Viscoelasticity in Dense Hard Sphere Colloids

I. M. de Schepper and H. E. Smorenburg
Interfaculty Reactor Institute, Delft University of Technology, 2629 JB Delft, The Netherlands

E. G. D. Cohen
The Rockefeller University, New York, New York 10021

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We present a new microscopic theory for the frequency (ω) and density (ϕ) dependent complex shear viscosity $\eta(\phi,\omega)$ of dense hard sphere colloids near equilibrium. The predictions are in good agreement with experimental results for silica spheres dissolved in cyclohexane.

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Recently, a number of measurements have been performed to determine the viscoelastic behavior of a series of typical dense monodisperse colloidal systems consisting of neutral silica hard spheres with various diameters σ dispersed in cyclohexane [1]. One measures the complex shear viscosity $\eta(\phi,\omega)$ as a function of the frequency ω of a small oscillating externally applied velocity disturbance at volume fraction $\phi=\pi n\sigma^3/6$ with $n=N/V$ the number density of N colloidal particles in a volume V. One finds that $\eta(\phi,\omega)$ depends on ϕ (but not on the particular value of σ) while the dependence on ω is very similar for all high densities $0.3<\phi<0.6$. In fact, at each ϕ one observes a very smooth transition of the complex shear viscosity $\eta(\phi,\omega)$ from its initial value $\eta(\phi,0)$, which is real, to its (real) final value $\eta(\phi,\infty)$, which is much smaller than $\eta(\phi,0)$ and roughly of the order of the viscosity η_0 of the pure solvent. The initial value $\eta(\phi,0)$ for $\omega=0$ of the viscosity strongly increases with increasing ϕ and is many times larger than η_0, as can be seen in Fig. 1, where the experimental values of $\eta(\phi,0)/\eta_0$ [1,2] are plotted as a function of ϕ. For large frequencies ω one finds that both the real part $\mathrm{Re}\,\eta(\phi,\omega)$ and the imaginary part $\mathrm{Im}\,\eta(\phi,\omega)$ of $\eta(\phi,\omega)$ decay to their final asymptotic values proportional to $\omega^{-1/2}$ with the same coefficient. One has for $\omega\to\infty$ [1]

$$\mathrm{Re}\frac{\eta(\phi,\omega)-\eta(\phi,\infty)}{\eta(\phi,0)-\eta(\phi,\infty)}=\mathrm{Im}\frac{\eta(\phi,\omega)-\eta(\phi,\infty)}{\eta(\phi,0)-\eta(\phi,\infty)}=\frac{3\sqrt{2}}{2\pi}[\omega\tau_1(\phi)]^{-1/2}, \qquad (1)$$

where the phenomenological time $\tau_1(\phi)$ is determined from experiment. The experimental results for $\tau_1(\phi)/\tau_p$ are given in Fig. 2 as a function of ϕ. Here $\tau_p=(\sigma/2)^2/D_0$ is the so-called Peclet time with $D_0=k_BT/3\pi\eta_0\sigma$ the Stokes-Einstein diffusion coefficient, k_B the Boltzmann constant, and T the temperature. Thus, τ_p is the time a free colloidal particle needs to diffuse over a distance $\sigma/2$ in the solvent. For concentrated colloids, τ_p is of the order of the "interaction time," i.e., the time a colloidal particle needs to interact with its neighbors. Furthermore, it appears from experiment that the reduced complex viscosity $[\eta(\phi,\omega)-\eta(\phi,\infty)]/[\eta(\phi,0)-\eta(\phi,\infty)]$ as a function of $\omega\tau_1(\phi)$ is virtually independent of the density ϕ. This is shown in Fig. 3, where the real and imaginary parts of the reduced viscosity are plotted as a function of $\omega\tau_1(\phi)$ for all $0.3<\phi<0.6$.

To our knowledge no microscopic theory is available at present to understand these experimental results. Here we discuss a new but approximate theory for the viscoelastic behavior of dense neutral colloids of hard spheres based on direct (pair) interactions between the colloidal particles only. We start from the more general viscosity $\eta(\gamma,\phi,\omega)$ of colloids when the externally applied velocity disturbance has both an oscillatory contribution (with frequency ω and very small amplitude) and a constant contribution in time [with shear rate $\gamma=\partial u_x(y)/\partial y$, where $u_x(y)$ is the fluid velocity in the x direction which only depends on y]. Then $\eta(\phi,\omega)=\eta(\gamma=0,\phi,\omega)$, where the limit $\gamma=0$ will be taken at the end. For $\eta(\gamma,\phi,\omega)$ one has for low densities and general (realistic) interactions [3-5]

$$\eta(\gamma,\phi,\omega)=\eta_0+\frac{1}{2}\frac{n^2}{\gamma}\int d\mathbf{r}\,g(\mathbf{r},\gamma,\omega)\,y\frac{\partial V(r)}{\partial x}, \qquad (2)$$

where $\mathbf{r}=(x,y,z)$ is a vector with length r, $g(\mathbf{r},\gamma,\omega)$ is the pair correlation function of the fluid under shear ($\gamma\neq0,\omega\neq0$), and $V(r)$ is the pair interaction potential

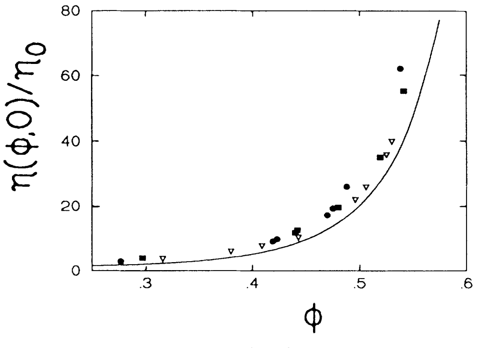

FIG. 1. Reduced viscosity $\eta(\phi,0)/\eta_0$ as a function of ϕ for silica spheres in cyclohexane [1,2]: squares, $\sigma=92$ nm; triangles, $\sigma=152$ nm; circles, $\sigma=220$ nm. Full curve is from theory [Eq. (9)].

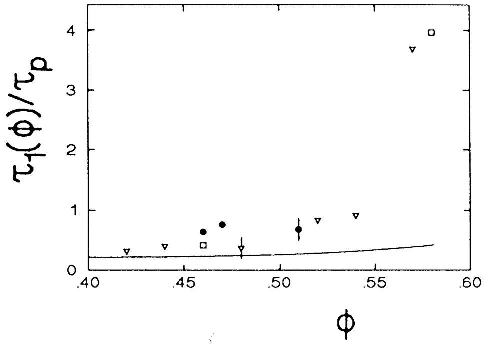

FIG. 2. Reduced relaxation time $\tau_1(\phi)/\tau_p$ as a function of ϕ for silica spheres in cyclohexane [1]: squares, $\sigma=56$ nm; triangles, $\sigma=92$ nm; circles, $\sigma=152$ nm. Full curve is from theory [Eq. (14)].

between two colloidal particles at distance r. Equation (2) has been discussed in Ref. [5] for $\phi \rightarrow 0$, $\omega=0$, and Debye-Hückel (shielded Coulomb) potentials $V(r)$. We extend Eq. (2) to hard spheres and high densities using the mean spherical approximation [6], i.e., we replace $V(r)$ in Eq. (2) by $V(r)=-k_BTC(r)$ with $C(r)$ the direct correlation function of hard spheres in equilibrium $(\gamma=0,\omega=0)$. The spatial Fourier transform $C(k)$ of $C(r)$ is $C(k)=[S(k)-1]/nS(k)$, where $S(k)$ is the static structure factor of the hard sphere colloidal particles in equilibrium. Using these results we can write Eq. (2) in Fourier representation as

$$\eta(\gamma,\phi,\omega)=\eta_0+\frac{k_BT}{16\pi^3\gamma}\int d\mathbf{k}\,\frac{k_xk_y}{k}\,\frac{S'(k)}{S(k)^2}\,\delta S(\mathbf{k},\gamma,\omega)\,, \tag{3}$$

with $\mathbf{k}=(k_x,k_y,k_z)$ a wave vector with length k, $S'(k)=\partial S(k)/\partial k$, and $\delta S(\mathbf{k},\gamma,\omega)=S(\mathbf{k},\gamma,\omega)-S(k)$, where $S(\mathbf{k},\gamma,\omega)$ is the static structure factor of the suspension under shear $(\gamma\neq 0,\omega\neq 0)$ given by

$$S(\mathbf{k},\gamma,\omega)=1+n\int d\mathbf{r}\exp(i\mathbf{k}\cdot\mathbf{r})[g(\mathbf{r},\gamma,\omega)-1]\,. \tag{4}$$

In Eq. (3), the distortion $\delta S(\mathbf{k},\gamma,\omega)$ of the static structure by the shear satisfies the balance equation [3-5]

$$\left[-\gamma k_y\frac{\partial}{\partial k_x}-i\omega+2\omega_H(k)\right]\delta S(\mathbf{k},\gamma,\omega)=\gamma k_y\frac{\partial}{\partial k_x}S(k)\,, \tag{5}$$

where $\omega_H(k)$ is the decay rate of equilibrium fluctuations in the density of colloidal particles for times t of the order of τ_p, i.e., $(t\lesssim\tau_p)$

$$\begin{aligned}F(k,t)&\equiv\frac{1}{N}\sum_{i,j=1}^{N}\langle\exp[i\mathbf{k}\cdot[\mathbf{r}_i(0)-\mathbf{r}_j(t)]]\rangle_0\\&=S(k)\exp[-\omega_H(k)t]\,.\end{aligned} \tag{6}$$

Here $\mathbf{r}_j(t)$ is the position of colloidal particle j at time t and the brackets denote an equilibrium ensemble average $(\gamma=0,\omega=0)$. $F(k,t)$ is the equilibrium intermediate dynamic structure factor and can be obtained experimentally by dynamic light scattering [7]. Its Fourier transform in time is the dynamic structure factor $S(k,\omega)$ [with half-width $\omega_H(k)$] which is experimentally accessible through neutron scattering.

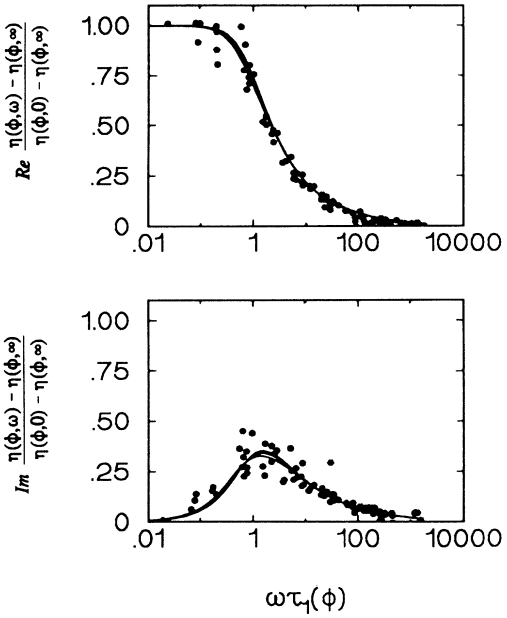

FIG. 3. Reduced complex shear viscosity $\eta(\phi,\omega)$ as a function of $\omega\tau_1(\phi)$. The data points refer to silica in cyclohexane [1] $(0.3<\phi<0.6)$. The full curves are from theory for $\phi=0.4$, 0.5, and 0.55 [Eq. (9)] (hardly distinguishable).

The balance equation (5) has been derived from the Smoluchowski equation by Dhont, van der Werff, and de Kruif [Ref. [5], Eq. (3.11)] for $\omega=0$ and low densities ϕ, where $\omega_H(k)=D_0k^2$. A low density theory for $\eta(\phi,\omega)$ similar to that of Dhont, van der Werff, and de Kruif has been discussed by Cichocki and Felderhof [8]. For high densities $0.3<\phi<0.6$ we use Eq. (5) with $\omega\neq 0$ and $\omega_H(k)$ defined by Eq. (6). It appears from experiments that for high densities and the reduced wave numbers $k\sigma>1$, relevant here, $\omega_H(k)$ can be represented very well by [7,9-11]

$$\omega_H(k)=\frac{D_0k^2}{\chi S(k)[1-J_0(k\sigma)+2J_2(k\sigma)]}\,, \tag{7}$$

where $J_0(x)$ and $J_2(x)$ are the spherical Bessel functions of orders 0 and 2, respectively, and $\chi=g(\sigma)$ is the value of the pair correlation function $g(r)=g(\mathbf{r},0,0)$ at contact in equilibrium $(\gamma=0,\omega=0)$.

Thus we arrive at a set of equations for $\eta(\gamma,\phi,\omega)$, i.e., Eqs. (3), (5), and (7), which we will now solve for $\gamma\rightarrow 0$. In that case Eq. (5) yields

$$\delta S(\mathbf{k},\gamma,\omega)=\gamma k_y\frac{\partial S(k)}{\partial k_x}[2\omega_H(k)-i\omega]^{-1}+O(\gamma^2)\,. \tag{8}$$

Substituting this result in Eq. (3), taking the limit $\gamma \to 0$, and performing trivial angular integrations in **k** space, our final result for $\eta(\phi,\omega)=\eta(\gamma=0,\phi,\omega)$ becomes

$$\eta(\phi,\omega)=\eta_0+\frac{k_BT}{60\pi^2}\int_0^\infty dk\,k^4\left(\frac{S'(k)}{S(k)}\right)^2\frac{1}{2\omega_H(k)-i\omega}\,. \tag{9}$$

First, we note that the k integral is convergent for all ω since the integrand vanishes for $k\to 0$, while for large k ($k\to\infty$)

$$\omega_H(k)=\frac{D_0}{\chi}k^2[1+O(k^{-2})]\,, \tag{10}$$

$$S(k)=1-24\phi\chi\frac{J_1(k\sigma)}{k\sigma}[1+O(k^{-2})]\,, \tag{11}$$

$$S'(k)=24\phi\chi\frac{J_2(k\sigma)}{k}[1+O(k^{-2})]\,, \tag{12}$$

and $J_n(x)\sim x^{-1}$ for $x\to\infty$. Therefore, the second term on the right-hand side of Eq. (9) vanishes for $\omega\to\infty$, so that, according to the theory, $\eta(\phi,\infty)=\eta_0$. Second, we remark that Eq. (9) implies that $\eta(\phi,\omega)/\eta_0$ is a function of ϕ and $\omega\tau_p$ only [because $S(k)$ is a function of ϕ and $k\sigma$ alone].

We have evaluated Eq. (9) for $\eta(\phi,\omega)$ and $\omega=0$ numerically, using Eq. (7) for $\omega_H(k)$ and the Percus-Yevick expressions for $S(k)$ and $\chi=(1+\phi/2)/(1-\phi)^2$ [12]. The theoretical result for $\eta(\phi,0)/\eta_0$, shown in Fig. 1 as a function of ϕ, describes the experimentally observed strong increase of $\eta(\phi,0)$ with increasing ϕ quite well.

The *large* k behavior of $S(k)$ [$=1$, cf. Eq. (11)], $S'(k)$ [from Eq. (12)], and $\omega_H(k)$ [from Eq. (10)] induces in Eq. (9) for $\eta(\phi,\omega)$ a square root singularity for *large* ω, i.e., for $\omega\to\infty$,

$$\eta(\phi,\omega)=\eta_0+\tfrac{9}{5}\phi^2\chi^{5/2}\eta_0(\omega\tau_p)^{-1/2}(1+i)+O(\omega^{-1})\,. \tag{13}$$

Thus, Eq. (1) follows immediately, with

$$\tau_1(\phi)=\left(\frac{\eta(\phi,0)}{\eta_0}-1\right)^2\frac{25}{18\pi^2\phi^4\chi^5}\tau_p\,. \tag{14}$$

This theoretical result for $\tau_1(\phi)$ is in reasonable agreement with experiment, at least below $\phi=0.55$ as can be seen in Fig. 2.

Finally we calculate $\eta(\phi,\omega)$ numerically from Eq. (9) as a function of ω for $\phi=0.4$, 0.5, and 0.55. We find that the reduced complex viscosity $[\eta(\phi,\omega)-\eta(\phi,\infty)]/[\eta(\phi,0)-\eta(\phi,\infty)]$ as a function of $\omega\tau_1(\phi)$ is indeed virtually independent of ϕ. Theoretical results, shown in Fig. 3, are in excellent agreement with experiment.

We conclude therefore that the approximate theory presented here [cf. Eqs. (3) and (5)] captures the basic mechanisms relevant for the viscoelastic behavior of dense neutral hard sphere colloids up to about $\phi\approx 0.55$.

We end with a number of open questions and remarks. (i) One observes in Fig. 2 a sudden increase in $\tau_1(\phi)$ when $\phi\gtrsim 0.55$ which is not predicted by the theory. This is possibly related to the fact that near the glass transition ($\phi\approx 0.6$), $F(k,t)$ in Eq. (6) decays extremely slowly for very long times $t\gg\tau_p$, with a decay rate much smaller than $\omega_H(k)$ of Eq. (7), which describes $F(k,t)$ in the liquid phase for $t\lesssim\tau_p$ [7]. It follows straightforwardly from Eqs. (9), (13), and (1) that when $\omega_H(k)$ in Eq. (5) is replaced by $\omega_H(k)/\alpha$ (with $\alpha>1$ a scaling factor), $\tau_1(\phi)$ in Eq. (1) will increase ($\sim\alpha^{1/2}$) with increasing $\alpha>1$. Thus, lower decay rates $\omega_H(k)$ of $F(k,t)$ cause higher relaxation times $\tau_1(\phi)$ in $\eta(\phi,\omega)$, so that the sudden increase in $\tau_1(\phi)$ might signal the onset of the glass transition. (ii) The present theory is based on Eq. (5) derived for the pair correlation function from the Smoluchowski equation in the absence of hydrodynamic interactions. This implies that, theoretically, $\eta(\phi,\infty)=\eta_0$ for all ϕ as noted below Eq. (12). However, experimentally one finds that $\eta(\phi,\infty)$ slowly increases from η_0 at $\phi=0$ to about $10\eta_0$ at $\phi=0.55$ [1,13]. Up to about $\phi\approx 0.4$, the observed behavior of $\eta(\phi,\infty)$ agrees rather well [1] with the low density theory of Beenakker [14] in which hydrodynamic interactions are included. Thus, it would clearly be important to develop a theory similar to that presented here, which includes hydrodynamic interactions. (iii) For monatomic dense fluids of hard spheres with diameter σ and mass m, expressions have been derived for the viscosity $\eta_{\text{hs}}(\phi,\omega)$ [15–17], which are very similar to those presented here [i.e., Eqs. (3), (5), and (6)]. The equilibrium viscosity $\eta_{\text{hs}}(\phi,0)$ at $\omega=0$ is then given by [17]

$$\eta_{\text{hs}}(\phi,0)=\eta_E+\frac{k_BT}{60\pi^2}\int_{6t_E}^\infty dt\int_0^\infty dk\,k^4\left(\frac{S'(k)}{S(k)}\right)^2\times\exp[-2\omega_H(k)t]\,. \tag{15}$$

Here η_E is the Enskog shear viscosity, t_E is the mean free time between collisions, and the decay rate $\omega_H(k)$ of $F(k,t)$ is defined as in Eq. (6). $\omega_H(k)$ is given by Eq. (7) with D_0 replaced by $D_B=0.216(k_BT/m)^{1/2}n\sigma^2$, the Boltzmann value of the self-diffusion coefficient, $t_E=(m/\pi k_BT)^{1/2}/4n\sigma^2\chi$, and $\eta_E/\eta_B=(1+3.2\phi\chi+12.18\phi^2\chi^2)/\chi$ where $\eta_B=0.179(mk_BT)^{1/2}/\sigma^2$ is the Boltzmann value of the viscosity.

We note the remarkable similarity of the second terms on the right-hand sides of Eq. (9) (with $\omega=0$) and Eq. (15). In fact, they are equal when the lower limit $6t_E$ in the time integral of Eq. (15) is replaced by zero. Equation (15) for $\eta_{\text{hs}}(\phi,0)$ leads to a strong increase in $\eta_{\text{hs}}(\phi,0)$ with increasing ϕ, similar to that shown in Fig. 1 for colloids. Moreover, in particular one finds that $\eta_{\text{hs}}(\phi,0)/\eta_B\approx\eta(\phi,0)/\eta_0$. We note that both terms on the right-hand side of Eq. (15) contribute to the increase of $\eta_{\rm hs}(\phi,0)/\eta_B$ with the first term given by η_E/η_B, while the second term contributes significantly for $\phi > 0.45$ only. Similarities in the (viscoelastic) ω behavior of $\eta_{\rm hs}(\phi,\omega)$ for dense hard sphere fluids and $\eta(\phi,\omega)$ for concentrated hard sphere colloids have not been studied so far.

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