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On the viscosity and shear modulus of strongly interacting colloids

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Abstract. We have studied the viscosity of dilute suspensions of strongly interacting monodispersed colloidal particles. Theoretically we find that the viscosity can be calculated from the infinite frequency shear modulus times a Maxwellian relaxation time $G^{\infty}\tau$, where G^{∞} is obtained from the interactions and τ depends on the interparticle spacing but is independent of the interactions over the physically interesting range. Experimentally we find that this relation holds quantitatively when G is identified with the shear modulus extrapolated from measurements on colloidal crystals, and when τ is taken as a 'Lindemann time'—the time for a particle to diffuse $\sim\frac{1}{10}$ of the distance to a near neighbour—a similar value results from the calculations. Thus for the Brownian dynamics of colloids it is possible to completely determine the viscosity of the melted state from measurements of the solid.

During the past decade there has been considerable progress and interest in understanding the dynamics of interacting particles in suspension (Batchelor 1972, 1976, 1983, Brown *et al* 1975, Pusey and Tough 1984, Ackerson 1976, Hess and Klein 1983, Klein and Hess 1983). An ideal system for the investigation of such phenomena, both theoretically and experimentally, is that of monodispersed lattices (Schaeffer and Berne 1974, Goodwin and Khider 1976, Schaeffer 1977, Ackerson and Clark 1980, Pieranski 1983, Gruner and Lehmann 1979, 1982, Les Houches 1985) composed of charged polymer spheres. For weak electrostatic interactions hydrodynamic forces dominate and for small volume fraction ϕ the linear corrections have been successfully calculated. In the opposite limit of strong electrostatic interactions (but small volume fraction), the hydrodynamic forces play a less important role and one might expect the system to approximate a simple fluid, i.e. without a solvent. However, the Brownian as opposed to ballistic dynamics still plays a crucial role which in the present case leads to both a simplification of the calculations of the viscosity and a physically intuitive way of understanding the results.

The system under consideration consists of charged polystyrene spheres of diameter $\sim 0.1\ \mu\text{m}$, $\phi \sim 1\%$, effective charge $Z^* \sim 300e$ interacting via a screened Coulomb (Alexander *et al* 1984, Lindsay and Chaikin 1983, 1985) potential. Such systems have been well characterised and have easily controllable interactions adjusted by independently varying the volume fraction ϕ, or the concentration of electrolyte which gives the range and strength of the interaction potential. They are known to form colloidal crystals which 'melt' on adding electrolyte and yield a liquid phase with a structure

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factor $S(K)$ with liquid-like shape (Schaeffer and Berne 1974, Schaeffer 1977, Ackerson and Clark 1980, Gruner and Lehmann 1979, 1982). The amplitude of the structures in $S(K)$ range from a maximum of ~3 (the Hansen-Verlet criterion) near melting (Hansen and Verlet 1969) to essentially flat ($S(K)=1$) for high electrolyte concentration (Hess and Klein 1983, Klein and Hess 1983). The viscosity of the liquid phase similarly varies from several times the solvent viscosity η_0 near melting to $\eta_0(1+2.5\phi)$ (Lindsay and Chaikin 1985).

By experimentally studying a variety of samples as a function of particle and electrolyte concentration in both the solid and liquid phases, we were able to show that the shear modulus which characterises the instantaneous response to a strain in the liquid is essentially the extrapolated shear modulus of the solid, and that for fixed particle concentration this determines the viscosity of the liquid. This implies that the time to relax the stress in the liquid is independent of the interaction strength between the particles. The relaxation time experimentally determined is the free diffusion time for an independent particle to go $\sim\frac{1}{10}$ of the nearest-neighbour distance as confirmed by varying the particle density. Theoretically this result is confirmed by a direct calculation of the relaxation time using a mode coupling scheme. As the strength of interaction between particles of fixed density is varied, $S(K)$ varies dramatically. However, the relaxation time is virtually unchanged in going from small interactions with $S(K)\sim 1$ to just above melting. Quantitatively the time is the same as that found experimentally. Phenomenologically this introduces a new meaning to the Lindemann melting criterion. Traditionally this suggests that a material melts when the RMS displacement of a particle from its mean position (as determined by the temperature and the interactions) is ~0.1 of the interparticle spacing. In the present context it suggests that the time for a material to 'melt' locally is given by the same criterion.

The interaction between the charged colloidal spheres is well described by a screened Coulomb or Yukawa potential of the form

$$V=\frac{Z^2e^2}{\varepsilon r}\,\mathrm{e}^{-kr} \qquad k^2=\frac{4\pi n_{\mathrm{ions}}e^2}{\varepsilon k_{\mathrm{B}}T} \tag{1}$$

where Z^* is the effective charge, ε is the dielectric constant of the solvent and n_{ions} is the total number of ions in solution including the countercharge to Z^* and any added electrolyte. In our experiments we determined Z^* by a measurement of the shear modulus of a colloidal crystal with no added electrolyte. The experiment has been described in detail elsewhere (Lindsay and Chaikin 1983, 1985). It consists of observing the shear elastic wave resonances of the colloidal crystal in a cylindrical geometry. The form of the potential is then tested by measuring the shear modulus as HCl is added to vary k. There is excellent experimental agreement with equation (1) up to the point at which a first-order melting transition is observed. The extrapolation of the shear modulus G is then accomplished either by using the value of Z^* in equation (1), or directly fitting the experimental data to a smooth function against c_{HCl} and extending this curve past the melting point. The results are equivalent to within experimental error.

The viscosity in the liquid state has been determined using several viscometers (Lindsay and Chaikin 1985). However, for the more concentrated samples, $0.01<\phi<0.05$, the viscosity just past the melting curve is slightly non-Newtonian and in this case we have used a Zimm viscometer (Mitaku *et al* 1978) which directly measures the strain rate for an applied stress in a small gap Couette geometry. The small gap ensures constant stress and data are only presented for the linear regime at low stress

If the electrostatic interactions dominate the hydrodynamic interactions, as is the case for most of this study, then the measured viscosity can be separated into two parts:

$$\eta \equiv \eta_0 + \eta_1 + O(\phi) \tag{2}$$

where η_0 is the viscosity of the solvent (water in our experiments), η_1 is the additional viscosity due to the interactions of the particles and the third term represents the hydrodynamic corrections which are of order ϕ for dilute suspensions. Equation (2) can be derived from a two-fluid model in which the colloidal particles are imagined to be a separate fluid interacting with the potential given in equation (1) and giving rise to the viscosity η_1, superposed on the solvent. A more rigorous treatment leading to equation (2) can be obtained from a generalised Fokker-Planck equation (Klein and Hess 1983, 1985).

In figures 1 and 2 we plot the measured viscosity against the extrapolated shear modulus for two samples with different particle density. The quantity which is being varied is c_{HCl}. It is clear from these figures that the viscosity varies linearly with the extrapolated shear modulus. Moreover, in figure 2 we see that the hydrodynamic correction to equation (2) gives the expected 2.5ϕ, as the strength of the interactions goes to zero.

In viscoelastic theory it is conventional to write the viscosity as

$$\eta \equiv G^{\infty} \tau \tag{3}$$

where G^{∞} is the infinite frequency or instantaneous shear modulus and τ is the Maxwellian relaxation time, the time for the fluid to relax a stress (Landau and Lifshitz 1970). Associating G^{∞} with the extrapolated shear modulus we are led to the conclusion that τ is independent of the strength of the interaction and moreover is numerically equal to $(0.1d)^2/D_0$ where d is the mean interparticle separation and $D_0 = k_B T / 6\pi\eta_0 a$ is the diffusion constant of the non-interacting sphere of radius a in the solvent.

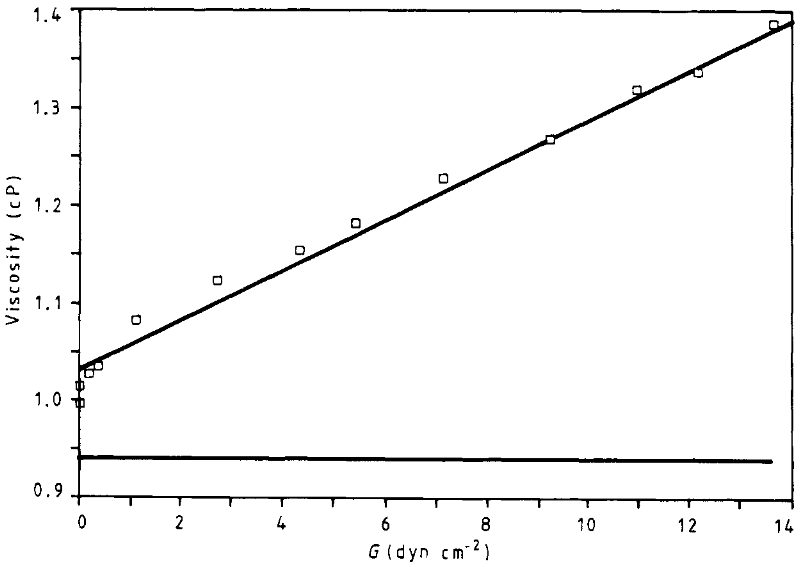

Figure 1. Viscosity of a sample of 0.109 μm spheres and 2% volume fraction plotted against the calculated shear modulus using an effective charge of 305. The horizontal line is the viscosity of water given for reference.

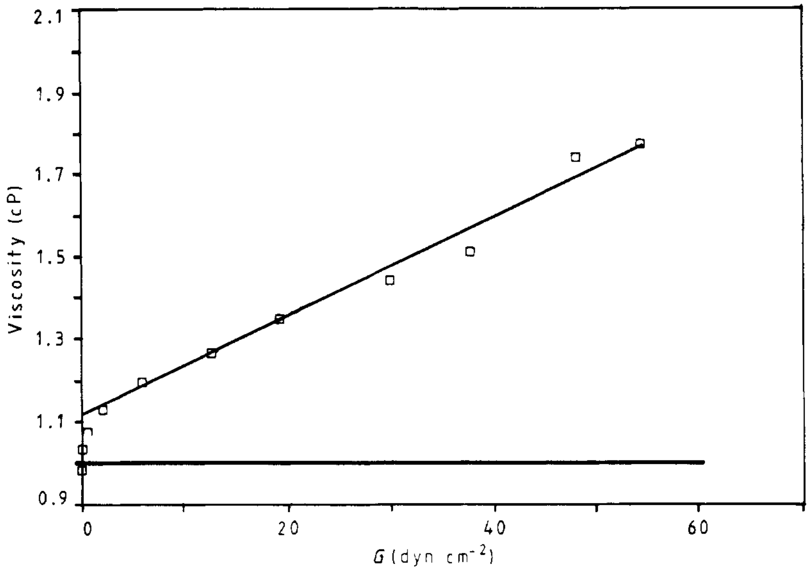

Figure 2. Viscosity of a sample of 0.109 μm spheres and 5% volume fraction plotted against the calculated shear modulus. The horizontal line is the Einstein value for non-interacting spheres. □, colloid; horizontal line, $(1+2.5)\eta_0$.

The theoretical treatment we will use is based on the Fokker–Planck description of the colloidal fluid elaborated in more detail in Batchelor (1972) and Klein and Hess (1983) and successfully applied to the cooperative and self-diffusion coefficients of colloidal liquids previously. Using a mode coupling approximation, the wavevector and time dependent viscosity function may be written in terms of the dynamic structure factor $S(k, t)$ and the total correlation function as

$$\eta(k, t) = \frac{2c^2}{k_B T(2\pi)^3} \int \mathrm{d}^3k' \frac{1}{k^2} g(\boldsymbol{k}, \boldsymbol{k}') g(-\boldsymbol{k}, -\boldsymbol{k}') S(\boldsymbol{k}_1', t) S(\boldsymbol{k}_2', t) \tag{4}$$

where

$$g(\boldsymbol{k}, \boldsymbol{k}') = \frac{\mathrm{i}k_B T}{2S(k_1')S(k_2')} [k_{1x}' h(\boldsymbol{k}_1') + k_{2x}' h(\boldsymbol{k}_2')] \qquad \boldsymbol{k}_{1,2}' = \tfrac{1}{2}(\boldsymbol{k} \pm \boldsymbol{k}')$$

and $h(k) = (S(k) - 1)/c$.

$S(k, t)$ in equation (4) is replaced by its mean-field expression

$$S(k, t) = S(k) \exp(-D_0 k^2 t / S(k)).$$

For the static structure factor we take the Hansen and Hayter form (Hansen and Hayter 1982) plus a correction for the long wavelength behaviour. The stress relaxation at zero wavevector as a function of time is seen from the behaviour of

$$f(t) \equiv \frac{\eta(0, t)}{\eta(0, 0)} = \frac{\eta(0, t)}{G^\infty}.$$

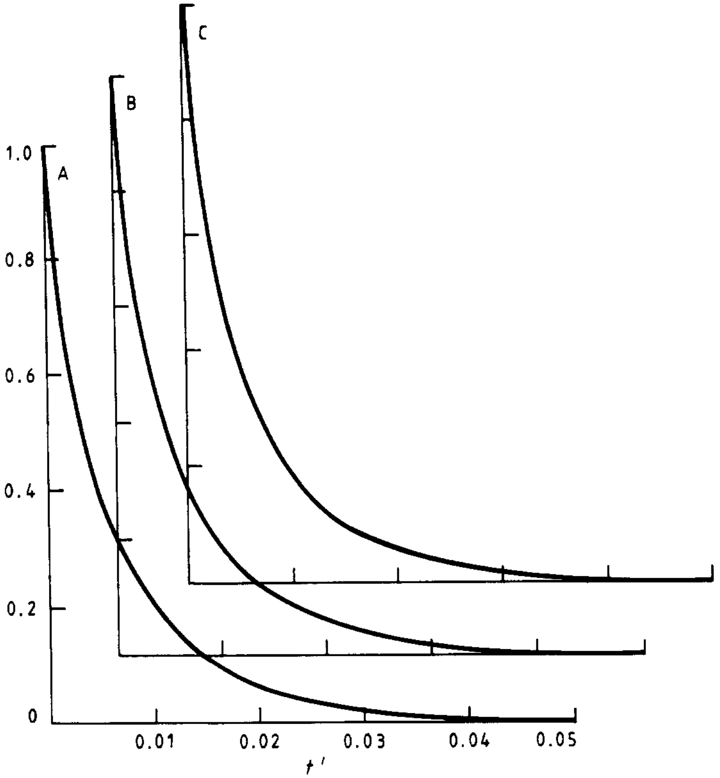

Figure 3. Normalised dynamic viscosity against reduced time $t' = D_0 t/d^2$ for several volume fractions (theory). Curve A is for $\phi = 10^{-4}$, curve B for $\phi = 1.5 \times 10^{-3}$ and curve C for $\phi = 4.5 \times 10^{-3}$.

As a function of the reduced time $t' = D_0 t/d^2 \equiv t/T$, figure 3 shows that the normalised dynamic viscosity is numerically identical for $10^{-4} < \phi < 4.5 \times 10^{-3}$. This spans the interaction regime (for the particular Z^*) from an essentially flat $S(K)$ to freezing. The time $T = d^2/D_0$ is the time a non-interacting particle would need to diffuse a distance $d = 2(3/4\pi c)^{1/3}$, which is the mean interparticle separation at concentration c. The only concentration dependence of the stress relaxation is contained in the concentration dependence of t' and therefore of d.

The contribution to the static shear viscosity due to interactions among the macroparticles is

$$\eta_1 = \int_0^\infty \eta(0, t)\,\mathrm{d}t.$$

Therefore

$$\eta_1 = G^\infty \frac{d^2}{D_0} \int_0^\infty \mathrm{d}t'\, f(t').$$

The integral is found to be approximately equal to 10^{-2}. Therefore

$$\eta_1/G^\infty = (d/10)^2/D_0 \equiv t_m$$

where t_m is the time which a particle needs to travel one-tenth of the distance to its nearest neighbour.

Although our mode coupling result for $\eta(0, t)$ deviates somewhat from a simple exponential, a simpler determination of this characteristic time is to approximate $\eta(0, t)$ by $\eta(0, t) = G^\infty \exp(-t/t'_m)$. Defining the transition from elastic to viscous behaviour by that time at which $\eta(0, t)$ has decreased to 1/e of its initial value, one obtains $t'_m = (d/7)^2/D_0$. Thus the suspension behaves elastically on a timescale which is given by the time the particle needs to travel one-seventh of the nearest-neighbour separation. More rigorously, the dynamical equations of Batchelor (1972, 1976, 1983) show that for short times the equation of motion for the transverse current fluctuations is that of a damped harmonic oscillator with a restoring force characterised by $\eta(k, 0) \equiv G^\infty$, the wavevector dependent high frequency elastic constant.

Physically for short times a particle is trapped in a glasslike cage of near neighbours which elastically resists shear. The 'melting' time for the local structure is the time in which the stress relaxes and this corresponds to the time required for the particles to diffuse a 'Lindemann' distance. What seems to be somewhat surprising is that the diffusion is essentially not retarded by the interactions with neighbouring particles since it is known that the self-diffusion of colloidal particles is strongly interaction dependent. However, theoretical calculations as well as molecular dynamic simulations indicate that a colloidal particle in such a cage has a mean square displacement $W(t)$ which for short times and distances is governed by D_0 and evolves at large times and displacements to a reduced value, D_s, largely governed by the difficulty encountered in leaving its cage. Using a 'time dependent' self-diffusion constant $D_s(t) = W(t)/t$, it is found that the characteristic time for reaching its asymptotic value D_s is much larger than t_m; therefore, it is more appropriate to connect the characteristic distance for the crossover from D_0 to D_s to the cage size or mean particle separation d. For solids the particle diffusion begins to slow down for distances less than $0.1d$, whereas for liquids the crossover is closer to d itself. Thus, in a liquid D_0 correctly describes the Brownian motion for the short distances given by the Lindemann criterion. For a simple liquid the only Brownian dynamics is given by the interactions of the particles themselves, and the diffusion coefficient is clearly related to the interaction strength.

It is, however, interesting to note that a fit of computer simulations for argon (Levesque *et al* 1973) as a Lennard-Jones fluid near its triple point to a single exponential dynamic viscosity function gives a shear stress relaxation time $\tau_t = 3.6 \times 10^{-13}$ s. During this time an argon atom in free flight with thermal velocity $(kT/M)^{1/2}$ spans about one-seventh of the interparticle distance, which is a similar value to the one obtained for the colloidal fluid. This is quite remarkable, since G^∞ in the two systems differs by roughly ten orders of magnitude, whereas the values of η_1 are rather similar. This might suggest further investigations to see whether the stress relaxation time is often given by the time required for displacement by a small fraction of the interparticle spacing.

In conclusion, we have demonstrated both theoretically and experimentally that the relation $\eta = G\tau$ has a quantitative and physically intuitive applicability in the case of colloidal liquids. This allows for the direct prediction of the viscosity of the liquid phase in terms of properties measured entirely in the solid phase (or in terms of the charge per sphere), a calculation which is not presently possible for any other materials of which we know. We have also introduced a new use of the phenomenological Lindemann criterion in which the local 'melting' time or stress relaxation time is given by the time required for a particle to diffuse a Lindemann distance. It is interesting to note that this criterion 'works' for systems which have long range or rather soft potentials in contrast to simple liquids and solids which are characterised by short range and rather hard potentials.

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