

Viscoelastic and Rheological Behavior of Concentrated Colloidal Suspensions¹

I. M. de Schepper^{2,3} and E. G. D. Cohen⁴

Molecular approaches are discussed to the density (ϕ), viscoelastic (ω), and rheological ($\dot{\gamma}$) behavior of the viscosity $\eta(\phi, \omega, \dot{\gamma})$ of concentrated colloidal suspensions with $0.3 < \phi < 0.6$, where ϕ is the volume fraction, ω the applied frequency, and $\dot{\gamma}$ the shear rate. These theories are based on the calculation of the pair distribution function $P_2(\mathbf{r}; \omega, \dot{\gamma})$, where \mathbf{r} is the relative position of a pair of colloidal particles. The linear viscoelastic behavior $\eta(\phi, \omega, \dot{\gamma} = 0)$ follows from an equation for $P_2(\mathbf{r}, \omega, \dot{\gamma})$ derived from the Smoluchowski equation for small ϕ , generalized to large ϕ by introducing the spatial ordering and (cage) diffusion typical for concentrated suspensions. The rheological behavior $\eta(\phi, \omega = 0, \dot{\gamma})$ follows from an equation for $P_2(\mathbf{r}; \dot{\gamma})$ of a dense hard-sphere fluid derived from the Liouville equation. This leads to a hard-sphere viscosity $\eta^h(\phi, \dot{\gamma})$ which yields the colloidal one $\eta(\phi, \dot{\gamma})$ by the scaling relation $\eta(\phi, \dot{\gamma})/\eta_0 = \eta^h(\phi, \dot{\gamma})/\eta_h$, where η_0 is the solvent viscosity, η_h is the dilute hard-sphere (Boltzmann) viscosity, and the $\dot{\gamma}$'s are appropriately scaled. $\eta(\phi, \omega)$ and $\eta(\phi, \dot{\gamma})$ agree well with experiment. A unified theory for $\eta(\phi, \omega, \dot{\gamma})$ is clearly needed and pursued.

KEY WORDS: concentrated colloids; rheology; viscoelasticity; viscosity.

1. INTRODUCTION

In this paper we are interested in the shear viscosity $\eta(\phi, \omega, \dot{\gamma})$ of neutral concentrated colloidal suspensions, not only in its dependence on the volume fraction ϕ , but especially in its dependence on an imposed frequency ω (viscoelastic behavior) or on an imposed shear rate $\dot{\gamma}$ (rheological behavior). We discuss two theoretical approaches and compare them with experimental results. In both theoretical approaches hydrodynamic interactions are

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² I.R.I., Delft University of Technology, 2629 JB Delft, The Netherlands.

³ To whom correspondence should be addressed.

⁴ The Rockefeller University, New York, New York 10021, U.S.A.

neglected. One approach is based on the Smoluchowski equation for the pair distribution function of a colloidal suspension and allows a discussion of the viscoelastic behavior; the other is based on the Liouville equation for a fluid of hard spheres and allows, by a scaling procedure, a discussion of the rheological behavior of concentrated colloidal suspensions. We only sketch the derivations and refer to the literature for details. In Section 2 we discuss the viscoelastic behavior, in Section 3 the rheological behavior, and in Section 4 we comment on the results.

2. VISCOELASTIC BEHAVIOR

Starting from the Smoluchowski equation for N neutral spherical Brownian particles without hydrodynamical interactions in a solvent under an imposed time-dependent shear rate $\dot{\gamma}(t) = \dot{\gamma} \exp(i\omega t)$ and integrating this equation over the positions of all particles but two, one obtains an equation for the nonequilibrium pair distribution function $P_2(\mathbf{R}; \mathbf{r}, \phi, \omega, \dot{\gamma}, t)$ involving the three-particle distribution function. Here $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the center of mass and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ the relative location, with \mathbf{r}_i the position of particle i ($i = 1, 2$). Neglecting the terms that involve the three-particle distribution function and ignoring spatial inhomogeneity (i.e., the dependence on \mathbf{R}), one arrives at the equation [1–4].

$$\begin{aligned} & \left[\frac{\hat{c}}{\hat{c}t} + 2\beta D_0 \nabla \cdot \mathbf{F}(\mathbf{r}) - 2D_0 \nabla^2 + \dot{\gamma} e^{i\omega t} x \frac{\hat{c}}{\hat{c}y} \right] \delta P(\mathbf{r}; \phi, \omega, \dot{\gamma}, t) \\ & = -\dot{\gamma} e^{i\omega t} x \frac{\hat{c}}{\hat{c}y} g(r; \phi) \end{aligned} \quad (1)$$

Here $\mathbf{r} = (x, y, z)$, $\delta P(\mathbf{r}; \phi, \omega, \dot{\gamma}, t) = P_2(\mathbf{r}; \phi, \omega, \dot{\gamma}, t) - g(r; \phi) = P_2(\mathbf{r}; \phi, \omega = 0, \dot{\gamma} = 0, t)$ the equilibrium radial distribution function, $\mathbf{F}(\mathbf{r})$ is the force between two particles, $\beta = 1/k_B T$, with T the temperature and k_B Boltzmann's constant, and D_0 is the Brownian (Stokes–Einstein) diffusion coefficient of a colloidal particle in a dilute suspension. Taking a Fourier transform of Eq. (1) with respect to \mathbf{r} , one can derive an equation for the deviation $\delta S(\mathbf{k}; \phi, \dot{\gamma}, \omega, t)$ of the structure factor from equilibrium:

$$\delta S(\mathbf{k}; \phi, \omega, \dot{\gamma}, t) = S(\mathbf{k}; \phi, \omega, \dot{\gamma}, t) - S(k; \phi) \quad (2)$$

where $S(k; \phi) = S(\mathbf{k}; \phi, \omega = 0, \dot{\gamma} = 0, t)$ is the equilibrium static structure factor [i.e., the spatial Fourier transform of $g(r; \phi)$]. We are particularly interested in values of ϕ and k for which $S(k; \phi)$ has a sharp maximum, i.e., in $0.3 < \phi < 0.6$ and $k \approx k^*$ with $k^* \sigma = 2\pi$. Here σ is the diameter of the colloidal particles and $\phi = \pi n \sigma^3 / 6$, the volume fraction with n the number

density. This sharp maximum of $S(k; \phi)$ at $k = k^*$ reflects the highly ordered state of the colloidal particles in the suspension on a length scale $\lambda^* = 2\pi/k^* = \sigma$ in cages, i.e., each particle finds itself in a cage, formed by its nearest neighbors, out of which it can escape only with difficulty. Then one derives from Eq. (1) the following equation for $\delta S(\mathbf{k}; \phi, \omega, \gamma, t)$ [5]:

$$\left[\frac{\partial}{\partial t} + \frac{2}{\tau_c(k; \phi)} - \gamma e^{i\omega t} k_y \frac{\partial}{\partial k_x} \right] \delta S(\mathbf{k}; \phi, \omega, \gamma, t) = \gamma e^{i\omega t} k_y \frac{\partial}{\partial k_x} S(k; \phi) \quad (3)$$

The only *dynamical* fluid property in Eq. (3) is the cage diffusion time $\tau_c(k; \phi)$, which determines the rate at which a particle can diffuse out of its cage. It is a collective diffusion process involving not only the motion of the particle inside the cage, but also that of its neighbors, which form the cage. The crucial cage diffusion time $\tau_c(k; \phi)$ is obtained from that of a corresponding dense fluid of hard spheres, where the particles move between collisions ballistically *in vacuo*, rather than carry out Brownian motion in a solvent, as in a suspension (cf. Fig. 1). Although at first sight these two types of motions appear to be very different, a closer observation of them on long time scales shows that for dense fluids they are qualitatively hardly distinguishable, as has been noticed by Löwen *et al.* [6]. Quantitatively, they take place on very different time scales, determined, for instance, by their low-density diffusion coefficients: D_B^{hs} , the Boltzmann diffusion coefficient for a hard-sphere gas, and D_0 , the Stokes-Einstein diffusion coefficient for a very dilute suspension, respectively. Since $D_B^{hs}/D_0 \approx 1000$ the cage-diffusion time scales of the two fluid systems will differ by about

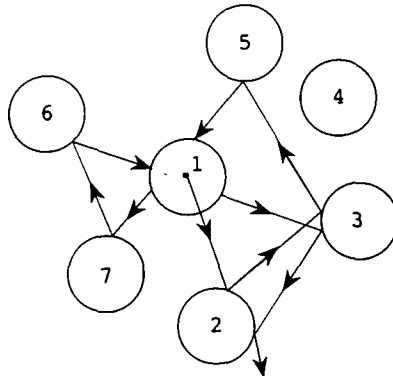


Fig. 1. Cage diffusion collisions of central particle 1. The motion of the wall particles 2 to 7 is not indicated. For clarity the distances between the hard spheres forming the cage have been enlarged considerably.

a factor of 1000, i.e., Newtonian motion proceeds on an asymptotic time scale similarly as Brownian motion, except a thousand times faster.

Using this analogy, one can determine $\tau_c(k; \phi)$ for the concentrated colloidal suspension from that of a dense hard-sphere fluid at the same volume fraction $\tau_c^{hs}(k; \phi)$, by scaling, i.e., by replacing D_B^{hs} [5] by D_0 [7]:

$$\tau_c^{hs}(k; \phi) = \tau_c^{hs}(k; \phi; D_B^{hs}) \tag{4}$$

so that

$$\tau_c(k; \phi) = \tau_c^{hs}(k; \phi; D_0)$$

where $\tau_c^{hs}(k; \phi; D_B^{hs})$ follows from kinetic theory [8]:

$$\frac{1}{\tau_c^{hs}(k; \phi; D_B^{hs})} = \frac{D_B^{hs} k^2}{g(r = \sigma; \phi) S(k; \phi) [1 - j_0(k\sigma) + 2j_2(k\sigma)]} \tag{5}$$

with $j_0(x)$ and $j_2(x)$ spherical Bessel functions and $g(r = \sigma; \phi)$ the radial distribution function at contact for the hard-sphere fluid in equilibrium.

Using Eq. (5) in Eq. (3), solving the so-obtained equation for $\delta S(\mathbf{k}; \phi, \omega, \gamma, t)$, integrating the solution over \mathbf{k} , and then setting $\gamma = 0$, one obtains for the viscoelastic behavior $\eta(\phi; \omega) = \eta(\phi; \omega, \gamma = 0)$ [5]:

$$\eta(\phi; \omega) = \eta_0 + \eta_c [S(k; \phi); \tau_c(k; \phi); \omega] \tag{6}$$

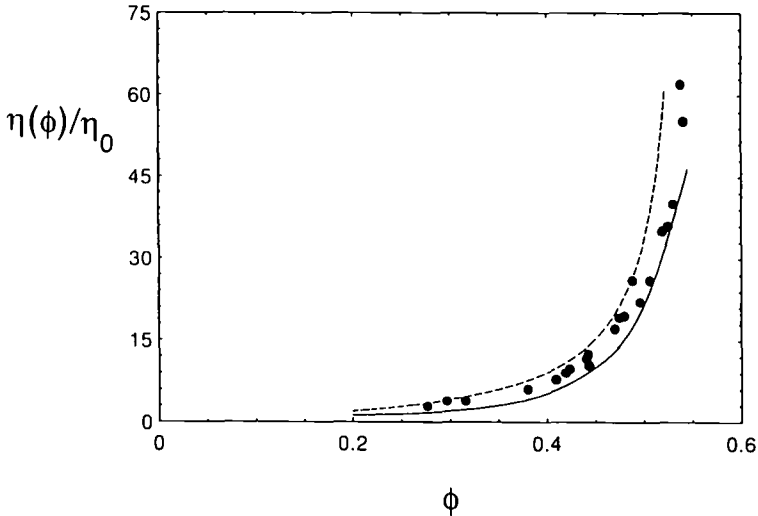


Fig. 2. Reduced viscosity as a function of volume fraction for silica spheres in cyclohexane [9] (filled circles), from Eq. (6) (solid line) and from Eqs. (8) and (9) (dashed line).

Here η_0 is the viscosity of the solvent and the ω -dependence of η is via η_c , the correction to η_0 due to the cage diffusion process of the Brownian particles in the fluid, which depends functionally on the equilibrium static structure factor $S(k; \phi)$ and the cage diffusion time $\tau_c(k; \phi)$. We remark the following:

1. For $\omega = 0$, one obtains the concentration dependence of the Newtonian viscosity $\eta(\phi) = \eta(\phi; \omega = 0)$. A comparison of theory and experiment [9] is made in Fig. 2. The agreement is good.
2. For $\omega \neq 0$, the viscosity is a complex function of ω : $\eta(\phi, \omega) = \eta'(\phi; \omega) - i\eta''(\phi; \omega)$, and in Fig. 3 the real and imaginary parts of a reduced viscosity $\eta^*(\phi; \omega) = [\eta(\phi; \omega) - \eta(\phi; \infty)] / [\eta(\phi; 0) - \eta(\phi; \infty)]$ are plotted for $0.3 < \phi < 0.6$ as a function of a reduced frequency $\omega^* = \omega\tau_1(\phi)$ for a number of concentrations. Here $\tau_1(\phi) \approx \tau_p/4$ [5], where $\tau_p = \sigma^2/4D_0$ is the Péclet time. We note in Fig. 3,

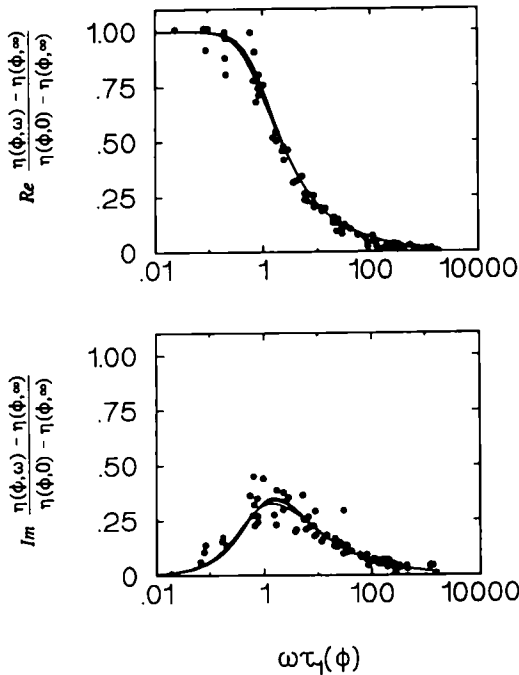


Fig. 3. Reduced complex shear viscosity $\eta^*(\phi, \omega)$ as a function of $\omega\tau_1(\phi)$. The data points refer to silica spheres in cyclohexane [9] ($0.3 < \phi < 0.6$). The full curves are from theory for $\phi = 0.4, 0.5,$ and 0.55 [Eq. (6)] (hardly distinguishable).

for both theory and experiment [9], (a) the independence of $\eta^*(\phi; \omega)$ of ϕ and (b) $\lim_{\omega \rightarrow \infty} \text{Re } \eta^*(\phi; \omega) = \lim_{\omega \rightarrow \infty} \text{Im } \eta^*(\phi; \omega) = 0.675(\omega\tau_1(\phi))^{-1/2}$.

Although the rheological behavior $\eta(\phi; \dot{\gamma}) = \eta(\phi; \omega = 0; \dot{\gamma})$ can also be derived from Eq. (3), we postpone its discussion to the next section.

3. RHEOLOGICAL BEHAVIOR

Starting from the Liouville equation for N hard spheres under an imposed time-dependent shear rate $\dot{\gamma}(t) = \dot{\gamma} \exp^{i\omega t}$ and integrating this equation over the momenta of all the particles and the positions of all the particles but two, one obtains an equation for the nonequilibrium pair distribution function $P_2^{\text{hs}}(\mathbf{R}, \mathbf{r}; \phi, \omega, \dot{\gamma}, t)$ involving the three-particle distribution function. Neglecting the terms that involve the latter and ignoring spatial inhomogeneity, one finds an equation for the deviation $\delta S^{\text{hs}}(\mathbf{k}; \phi, \omega, \dot{\gamma}, t)$, defined as in Eq. (2), which reads [10, 11]

$$\left[\frac{\partial}{\partial t} + \frac{2}{\tau_c^{\text{hs}}(k; \phi)} - \dot{\gamma} e^{i\omega t} k_y \frac{\partial}{\partial k_y} \right] \delta S^{\text{hs}}(\mathbf{k}; \phi, \omega, \dot{\gamma}, t) = \dot{\gamma} e^{i\omega t} k_y \frac{\partial}{\partial k_y} S^{\text{hs}}(k; \phi) \quad (7)$$

This equation is the same as Eq. (3), except that $\tau_c(k; \phi)$ in Eq. (3) is replaced in Eq. (7) by $\tau_c^{\text{hs}}(k; \phi)$ of Eq. (5). For a stationary state, where $\omega = 0$, a solution of this equation leads, after integration over \mathbf{k} , to an expression for the rheological viscosity $\eta^{\text{hs}}(\phi; \dot{\gamma}) = \eta^{\text{hs}}(\phi; \omega = 0; \dot{\gamma})$ of a dense fluid of hard spheres of the form [5, 10]

$$\eta^{\text{hs}}(\phi; \dot{\gamma}) = \eta_E^{\text{hs}}(\phi) + \eta_c^{\text{hs}}[S^{\text{hs}}(k; \phi); \tau_c^{\text{hs}}(k; \phi); \dot{\gamma}] \quad (8)$$

where $\eta_E^{\text{hs}}(\phi)$ is the viscosity of a dense hard-sphere fluid given by the Enskog kinetic theory and η_c^{hs} gives the correction to η_E^{hs} due to cage diffusion.

In order to obtain from Eq. (8) the corresponding values of $\eta(\phi; \dot{\gamma})$ for a concentrated colloidal suspension, we apply a scaling procedure to the relative viscosity of the colloidal suspension [12]:

$$\frac{\eta(\phi; \dot{\gamma}\tau_\eta)}{\eta_0} = \frac{\eta^{\text{hs}}(\phi; \dot{\gamma}\tau_\eta^{\text{hs}})}{\eta_B^{\text{hs}}} \quad (9)$$

Here η_B^{hs} is the viscosity of a hard-sphere gas obtained from the Boltzmann equation [5] and $\tau_\eta^{\text{hs}} = 3\pi\eta_B^{\text{hs}}\sigma^3/(4k_B T)$ for the hard-sphere fluid and

$\tau_\eta = 3\pi\eta_0\sigma^3/(4k_B T)$ for the colloidal suspension, are characteristic Péclet-like relaxation times. We make the following remarks.

1. For $\gamma = 0$, the Newtonian viscosity $\eta(\phi, 0)$ of the concentrated colloidal suspension is obtained from Eqs. (8) and (9). The result is shown in Fig. 2 and compares well with experiment.
2. For $\gamma \neq 0$, Eqs. (8) and (9) give that the viscosity is a real function of γ of the form

$$\eta^*(\phi; \gamma\tau_\eta) = \frac{\eta(\phi; \gamma\tau_\eta)}{\eta(\phi; 0)} = C - S(\phi)(\gamma\tau_\eta)^{1/2} \tag{10}$$

where C is a constant. $\eta^*(\phi; \gamma)$ is plotted in Fig. 4. We note (a) in both theory and experiment [13] a γ -dependence $\sim \gamma^{1/2}$ after (b) an initial small γ behavior as $\eta^*(\phi; \gamma) = 1 - C_1(\phi)\gamma^2$. The former is clearly shown, but the latter can only be said at present to be consistent with experiments. The theoretical values for $C_1(\phi)$ are somewhat smaller than those suggested by experiment, leading to similar but slightly displaced curves with the same slope (cf. Fig. 4). In fact, in Fig. 5 we plot the coefficient $S(\phi)$ in Eq. (10), both for the scaled-hard-sphere theory [cf. Eqs. (8) and (9)]

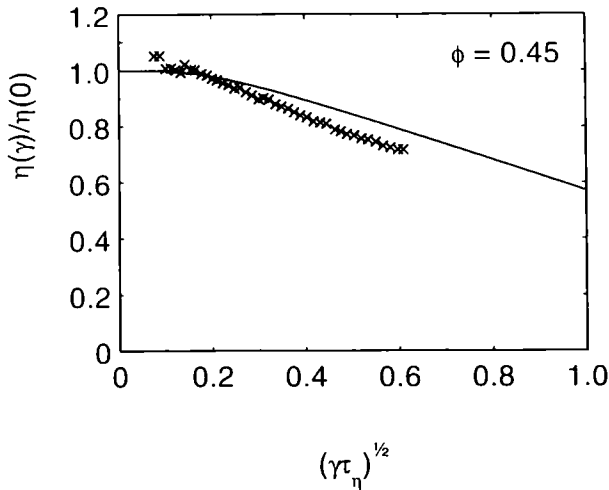


Fig. 4. Reduced shear viscosity $\eta(\phi, \gamma)/\eta(\phi, 0)$ as a function of reduced shear rate $(\gamma\tau_\eta)^{1/2}$ for $\phi = 0.45$. Silica spheres in cyclohexane [13] (crosses). Scaled hard-sphere theory [Eqs. (8) and (9)] (full curve).

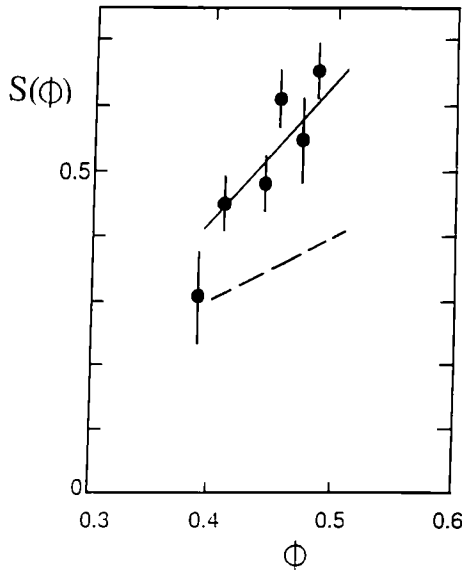


Fig. 5. Reduced slopes $S(\phi)$ defined by Eq. (10) as a function of ϕ for silica spheres in cyclohexane [13] (filled circles) and from theory: scaled hard spheres, cf. Eqs. (8) and (9) (solid curve); and Smoluchowski, cf. Eq. (3) (dashed curve).

and as derived from the Smoluchowski equation, discussed in Section 2. The latter approach appears not to lead to a behavior consistent with experiment.

4. CONCLUSIONS

We mention here a few points emanating from the results given in the previous sections.

1. The two essential physical features of the above-sketched two theoretical approaches to an understanding of the viscoelastic and rheological behavior of concentrated colloidal suspensions are

- (a) the qualitative similarity for long times, i.e., on a macroscopic time scale, of Newtonian and Brownian dynamics, and
- (b) the qualitative similarity of the cage diffusion process in concentrated colloidal suspensions and dense hard-sphere fluids.

2. Problems to consider are
 - (a) the viscoelastic behavior of a concentrated colloidal suspension obtained by scaling [cf. Eq. (9)] from that of dense hard-sphere fluids derived from the Liouville equation;
 - (b) the rheological behavior of concentrated colloidal suspensions from the Smoluchowski equation;
 - (c) that although we used the Smoluchowski theory for the colloidal suspensions neglecting hydrodynamical effects, we believe that the good agreement with experiment, at least for the viscoelastic behavior of neutral colloidal suspensions, implies that these effects are not important at high concentrations and that a similar good agreement would be obtained for charged colloidal suspensions. This would, however, obtain only, as long as the imposed frequencies ω are such that they will not seriously distort the Debye clouds surrounding the colloidal particles. This implies that we conjecture—at least for the viscoelastic behavior of concentrated colloidal suspensions—(i) the hard-sphere potential with an effective hard-sphere diameter σ determined from the experimental $S(k)$ [7] can be a good approximation for the Debye–Hückel interaction potential, and (ii) hydrodynamic effects largely cancel each other at high concentrations. Previous work on the self-diffusion coefficient of concentrated colloids seem to corroborate this conjecture [14].
3. There appears to be an interesting similarity between the ω - and the γ -dependence of $\eta(\phi; \omega; \gamma)$ which we intend to explore further.
4. What is the connection between the two theoretical approaches, discussed in Sections 3 and 4, i.e., Why are the Smoluchowski and the (scaled) Liouville equation results for concentrated colloidal suspensions so similar?

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