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Square Root Singularity in the Viscosity of Neutral Colloidal Suspensions at Large Frequencies

R. Verberg,[1] I. M. de Schepper,[1] M. J. Feigenbaum,[2] and E. G. D. Cohen[2]

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The asymptotic frequency, ω, dependence of the dynamic viscosity of neutral hard-sphere colloidal suspensions is shown to be of the form $\eta_0 A(\phi)(\omega\tau_P)^{-1/2}$, where $A(\phi)$ has been determined as a function of the volume fraction ϕ, for all concentrations in the fluid range, η_0 is the solvent viscosity, and τ_P is the Péclet time. For a soft potential it is shown that, to leading order in the steepness, the asymptotic behavior is the same as that for the hard-sphere potential and a condition for the crossover behavior to $1/\omega\tau_P$ is given. Our result for the hard-sphere potential generalizes a result of Cichocki and Felderhof obtained at low concentrations and agrees well with the experiments of van der Werff *et al.* if the usual Stokes–Einstein diffusion coefficient D_0 in the Smoluchowski operator is consistently replaced by the short-time self-diffusion coefficient $D_s(\phi)$ for nondilute colloidal suspensions.

KEY WORDS: Viscosity; viscoelasticity; rheology; colloidal suspensions; hardspheres; softspheres.

1. INTRODUCTION

The viscoelastic behavior, i.e., the frequency-dependent viscosity $\eta(\phi, \omega)$, of concentrated neutral hard-sphere colloidal suspensions has been obtained in the benchmark experiments of Van der Werff *et al.*(2) for volume fractions $0.44 < \phi < 0.58$, where $\phi = \pi n \sigma^3/6$, with n the number density of the colloidal particles of diameter σ. The frequency dependence was found to be qualitatively similar to that obtained theoretically by Cichocki and Felderhof(1) for dilute suspensions from an exact solution of the two-particle Smoluchowski equation for two Brownian particles without hydrodynamic interactions.

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[1] I. R. I. Delft University of Technology, 2629 JB Delft, The Netherlands.

[2] The Rockefeller University, New York, New York 10021.

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An approximate theory for concentrated colloidal suspensions was developed by Verberg *et al.*(3) which agreed well with the experimental results of Van der Werff *et al.* for such suspensions. In particular, the asymptotic behavior of the (complex) viscosity for large frequencies ω was given correctly as $\sim\eta_0 A(\phi)(1+i)/\sqrt{\omega\tau_P}$, where η_0 is the viscosity of the solvent, $A(\phi)$ an amplitude, and τ_P a characteristic Brownian particle interaction time, the Péclet time, defined below. However, the amplitude $A(\phi)$ was at small ϕ a factor two smaller than the exact value obtained by Cichocki and Felderhof at low densities and it was too high when compared with the experiments of Van der Werff *et al.* at high densities. This difference in asymptotic behavior did not affect the good agreement with experiments carried out in the reduced form used by Van der Werff *et al.*(3-5)

In the theory of Verberg *et al.* $\eta(\phi, \omega)$ was obtained as a sum of two terms: a short-time (infinite-frequency) contribution $\eta_\infty(\phi)$ on the very short Brownian time scale $\tau_B(\sim 10^{-9}\,\text{sec})$ where the Brownian particle forgets its initial velocity, and a long-time contribution, on the very much longer Péclet time scale $\tau_P(\sim 10^{-4}\,\text{sec})$, involving mode–mode coupling contributions associated with two cage-diffusion modes that describe the diffusion of each colloidal particle out of the cage in which it finds itself in a concentrated colloidal suspension(3):

$$\eta(\phi, \omega) = \eta_\infty(\phi) + \eta_{\text{mc}}(\phi, \omega) \tag{1.1}$$

For large ω, the mode–mode coupling contributions $\eta_{\text{mc}}(\phi, \omega)$ reduces to

$$\eta_{\text{mc}}(\phi, \omega) = \frac{9}{5}\, \phi^2 \chi(\phi)^{5/2} \frac{1}{\sqrt{\omega\tau_P}} (1+i)\, \eta_0 + O\left(\frac{1}{\omega}\right) \tag{1.2}$$

where $\chi(\phi)$ is the equilibrium radial distribution function $g_{\text{eq}}(r; \phi)$ at contact, i.e., $\chi(\phi) = g_{\text{eq}}(r=\sigma; \phi)$, where r is the distance between two hard spheres of diameter σ and $\tau_P = \sigma^2/4D_0$. Here D_0 is the Stokes–Einstein diffusion coefficient

$$D_0 = \frac{k_B T}{3\pi\eta_0\sigma} \tag{1.3}$$

where k_B is Boltzmann's constant and T the temperature of the colloidal suspension.

For low concentrations $\phi \to 0$, $\chi(\phi) \to 1$ and $\eta_{\text{mc}}(\phi, \omega)$ reduces to

$$\eta_{\text{mc}}(\phi, \omega) = \eta(\phi, \omega) - \eta_\infty(\phi) \xrightarrow{\phi \to 0} \frac{9}{5} \frac{\phi^2}{\sqrt{\omega\tau_P}} (1+i)\, \eta_0 \tag{1.4}$$

while Cichocki and Felderhof obtain(1)

$$\eta_{\mathrm{CF}}(\phi, \omega) - \eta_{\infty}(\phi) \xrightarrow{\phi \to 0} \frac{18}{5} \frac{\phi^2}{\sqrt{\omega \tau_{\mathrm{P}}}} (1+i)\,\eta_0 \tag{1.5}$$

The different coefficient in Eq. (1.4) for the approach to $\eta_{\infty}(\phi)$ is due to the approximate nature of $\eta_{\mathrm{mc}}(\phi, \omega)$.(3)

The purpose of this paper is to obtain the exact asymptotic behavior of $\eta(\phi, \omega)$ for large ω for *all* ϕ studied by van der Werff *et al.*,(2) i.e., an extension of Cichocki and Felderhof's result to high concentrations, as well as its behavior for a soft potential.

In the next section we will give the basic equations. In Section 3 we will calculate the asymptotic frequency-dependent viscosity for a soft, but very steep potential, starting from the Green–Kubo expression. In Section 4 we will give the result for a hard-sphere potential, as the limit of a soft potential. We will end with a short discussion on the soft-potential result.

2. BASIC EQUATIONS

In order to obtain the asymptotic behavior of $\eta(\phi, \omega)$ for large ω for concentrated suspensions we start from a general Green–Kubo expression for the frequency-dependent viscosity of a colloidal suspension(6):

$$\eta(\phi, \omega) = \eta_{\infty}(\phi) + \frac{\beta}{V} \int_0^{\infty} dt\, \rho_{\eta}(t; \phi)\, e^{i\omega t} \tag{2.1}$$

Equation (2.1) gives the linear response of the suspension to an applied shear rate $\gamma(t) = \gamma_0 e^{-i\omega t}$ with finite frequency ω and vanishing shear rate amplitude $\gamma_0 \to 0$. In Eq. (2.1), $\beta = 1/k_{\mathrm{B}} T$, V is the volume of the colloidal suspension, while $\rho_{\eta}(t; \phi)$ is the stress–stress autocorrelation function defined by

$$\rho_{\eta}(t; \phi) = \langle \Sigma^{\eta}_{xy}(r^N)\, e^{t\Omega(r^N; \phi)} \Sigma^{\eta}_{xy}(r^N) \rangle_{\mathrm{eq}} \tag{2.2}$$

where the brackets denote a canonical equilibrium ensemble average. The microscopic stress tensor $\Sigma^{\eta}_{xy}(r^N)$ is given by

$$\Sigma^{\eta}_{xy}(r^N) = \sum_{i=1}^{N} r_{i,x} F_{i,y}(r^N) \tag{2.3}$$

with $\mathbf{r}_i$ the position of particles $i(i=1,\ldots,N)$, $r^N=\mathbf{r}_1,\ldots,\mathbf{r}_N$, $\mathbf{F}_i=-\nabla_i\Phi(r^N)$ the total force on particle $i(\nabla_i=\partial/\partial\mathbf{r}_i)$, $\Phi(r^N)$ the total potential energy of the colloidal particles, and

$$\Omega(r^N;\phi)=\sum_{i,j=1}^{N}(\nabla_i+\beta\mathbf{F}_i(r^N))\cdot\mathbf{D}_{ij}(r^N)\cdot\nabla_j \tag{2.4}$$

the N-particle Smoluchowski operator,(7-9) the colloidal analogue of the Liouville operator for atomic liquids,(10) with $\mathbf{D}_{ij}(r^N)$ the diffusion tensor, incorporating hydrodynamic interactions. This diffusion tensor determines the velocity imparted to particle i by a force acting on particle j. In the absence of hydrodynamic interactions, i.e., for $\phi\to 0$, the diffusion tensor becomes diagonal and independent of r^N,

$$\mathbf{D}_{ij}(r^N)=D_0\mathbf{1}\,\delta_{ij} \tag{2.5}$$

with $\mathbf{1}$ the unit tensor and δ_{ij} the Kronecker symbol. However, in concentrated suspensions, where hydrodynamic interactions no longer can be neglected, $\mathbf{D}_{ij}(r^N)$ becomes a function of the positions of all particles, involving therefore many-particle interactions.

The diffusion tensor $\mathbf{D}_{ii}(r^N)$ is directly related to the experimental short-time self-diffusion coefficient $D_s(\phi)$ by(7,8)

$$D_s(\phi)\equiv\langle\hat{\mathbf{Q}}\cdot\mathbf{D}_{ii}(r^N)\cdot\hat{\mathbf{Q}}\rangle_{\mathrm{eq}} \tag{2.6}$$

for any particle i. Here $\hat{\mathbf{Q}}$ is a 3-dimensional unit vector. $D_s(\phi)$ reduces in the dilute limit to the Stokes–Einstein diffusion coefficient D_0 [cf. Eq. (2.5)]. $D_s(\phi)$ is a purely hydrodynamic quantity, which involves the calculation of the very complicated many-particle interactions, and has been the subject of research for many years, both theoretically(11-18) and experimentally.(19-24) By now the behavior of $\mathbf{D}_{ij}(r^N)$ and $D_s(\phi)$ for intermediate volume fractions up to $\phi\approx 0.45$ is fairly well understood theoretically. For higher concentrations to the best of our knowledge only semiempirical results exist.

However, in this paper we are particularly interested in the high volume fractions $\phi>0.40$. Therefore we were forced to incorporate hydrodynamic interactions in an approximate (mean-field-like) fashion, using Eq. (2.6). This approximation seems justified for high frequencies, where the particle distribution in the suspension is very close to the equilibrium particle distribution, so that the hydrodynamic interactions are described in first order by the hydrodynamic interactions of the suspension at infinite frequency. The mean-field approximation will be done explicitly in the next section. For $D_s(\phi)$ we use at the end a semiempirical relation which is consistent with experiments and hard-sphere computer simulations for all ϕ up to $\phi \approx 0.60$.(25)

3. LARGE-FREQUENCY VISCOSITY FOR SOFT POTENTIALS

We will proceed with the calculation of the asymptotic behavior of $\eta(\phi, \omega)$ for large ω by calculating the stress–stress autocorrelation function $\rho_\eta(t; \phi)$ of Eq. (2.2) with the microscopic stress tensor of Eq. (2.3) and the N-particle Smoluchowski operator of Eq. (2.4) for a soft, but very steep potential.

We restrict ourselves to pairwise additive potentials, i.e., $\Phi(r^N) = \sum_{i<j=1}^{N} V(r_{ij})$, with $V(r_{ij})$ the two-particle potential and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$. We can then write Eqs. (2.3) and (2.4), respectively, as

$$\Sigma^{\eta}_{xy}(r^N) = -\frac{1}{2} \sum_{i \neq j}^{N} r_{ij,x} \frac{\partial V(r_{ij})}{\partial r_{i,y}} \tag{3.1}$$

and

$$\Omega(r^N; \phi) = \sum_{i,j,k=1}^{N} \left(\delta_{ik} \nabla_i - \beta(1-\delta_{ik}) \frac{\partial V(r_{ik})}{\partial \mathbf{r}_i}\right) \cdot \mathbf{D}_{ij}(r^N) \cdot \nabla_j \tag{3.2}$$

We determine the asymptotic behavior of $\eta(\phi, \omega)$ from Eq. (2.1) for a soft, but steep pair potential $V_l(r) = \varepsilon(\sigma/r)^l$, with ε the pair interaction energy at $r = \sigma$ and $l = |r(\partial/\partial r) \ln V_l(r)|$ the steepness of the potential. Since the hard-sphere potential is the limit for $l \to \infty$ of $V_l(r)$, one can obtain the hard-sphere result by letting $l \to \infty$ at the end of the calculation. This is discussed in the next section.

In order to compute $\rho_\eta(t; \phi)$ for short time, we first expand $\rho_\eta(t; \phi)$ for $V_l(r)$ in powers of t. Thus, we first write Eq. (2.2) for $\rho_\eta(t; \phi)$ as

$$\rho_\eta(t; \phi) = \sum_{n=0}^{\infty} \frac{1}{n!} t^n \rho^n_\eta(\phi) \tag{3.3}$$

and then calculate

$$\rho^n_\eta(\phi) = \langle \Sigma^{\eta}_{xy}(r^N)\, \Omega^n(r^N; \phi)\, \Sigma^{\eta}_{xy}(r^N) \rangle_{\mathrm{eq}}$$

using Eq. (3.1) for the second $\Sigma^{\eta}_{xy}(r^N)$ within the brackets, i.e.,

$$\rho^n_\eta(\phi) = -\frac{1}{2} N(N-1) \left\langle \Sigma^{\eta}_{xy}(r^N)\, \Omega^n(r^N; \phi)\, r_{12,x} \frac{\partial V_l(r_{12})}{\partial r_{1,y}} \right\rangle_{\mathrm{eq}} \tag{3.4}$$

for the soft potential $V_l(r)$.

In this paper we will restrict ourselves to only the leading order in the steepness. Thus, we take into account, for each n, only the most divergent terms in l. This implies that, for short times, we can neglect all the contributions of more than two particles to the equilibrium ensemble average $\langle \cdot \rangle_{\mathrm{eq}}$, i.e., we only have to calculate the two-particle contributions, involving the equilibrium radial distribution function $g_{\mathrm{eq}}(r;\phi)$. This is because, relative to the two-particle contributions, the n-particle contributions are of the order $l^{-(n-2)}$, so that they can be neglected in the limit $l \to \infty$.(26)

Thus, for $\Omega(r^N;\phi)$ in Eq. (3.4) we can use Eq. (3.2) with only $i, j \in \{1, 2\}$, giving

$$\rho_\eta^n(\phi) = -\frac{1}{2} N(N-1) \left\langle \Sigma_{xy}^n(r^N) \left[\left(\nabla_1 - \beta \frac{\partial V_l(r_{12})}{\partial \mathbf{r}_1} \right) \cdot \mathbf{D}_r(r^N) \cdot \nabla_1 \right]^n \times r_{12,x} \frac{\partial V_l(r_{12})}{\partial r_{1,y}} \right\rangle_{\mathrm{eq}} \tag{3.5}$$

Here we used the symmetry of $\Omega(r^N;\phi)$ in the particles 1 and 2 when applied to functions of $\mathbf{r}_{12}$. We have introduced the relative diffusion coefficient of two interacting spheres $\mathbf{D}_r(r^N) = 2(\mathbf{D}_{11}(r^N) - \mathbf{D}_{12}(r^N))$.(25, 9) In the dilute limit for just two particles, distant from all others, the diffusion tensors $\mathbf{D}_{11}(\mathbf{r}_1, \mathbf{r}_2)$ and $\mathbf{D}_{12}(\mathbf{r}_1, \mathbf{r}_2)$ are known.(11, 27, 28)

For concentrated suspensions we make a mean-field approximation. We replace $\mathbf{D}_r(r^N)$ in Eq. (3.5) by its mean value $\langle \mathbf{D}_r(r^N) \rangle_{\mathrm{eq}}$, which reduces for high frequencies, i.e., for short times, to twice the single-particle short-time self-diffusion coefficient $D_s(\phi)$ as given in Eq. (2.6).(25, 29, 30) Thus we write in Eq. (3.5)

$$\mathbf{D}_r(r^N) = \langle \mathbf{D}_r(r^N) \rangle_{\mathrm{eq}} = 2 D_s(\phi)\, \mathbf{1} \tag{3.6}$$

consistently with Eq. (2.6).

Using this approximation and Eq. (3.1) for $i, j \in \{1, 2\}$, i.e., neglecting again all but two-particle contributions, we find straightforwardly

$$\rho_\eta^n(\phi) = \frac{1}{2} N(N-1)(2D_s(\phi))^n \times \left\langle r_{12,x} \frac{\partial V_l(r_{12})}{\partial r_{1,y}} \left[\left(\nabla_1 - \beta \frac{\partial V_l(r_{12})}{\partial \mathbf{r}_1} \right) \cdot \nabla_1 \right]^n r_{12,x} \frac{\partial V_l(r_{12})}{\partial r_{1,y}} \right\rangle_{\mathrm{eq}} \tag{3.7}$$

Since $\nabla_1 \mathbf{r}_{12} V_l(r_{12}) = \mathbf{r}_{12} \nabla_1 V_l(r_{12})(1 + O(l^{-1}))$, we can shift, to leading order in the steepness, the differential operator ∇_1 through $\mathbf{r}_{12}$ in any product of $\mathbf{r}_{12}$ and $V_l(r_{12})$ or its derivatives. Thus, from Eq. (3.7) we obtain

$$\rho_\eta^n(\phi) = \frac{1}{2} N(N-1)(2D_s(\phi))^n \times \left\langle \frac{r_x^2 r_y^2}{r^2} V_l'(r)[(\nabla_1 - \beta V_l'(r)\,\hat{\mathbf{r}}) \cdot \nabla_1]^n \, V_l'(r) \right\rangle_{\text{eq}} \tag{3.8}$$

with $\mathbf{r} = \mathbf{r}_{12}$, $r = |\mathbf{r}_{12}|$, $\hat{\mathbf{r}} = \mathbf{r}/r$, $\partial V_l(r_{12})/\partial r_{12} = V_l'(r)$.

Changing to spherical coordinates, using the definition of the equilibrium radial distribution function $g_{\text{eq}}(r;\phi)$ for the soft potential $V_l(r)$, and performing the angular integration, we find from Eqs. (3.3) and (3.7)

$$\rho_\eta(t;\phi) = \frac{2}{15}\pi n^2 V \int_0^\infty dr\, g_{\text{eq}}(r;\phi)\, r^4 \times V_l'(r)\{\exp[2tD_s(\phi)(\nabla_r^2 - \beta V_l'(r)\,\nabla_r)]\}\, V_l'(r) \tag{3.9}$$

where $\nabla_r = \partial/\partial r$.

Thus we have expressed $\rho_\eta(t;\phi)$ at large volume fractions ϕ and to leading order in the steepness l in terms of a one-dimensional integral over r involving the high-density equilibrium radial distribution function $g_{\text{eq}}(r;\phi)$ for a potential $V_l(r)$ of finite but large l and the effective short-time self-diffusion coefficient $D_s(\phi)$. In the next section we consider the hard-sphere limit ($l \to \infty$) of Eq. (3.9).

4. HARD-SPHERE LIMIT

To evaluate Eq. (3.9) for hard spheres, we introduce the function

$$y_{\text{eq}}(r;\phi) = g_{\text{eq}}(r;\phi)\, e^{\beta V_l(r)} \tag{4.1}$$

As discussed in Ref. 10, $y_{\text{eq}}(r;\phi)$ is, unlike $g_{\text{eq}}(r;\phi)$, a smooth continuous function of r for *all* r and l. For hard spheres $g_{\text{eq}}^{\text{hs}}(r;\phi) = y_{\text{eq}}^{\text{hs}}(r;\phi)$ for $r \geqslant \sigma$ and $\chi(\phi) \equiv g_{\text{eq}}^{\text{hs}}(r=\sigma;\phi) = y_{\text{eq}}^{\text{hs}}(r=\sigma;\phi)$ is the pair correlation function at contact. Writing $V_{\text{hs}}(r) = V_{l\to\infty}(r)$, using that

$$e^{-\beta V_{\text{hs}}(r)} V_{\text{hs}}'(r) = -\frac{1}{\beta}\delta(r-\sigma) \tag{4.2}$$

and using Eq. (4.1), we can write for the stress–stress autocorrelation $\rho_\eta(t;\phi)$ of Eq. (3.9) in the hard-sphere limit $l \to \infty$

$$\rho_\eta(t;\phi) = \frac{2}{15}\pi n^2 V \chi(\phi) \int_0^\infty dr\, r^4 e^{-\beta V_{\text{hs}}(r)} V_{\text{hs}}'(r)\, e^{\Omega_r^{\text{hs}} t}\, V_{\text{hs}}'(r) \tag{4.3}$$

Here we have defined $\Omega_r^{\rm hs} = 2D_s(\phi)(\nabla_r^2 - \beta V'_{\rm hs}(r)\,\nabla_r)$, the radial part of the two-particle Smolochowski operator for a hard-sphere potential in relative coordinates.

This expression can be calculated by a method similar to that of Cichocki and Felderhof.(1) The actual calculation is given in more detail in the Appendix, giving

$$\rho_\eta(t;\phi) = \frac{18}{5}\,\phi^2\chi(\phi)\left(\frac{2D_0}{\pi D_s(\phi)}\right)^{1/2}\frac{V}{\beta}\,\frac{1}{\sqrt{t\tau_{\rm P}}}\,\eta_0 \tag{4.4}$$

Equation (4.4) leads, with Eq. (2.1), to our final result for hard spheres:

$$\eta(\phi,\omega)\xrightarrow{\omega\to\infty}\eta_\infty(\phi) + A(\phi)\,\frac{1+i}{\sqrt{\omega\tau_{\rm P}}}\,\eta_0 \tag{4.5}$$

with the coefficient of the square root singularity $A(\phi)$ given by

$$A(\phi) = \frac{18}{5}\,\phi^2\chi(\phi)\left(\frac{D_0}{D_s(\phi)}\right)^{1/2} \tag{4.6}$$

This result, based on the Green–Kubo formula(6) for the frequency-dependent viscosity $\eta(\phi,\omega)$ of a colloidal suspension consisting of hard spheres with hydrodynamic interactions included, is compared with experiments of van der Werff *et al.*(2) in Fig. 1. Here we have used for $\chi(\phi)$ the Carnahan–Starling approximation (Ref. 25; Ref. 10, pp. 36, 95) $\chi(\phi) = (1-0.5\phi)/(1-\phi)^3$ for $\phi \leqslant 0.5$ and a one-pole approximation(25) $\chi(\phi) = 1.2/(1-\phi/\phi_m)$ for $\phi > 0.5$, with $\phi_m = 0.63$ the volume fraction at random close packing. For $D_s(\phi)/D_0$ we have used Beenakker and Mazur's expression(17) for $\phi \leqslant 0.45$ and $D_s(\phi)/D_0 = 0.85(1-\phi/\phi_m)$ for $\phi > 0.45$.(25)

Figure 1 clearly shows that in order to obtain agreement with experiment it is neccesary to include hydrodynamic interactions, i.e., to take into account the diffusion tensor $\mathbf{D}_{ij}(r^N)$ in the basic N-particle Smoluchowski equation. In a mean-field approximation this leads to the replacement of the Stokes–Einstein diffusion coefficient D_0 by the short-time self-diffusion coefficient $D_s(\phi)$, a replacement also made by Brady.(25) Equations (4.5) and (4.6) reduce to the exact expression [Eq. (1.5)] obtained before by Cichocki and Felderhof for low densities(1) to $O(\phi^2)$ (see Appendix).

We will show in the next section [Eqs. (5.1) and (5.3)] that the right-hand side of Eq. (4.4) is the leading term of the expansion in powers of l of $\rho(t;\phi)$ for a soft potential, i.e., for finite l and for frequencies ω up to $\sim(l^2/\tau_{\rm P})\,D_s(\phi)/D_0$.

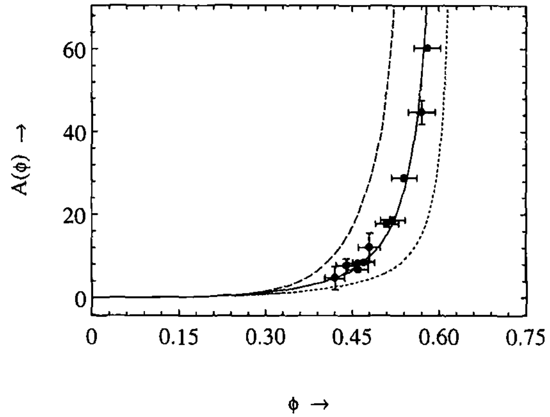

Fig. 1. Coefficient $A(\phi)$ of the square root singularity in ω, i.e., $\sim A(\phi)(1+i)\,\eta_0/\sqrt{\omega\tau_P}$, of $\eta(\phi,\omega)$ as a function of the volume fraction ϕ. Experimental points (•) of van der Werff *et al.*;(2) the vertical lines indicate the estimated errors in the experimental values of $A(\phi)$, while the horizontal lines indicate the effect of the 4% uncertainty in ϕ (C. B. de Kruif, private communication). The long-dashed line represents the mode-coupling result, Eq. (1.2), and the solid line our result given in Eq. (4.6). Here we have used for $\chi(\phi)$ the Carnahan–Starling approximation (Ref. 10, pp. 36, 95) $\chi(\phi)=(1-0.5\phi)/(1-\phi)^3$ for $\phi\leqslant 0.5$ and a one-pole approximation(25) $\chi(\phi)=1.2/(1-\phi/\phi_m)$ for $\phi>0.5$, with $\phi_m=0.63$ the volume fraction at random close packing. For $D_s(\phi)/D_0$ we have used Beenakker and Mazur's expression(17) for $\phi\leqslant 0.45$ and $D_s(\phi)/D_0=0.85(1-\phi/\phi_m)$ for $\phi>0.45$.(25) The short-dashed line represents Eq. (4.6) with $D_s(\phi)=D_0$, i.e., when hydrodynamic interactions are neglected.

5. SOFT POTENTIAL

We note that the large-ω behavior of $\eta(\phi,\omega)\sim 1/\sqrt{\omega}$ is typical for hard spheres. For any soft, but steep potential, $\eta(\phi,\omega)\sim 1/\omega$ for $\omega\to\infty$. For example, the presence of a lubrication layer causes a change in the relative diffusion of two spheres at very short times, which leads to $1/\omega$ behavior at very high frequencies, as discussed by Cichocki and Felderhof(31) and Rallison and Hinch.(32) To study the transition from the $1/\omega$ behavior (for any finite l) to the $1/\sqrt{\omega}$ behavior ($l=\infty$) we have calculated $\rho_{ll}(t;\phi)$ of Eq. (3.9) for finite l. For finite l Eq. (3.9) can no longer be calculated by a method similar to that of Cichocki and Felderhof,(1) described in the Appendix, but involves the calculation of the complete eigenvalue problem of the radial part of $\Omega_r=2D_s(\phi)(\nabla_r^2-\beta V_l'(r)\,\nabla_r)$, the two-particle Smoluchowski operator in relative coordinates, for finite l.(33) The result for $\rho_{ll}(t;\phi)$ in Eq. (3.9) can be written as(33)

$$\rho_{ll}(t;\phi)=\frac{2\pi n^2 V l\sigma^3\chi(\phi)}{15\beta^2}\,r(\tau(\phi)) \qquad (5.1)$$

with $\tau(\phi) = 2D_s(\phi)\, tl^2/\sigma^2$. The function $r(x)$ can be expanded for $x \ll 1$ as

$$r(x) = 1 - x + \tfrac{3}{2}x^2 + O(x^3) \tag{5.2}$$

and for $x > 1$ as[33]

$$r(x) = \frac{1}{\sqrt{\pi x}}\left(1 + \frac{\pi^2}{12x} + O\left(\frac{1}{x^2}\right)\right) \tag{5.3}$$

Thus, to leading order in the steepness l, we obtain from Eqs. (5.1) and (5.3)

$$\rho_\eta(t;\phi) = \frac{2\pi n^2 V l \sigma^3 \chi(\phi)}{15\beta^2}\frac{1}{\sqrt{\pi\tau(\phi)}}, \qquad t > \frac{\tau_{\mathrm{P}}}{l^2}\frac{D_0}{D_s(\phi)} \tag{5.4}$$

consistent with Eq. (4.4) when $l \to \infty$. For finite l, $\eta(\phi, \omega) \sim 1/\sqrt{\omega}$ for frequencies ω up to $\sim (l^2/\tau_{\mathrm{P}})\, D_s(\phi)/D_0$, while for larger ω, $\eta(\phi, \omega)$ behaves as $1/\omega$, as is typical for soft potentials. It might be interesting to see whether such a transition in the asymptotic behavior of $\eta(\phi, \omega)$ can be observed in concentrated colloidal suspensions, where the interaction potential is steep.

APPENDIX

Here we calculate the stress–stress autocorrelation function $\rho_\eta(t;\phi)$ for hard spheres. We start with Eq. (4.3) for $\rho_\eta(t;\phi)$ in the hard-sphere limit, i.e., $l \to \infty$:

$$\rho_\eta(t;\phi) = \frac{2}{15}\pi n^2 V \chi(\phi) \int_0^\infty dr\, r^4 e^{-\beta V_{\mathrm{hs}}(r)} V'_{\mathrm{hs}}(r)\, e^{\Omega_r^{\mathrm{hs}} t} V'_{\mathrm{hs}}(r) \tag{A.1}$$

with $V_{\mathrm{hs}}(r)$ the hard-sphere potential and

$$\Omega_r^{\mathrm{hs}} = 2D_s(\phi)(\nabla_r^2 - \beta V'_{\mathrm{hs}}(r)\, \nabla_r) \tag{A.2}$$

Using that $\exp(-\beta V_{\mathrm{hs}}(r))\, V'_{\mathrm{hs}}(r) = -(1/\beta)\, \delta(r - \sigma)$ gives

$$\rho_\eta(t;\phi) = -\frac{2\pi n^2 V \sigma^4 \chi(\phi)}{15\beta} \int_0^\infty dr\, \delta(r-\sigma)\, e^{\Omega_r^{\mathrm{hs}} t} V'_{\mathrm{hs}}(r) \tag{A.3}$$

With Eq. (2.1), Eq. (A.3) gives

$$\begin{aligned}\eta(\phi,\omega) &= \eta_{\infty}(\phi) - \frac{2}{15}\pi n^2\sigma^4\chi(\phi)\int_0^{\infty} dt \int_0^{\infty} dr\, \delta(r-\sigma)^{(\Omega_r^{\text{hs}}+i\omega)\,t}V'_{\text{hs}}(r) \\ &= \eta_{\infty}(\phi) + \frac{2}{15}\pi n^2\sigma^4\chi(\phi)\int_0^{\infty} dr\, \delta(r-\sigma)\frac{1}{(\Omega_r^{\text{hs}}+i\omega)}\,V'_{\text{hs}}(r) \end{aligned} \tag{A.4}$$

We define

$$f(r,\omega) = \frac{1}{(\Omega_r^{\text{hs}}+i\omega)}\,V'_{\text{hs}}(r) \tag{A.5}$$

and deduce the following differential equation for $f(r,\omega)$:

$$(2D_s\nabla_r^2 - 2D_s\beta V'_{\text{hs}}(r)\,\nabla_r + i\omega)\,f(r,\omega) = V'_{\text{hs}}(r) \tag{A.6}$$

Due to the singular behavior of the hard-sphere potential at $r=\sigma$, Eq. (A.6) reduces to the boundary value problem

$$\begin{cases}(2D_s\nabla_r^2 + i\omega)\,f(r,\omega) = 0, & r>\sigma \\ 2D_s\beta\,\nabla_r f(r,\omega) = -1, & r=\sigma\end{cases} \tag{A.7}$$

with the solution, bounded for $r \geqslant \sigma$,

$$f(r,\omega) = \frac{1}{2\alpha\beta D_s}\,e^{-\alpha(r-\sigma)} \tag{A.8}$$

where $\alpha^2 = -i\omega/2D_s$. Equation (A.5) with Eqs. (A.5) and (A.8) gives the asymptotic result for the frequency-dependent viscosity as given in Eqs. (4.4) and (4.5),

$$\eta(\phi,\omega) = \eta_{\infty}(\phi) + \frac{18}{5}\phi^2\chi(\phi)\left(\frac{D_0}{D_s(\phi)}\right)^{1/2}\frac{1+i}{\sqrt{\omega\tau_{\text{P}}}}\,\eta_0 \tag{A.9}$$

where we have used the Péclet time $\tau_{\text{P}} = \sigma^2/4D_0$ and the Stokes–Einstein relation for D_0 as given in Eq. (1.3). Equation (A.9) with Eq. (2.1) yields for $\rho_\eta(t;\phi)$

$$\rho_\eta(t;\phi) = \frac{18}{5}\phi^2\chi(\phi)\left(\frac{2D_0}{\pi D_s(\phi)}\right)^{1/2}\frac{1}{\sqrt{t\tau_{\text{P}}}}\,\eta_0 \tag{A.10}$$

For low concentrations ($\phi \to 0$), $\chi(\phi) = 1$ and $D_s(\phi) = D_0$ and $\rho_\eta(t; \phi)$ reduces to the result of Cichocki and Felderhof[11] for $\rho_\eta(t; \phi \to 0)$ for short times. These authors calculate $\rho_\eta(t; \phi \to 0)$ for hard spheres, on the basis of Eq. (2.2) restricted from the beginning to two hard-sphere particles only, but for all times t. One can show that the angular dependences in Eq. (2.2) (i.e., in Σ_{xy}) are irrelevant for short times. Thus, for $t \to 0$, both approaches are similarly leading to identical results for $\rho_\eta(t; \phi)$ and $\eta(\phi, \omega)$.

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