Random Packings of Spheres and Fluidity Limits of Monodisperse and Bidisperse Suspensions

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The transition from a fluid to solid state is investigated by studying the viscosity of concentrated noncolloidal monodisperse and bidisperse suspensions of hard spheres. The notion of a range of fluidity limits, analogous to glass transition densities, is introduced. Lower bounds to this range are determined and compared with dry random close packings of the spheres. The ratio of the random-close-packing fraction to the lower bound fluidity limit of the bidisperse suspensions is found to be the same as for monodisperse spheres, a constant of 1.19, suggesting a random structure at this limit.

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The fluidity limit ϕ_m of a suspension of solid particles in a fluid is the concentration or volume fraction of the solid below which the suspension behaves like a liquid in that an applied shear stress induces velocity gradients in the mixture. Above the fluidity limit the suspension can support a finite shear stress and hence exhibits the properties of a solid. It is generally understood that for a given suspension there exist two fluidity limits: a low and a high shear rate limit. At low shear rates Brownian motion and surface forces are significant and affect the rheological behavior of the suspension. At high shear rates hydrodynamic forces dominate and the fluidity limit depends only on particle size and shape distribution. The ratio of hydrodynamic forces to Brownian motion is given by the Peclet number, $\mathrm{Pe}=\mu a^3\dot{\gamma}/kT$, where μ is the fluid viscosity, a the characteristic particle size, $\dot{\gamma}$ the shear rate, k the Boltzmann constant, and T the absolute temperature. In this work we are concerned *only with the high shear rate behavior* and therefore examine suspensions for which the Peclet number is large. For suspensions of uniform spherical particles, there is considerable variation in the reported high shear rate fluidity limit ranging from 0.55 to 0.71 [1-3] (note that the maximum attainable solid fraction is 0.74). It is one thesis of this paper that there is not a single value for the fluidity limit, and that the higher values can be ascribed to greater degrees of ordering of the particles. A similar range is observed in glass transition volume fractions (0.49-0.64) for hard-sphere fluids [4], for what is suggested below to be analogous reasons.

The fluidity limit is sometimes referred to as the maximum packing fraction (or concentration), implying that the suspension cannot be packed in a denser fashion and still retain its fluidlike behavior. This maximum packing is usually inferred by extrapolation from rheological experiments in which the viscosity of the suspension is measured as a function of solid fraction. Figure 1 shows Couette viscometer data for monodisperse and bidisperse suspensions of glass spheres in glycerine. Data from Lewis and Nielsen [5], which are consistent with the present measurements, are included on the monodisperse curve for comparison. The viscosity of the suspension increases with the solid fraction because of the increased energy dissipation associated with particles within the shear flow. As the solid fraction approaches the fluidity limit the suspension viscosity asymptotes to infinity.

Consistent with the fact that there is a range for the fluidity limit, one objective of this work is to measure a lower bound of the high shear rate fluidity limit for monodisperse and bidisperse suspensions of spherical particles. A second objective is to show the existence of a correlation between this fluidity limit and the random packing of the dry solid fraction. This correlation allows the lower bound fluidity limit, and hence the rheology of concentrated suspensions, to be determined independently of viscometry experiments and provides evidence that this lower bound fluidity limit is random in structure.

Recent studies [1,6] have suggested that the fluidity limit of monodisperse suspensions may be related to the random packing fraction, that is, the volume fraction of solids in an ensemble of a random arrangement of particles. In this work we extend this idea to suspensions of

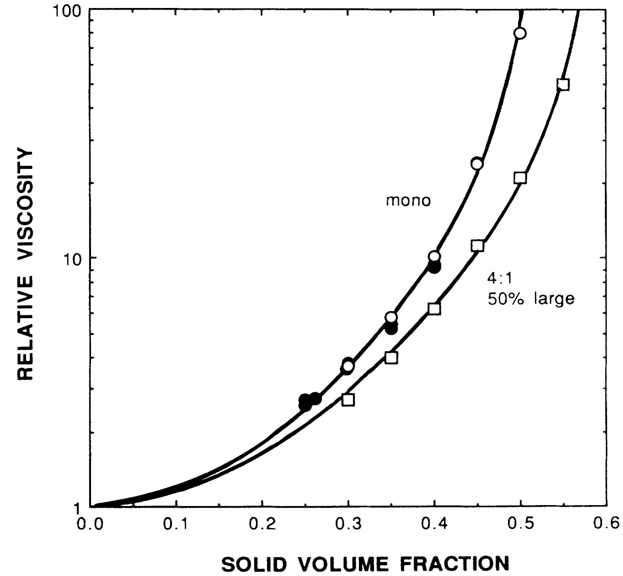

FIG. 1. Relative viscosity vs solid fraction ϕ; comparison of viscometry measurements and semiempirical model by Sengun and Probstein [8]. Circles are for monodisperse suspensions; solid circles are from Lewis and Nielsen [5]. Squares are for 4:1 particle size ratio, 50% large particles.

nonuniform size spheres. The experimental data presented here reveal a single constant of proportionality relating the fluidity limit as determined by viscosity measurements to *random-close-packing* fractions of monodisperse and bidisperse mixtures of spheres.

To calculate the fluidity limit from Couette viscometer measurements, one must employ a model to characterize the asymptotic behavior of the viscosity near this limit. Several models have been used successfully to describe the relative viscosity of concentrated suspensions [2,7,8]. In this work we employ the model developed by Sengun and Probstein [8]. For monodisperse suspensions of spherical particles and particles whose aspect ratio was not too far from 1 the model was shown to correlate well with measurements made over a wide range of solid concentrations. Though this semiempirical model was derived for monodisperse suspensions, it is shown in Fig. 1 that it matches our bidisperse suspension data quite well. The expression derived for the relative viscosity η as a function of solid volume fraction ϕ is

$$\eta = 1 + C\frac{3\pi}{8}\frac{\beta}{\beta+1}\left\{\frac{3+4.5\beta+\beta^2}{\beta+1} - 3\left(1+\frac{1}{\beta}\right)\ln(\beta+1)\right\},$$

where

$$\beta = \frac{(\phi/\phi_m)^{1/3}}{1-(\phi/\phi_m)^{1/3}}\,.$$

Here, the two free parameters are ϕ_m, the fluidity limit, and C, a constant of order unity. This model combines the asymptotic behavior near the fluidity limit developed by Frankel and Acrivos [7] with an approximation to the dilute limit behavior where the suspension viscosity must approach that of the suspending fluid as the solid fraction vanishes. The equation for relative viscosity is appropriate only for high solid volume fractions (say, $\phi > 0.2$) and is not a valid expression for dilute suspensions.

Viscosity measurements were made of suspensions of glass beads (40–160 μm) in glycerine (5% water) at a temperature of 11.5 °C using a Couette viscometer with a gap width of 2.6 mm and an outer radius of 21 mm (Haake model RV12/MVII). The fluidity limits are determined by using the least-squares error method, on a logarithmic basis, to calculate the two free parameters ϕ_m and C. Table I presents the calculated ϕ_m and C for several suspensions. The agreement between this model and data over a wide range of solid fractions is demonstrated in Fig. 1 for bidisperse and monodisperse suspensions. Note that the monodisperse ϕ_m of 0.524 is consistent with the data of Lewis and Nielsen [5]. Interestingly this lower bound fluidity limit corresponds precisely with the volume fraction $\pi/6$ of a simple cubic packing. As expected ϕ_m is higher in bidisperse suspensions because the small particles can move freely in the interstices between large particles. It is observed that C is indeed of order unity in all cases, falling in the range 1.35–1.58. While the precise value of the fluidity limit for a given suspension is dependent on the model used for extrapolation, similar values are obtained for ϕ_m using the single parameter empirical model developed by Kreiger [2].

TABLE I. ϕ_m and C from best fit of viscosity data.

Fraction large particles	Particle size ratio 2:1 ϕ_m	2:1 C	4:1 ϕ_m	4:1 C
0.25	0.536	1.35	0.558	1.42
0.50	0.550	1.49	0.597	1.51
0.65	0.550	1.53	0.597	1.58
0.75	0.546	1.50	0.588	1.48
Monomodal	0.524	1.50		

The measurements of the relative viscosity of suspensions near the fluidity limit are subject to experimental difficulties related to wall slip or, more precisely, the development of lubrication layers of low solid content on the viscometer surfaces across which there is a significant drop in the shear rate [9]. This can result in lower measured viscosities that are dependent on both the shear rate and viscometer gap width. The apparent shear thinning behavior is not due to non-Newtonian fluid properties but is associated with the experimental apparatus. Figure 2 shows typical relative viscosity data as a function of applied shear rate for three concentrated suspensions of glass particles. Visual observations confirm the presence of wall slip at high shear rates. The relative viscosities reported in this work are those measured at the lower shear rates where the viscosity is seen to be independent of shear rate. We emphasize that in this regime the shear rates are still high enough that surface forces and Brownian effects are negligible (Pe $> 10^7$). Below a solid

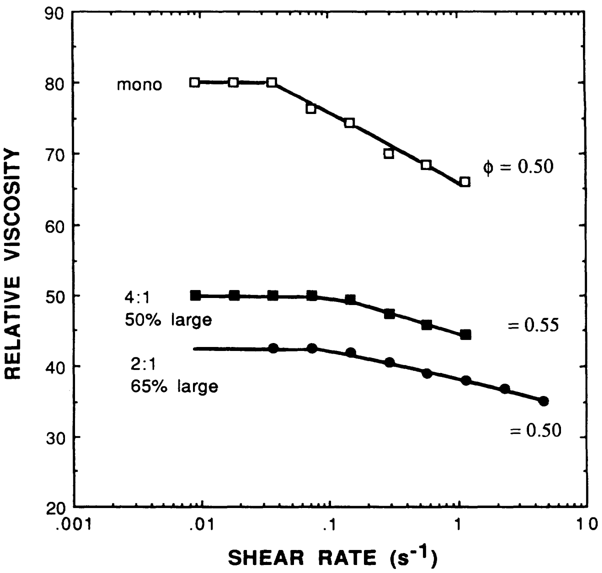

FIG. 2. Relative viscosity vs shear rate, illustrating the effect of wall slip at large solid volume fractions (ϕ).

fraction of about 40% no shear dependence is observed, indicating the absence of significant lubrication layers. Using the same apparatus Sengun and Probstein [8] obtained data which gave $\phi_m = 0.625$ compared to 0.524 reported here. This is ascribed to an underestimate of the higher concentration relative viscosities associated with wall slip.

As noted, suspensions may behave as fluids at concentrations above the fluidity limits reported here. We propose that the lower bound fluidity limit values reported here are characterized by random suspensions. The fluidity limits presented here are quite insensitive to the values of the viscosities measured at the highest solid fractions. In other words, the semiempirical model based on viscosity measurements made at solid fractions below 45% can accurately predict the viscosities at solid fractions near 50%. For suspensions with solid fractions above this lower bound, *ordering must take place to enable fluidization.*

To directly validate this conjecture, measurements of pair correlation functions would be required. At present such measurements in highly concentrated shear flows are not readily obtained. Indirect evidence for random suspension structure at the lower bound fluidity limits can be derived from comparison of these limits with random packing fractions of spheres. Random packings of spheres have been studied in connection with a variety of physical systems. The literature on molecular hard-sphere fluid models and glass transitions [4,10,11] is perhaps the most extensive. Recent work has examined the relation of random packings to the rheology of monodisperse suspensions. Sengun and Probstein [6] compared the fluidity limit to random close packings of uniform spheres and Onoda and Liniger [1] have related dilatancy onset to random loose packings of solid particles in liquids. Dilatancy describes the expansion of a close-packed bed of particles that results from an applied shear rate. While the term "random packing" is rather imprecise, Onoda and Liniger describe two limits: random *close* packing (RCP) and random *loose* packing (RLP). Random close packings are the type studied most extensively (e.g., Scott [12]) and represent the densest packing having random structure [1]. For uniform spheres the RCP has a solid volume fraction of 0.63 ± 0.01. Close packings can be measured by pouring a known volume of particles into a large rigid container and shaking the container to achieve an equilibrium state. The presence of an external force field, in this case gravity, is required to achieve the RCP. Random loose packings represent the least dense packing that can support an external load. It may be identified with the lower bound fluidity limit introduced in this paper. Onoda and Liniger [1] have measured the RLP of uniform spheres through sedimentation experiments with a number of fluids of densities differing from the sphere densities. The solid volume fraction of the RLP is determined by extrapolation to the limit of vanishing density difference between the solid and suspending liquid. Their sedimentation and dilatancy experiments determined the RLP solid fraction to be 0.555 ± 0.005. This 5% larger value than the 0.524 reported here may be associated with the different experimental procedures used.

Random close packings of the bidisperse mixtures of spheres used in the viscosity experiments reported here were measured by pouring a particle volume V_p of dry

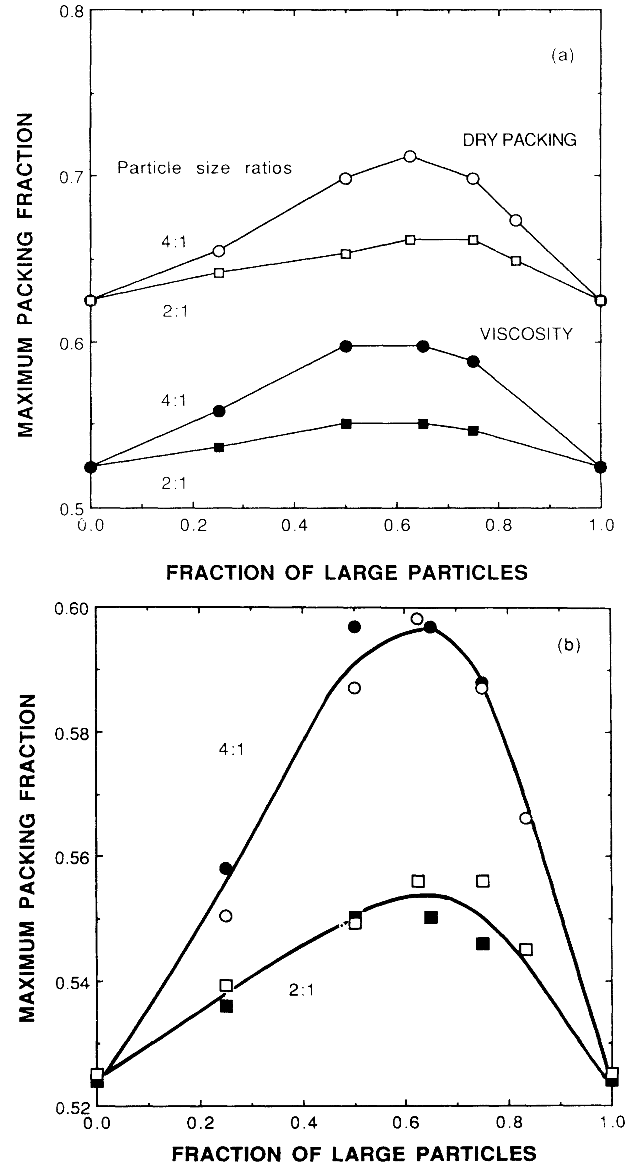

FIG. 3. (a) Comparison of lower bound fluidity limit and dry random-close-packing fraction for bidisperse suspensions with particle size ratios of 2:1 and 4:1. Open symbols are dry random-close-packing measurements; solid symbols are viscosity measurements. (b) Comparison of lower bound fluidity limit and dry random-close-packing fraction for bidisperse suspensions with particle size ratios of 2:1 and 4:1. Open symbols are dry random-close-packing measurements divided by 1.19; solid symbols are viscosity measurements.

glass beads into graduated cylinders, vibrating the cylinder for several hours, and measuring the total volume V_t in the cylinder. The solid volume fraction is simply V_p/V_t. Following Scott [12] the wall effects on the packing fraction were determined to be unimportant by varying the cylinder size and observing no change in the solid volume fractions. The RCP solid volume fractions for different ratios of large to small particle diameters combined in a range of proportions are plotted in Fig. 3(a) and are compared to the fluidity limits for the same bidisperse glass particle mixtures in glycerine as determined by viscosity measurements.

It was observed that the shapes of these curves are very similar and that a constant of proportionality related the fluidity limit and the RCP concentration. Figure 3(b) shows the same data as in Fig. 3(a) except that the RCP concentrations have been scaled by dividing by the ratio $0.625/0.524 = 1.19$ characterizing the monodisperse spheres. The good agreement between the scaled dry packing fractions and the lower bound fluidity limits suggests that the state of the suspension near the fluidity limit is indeed of random structure.

The correlation of the lower bound fluidity limit and random-close-packing fraction in bidisperse suspensions of spheres provides evidence for two important conclusions. First, the lower bound fluidity limit and hence the high-shear-limit rheology of polydisperse suspensions can be predicted by simple dry packing measurements independent of viscosity experiments. Second, the structure of these lower bounds of fluidity limits are random. It is our contention that there does not exist one well-defined fluidity limit for a given suspension; rather the rheology of the suspension can be predicted up to the lower bound of the fluidity limit in which no short-range order has developed. As the solid fraction of the suspension approaches this lower bound the degree of ordering of the suspension must increase to enable fluidization. In this manner the fluidity limit is analogous to the structure of glasses in which varying degrees of short-range order may be imbedded in a structure which is amorphous on a larger scale [13]. This interpretation may explain the wide range of values reported for both the fluidity limits and glass transition densities.

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