

High frequency rheology of hard sphere colloidal dispersions measured with a torsional resonator

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Abstract

The high frequency rheology of model, hard sphere dispersions of charge-neutralized, coated silica particles in tetrahydrofurfuryl alcohol (THFA) was measured using two torsional resonators at five frequencies. The resulting elastic modulus shows $\omega^{1/2}$ limiting behavior at high frequencies and is in quantitative agreement with the theoretical predictions of Lionberger and Russel [J. Rheol. 38 (1994) 1885]. The lack of a high frequency plateau is a signature of weaker hydrodynamic interactions acting at very small separations. Calculations verify that despite the lack of a high frequency plateau, these dispersions can exhibit reversible shear thickening at high shear rates, in agreement with experiment. Thus, the experiments verify the unique sensitivity of high frequency rheology to hydrodynamic properties at the particle surface. © 2002 Published by Elsevier Science B.V.

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1. Introduction

The high frequency elastic modulus (G'_{∞}) is a useful tool to study the interactions at small separations between colloidal particles [1–3]. The frequency dependence of G' in the limit of high frequency is of special interest for the case of the hard sphere potential because in the absence of singular, lubrication hydrodynamic interactions, the discontinuity in the potential leads to a limiting $G' \propto \omega^{1/2}$ behavior, where ω is the frequency of oscillation of the applied flow [4,5]. However, the presence of near-field hydrodynamic interactions has been shown theoretically to lead to a limiting value G'_{∞} [2]. These authors prove that lubrication hydrodynamic interactions eliminate the diffusional boundary layer that leads to $\omega^{1/2}$ dependence. Consequently, theoretical considerations demonstrate that the qualitative behavior of

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Dedicated to Professor Acrivos on the occasion of his retirement from the Levich Institute and the CCNY.

the high frequency elastic modulus of hard sphere colloidal dispersions is very sensitive to the presence of short-range hydrodynamic interactions.

Interestingly, there are only two experimental data sets for the high frequency modulus of model hard sphere dispersions. de Kruif and coworkers [6] studied octadecyl coated silica in cyclohexane, an index matching solvent. Their results, which were obtained on a series of torsional and nickel-tube resonators developed by Mellema and coworkers [6], clearly show a $\omega^{1/2}$ dependence for the high frequency elastic modulus. Small angle neutron scattering (SANS) measurements of similar dispersions were shown to quantitatively agree with hard-sphere predictions up to volume fractions of 50% [7].

Shikata and Pearson [8] studied a commercial silica in index matching solvent, consisting of an ethylene glycol and glycerol mixture. They report evidence for a high frequency plateau, in contrast to the former investigators. They used a conventional rheometer and the method of time–temperature superposition to obtain the high frequency moduli. As noted by the authors, definitive plateaus were not obtained for many of the concentrations investigated and those that appeared to limit to a plateau often did not demonstrate a definitive plateau over a broad frequency range, which was a consequence of measurement limitations. Further, due to the viscous solvent, the viscous modulus greatly exceeded the elastic modulus at high frequencies, making extraction of the elastic modulus difficult. As importantly, the data of Shikata and Pearson [8] has no independent verification of the hard-sphere interaction potential other than comparison of the zero shear viscosity.

The importance of short-range hydrodynamic interactions in particle dispersion rheology has been recognized for some time. The work of Jeffrey and Acrivos [9] and Frankel and Acrivos [10] demonstrated that these interactions alone can drive a divergence in the viscosity at high packing fractions. Simulations [11,12], experiment [13,14] and theory [5,15] have all shown that the high shear rate rheology of hard-sphere-like dispersions is dominated at high concentrations by shear thickening, which is a consequence of these short-range hydrodynamic interactions driving the formation of a self-organized, “hydroclustered” microstructure. Thus, experimental methods to detect and quantify, directly, these short-range hydrodynamic interactions are vital to further our understanding of dense dispersion rheology.

The recent development of a model, hard-sphere system consisting of acid titrated 3-(trimethoxysilyl)propyl methacrylate (TPM) coated Stöber silica in index matching tetrahydrofurfuryl alcohol (THFA) [14,16] and the commensurate development of a calibrated series of high-frequency torsional resonators afforded an opportunity to provide additional measurements on a model hard-sphere system with independent verification of the interaction potential and without reliance on the validity of time–temperature superposition. In this contribution, we report on the quantitative comparison between measurements of the high frequency modulus to the theoretical predictions for hard spheres [2].

2. Experimental

The synthesis of the Stöber-silica particles and their characterization has been reported in detail [14,16,17], so only the essential features will be discussed here. The dispersions used here consist of 302 ± 26 nm diameter (by TEM) TPM-coated silica dispersed in index matching THFA ($\mu = 5.44$ cP at 20°C). Index matching greatly reduces the Hamaker constant so that van der Waals dispersion forces are removed. Nitric acid is added (0.1 M) to eliminate any residual surface charge, as verified by zeta-PALS measurements. SANS measurements verified both the particle size and polydispersity (318 ± 17 nm), and from a concentration series, the hard-sphere interaction potential [14]. The particle

density (1.82 ± 0.08 g/ml) extracted by matching the Einstein coefficient for the intrinsic viscosity agrees exactly with that determined by solution densitometry (1.82 ± 0.01 g/ml), and the measured Huggins coefficient (0.63 ± 0.93) is in agreement with the hard sphere value of ~ 1.0 . Thus, by all conventional measures, the particles are nearly monodisperse, spherical, hard spheres. Note that these samples show extensive but reversible shear thickening for volume fractions $>35\%$, which is thought to be due to the influence of short-range hydrodynamic interactions [14].

The high frequency rheology was measured with two torsional resonators supplied by the Institut für Dynamische Materialprüfung, Ulm, Germany. These instruments are similar to the one used by Bergenholtz [1], and so the operation and analysis of the signal are not discussed here. The frequencies ω accessible by these resonators are 23,000, 63,000, 119,000, 239,000 and 358,000 rad/s. All frequencies were examined for the sample $\phi = 0.50$, while the diluted samples were only measured at 119,000 and 358,000 rad/s. Due to the instrument design, the 23,000 rad/s frequency yields a weaker signal to noise, so these results are not reported here. The sample measurement volume is 18 or 11 ml, depending on the resonator. All measurements were performed at 20 ± 0.1 °C.

The rheological properties of a charge-neutralized dispersion ($\phi = 0.50$) were measured. Due to sample limitations, this sample was recovered after the experiment and 0.1 M HNO₃ solution in THFFA was added by weight to give $\phi = 0.49$. This procedure was repeated in volume fraction steps of 0.01 to reach a final $\phi = 0.45$.

3. Theory

The derivations and discussion of the theoretical analysis of the high frequency modulus can be found in Lionberger and Russel [2]. Neglecting the lubrication hydrodynamic interactions yields the free draining model for the high frequency elastic modulus

$$\frac{G'_{\infty} d^3}{k_B T} = \left(\frac{d^2 \omega}{D_S^0(\phi)} \right)^{1/2} \frac{24\phi^2}{5\pi} g(1) \quad (1)$$

where d is the particle's diameter, $D_S^0(\phi)$ the short time self diffusion coefficient, which depends on volume fraction (ϕ), k_B the Boltzmann constant, T the absolute temperature and $g(1)$ is the value of the radial distribution function at contact.

Calculating G'_{∞} from Eq. (1) requires approximations for $g(1)$ given by Carnahan and Starling in 1969, and D_S^0 provided by Lionberger and Russel [2].

$$g(1) = \begin{cases} \frac{1 - (1/2)\phi}{(1 - \phi)^3}, & \phi < 0.5 \\ \frac{0.78}{0.64 - \phi}, & \phi \geq 0.5 \end{cases} \quad (2)$$

$$D_S^0 = D_0(1 - 1.56\phi)(1 - 0.27\phi) \quad (3)$$

where D_0 is the single particle diffusion coefficient and can be calculated from the Stokes–Einstein equation. Note that these approximations for $g(1)$ and D_S^0 diverge or vanish at a maximum volume fraction of 0.64.

The high frequency viscosity, which is a consequence purely of viscous dissipation, can be approximated by an expression for the reduced viscosity [2]

$$\frac{\eta'_{\infty}}{\mu} = \frac{1 + (3/2)\phi(1 + \phi - 0.189\phi^2)}{1 - \phi(1 + \phi - 0.189\phi^2)} \quad (4)$$

where η'_{∞} is the high frequency viscosity of the sample and μ is the viscosity of the solvent. Note that this equation and that for the self-diffusivity (Eq. (3)) are correlations of the data of Shikata and Pearson [8].

4. Results and discussion

The measured elastic modulus of a 50 vol.% dispersion (Fig. 1) shows a ω^n behavior with $n = 0.70 \pm 0.11$. An average over all measurements at all volume fractions yields $n = 0.59 \pm 0.17$. Note that each

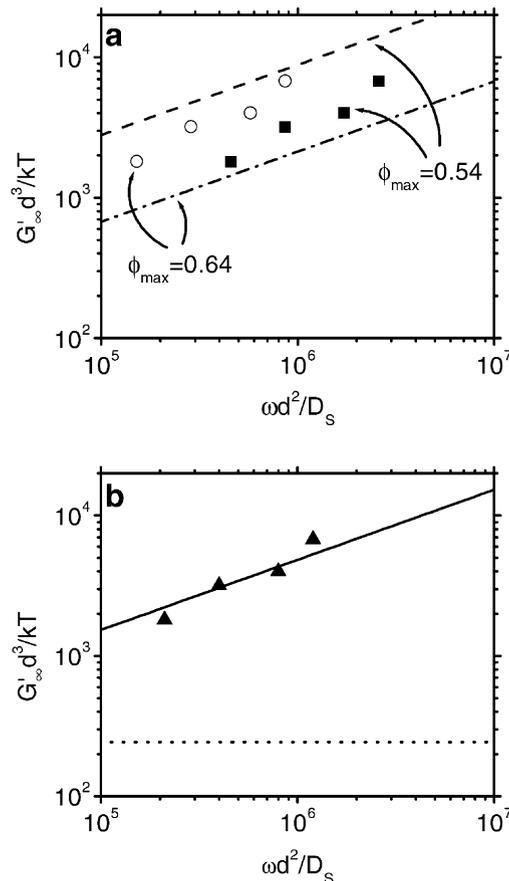


Fig. 1. Frequency dependence of the elastic modulus for the 50% dispersion. The value of D_s used in reducing the frequency is calculated for various maximum volume fractions—(a) $\phi_{\max} = 0.64$: (○), experimental; (---), theory; $\phi_{\max} = 0.54$: (■), experimental; (---), theory; (b) best-fit result of $\phi_{\max} = 0.57$: (▲), experimental, (—), free draining theory; (···), lubrication theory.

measurement is plotted three times in Fig. 1 according to choice of the maximum packing fraction, as will be discussed later on. This overall value for the frequency power law index is in agreement with the value of $1/2$, which has been predicted by theory if lubrication hydrodynamics are not dominant. Also note that our values of scaled frequency are significantly higher than those measured previously [2] and cover a broader range of values above the critical frequency. Also shown in Fig. 1b is the prediction of the lubrication theory, which is substantially below the measurements.

As a first step toward understanding these measurements, it is necessary to check if the time scale separation assumed in theory applies for the measurement and the dispersion. This requires that the vorticity diffusion time for the hydrodynamic interactions to propagate and the relaxation time for particle inertia are much shorter than the fastest time for one period of oscillation. Calculations of the relations given by Lionberger and Russel [2] demonstrate that these processes are faster than the fastest oscillation frequency by factors of 91 and 1600, respectively. Therefore, the time scale separation is respected.

Equally as important is the requirement of being in the high frequency limit. The onset of the high frequency regime is defined by the relative thickness of the diffusion to the lubrication boundary layers. The region near contact, where diffusion is equal in magnitude to convection, determines the thickness of the diffusion boundary layer, which is frequency dependent. On the other hand, the distance where two approaching particles start to slow down because the liquid between them is squeezed out, defines the lubrication layer, which is frequency independent. Balancing these two yields an estimate of the critical frequency at which the elastic modulus should reach its plateau value. Using this approximation leads to a critical ω_c of 4200 rad/s (for $\phi = 0.50$ and $\phi_{\max} = 0.57$) which is nearly an order of magnitude smaller than the lowest frequency accessible with the resonators used. In summary, our measurements are safely within the high frequency limit for this dispersion, and are safely below frequencies where particle inertia and unsteady hydrodynamics become important.

A quantitative comparison between theory and experimental data reveals discrepancies (Fig. 1a). Note that the theory has one parameter in it, the maximum packing fraction, which appears in the calculation of the nearest neighbor distribution as well as in the diffusivity correlation. One reason for the discrepancy is that the maximum volume fraction used in the theory is 0.64 (random close packing), while fitting zero shear viscosities to the Krieger–Dougherty equation yields an estimated value of 0.54. This value is low compared to the values for random closed packing (0.64) or the glass transition (0.58), but could possibly be due to a small amount of surface roughness or adsorbed water and ions. Rescaling $g(1)$ and D_S^0 relative to this maximum volume fraction (0.54) results in predicted values of G'_∞ that are considerably higher than the experimental ones. To compare theory and experiment, we plot both on a master plot as a function of scaled volume fraction (ϕ/ϕ_{\max}) and fit the data to the theory to determine the maximum packing fraction for our dispersion. A best-fit value is determined to be $\phi_{\max} = 0.57$, which is shown in Fig. 1b. This value is close (to within experimental uncertainty) to the hard sphere glass transition concentration $\phi_G = 0.58$, as found by van Meegen and Underwood [18], and Pusey and van Meegen [19], which is also the value for the maximum packing of hard spheres as determined by our previous investigations [1,20,21].

Limited sample quantities limited the investigation to two frequencies for the lower volume fractions. This data is shown in Fig. 2 and compared directly with theoretical calculations of Eq. (1), where again $\phi_{\max} = 0.64$ for the theory and 0.57 for the experimental data. The ratio between the G'_∞ values obtained for the two frequencies is, to within uncertainty, constant for all the volume fractions and is consistent with the $\omega^{1/2}$ behavior.

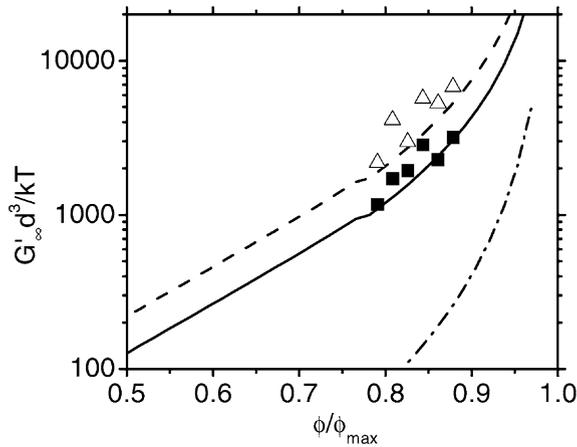


Fig. 2. Volume fraction dependence of the high frequency elastic modulus for two frequencies. The experimental data are scaled for $\phi_{\max} = 0.57$, $\omega = 119,000$ rad/s (■), $\omega = 358,000$ rad/s (Δ). The solid and the dashed lines are the results of the free draining model while the dash dotted line represents the frequency independent plateau value predicted by the lubrication model.

Over the volume fraction range of 45–50%, no high frequency plateau is observed for the elastic modulus and, therefore, the lubrication singularity does not hold for this system. Possible reasons for this might be the small amount of surface roughness and adsorbed ions and water. However, the range of these interactions would have to be on the order of a few nanometers to give this effect because the thickness of the lubrication layer is estimated to be 2.5 nm (for $\phi = 0.50$ and $\phi_{\max} = 0.57$, as given by Eq. (5.7) in [2]). As noted by Philipse [22], the TPM coating layer is a “loosely structured layer” of a few nanometers, which is consistent with our observations.

Interestingly, the distance of separation at the onset of shear thickening, which is known to be a consequence of lubrication interactions at high shear rates, is approximately 15 nm [14]. Consequently, there is no inconsistency between the observation of shear thickening and the lack of a high frequency modulus. Indeed, the presence of extremely short-range forces has been invoked to explain the apparent deviation from the predicted, weak, logarithmic divergence in the viscosity [14].

A final crosscheck for the frequency dependence of the measured moduli is the loss modulus, because both moduli are obtained simultaneously from the measured frequency shifts and damping coefficients. The experimentally obtained η'_{∞} (Fig. 3) follow the volume fraction dependence predicted by Eq. (4), again using the same scaling with maximum packing fraction. No frequency dependence is observed for this quantity, in agreement with theoretical expectations.

van der Werff et al. [6] determined η'_{∞} by extrapolating their data to high frequencies using a Rouse-like model. In contrast Shikata and Pearson [8], with their relatively higher solvent viscosity, obtained a frequency independent η'_{∞} as observed here. Their data is represented by the correlation line (Eq. (4)) in Fig. 3. As seen, our results for the high frequency viscosity agree with the previous two measurements. Despite the extreme differences in the measured η'_{∞} values between experiments, the agreement for η'_{∞} is to be expected. As discussed previously [1,20], η'_{∞} is dominated by the far-field hydrodynamic interactions and is relatively insensitive to the near-field lubrication interactions. Consequently, the presence of a

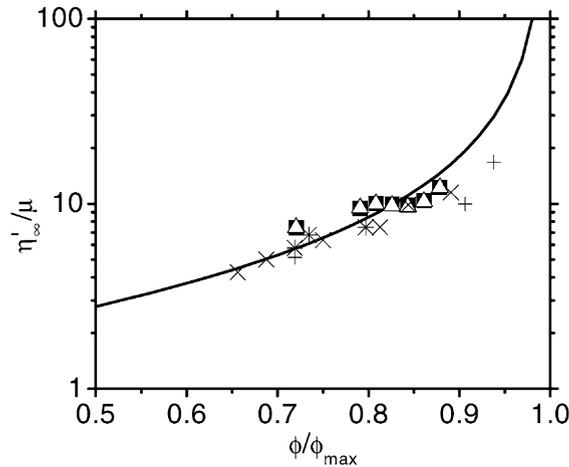


Fig. 3. Volume fraction dependence of the reduced viscosity. The experimental data are scaled for $\phi_{\max} = 0.57$. The two frequencies $\omega = 119,000$ rad/s (■) and $\omega = 358,000$ rad/s (△) give nearly the same results. The solid line is the approximation given by Lionberger and Russel [2]. Data by van der Werff et al. [6] are included in this plot: SP23 (+), SSF1(x), SJ18 (*).

diffusive boundary layer exceeding the lubrication layer in extent is largely irrelevant in the calculation of the high frequency loss modulus. This suggests that accurate measurements of the loss modulus could be used to determine the hydrodynamic volume fraction of dispersions.

In conclusion, the results presented here demonstrate the lack of a high frequency plateau and consequently, the loss of singular lubrication hydrodynamic interactions at the particle surface, in a model hard sphere dispersion. Quantitative agreement is obtained with the theoretical predictions of Lionberger and Russel [2]. These results are consistent with previous observations on a sterically stabilized dispersion by van der Werff et al. [6], and are in contrast to the plateau observed by Shikata and Pearson [8] for a commercial silica in a more viscous solvent. These measurements cover a relatively higher frequency range than the previous measurements and are safely within the upper and lower limits that define G'_{∞} . As expected, the high frequency viscosities are comparable to both previous measurements, as this property is relatively insensitive to the near-field lubrication hydrodynamics. Finally, we note that these samples show strong, reversible shear thickening at higher shear rates. Estimates of the separation distance at the onset of hydrocluster formation, however, are significantly larger than the lubrication boundary layer required for a plateau in G'_{∞} . Consequently, there is no dichotomy in the observation of shear thickening and the $G' \propto \omega^{1/2}$ at high frequencies.

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