Viscosity and Structural Relaxation in Suspensions of Hard-Sphere Colloids

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Viscometry and dynamic light scattering (DLS) were used to study suspensions of colloidal particles which interact like hard spheres. The rate of "structural relaxation" of microscopic density fluctuations, indicated by the long-time diffusion coefficient measured by DLS at the peak of the static structure factor, was found to vary with particle concentration quantitatively like the inverse of the low-shear-rate viscosity. Sample concentrations were calibrated with respect to the thermodynamic "freezing" transition of the suspension.

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By viscometry and dynamic light scattering (DLS) we have studied suspensions of colloidal particles, which interact like hard spheres, in the range of volume fractions $0 < \phi < 0.494$. Sample volume fractions were calibrated directly with respect to the thermodynamic hard-sphere disorder-order transition at $\phi_F = 0.494$ [1], where the suspension freezes to a colloidal crystal. The low-shear-rate viscosity of a suspension at freezing was found to be $\sim 50\eta_0$, where η_0 is the viscosity of the solvent. Diffusion was studied using the new technique of two-color dynamic light scattering, which gives good discrimination against multiple scattering (so that complications associated with the use of solvent mixtures for refractive index matching are avoided). We found that the rate of relaxation of microscopic density fluctuations ("structural relaxation") scales like the inverse of the viscosity for all volume fractions studied up to freezing. To be specific, our results show that

$$\frac{D_0}{D_L(Q_m)} = \frac{\eta}{\eta_0}. \tag{1}$$

Here D_0 is the low-concentration (Stokes-Einstein) diffusion constant of the particles, $D_L(Q_m)$ is the diffusion coefficient describing the long-time decay of density fluctuations that have wave vector Q_m corresponding to the main peak of the suspension's static structure factor, and η is the low-shear-rate viscosity of the suspension. While structural relaxation and inverse viscosity might be expected to show *similar* dependences on concentration, what is unexpected, and suggestive, about our findings is the *identity*, to within relatively small experimental uncertainties, expressed in Eq. (1) and displayed in Fig. 1.

The particles used in these experiments comprised cores of polymethylmethacrylate (PMMA) stabilized by thin layers of poly-12-hydroxystearic acid. They were suspended in *cis*-decalin. Previous work on similar systems has shown that the interaction between the particles is well approximated by that of hard spheres [2,3]. Precise determination of the volume fraction of suspensions of this type is complicated by the core-shell structure of the particles. Thus, as in previous work, we take the volume fraction of the fluid phase in a sample showing crystal-fluid coexistence to be $\phi_F = 0.494$. Addition of *cis*-decalin gave more dilute samples, the concentrations of which were calculated using literature values for the densities of PMMA and *cis*-decalin. The hard-sphere volume fractions ϕ calculated by this procedure are accurate near $\phi = 0$ and $\phi = 0.494$ and have a maximum uncertainty of ± 0.006 around $\phi = 0.3$, arising from the uncertain density of the slightly solvated particles. Particles of mean radii $R = 178$ and 301 nm were used for the light scattering. The viscometry was performed with the particles having $R = 301$ nm. The polydispersity of the particles was about 0.05 in each case.

Measurements of the viscosity were made using a concentric-cylinder arrangement of the type described first by Zimm and Crothers [4]. The inner cylinder floats in the suspension and stress is applied through the action of a rotating magnetic field on eddy currents induced in an aluminum disk fixed to the cylinder. The shear stress can be shown [5] to be proportional to the difference between the angular speeds of the rotating magnetic field and the

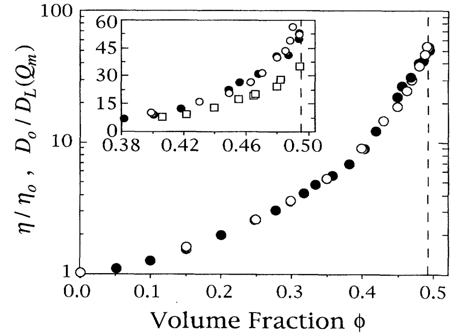

FIG. 1. Viscosity and inverse structural relaxation rate versus volume fraction ϕ of suspensions of PMMA spheres. The open circles are values of η/η_0, the filled circles represent $D_0/D_L(Q_m)$. The size of the symbols represents the estimated uncertainty in both measurements. Inset: Upper curve: same as main plot. Lower curve: open squares, normalized values of the long-time self-diffusion coefficient, D_0/D_L^S, measured on spheres of mean radius $R = 247$ nm (in an index matched solvent).

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inner cylinder. The main advantage of this arrangement is that extraneous sources of friction are minimal, so that the effect of very small stresses can be studied. Thus the low-shear-rate Newtonian regimes of systems that shear thin at high shear rates can be investigated.

The viscometer was calibrated using water and *cis*-decalin as standard liquids. Figure 2 shows plots of stress against strain for PMMA suspensions of various concentrations. At the higher concentrations, linear regions of the plots, whose slopes give low-shear-rate viscosities, are followed by curvature indicating some shear thinning of the samples. Figure 2 shows the relative Newtonian viscosity η/η_0 of the suspensions as a function of concentration; we estimate experimental uncertainties in the measurements of η to be $\pm 3\%$.

Our results for the viscosities of hard-sphere suspensions can be compared with those of others. Marshall and Zukoski [6] have plotted the results of a number of studies. The values, η_F, of η at a nominal concentration of $\phi_F = 0.494$ provide a sensitive comparison. Various factors could contribute to the very wide range of values found in the literature: $18 < \eta_F/\eta_0 < 400$. It is possible that not all the systems studied can be modeled accurately as hard spheres, and that significant polydispersity has an effect. The true low-shear-rate regime may not have been reached in all cases. The most likely cause of the discrepancies is uncertainty in the determination of suspension volume fractions. Since η varies strongly with ϕ at high concentrations (Fig. 1), small errors in ϕ translate to large uncertainties in η. We emphasize that our measurements, which give $\eta_F/\eta_0 \approx 50$, appear to be the only ones in which particle concentrations are calibrated directly to the hard-sphere freezing transition. In many previous studies, use is made of the known low-concentration prediction for hard spheres [7], $\eta = \eta_0[1 + 2.5\phi + 6.2\phi^2 + \cdots]$, to convert measured weight fractions to volume fractions. With this method extremely accurate measurements of η must be made at low concentrations to obtain reliable estimates of ϕ (see, e.g., [3]).

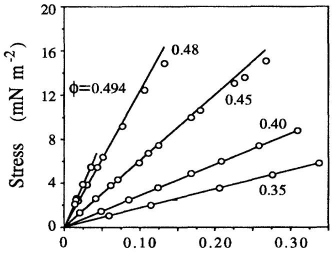

FIG. 2. Shear stress versus strain rate for several concentrated PMMA suspensions. At low rates of strain (or stresses), the points in each case lie on a straight line (shown), the slope of which is the low-shear-rate viscosity. All of these lines extrapolate through the origin to within experimental error. In the samples at $\phi = 0.45$ and 0.48, deviations from linearity are observed. This is the beginning of shear thinning.

Dynamic light scattering measurements were made using a two-color DLS (TCDLS) equipment which has been described in detail elsewhere [8]. Briefly, by cross correlating the light scattered, *at the same scattering vector* $\vec{Q}$, from laser beams of different colors, single scattering is selected and multiple scattering is suppressed. The technique has several advantages compared to conventional DLS. Moderately turbid samples, such as PMMA particles in *cis*-decalin, which give strong single scattering and appreciable multiple scattering, can be studied directly. Thus complications associated with using a mixture of two liquids to match the refractive index of the particles and minimize multiple scattering, as in previous work, are avoided. Furthermore, the strong scattering dominates that from dust and sample cell walls. These factors combine to make the collection of high-quality data possible.

DLS measures the normalized intermediate scattering function $f(Q,\tau) = F(Q,\tau)/F(Q,0)$, where $F(Q,\tau) = N^{-1}\sum_{j=1}^{N}\sum_{k=1}^{N}\langle \exp(i\vec{Q}\cdot[\vec{r}_j(0) - \vec{r}_k(\tau)])\rangle$ and the static structure factor is $S(Q) \equiv F(Q,0)$ (see, e.g., [2]); N is the number of particles in the scattering volume, assumed to be large, and $\vec{r}_j(t)$ is the position of particle j at time t. We have measured $f(Q,\tau)$ for a wide range of scattering vectors which span the position Q_m of the main peak in $S(Q)$ [9]; first we discuss measurements made at the peak, $Q = Q_m$. In a dense fluidlike assembly of hard spheres at $\phi < \phi_F$, the dominant structure, which gives rise to the peak in $S(Q)$, is the short-ranged ordering, or "cage," of particles surrounding a given particle. Thus it can be argued that the decay of $f(Q_m,\tau)$, the intermediate scattering function measured at $Q = Q_m$, reflects the *dominant structural relaxation* of the system [10].

Figure 3 shows plots of $\ln f(Q_m,\tau)$ against $D_0 Q_m^2 \tau$ for various suspension concentrations. For a dilute suspen-

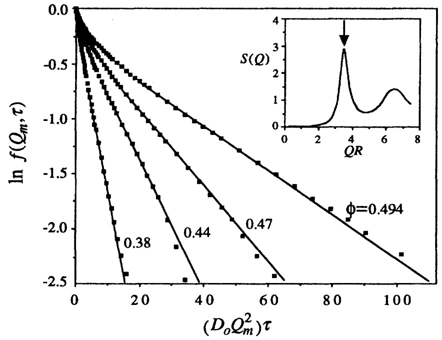

FIG. 3. Intermediate scattering functions $f(Q,\tau)$ of PMMA spheres suspended in *cis*-decalin versus scaled (to free diffusion) delay times. All measurements were made at Q values corresponding to the main (first) peak of the structure factor $S(Q)$. The volume fractions are as indicated, with $\phi = 0.494$ being a colloidal fluid in coexistence with a colloidal crystal. For all volume fractions ϕ, the long-time behaviors are fitted well by $f(Q, \text{large}\,\tau) \propto \exp(-D_L(Q_m)Q_m^2\tau)$ yielding a long-time diffusion coefficient $D_L(Q_m)$. The inset shows the structure factor for a hard-sphere fluid at $\phi = 0.494$.

sion [2], $f(Q,\tau) = \exp(-D_0 Q^2 \tau)$, which would give a straight line of slope -1 in Fig. 3. At higher concentrations much slower, two-stage, decays are observed. Qualitatively, the initial decays of $f(Q_m,\tau)$ can be associated with local motions of the particles within their neighbor cages. The (larger amplitude) longer-time decays reflect substantial rearrangement of the cages, or structural relaxation. Since these are observed to be roughly exponential, as is also found to be the case for atomic fluids [11], we fit them by $f(Q_m, \text{large}\,\tau) \propto \exp[-D_L(Q_m)Q_m^2\tau]$ and identify $D_L(Q_m)$ as the long-time diffusion coefficient describing structural relaxation. We estimate experimental uncertainties in $D_L(Q_m)$ to be ±5%. In Fig. 1, $D_0/D_L(Q_m)$ is plotted against ϕ. A strong slowing down of the rate of structural relaxations is observed, particularly at the higher concentrations, which corresponds to tightening of the neighbor cages surrounding the particles.

We see further from Fig. 1 that the rate of structural relaxation decreases by a factor of $\sim$50 as the suspension concentration increases from dilute to the freezing point [12]. Our viscosity measurements show that the low-shear-rate viscosity increases by essentially the same factor. Moreover, the relative inverse structural relaxation rate, $D_0/D_L(Q_m)$, and the relative viscosity, η/η_0, are, within experimental uncertainties, *the same at all intermediate concentrations*. It is not surprising that the two quantities show similar trends: The processes of simple shear flow and local structural rearrangement both involve the relative motions of neighboring particles. Furthermore it has been suggested that the structural relaxation and viscosity of simple liquids are coupled, particularly in the vicinity of the glass transition [13]. However, the apparent *identity* of the two quantities [Fig. 1 and Eq. (1)] *is* surprising. Indeed Green-Kubo relationships [14] give apparently different expressions, the structural relaxation in terms of the correlation of longitudinal components of spatial Fourier components of the particles' velocities, and the suspension viscosity in terms of the correlation of transverse components of the stress tensor.

At other values of the scattering vector Q, $f(Q,\tau)$ also showed two-stage decays with roughly exponential tails at long times. The diffusion coefficients $D_L(Q)$ describing the long-time decays, which will be considered in more detail elsewhere [9], depended strongly on Q. Thus Eq. (1) was only obeyed at $Q = Q_m$ where the smallest values of $D_L(Q)$, discussed above, were found.

At values of Q where the structure factor $S(Q) = 1$, only self-terms ($j = k$) contribute to the structure. While the absence of static correlations in $S(Q)$ does not ensure the absence of dynamic correlations in $f(Q,\tau)$, it has been argued [15] that, under these conditions, $f(Q,\tau)$ should represent, at least approximately, the self-motions of individual particles in the suspension. Thus we are able to estimate the long-time self-diffusion coefficients D_L^S. DLS measurements of $f(Q,\tau)$ were made at $QR \sim 4.0$ [just beyond the main peak of $S(Q)$ at $Q_m R \sim 3.4$] where $S(Q) \sim 1$; here R is the particle radius. Values of D_L^S were extracted from $f(Q, \text{large}\,\tau) \propto \exp[-D_L^S Q^2 \tau]$ by the same procedure as was used for $D_L(Q_m)$. The results for D_0/D_L^S at high volume fractions are shown in the inset of Fig. 1. At freezing, $D_0/D_L^S \sim 30$, significantly less that the factor $\sim$50 found for structural relaxation. Moreover, η and D_L^S do *not* scale in the same fashion as that found in Eq. (1).

The "generalized Stokes-Einstein" relation

$$D_L^S = \frac{k_B T}{C\pi\eta R} \tag{2}$$

provides a useful framework in which to discuss the relationship between viscosity and long-time self-diffusion at arbitrary suspension concentration. The experimental values of the parameter C, calculated from Eq. (2) using measured values of D_L^S and values of η interpolated from the measurements, are plotted in Fig. 4. In the dilute limit, $\phi \sim 0$, D_L^S [as well as all the diffusion coefficients $D(Q)$] approaches the value $D_0 = k_B T/6\pi\eta R$, corresponding to using a stick boundary condition in the solution of the Stokes equation for the flow of a liquid around an isolated sphere [16]. With increasing volume fraction, C decreases from 6 to about 4 at freezing (Fig. 4). The finding $C = 4$ could be interpreted as arising from the solution of the Stokes equation for a colloidal particle in an "effective medium" formed by the other particles of the dense suspension using a *slip* boundary condition [16]. A low value, $C \sim 3$, was reported by Imhof *et al.* [17] in suspensions of charged colloidal particles which interact through a softer, screened Coulombic interaction and freeze at concentrations significantly below $\phi = 0.494$. In addition, a value $C \sim 4$ has been observed for simple atomic and molecular fluids [18].

The development of rigorous theories of the dynamical properties of concentrated suspensions has been limited by the complexities of the interparticle hydrodynamic interactions. Predictions for both viscosity and self-diffusion exist, e.g., [19]. The predicted values, however, are divergent among themselves, so that we do not attempt a comparison here. We are not aware of any predictions

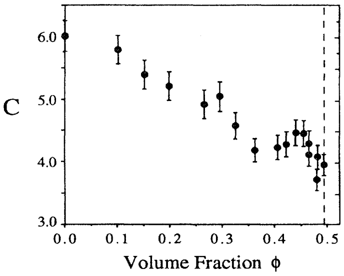

FIG. 4. Values of $C = k_B T/\pi R\eta D_L^S$ versus volume fraction ϕ. The variation of C with ϕ means that viscosity and self-diffusion do not scale with each other in a simple way.

for the structural relaxation rate $D_L(Q_m)$ which include the effects of hydrodynamic interactions.

Finally we mention that recent experiments by Mason and Weitz [20] have suggested a connection between the *frequency-dependent* viscosities and particle diffusion in a number of complex fluids.

Our main finding, for which there appears to be no theory, is the precise scaling, expressed in Eq. (1) and displayed in Fig. 1, of the structural relaxation rates and inverse viscosities of suspensions of hard-sphere colloids. We intend to investigate the generality of this result by making similar measurements on the charged colloidal particles described in [17].

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Note added.—Since submitting this Letter we have discovered that Reuvers [21] has measured the low-shear-rate viscosities of suspensions of charged colloidal particles. The particle charges were screened by added electrolyte and the particles stabilized by added surfactant to give nearly hard-sphere interactions. As in our work, concentrations were determined relative to the freezing transition. His results are very similar to ours, giving a relative viscosity at freezing of 49 (cf. our ~50).

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