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Concentration dependence of the low-shear viscosity of suspensions of hard-sphere colloids

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Experimental measurements are presented of the concentration dependence of the low-shear limit viscosity of nearly monodisperse polymethylmethacrylate spheres dispersed in cis-decalin, a system that models a suspension of hard spheres. The suspension volume fractions are calibrated with reference to the volume fraction at which the particles undergo the thermodynamic freezing transition to a colloidal crystal, providing accurate estimates of the volume fractions of concentrated suspensions. At the freezing volume fraction ($\phi_f \approx 0.50$) we find the relative low-shear viscosity η_r^0 (low-shear viscosity normalized by the solvent viscosity) to be 53 ± 6, compared with results from previous studies that vary from ≈ 20 to 400.

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I. INTRODUCTION

Colloidal suspensions are found in many products and applications throughout industry and are of interest in various branches of science. Their response to deformation and flow is often of importance, so knowledge of the viscosity of a suspension is desirable. A dispersion of identical hard spheres is the simplest basis from which to work. Previous studies [1,2] have shown that the relative viscosity

$$\eta_r = \frac{\eta}{\eta_0}, \tag{1}$$

where η and η_0 are the suspension viscosity and pure solvent viscosity, respectively, of a collection of monodisperse hard spheres dispersed in solvent depends not only on the volume fraction of particles ϕ, but also (for $\phi \gtrsim 0.2$) on the dimensionless shear stress $\sigma_r = \sigma a^3/k_B T$, where σ is the actual stress, a is the particle radius, k_B is Boltzmann's constant, and T is the absolute temperature. At suitably low-shear stresses the viscosity at any one volume fraction is constant: the Newtonian regime. At higher stresses, the viscosity decreases with increasing shear rate (shear thinning), eventually reaching a ''second Newtonian plateau.'' Concentrated dispersions often exhibit shear thickening as the shear stress is increased further. Here we focus our attention on the relative viscosity in the low-shear limit η_r^0, where the motion imposed on the particles due to shearing is much smaller than their Brownian fluctuations.

Theoretical calculation and computer simulation of the dependence of the low-shear viscosity on volume fraction are hampered by the complex interplay of hydrodynamics and Brownian motion set in a many-body scenario. Faced with such problems, one would hope to have definitive measurements of the low-shear viscosity as a function of particle volume fraction for a hard-sphere dispersion. However, previous experimental measurements of η_r^0 for different hard-sphere suspensions give varying results as the suspensions become concentrated [2–6] (see Table I).

Several problems are encountered when attempting such measurements. Many viscometers are not capable of imposing small enough shear stresses to reach the low-shear regime of concentrated suspensions. Here we use a viscometer of Zimm-Crothers design [7,8], suited for measurements requiring small stresses. Another important factor is the precision to which the volume fraction of the suspension can be determined. The low-shear viscosity rapidly increases as the volume fraction approaches 0.50: a discrepancy of only ≈ 0.025 in concentration could lead to an error in low-shear viscosity of a factor ≈ 2 or more. Here we calibrate our suspensions by referring them to the disorder-order, or freezing, phase transition of an assembly of identical hard spheres.

II. MODEL SYSTEM

Our system comprises sterically stabilized nearly monodisperse spheres of polymethylmethacrylate (PMMA) dispersed in cis-decalin. The stabilizer layer consists of chemically grafted poly-12-hydroxystearic acid. This system is observed to depart from the fluid state at a volume fraction of ≈ 0.50, undergoing a thermodynamic phase transition to a state consisting of coexisting colloidal fluid and colloidal crystal [9]. Previous work on similar systems has shown that the interaction between the particles is well approximated by that of hard spheres [10–12], so we relate the transition to the freezing point of an assembly of identical hard spheres as calculated in computer simulations [13], with the fluid-crystal coexistence region given by $0.494 < \phi < 0.545$. The majority of our measurements were performed using particles with radius 301 ± 3 nm with a polydispersity of about

TABLE I. Comparison of low-shear limit viscosity measurements on various hard-sphere suspensions at ~0.50 volume fraction.

Study	Low-shear viscosity $\eta_r^0(\phi \approx 0.50)$
Papir and Krieger [2]	~ 24
de Kruif *et al.* [3]	~ 21
Choi and Krieger [4]	~ 70
Mewis *et al.* [5]	~ 100
Marshall and Zukoski [6]	~ 80–400
this work	~ 50

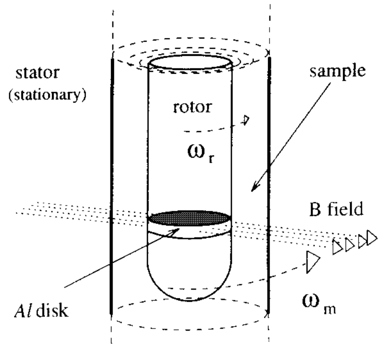

FIG. 1. Schematic representation of the Zimm-Crothers viscometer. The neutrally buoyant inner cylinder (rotor) floats concentrically within the outer cylinder (stator). The rotating magnetic field (angular velocity ω_m) induces a torque on the aluminum disk fixed inside the rotor and causes it to rotate (angular velocity ω_r), subjecting the sample to shear.

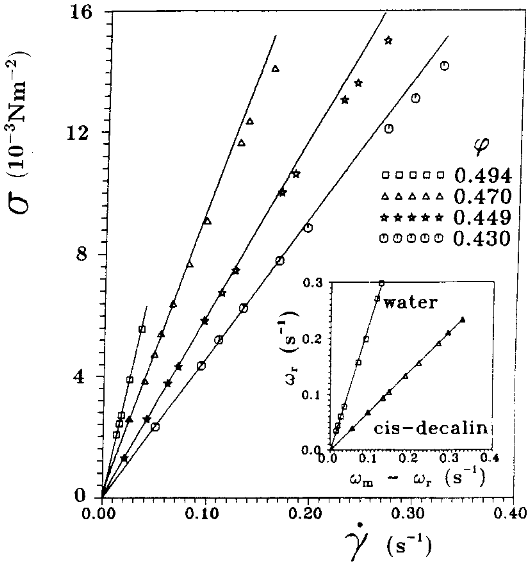

FIG. 2. Shear stress σ versus strain rate $\dot{\gamma}$ for several concentrated PMMA suspensions ($R = 301$ nm). At low rates of strain (or stresses) the points in each case lie on a straight line (shown), the slope of which is the low-shear viscosity. All of these lines extrapolate through the origin to within experimental error. At higher rates of strain deviations from linearity are observed: this is the beginning of shear thinning. The inset graph shows calibration curves (water and cis-decalin) from which the apparatus constant C for the viscometer is determined [see Eqs. (2)–(4)].

0.05 (both determined by dynamic light scattering [14]). A few measurements were performed using particles with $R = 240$ and 500 nm and polydispersities comparable to the $R = 301$ nm particles.

III. SAMPLE PREPARATION

Batches of colloidal stock solution were prepared with concentrations within the coexistence region. They were calibrated by taking small samples in glass cuvettes and monitoring the amount of crystal phase over a period of a week. Using the lever rule, this method yields the sample volume fraction to an accuracy of ± 0.002 [12]. Once the batch is calibrated amounts are removed and diluted to the desired volume fractions (cis-decalin added by weight), calculated using literature values for the densities of PMMA and cis-decalin. There is uncertainty in this estimate of the volume fraction as it does not include the solvated stabilizer layer, whose thickness and density are not known precisely. Possible solvent imbibition by the particles is a further complication. These uncertainties lead to a ''dilution'' error in volume fraction that is quadratic in form: zero at $\phi = 0$, increasing to a maximum error of ± 0.002 at $\phi = 0.247$, and decreasing to zero at the reference volume fraction $\phi_f = 0.494$. A number of samples were also prepared by carefully removing the colloidal fluid (deemed to be at $\phi = 0.494$) from batches with coexisting fluid and crystal and then diluting to the required concentrations. The weights of all colloidal batches and samples were periodically measured to monitor any solvent evaporation, which was then included as part of the final uncertainty in volume fraction.

IV. VISCOSITY MEASUREMENT

Measurements of the low-shear viscosity were obtained using an updated version of the Zimm-Crothers viscometer [7,8]; see Fig. 1. The apparatus is of Couette geometry, the sample of interest trapped between the two concentric cylinders. Surface forces cause the inner cylinder (rotor) to float concentrically within the outer cylinder (stator) [7]. A disk of nonferrous metal (aluminum) is fixed inside the rotor, and by centering a rotating magnetic field (angular velocity ω_m, contolled via a stepper motor) on the disk (inducing eddy currents) a torque is generated, causing the rotor to rotate with angular velocity ω_r and subjecting the sample to shear.

The average shear rate for this geometry is [8,15]

$$\langle \dot{\gamma} \rangle = f(r_1, r_2)\,\omega_r, \tag{2}$$

where $f(r_1, r_2) = [4r_1^2 r_2^2/(r_2^2 - r_1^2)^2]\ln(r_2/r_1)$ depends on the radii of the rotor ($r_1 = 9.94 \pm 0.01$ mm) and stator ($r_2 = 10.86 \pm 0.01$ mm). The magnetically generated torque is proportional to the relative motion of the applied magnetic field and the disk:

$$\langle \sigma \rangle = C(\omega_m - \omega_r), \tag{3}$$

where C is an apparatus constant that depends on such things as the dimensions of the rotor and stator, applied field strength, metal disk size, and conductivity. An unknown viscosity, given by

$$\eta = \frac{\langle \sigma \rangle}{\langle \dot{\gamma} \rangle}, \tag{4}$$

can therefore be measured provided the apparatus is calibrated using liquids of known viscosities. The lowest stress achievable is of the order of 10^{-4} N m^{-2}.

The samples were temperature controlled at 23.0±0.1°C using a recirculating bath and the viscometer was sealed to avoid solvent evaporation. The inset in Fig. 2 shows a cis-decalin calibration curve (see [16] for a listing of the viscosity of cis-decalin as a function of temperature). Successive calibrations deviated by 2%. The calibrated viscometer

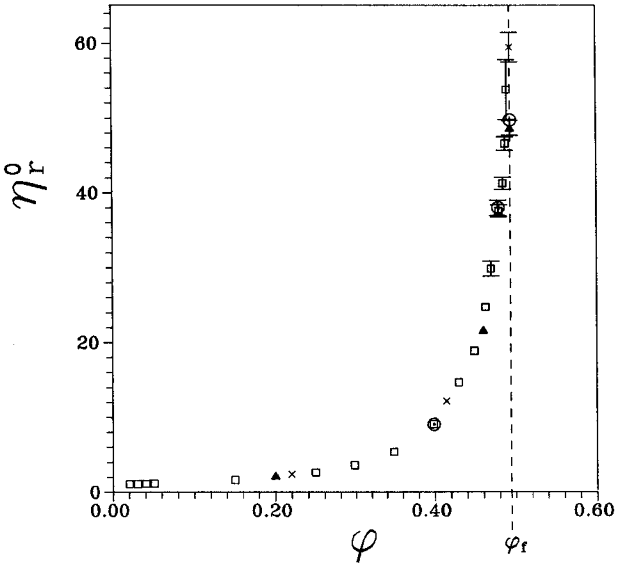

FIG. 3. Dependence of the low-shear viscosity η_r^0 on volume fraction ϕ. Data from particles of three different sizes are shown: 301 nm (□, ○), 500 nm (×), and 240 nm (▲). For the 301-nm particles, squares indicate samples that were diluted from batches consisting of coexisting fluid and colloidal crystal, whereas circles indicate samples diluted from the coexistence fluid (ϕ_f=0.494).

yielded the viscosity of water, a liquid that is less viscous, to within 3% of the literature value. The straight lines show good agreement with theory; the surface tension of the meniscus and end effects are negligible.

V. RESULTS

Some examples of the shear stress σ versus strain rate $\dot{\gamma}$ curves obtained for dispersions of volume fractions 0.430–0.494 are shown in Fig. 2. Emergence from the shear-thinning regime into the low-shear viscosity limit can clearly be seen; data points in the low-shear limit at each volume fraction lie on a straight line extrapolating through the origin. The slope of this straight line gives the low-shear viscosity, while the standard deviation of the slope is the random error. Figure 3 displays the relative low-shear viscosity η_r^0 as a function of volume fraction ϕ. Consistent results were achieved between samples that were prepared by diluting the coexistence fluid and those calibrated by measuring the amount of crystals. Uncertainties in calibrating the apparatus led to a systematic error of 2% in viscosity. The aforementioned uncertainty of the density of the composite shell-core PMMA particle, any swelling through solvent absorbtion, plus uncertainty in the reference concentration and any solvent evaporation led to a maximum uncertainty of ± 0.003 in volume fraction.

Most of the data points were for particles with $R=301$ nm. A few measurements for larger and smaller particles are also shown. Taken together, the different data sets give $\eta_r^0 \approx 53 \pm 6$ at the freezing volume fraction, taken to be $\phi_f = 0.494$ for our system.

VI. DISCUSSION

Our value for the relative low-shear limit viscosity η_r^0 at the freezing concentration is compared with those determined by previous studies at $\phi \approx 0.50$ volume fraction in Table I. An attempt must be made to reconcile the different values reported. It is possible that not all the systems studied can be modeled accurately as hard spheres. For example, the polystyrene colloids used by Papir and Krieger were reported [2] to give iridescent colloidal crystals (as evidenced by Bragg peaks in laser diffraction) at $\phi \approx 0.3$, a density much below that at which hard spheres are expected to crystallize (at $\phi_f = 0.494$). Thus their data clearly cannot be taken as representative of the behavior of hard-sphere suspensions. The very-nearly hard-sphere nature of the PMMA particles used in our work has been established in a number of ways. Underwood *et al.* [17] have shown that the scaling of diffusion coefficients and sedimentation velocities of the colloidal fluid at ϕ_f with the particle radius is consistent with the particles being hard spheres. Segrè *et al.* [14] have measured the short-time self-diffusion coefficient accurately over a range of volume fractions (up to ϕ_f) using two-color dynamic light scattering; their data fit well theoretical calculations [18] and lattice Boltzmann simulations [14] of hard spheres. Finally, in this work, our low volume fraction measurements of the relative viscosity is fitted by $\eta_r - 1 = 2.6(\pm 0.2)\phi + 6(\pm 5)\phi^2$, compared to the expression expected for hard spheres, $2.5\phi + 5.9\phi^2$ [19].

A second possible source of discrepancy is polydispersity, which can have a significant effect [20]. This point will be discussed further below. Third, it is also possible that the true low-shear regime may not have been reached in all cases. The most likely cause of the discrepancy, however, is the determination of the suspension volume fractions. Previous studies measure the mass concentrations of the particles and convert these into volume fractions using literature or experimentally determined values for particle and solvent density. However, it is not clear that volume fraction can be related to mass concentration so simply. As mentioned before, the suspensions are likely to have an ''effective'' volume fraction arising from solvation of the stabilizing layer or the particle itself.

Some of the previous studies attempt to convert particle mass concentration into volume fraction by determining a particle specific volume q from specific viscosity measurements in the dilute limit. As mass concentration $c \rightarrow 0$

$$\eta_{\mathrm{sp}} = \eta_r - 1 = Kc = [\eta]\phi, \tag{5}$$

where K is a constant determined by the dilute viscometery measurements and $[\eta]$ is the intrinsic viscosity. Then $[\eta]$ is equated to the Einstein value of 5/2 (by assuming hard-sphere behavior), which yields a particle specific volume $q = 2K/5$. However, care has to be taken that such measurements are truly in the dilute limit. At ϕ as low as 0.03 the quadratic term $5.9\phi^2$ [19] contributes $\approx 7\%$ to the specific viscosity η_{sp}, which would be directly passed on as error in ϕ if ignored. In fact, a simple least-squares analysis [21] confirms that the procedure of fitting a straightline to low-dilution viscosity data, when applied using suspensions with ϕ up to ≈ 0.03, would lead to an overestimation of ϕ by $\approx 7\%$. Such discrepancy would have grave consequences when relating low-shear viscosity measurements to (calculated) volume fraction.

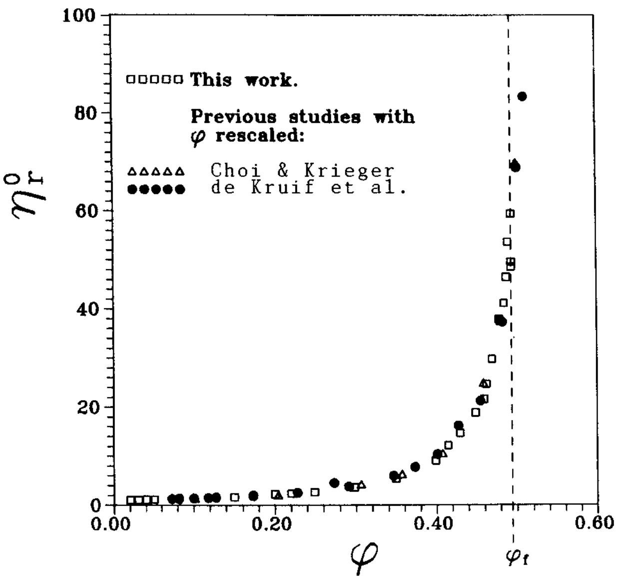

FIG. 4. Dependence of the relative low-shear viscosity η_r^0 on volume fraction ϕ measured in this work and the data of de Kruif *et al.* [3] and Choi and Krieger [4] *with volume fraction multiplied by a constant factor in each case* (0.91 and 1.02, respectively). All the data fall on a single curve, supporting the claim that uncertainty in the volume fraction is the main cause of the discrepancies between many existing data sets.

Even if measurements are on sufficiently dilute suspensions great accuracy is required [11]. For $\phi \approx 0.01$, η_{sp} accounts for only $\approx 3\%$ of the relative viscosity. In order to achieve an estimate of η_{sp} (and thereby ϕ) to a minimum precision of $\pm 2\%$ one would have to measure η_r to $\pm 0.06\%$. By calibrating our samples with respect to their freezing concentration we have a clearly defined volume fraction reference point with a physical significance.

Support for our contention that volume fraction uncertainty is the single most important cause of discrepancy between existing data sets comes from the plot shown in Fig. 4. Here we show again the dependence of the relative low-shear viscosity η_r^0 on volume fraction ϕ measured in this work. On the same plot, however, we also show the data of de Kruif *et al.* [3] and Choi and Krieger [4] *with volume fraction multiplied by a constant factor in each case* (0.91 and 1.02, respectively). The three data sets fall on a single curve. The data of Mewis *et al.* [5] failed to agree with our results even with volume-fraction rescaling. Our only explanation is possible deviation of their particles from the hard-sphere ideal, or uncertainties in determining the low-shear viscosity. The data of Marshall and Zukoski [6] did not lend themselves to such comparison, as the bulk of their measurements made were on suspensions near the glass transition.

It is tempting to seek a closed form expression for the "master curve" shown in Fig. 4. An obvious candidate is the Krieger-Dougherty equation [22]

$$\eta_r^0 = (1 - \phi/\phi_m)^{-[\eta]\phi_m}. \tag{6}$$

The intrinsic viscosity $[\eta]$ is expected to take the Einstein value for hard spheres $[\eta] = 2.5$. The other parameter ϕ_m is the volume fraction at which the low-shear viscosity diverges. Since the colloidal fluid becomes thermodynamically metastable with respect to the colloidal crystal above the freezing volume fraction $\phi_f = 0.494$, the viscosity is, strictly speaking, not defined above this density. If one nevertheless wants to enquire about the viscosity of the metastable colloidal fluid, the expectation must be (in common with the well-known situation in simple atomic and molecular fluids [23]) that it should diverge at the glass transition [6,10], which occurs in this system at $\phi_g \approx 0.58$ [24]. An unconstrained fit, returning the values $[\eta] = 3.2$ and $\phi_m = 0.55$, gave good agreement with the data in Fig. 4. However, we deem the fitted values of the parameters $[\eta]$ and ϕ_m to be unphysical. Constraining $[\eta]$ to the Einstein value and fitting to ϕ_m alone (returning a best-fit value of $\phi_m = 0.516$) did not produce satisfactory agreement.

Another possible expression for η_r^0 has been suggested recently by Brady [25]. At volume fractions greater than about 0.4, Brady's expression can be represented accurately by the asymptotic form

$$\eta_r^0 = 1.3(1 - \phi/\phi_m)^{-2}, \tag{7}$$

where ϕ_m is the volume fraction, ≈ 0.64, of random close packing of hard spheres. In Eq. (7), one factor $(1 - \phi/\phi_m)$ is associated with the divergence, at $\phi = \phi_m$, of the radial distribution function of the spheres at contact and the other factor is associated with a similar divergence of the short-time self-diffusion coefficient. Using the value of $\phi_m = 0.64$, Brady found that his (full) expression fitted the data of Papir and Krieger [2] and de Kruif *et al.* [3]. This means that the same expression is not expected to fit the master curve shown in Fig. 4. In any case, as mentioned above, we expect the low-shear viscosity to diverge at the glass transition $\phi_m = \phi_g \approx 0.58$, where the *long-time* diffusion coefficients vanish, and not at $\phi_m = 0.64$.

Finally, polydispersity affects all previous measurements as well as the present work. Differing or unavailable polydispersity values hinder meaningful comparison between data sets. Polydispersity also affects directly our method of volume fraction determination [20]. The freezing transition in a slightly polydisperse hard-sphere system occurs at a volume fraction ϕ_f' *above* that for a monodisperse system ($\phi_f = 0.494$). Two existing theoretical calculations [26] of ϕ_f' give conflicting predictions; neither reproduce exactly the value of ϕ_f obtained in computer simulations of monodisperse hard spheres. The best available estimate of the polydispersity dependence of ϕ_f' to date is probably the computer simulations of Bolhuis and Kofke [27] (which reproduce ϕ_f at the limit of zero polydispersity). These simulations show that $\phi_f' \approx 0.51$ for a polydispersity of $\approx 5\%$. Our volume fractions, calibrated with respect to the freezing transition for monodisperse hard spheres, are therefore likely to be too large by $\approx 3\%$.

VII. CONCLUSION

The low-shear limit relative viscosity η_r^0 of nearly monodisperse sterically stabilized PMMA spheres dispersed in cis-decalin, a hard-sphere suspension, was found to be $\approx$ 50 at the freezing concentration. This, as well as the general volume fraction dependence (referenced to the freezing concentration) of the low-shear relative viscosity, was found to be significantly different from previous measurements on hard-sphere suspensions. However, two previous data sets were brought into agreement with our measurements with a simple scaling of volume fractions in each case. Elsewhere we have discussed our results in relation to dynamic light scattering (DLS) measurements. An intriguing relationship was found between the low-shear viscosities and the rates of structural relaxation determined by DLS [28].

Note added. Since the submission of the original version of this work, Phan *et al.* [29] have published extensive data on the PMMA system, which agree with our results. These authors have also analyzed quantitatively the expected effects of polydispersity.

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