciable colloidal forces, suggest that the large scatter in reported values of μ_r and the onset of non-Newtonian behavior may be explained by variations in the suspension microstructure.

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ϕ	d_s (cm)		
	0.32	0.64	1.27
0.05	a		
0.10	a		
0.20	a,b,c,d		
0.25			a
0.30	a		
0.45	a,b,c,d		
0.50	a,e	a	a,e
0.55	a,f,g,h	f,h	a,f,g,h

Table 1. Experiments performed:

a – falling-ball measurements, D = 14.6 cm
b – falling-ball measurements, D = 11.4 cm
c – falling-ball measurements, D = 9.5 cm
d – falling-ball measurements, D = 6.4 cm
e – falling-ball measurements, D = 3.8 cm
f – capillary measurements, D = 14.6 cm
g – capillary measurements, D = 6.3 cm
h – capillary measurements, D = 3.5 cm

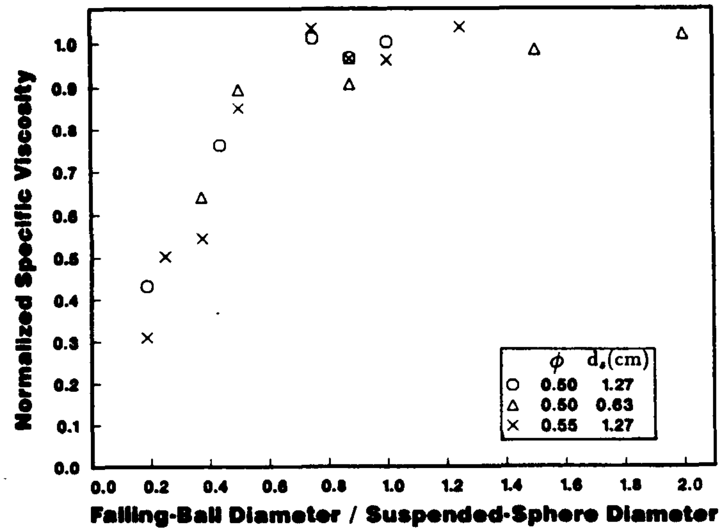

Figure 2. Reduction in apparent viscosity of highly concentrated suspensions when the falling-ball diameter, d, is smaller than the suspended-sphere diameter, d_s.

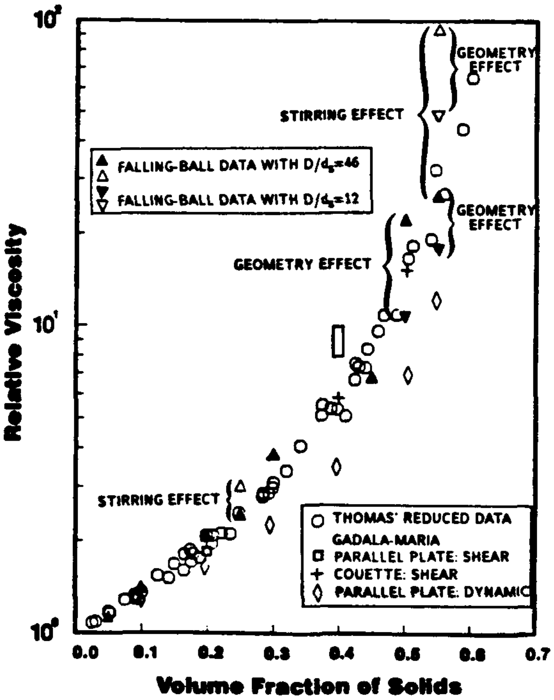

Figure 1. Relative viscosity, μ_r, from falling-ball experiments compared to data collected in shear and capillary rheometers [5,6]. Elongated symbol represents shear-rate dependence measured by Gadala-Maria. Triangles (solid and open) represent falling-ball data taken with two stirring techniques. Geometry effect is caused by lowering the ratio D/d_s.

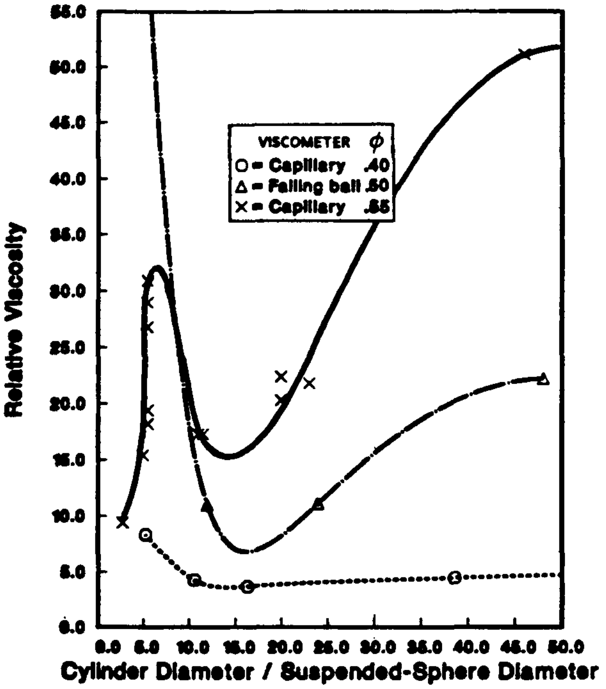

Figure 3. Relative viscosity, μ_r, measured in falling-ball and capillary experiments as a function of the ratio D/d_s. The viscosity minimization becomes more pronounced as the concentration ϕ increases. (Capillary data at ϕ=0.40 were taken by Seshadri and Sutera [9].)

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