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Viscosity of colloidal suspensions

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Simple expressions are given for the Newtonian viscosity $\eta_N(\phi)$ as well as the viscoelastic behavior of the viscosity $\eta(\phi,\omega)$ of neutral monodisperse hard-sphere colloidal suspensions as a function of volume fraction ϕ and frequency ω over the *entire* fluid range, i.e., for volume fractions $0<\phi<0.55$. These expressions are based on an approximate theory that considers the viscosity as composed as the sum of two relevant physical processes: $\eta(\phi,\omega)=\eta_\infty(\phi)+\eta_{cd}(\phi,\omega)$, where $\eta_\infty(\phi)=\eta_0\chi(\phi)$ is the infinite frequency (or very short time) viscosity, with η_0 the solvent viscosity, $\chi(\phi)$ the equilibrium hard-sphere radial distribution function at contact, and $\eta_{cd}(\phi,\omega)$ the contribution due to the diffusion of the colloidal particles out of cages formed by their neighbors, on the Péclet time scale τ_P, the dominant physical process in concentrated colloidal suspensions. The Newtonian viscosity $\eta_N(\phi)=\eta(\phi,\omega=0)$ agrees very well with the extensive experiments of van der Werff *et al.*, [Phys. Rev. A **39**, 795 (1989); J. Rheol. **33**, 421 (1989)] and others. Also, the asymptotic behavior for large ω is of the form $\eta_\infty(\phi)+\eta_0 A(\phi)(\omega\tau_P)^{-1/2}$, in agreement with these experiments, but the theoretical coefficient $A(\phi)$ differs by a constant factor $2/\chi(\phi)$ from the exact coefficient, computed from the Green-Kubo formula for $\eta(\phi,\omega)$. This still enables us to predict for practical purposes the viscoelastic behavior of monodisperse spherical colloidal suspensions for all volume fractions by a simple time rescaling. [S1063-651X(97)09303-3]

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I. INTRODUCTION

In a number of previous papers we have discussed the Newtonian viscosity as well as the viscoelastic behavior of concentrated colloidal suspensions, consisting of monodisperse neutral hard-sphere particles [1–4]. The motivation was to understand theoretically the very extensive viscosity measurements on colloidal suspensions carried out by van der Werff *et al.* [5,6] (see Table I). In particular, these experiments on carefully prepared systems seemed to be an ideal testing ground for the theory. In this paper a more complete and detailed account of the viscous behavior of colloidal suspensions over their fluid range will be given.

In the past, many theoretical investigations have been carried out of the rheological properties of colloidal suspensions. Most of this work concerned the shear-rate dependence of the viscosity of dilute or semidilute (charged) suspensions consisting of Brownian particles, interacting with soft potentials [7–9]. Therefore, a comparison between our results and those would only be possible for the Newtonian viscosity, except for the essential difference in the interparticle potential. The viscoelastic properties of neutral hard-sphere suspensions with which we are exclusively concerned here have been considered by Brady [10], and Cichocki and Felderhof [11,12]. Their work will be discussed and compared, where possible with ours, in some detail below. Blawzdziewicz and Szamel [13] have considered the shear-rate-dependent viscosity of semidilute neutral hard-sphere colloidal suspensions. We will show that our result for the Newtonian viscosity reduces in the semidilute limit to their result for vanishing shear rate.

Our theoretical approach is based on two physical processes related to the two widely separated basic time scales in a colloidal suspension: the Brownian time $\tau_B\sim10^{-8}$ s, during which a single Brownian particle ‘‘forgets’’ its initial velocity, and the interaction time or Péclet time $\tau_P=\sigma^2/4D_0\sim10^{-3}$ s, during and beyond which Brownian particle interactions take place. Here σ is the diameter of the hard-sphere colloidal particles and D_0 the Stokes-Einstein colloidal particle diffusion coefficient at infinite dilution. The viscosity is consequently considered as composed of a sum of contributions that take place on a short- and a long-time scale. Although the theory is constructed for concentrated colloidal suspensions with volume fractions $0.3<\phi<0.55$, it appears that the theory also gives good numerical results for lower concentrations, so that effectively formulas are obtained that cover the entire fluid range $0<\phi<0.55$. Here $\phi=n\pi\sigma^3/6$, where n is the number density of the hard-sphere colloidal particles.

The suspension is considered as a homogeneous fluid consisting of spherical particles immersed in a continuum solvent. As a consequence, formulas derived for simple homogeneous fluids in general, such as the Irving-Kirkwood expression for the pressure tensor [14,15] or the Green-Kubo formula for the viscosity [16], are also assumed to be applicable here. The formulas for the viscous behavior are derived

TABLE I. Characteristic values of the model systems used [5,6].

System	σ (nm)(DLS)	η_0 (10^{12} s^{-1} m^{-2})	τ_P (ms)
SP 23	28 ± 2	8.68	0.0903
SSF 1	46 ± 2	5.29	0.400
SJ 18	76 ± 2	3.20	1.81

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under a number of assumptions, which we will try to justify physically as well as possible, but which, considering the complexity of this strongly interacting system, we have not been able to derive from first principles or justify completely.

The two basic physical processes we referred to are as follows: (i) At short times $t \leqslant \tau_B \ll \tau_P$ and nonzero concentrations, the viscosity of the suspension effectively increases when compared to that of the (pure) solvent viscosity η_0 at infinite dilution, due to the finite probability to find two particles at contact, and (ii) at long times $t \sim \tau_P \gg \tau_B$, it is difficult for a Brownian particle to diffuse out of the cage formed around it by its neighbors, characterized by a cage-diffusion coefficient $D_c(k;\phi)$.

As for (i), the probability to find two particles in the suspension at contact is given by the equilibrium radial distribution function at contact: $g_{\mathrm{eq}}(\sigma;\phi) \equiv \chi(\phi)$ [17], which follows from the canonical distribution of the hard-sphere colloidal particles. As a result, the effective very-high-frequency viscosity of the suspension satisfies $\eta_\infty(\phi) = \eta_0 \chi(\phi)$, a relation that is consistent with experiment over the entire fluid range [4] (cf. Fig. 2). Similarly, the very-short-time self-diffusion coefficient of the Brownian particles past each other is decreased from the Stokes-Einstein value D_0 at infinite dilution to a value $D_s(\phi) = D_0/\chi(\phi)$, since $\chi(\phi)$ also gives the increase in the binary collision frequency in a dense hard-sphere gas in equilibrium as compared to that in a dilute gas. Also this relation has been confirmed by experiment [4].

As for (ii), the cage-diffusion coefficient $D_c(k;\phi)$ refers to the diffusion of a particle out of a cage formed by its neighbors when the particles are distributed periodically in the solvent with a wave number k. For concentrated suspensions one should bear in mind that a typical wave number is $k \approx k^* = 2\pi/\sigma$, corresponding to a surface to surface distance of two neighboring Brownian particles of typically 1/10 of their diameter σ, so that the particles "rattle" in their cages before they diffuse out in a time of the order of $\tau_P \approx \tau_c(k^*;\phi) = 1/D_c(k^*;\phi)k^{*2}$. In Fig. 1(a) $\tau_c(k;\phi)/\tau_P$ is plotted as a function of $\kappa = k\sigma$ for four values of ϕ. $\tau_c(k;\phi)$ and τ_P are clearly of the same order of magnitude, the pronounced maximum of $\tau_c(k;\phi)$ at $k = k^*$ corresponding to the "rattling in the cage." An explicit expression for the cage-diffusion coefficient $D_c(k;\phi)$ has been obtained from kinetic theory [18]. Since $D_c(k;\phi)$ also characterizes the decay of a spontaneous density fluctuation of wave number k in the suspension [19], it can be measured by light or neutron scattering and the expression we give for it below has been shown to be in good agreement with such experiments [cf. Fig. 1(b)] [20].

To incorporate the cage-diffusion process, i.e., $D_c(k;\phi)$ into the theory, we need to go to a Fourier (i.e., **k**) representation, while the starting point of our theory, the two-particle Smoluchowski equation [21], is expressed in ordinary (i.e., **r**) space. This will introduce a fundamental difficulty in the development of the theory since the impenetrability of two hard-sphere particles, which is easily accounted for in **r** space, will be violated in our theory in **k** space, a point that will be discussed further below.

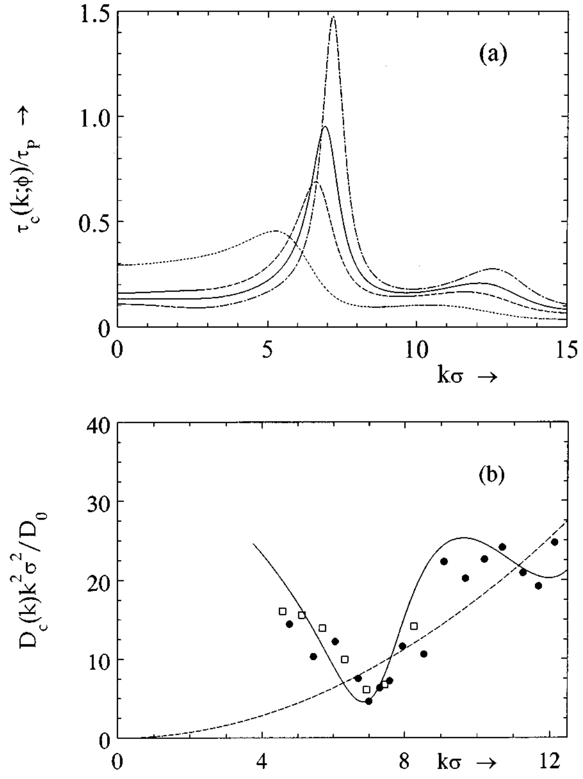

FIG. 1. (a) Reduced cage-diffusion time $\tau_c(\kappa;\phi)/\tau_P$ as a function of $\kappa = k\sigma$ for volume fractions ϕ = 0.30 (dotted line), 0.45 (dashed line), 0.50 (solid line), and 0.55 (dash-dotted line). For $k \approx k^* \approx 2\pi$ the two times are of the same order of magnitude. (b) Reduced cage-diffusion coefficient $D_c(k;\phi)k^2\sigma^2/D_0$ as a function of $k\sigma$ from light scattering experiments for a charged colloid (●) (σ=600 nm, ϕ=0.48 [56]), a neutral colloid (□) (σ=335 nm, ϕ=0.49 [57]), and from theory (solid line) [Eq. (13)]. The two minima correspond to the first two maxima of $S_{\mathrm{eq}}(k;\phi)$. Here the diameter of the Debye sphere of the charged colloid is replaced by an effective hard-sphere diameter that is determined by making a best fit of the experimental behavior of $S_{\mathrm{eq}}(k;\phi)$ of the charged colloid near k^*, with an $S_{\mathrm{eq}}(k;\phi)$ of a corresponding hard-sphere fluid [19]. Also plotted is the reduced high-density self-diffusion coefficient $D_s(\phi)k^2\sigma^2/D_0 = k^2\sigma^2/\chi(\phi)$ [cf. Eq. (45a)], around which the reduced cage diffusion coefficient oscillates and it approaches for $k \to \infty$.

The paper is constructed as follows. In Sec. II we give the basic equation for the viscosity of the colloidal suspension and that for the nonequilibrium pair distribution function of the colloidal particles to obtain this viscosity from a solution of the latter equation. In Sec. III this solution is used to obtain an explicit expression for the viscoelastic behavior $\eta(\phi,\omega)$ of the suspension. Section IV gives a simple formula for the zero-frequency or Newtonian viscosity $\eta_N(\phi) = \eta(\phi,\omega=0)$, while Sec. V contains the viscoelastic behavior of the fluid for finite frequencies. In Sec. VI the approach of $\eta(\phi,\omega)$ to its asymptotic value $\eta_\infty(\phi)$, via a behavior $\sim \eta_0 A(\phi)(\omega\tau_P)^{-1/2}$, is discussed and exact results for the coefficient $A(\phi)$ are compared with our theory and with experiment. In Sec. VII the behavior of $\eta(\phi,\omega)$ for small ω is given and Sec. VIII discusses a number of issues raised by the results obtained in the paper, especially in connection with the good agreement with experiment, in spite of the apparent neglect of hydrodynamic interactions between the Brownian particles.

II. BASIC EQUATIONS

The shear viscosity we are concerned with in this paper is defined as 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 amplitude γ_0 or, equivalently, by

$$P_{xy}(\phi,\omega,\gamma_0,t)=-\eta(\phi,\omega,\gamma_0,t)\gamma(t). \tag{1}$$

Here P_{xy} is the xy component of the pressure tensor of the suspension, defined by

$$P_{xy}(\phi,\omega,\gamma_0,t)=P_{xy,s}(\phi,\gamma_0,t)+P_{xy,d}(\phi,\omega,\gamma_0,t), \tag{2}$$

where $P_{xy,s}(\phi,\gamma_0,t)$ is the static contribution ($\omega=\infty$) to the xy component of the pressure tensor, associated with the pure solvent contribution and the solvent-colloid contribution (the stresslet contribution) [22,23], and $P_{xy,d}(\phi,\omega,\gamma_0,t)$ is the dynamic contribution given by [14,15]

$$P_{xy,d}(\phi,\omega,\gamma_0,t)=-\frac{1}{2V}\left\langle \sum_{j\neq i=1}^{N} r_{ij,x}\frac{\partial V(r_{ij})}{\partial r_{i,y}}\right\rangle_{\rm ne}. \tag{3}$$

Here V is the volume of the system, $\mathbf{r}_i$ is the position of particle $i(i=1,\dots,N)$, $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, $V(r_{ij})$ is the interparticle potential between particles i and j at a distance $r_{ij}=|\mathbf{r}_{ij}|$, and the average $\langle\ \rangle_{\rm ne}$ is taken with respect to a nonequilibrium distribution function derived from the N-particle Smoluchowski equation for a suspension under shear rate $\gamma(t)$. Kinetic contributions to the xy component of the pressure tensor can be neglected in the limit $\gamma_0=0$, as is the case in this paper [23,24].

The static contribution follows from the limit $\omega\to\infty$ when the dynamic contribution to the pressure tensor becomes zero, leaving in Eq. (1) only

$$P_{xy}(\phi,\omega=\infty,\gamma_0,t)=P_{xy,s}(\phi,\gamma_0,t)=-\eta_\infty(\phi)\gamma(t). \tag{4}$$

Carrying out the implied integration on the right-hand side (rhs) of Eq. (3) over the positions of all $N-2$ particles but particles 1 and 2, introducing center-of-mass and relative coordinates by $\mathbf{R}=(\mathbf{r}_1+\mathbf{r}_2)/2$ and $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$, respectively, and carrying out the integration over $\mathbf{R}$, one obtains for the dynamic contribution to the pressure tensor

$$P_{xy,d}(\phi,\omega,\gamma_0,t)=-\frac{n^2}{2}\int d\mathbf{r}\; g(\mathbf{r};\phi,\omega,\gamma_0,t)x\frac{\partial V(r)}{\partial y}. \tag{5}$$

This gives, with Eqs. (2) and (4), the expression for the total pressure tensor

$$P_{xy}(\phi,\omega,\gamma_0,t)=-\eta_\infty(\phi)\gamma(t) -\frac{n^2}{2}\int d\mathbf{r}\; g(\mathbf{r};\phi,\omega,\gamma_0,t)x\frac{\partial V(r)}{\partial y}. \tag{6}$$

Here $n^2 g(\mathbf{r};\phi,\omega,\gamma_0,t)$ is the nonequilibrium pair distribution function, giving the average number of colloidal particle pairs at a separation $\mathbf{r}$ in the suspension at a number density n of the colloidal particles, so that $g(\mathbf{r};\phi,\omega,\gamma_0,t)$ is the nonequilibrium generalization of the radial distribution function $g_{\rm eq}(r;\phi)$ in equilibrium, when $\gamma_0=0$. Introducing then

$$g(\mathbf{r};\phi,\omega,\gamma_0,t)=g_{\rm eq}(r;\phi)+\delta g(\mathbf{r};\phi,\omega,\gamma_0)e^{-i\omega t}, \tag{7a}$$

we have, for $\gamma_0\to 0$,

$$\delta g(\mathbf{r};\phi,\omega,\gamma_0)=\gamma_0\delta g(\mathbf{r};\phi,\omega)+O(\gamma_0^2) \tag{7b}$$

and one finds from Eq. (6) that in the limit of vanishing shear rate $\gamma_0\to 0$, $P_{xy}(\phi,\omega,\gamma_0,t)$ is proportional to $\gamma(t)$ since the contribution of $g_{\rm eq}(r;\phi)$ vanishes. Then, in Eq. (1), the viscosity $\eta(\phi,\omega)=\lim_{\gamma_0\to 0}\eta(\phi,\omega,\gamma_0,t)$ is independent of γ_0 and t and is given by

$$\eta(\phi,\omega)=\eta_\infty(\phi)+\frac{1}{2}n^2\int d\mathbf{r}\;\delta g(\mathbf{r};\phi,\omega)x\frac{\partial V(r)}{\partial y}. \tag{8}$$

An approximate equation for $\delta g(\mathbf{r};\phi,\omega)$ can be obtained in the following way. Neglecting the hydrodynamical interactions between the Brownian particles transmitted via the solvent, the N-particle Smoluchowski equation for this case in a shear field $\gamma(t)$ can be integrated over the positions of all $N-2$ particles but the two particles 1 and 2. This leads to an equation for the nonequilibrium pair distribution function, involving the nonequilibrium three-particle distribution function. Neglecting the latter, i.e., restricting ourselves to low densities, transforming to center-of-mass and relative coordinates of the two particles 1 and 2, neglecting the dependence on the former, i.e., assuming spatial homogeneity and using $g_{\rm eq}(r;\phi)=\exp[-\beta V(r)]$, one obtains the following equation for $g(\mathbf{r};\phi,\omega,\gamma_0,t)$ to lowest order in the density:

$$\left[\frac{\partial}{\partial t}+2\beta D_0\boldsymbol{\nabla}\cdot\mathbf{F}(\mathbf{r})-2D_0\nabla^2+\gamma(t)x\frac{\partial}{\partial y}\right]g(\mathbf{r};\phi,\omega,\gamma_0,t) =0. \tag{9}$$

Here $\mathbf{F}(\mathbf{r})=-\boldsymbol{\nabla}V(r)$ is the force on particle 1 at a separation $\mathbf{r}$ from particle 2, $\beta=1/k_BT$, with k_B Boltzmann's constant and T the absolute temperature. Equation (9) has been considered for charged colloidal suspensions in the stationary state, i.e., for $\omega=0$ by Dhont *et al.* [25]. With Eq. (7), Eq. (9) can be written as an equation for $\delta g(\mathbf{r};\phi,\omega)$,

$$[-i\omega+2\beta D_0\boldsymbol{\nabla}\cdot\mathbf{F}(\mathbf{r})-2D_0\nabla^2]\delta g(\mathbf{r};\phi,\omega) =-x\frac{\partial}{\partial y}e^{-\beta V(r)}, \tag{10}$$

which has been solved exactly by Cichocki and Felderhof [11] for hard-sphere particles (cf. Appendix A).

From now on we shall explicitly use a hard-sphere potential unless specified otherwise. Neglecting then the force term on the left-hand side (lhs) of Eq. (10) and taking the Fourier transform of Eq. (10) with respect to $\mathbf{r}$, an equation is obtained for

$$\delta S(\mathbf{k};\phi,\omega)=n\int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}\delta g(\mathbf{r};\phi,\omega). \tag{11a}$$

Using that

$$S_{\mathrm{eq}}(k;\phi)=1+n\int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}[g_{\mathrm{eq}}(r;\phi)-1] \tag{11b}$$

is the static structure factor in equilibrium in general, the equation for $\delta S(\mathbf{k};\phi,\omega)$ derived from Eq. (10) becomes, to lowest order in the density,

$$[-i\omega+2D_0k^2]\delta S(k;\phi,\omega)=24\phi\frac{k_xk_y}{k^2}j_2(k\sigma), \tag{12}$$

where $j_2(k\sigma)$ is the spherical Bessel function of order 2 [26].

As pointed out in the Introduction, the neglect of the force term (which is only justified for $r>\sigma$) in taking the Fourier transform of Eq. (10) is the source of an error in the theory used in this paper to obtain the viscosity $\eta(\phi,\omega)$. A more detailed discussion of the nature of this error, its consequences, and a way to partially correct for it can be found in Sec. VI and Appendix A.

Equation (12) is only valid for dilute suspensions where $g_{\mathrm{eq}}(r;\phi)=\exp[-\beta V(r)]$, i.e., $S_{\mathrm{eq}}(k;\phi)=1-24\phi j_1(k\sigma)/k\sigma$ and the basic diffusion process of the two particles is free diffusion, represented by the term $2D_0k^2$ on the lhs of Eq. (12). In order to obtain an equation for concentrated colloidal suspensions we make two corrections: a static one and a dynamic one. The first one replaces the low-density expression for $g_{\mathrm{eq}}(r;\phi)$ used above by the full $g_{\mathrm{eq}}(r;\phi)$ or, equivalently, the rhs of Eq. (12) by $k_y\partial S_{\mathrm{eq}}(k;\phi)/\partial k_x$, where $S_{\mathrm{eq}}(k;\phi)$ is the full equilibrium static structure factor of Eq. (11b). For the second correction we postulate that for such suspensions the basic diffusion process is cage diffusion rather than free diffusion. An expression for the relaxation time $\tau_c(k;\phi)$ for cage diffusion for concentrated colloidal suspensions has been derived before from the kinetic theory of a dense fluid of hard spheres, as the (scaled) reciprocal of the lowest eigenvalue $D_c(k;\phi)k^2$ of a linear generalized kinetic operator, discussed elsewhere [18–20,27]:

$$\frac{1}{\tau_c(k;\phi)}=D_c(k,\phi)k^2=\frac{D_0k^2}{\chi(\phi)S_{\mathrm{eq}}(k;\phi)}d(k). \tag{13}$$

Here $D_c(k;\phi)$ is the cage diffusion coefficient, $S_{\mathrm{eq}}(k;\phi)$ is again the equilibrium static structure, and $d(k)=1/[1-j_0(k)+2j_2(k)]$ is a combination of spherical Bessel functions $j_l(k)$ of order $l=0$ and $l=2$ [26]. We emphasize that $d(k)$ is due to the collisional transfer between two hard spheres at collision and plays an important role in $\tau_c(k;\phi)$. $D_c(k;\phi)$ is plotted as a function of k in Fig. 1(b). Writing

$$\frac{1}{\tau_c(k;\phi)}=\omega_H(k;\phi), \tag{14}$$

the frequency $\omega_H(k;\phi)$ is the half-width at half height of the dynamical structure factor $S_{\mathrm{eq}}(k;\omega)$ of the suspension in equilibrium, which is the quantity that can be measured in light scattering experiments. The equality (14) is very well supported by experiment [20] [cf. Fig. 1(b)]. Then Eq. (12) becomes, with Eqs. (13) and (14),

$$[-i\omega+2\omega_H(k;\phi)]\delta S(\mathbf{k};\phi,\omega)=k_y\frac{\partial}{\partial k_x}S_{\mathrm{eq}}(k;\phi), \tag{15}$$

which has the solution

$$\delta S(\mathbf{k};\phi,\omega)=\frac{k_xk_y}{k}\,\frac{S'_{\mathrm{eq}}(k;\phi)}{2\omega_H(k;\phi)-i\omega}, \tag{16}$$

where $S'_{\mathrm{eq}}(k;\phi)=dS_{\mathrm{eq}}(k;\phi)/dk$.

We note that $S_{\mathrm{eq}}(k;\phi)$ has a very sharp maximum at $k\sim k^*=2\pi/\sigma$ at high densities [20] indicating a quasiperiodic ordering of the colloidal particles on the length scale σ in cages. Equation (16) for $\delta S(\mathbf{k};\phi,\omega)$ can be used to compute $\eta(\phi,\omega)$ with Eqs. (8) and (11). This will be shown in the next section.

III. GENERAL EXPRESSION FOR THE VISCOSITY

In order to use Eq. (16) for $\delta S(\mathbf{k};\phi,\omega)$ to compute $\eta(\phi,\omega)$ we must Fourier transform Eq. (8). For a hard-sphere potential such a transformation is not possible. Therefore, we replace in the spirit of the mean spherical approximation [28] $V(r)$ on the rhs of Eq. (8) by the equilibrium hard-sphere direct correlation function $C_{\mathrm{eq}}(r;\phi)$, i.e.,

$$V(r)\rightarrow -k_BTC_{\mathrm{eq}}(r;\phi). \tag{17}$$

As discussed in Sec. VI and Appendix A, this replacement corrects partially for the neglect of the force term on the lhs of Eq. (10), which leads to unphysical contributions from overlapping particle configurations. Fourier transforming then Eq. (8) by using Parcival's theorem on the rhs and that the Fourier transform $C_{\mathrm{eq}}(k;\phi)$ of $C_{\mathrm{eq}}(r;\phi)$ is related to $S_{\mathrm{eq}}(k;\phi)$ by

$$nC_{\mathrm{eq}}(k;\phi)=1-\frac{1}{S_{\mathrm{eq}}(k;\phi)}, \tag{18}$$

one obtains straightforwardly from Eqs. (8) and (11) the expression

$$\eta(\phi,\omega)=\eta_\infty(\phi)+\frac{k_BT}{16\pi^3}\int d\mathbf{k}\frac{k_xk_y}{k}\,\frac{S'_{\mathrm{eq}}(k;\phi)}{S_{\mathrm{eq}}(k;\phi)^2}\,\delta S(\mathbf{k};\phi,\omega). \tag{19}$$

Substituting Eq. (16) into Eq. (19), we obtain, after an angular integration in $\mathbf{k}$ space,

$$\eta(\phi,\omega)=\eta_\infty(\phi)+\frac{k_BT}{60\pi^2}\int_0^\infty dk\,k^4\left[\frac{S'_{\mathrm{eq}}(k;\phi)}{S_{\mathrm{eq}}(k;\phi)}\right]^2\times\frac{1}{2\omega_H(k;\phi)-i\omega} \tag{20}$$

for the viscoelastic behavior of the suspension.

Insofar as the integrand in the second term on the rhs of Eq. (20) contains the eigenvalues $[\omega_H(k;\phi)]$ and amplitudes $[S'_{\mathrm{eq}}(k;\phi)/S_{\mathrm{eq}}(k;\phi)]$ of *two* cage-diffusion modes, this term can be called a mode-mode coupling contribution to the viscosity. The difference with the usual mode-mode coupling contributions is that here two cage-diffusion modes, which describe the diffusion process in and out of two neighboring particles' cages, rather than two hydrodynamic modes (as occur in the long-time tails or vortex diffusion [29]) are used. We also note that the same expression (20) for $\eta(\phi,\omega)$ can be derived for $\omega=0$, by a direct application of mode-mode coupling theory to the Green-Kubo expression for $\eta(\phi,\omega=0)$ [30]. Since the complete derivation appears not to be in the literature, we briefly sketch it in Appendix B. For the concentrated suspensions we are mainly interested in here, the most important contributions to the integral in Eq. (20) come from values of $k\approx k^*$.

We note that the k integral on the rhs of Eq. (20) is convergent for all ω, since the integrand vanishes for $k\to 0$ and the asymptotic behavior for $k\to\infty$ is $\sim k^{-2}$, as for large k:

$$S_{\mathrm{eq}}(k;\phi)=1-24\phi\chi(\phi)\frac{j_1(k\sigma)}{k\sigma}[1+O(k^{-2})], \tag{21a}$$

$$S'_{\mathrm{eq}}(k;\phi)=24\phi\chi(\phi)\frac{j_2(k\sigma)}{k}[1+O(k^{-2})], \tag{21b}$$

$$\omega_H(k;\phi)=\frac{D_0}{\chi(\phi)}k^2[1+O(k^{-2})]. \tag{21c}$$

This implies that the second term on the rhs of Eq. (20) vanishes for $\omega\to\infty$, as it should, since $\eta(\phi,\infty)\equiv\eta_\infty(\phi)$ by definition.

We still have to obtain $\eta_\infty(\phi)$ in order to compute $\eta(\phi,\omega)$. One often writes for $\eta_\infty(\phi)$ [9,11,12]

$$\eta_\infty(\phi)=\eta_0[1+\tfrac{5}{2}\phi+O(\phi^2)], \tag{22a}$$

where the terms containing ϕ are corrections to the pure solvent viscosity η_0, obtained by hydrodynamic interactions (stresslet contribution) [22,23]. For concentrated solutions, we propose to set

$$\eta_\infty(\phi)=\eta_0\chi(\phi), \tag{22b}$$

implying that the effective viscosity of the suspension at very high frequencies is not only determined by the pure solvent viscosity but increased by the fraction of colloidal particle pairs at contact $\chi(\phi)$. Physically one could argue that these touching, i.e., colliding, particles increase the effective viscosity proportional to the number of such pairs present in the suspension because they increase the viscous dissipation in the suspension due to the instantaneous exchange of momentum during their collisions, no matter how short the time scale. They constitute therefore an instantaneous contribution to $\eta(\phi,\omega)$. Since [17]

$$\chi(\phi)=1+\frac{5}{2}\phi+O(\phi^2), \tag{23}$$

Eq. (22b) reduces to the usual expression (22a) for $\eta_\infty(\phi)$ at small concentrations and can therefore be considered as a generalization of Eq. (22a) to high concentrations (see also Sec. VIII).

In Fig. 2 the behavior of $\eta_\infty(\phi)/\eta_0=\chi(\phi)$ is compared with the reduced viscosity measurements by van der Werff *et al.* [5] and Zhu *et al.* [31] at very high frequencies for ϕ over the entire fluid range $0<\phi<0.55$. Here we used the Carnahan-Starling approximation [17]

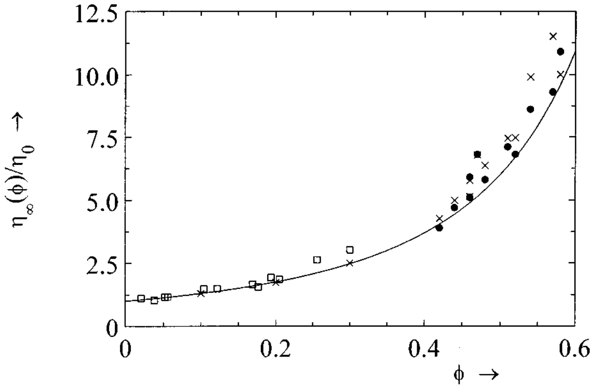

FIG. 2. Relative infinite frequency viscosity $\eta_\infty(\phi)/\eta_0$ as a function of the volume fraction ϕ. □, Zhu *et al.* [31]; ×, van der Werff *et al.* [5]; ●, Cichocki and Felderhof [12], whose points were obtained by an analysis of van der Werff *et al.* that is different from that of the authors (cf. Table II). The solid line corresponds to Eq. (24).

$$\chi(\phi)=\frac{1-0.5\phi}{(1-\phi)^3}, \tag{24}$$

which is very accurate for all such ϕ. The agreement between theory and experiment is good, thus confirming Eq. (22b). We note, however, that a theoretical justification of Eq. (22b) is still lacking (see Sec. VIII).

We also included in Fig. 2 the values for $\eta_\infty(\phi)$ as obtained by Cichocki and Felderhof [12]. These values differ from those used by van der Werff *et al.* since they obtained $\eta_\infty(\phi)$ by fitting the tails of the data for large ω to $\eta_\infty(\phi)+\eta_0 A(\phi)\sqrt{\omega\tau_P}$ instead of using a fit for all ω. We used Cichocki and Felderhof's values for $\eta_\infty(\phi)$ throughout the paper (cf. Table II).

We remark that Eq. (20), with Eq. (22b) and all the equations following from them, such as Eq. (25) in Sec. IV, contains no adjustable parameters and is completely determined by those characterizing the system: the viscosity of the solvent η_0, the volume fraction ϕ (or, equivalently, the number density n), and the diameter σ of the colloidal particles.

In Secs. IV and V we will compare the concentration dependence of Eq. (20) for the Newtonian viscosity

TABLE II. Parameters discussed in the text.

ϕ	System	$\tau_1(\phi)/\tau_P$	$\eta_\infty(\phi)/\eta_0$	$\eta_N(\phi)/\eta_0$	$A(\phi)$	ϕ^*
0.44	SSF 1	0.402	4.99	12.2	7.69	0.431
0.46	SP 23	0.421	5.13	13.1	8.33	0.438
0.47	SJ 18	0.776	6.78	17.8	8.45	0.458
0.48	SSF 1	0.372	6.36	17.3	12.1	0.458
0.51	SJ 18	0.665	7.45	28.8	17.7	0.498
0.52	SSF 1	0.834	7.47	32.7	18.6	0.508
0.54	SSF 1	0.912	9.9	50.7	28.8	0.535
0.57	SSF 1	3.70	11.5	139	44.7	0.593
0.58	SP 23	3.99	10.0	187	60.2	

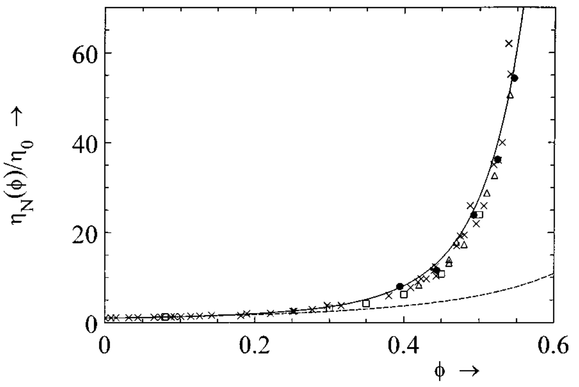

FIG. 3. Relative Newtonian viscosity $\eta_N(\phi)/\eta_0$ as a function of the volume fraction ϕ. ×, van der Werff and de Kruif [6]; △, van der Werff *et al.* [5] (cf. Table II); ●, Jones *et al.* [49]; □, Papir and Krieger [50]. The solid line corresponds to Eq. (25) and the dashed line to $\eta_\infty(\phi)/\eta_0 = \chi(\phi)$ [Eq. (24)].

$\eta_N(\phi) = \eta(\phi, \omega = 0)$ and the concentration and frequency dependence of $\eta(\phi, \omega)$ of Eq. (20) with the experimental results of van der Werff *et al.* and others.

IV. NEWTONIAN VISCOSITY

Setting $\omega = 0$ in Eq. (20) and using Eqs. (13), (14), and (22b), we obtain the simple expression for the Newtonian viscosity

$$\eta_N(\phi) = \eta_0 \chi(\phi) \left[1 + \frac{1}{40\pi} \int_0^\infty d\kappa\, \kappa^2 \frac{[S'_{\mathrm{eq}}(\kappa;\phi)]^2}{S_{\mathrm{eq}}(\kappa;\phi) d(\kappa)} \right], \tag{25}$$

where $\kappa = k\sigma$ and the Stokes-Einstein relation

$$D_0 = \frac{k_B T}{3\pi \eta_0 \sigma} \tag{26}$$

has been used. We note that for small ϕ, i.e., to $O(\phi^2)$, the second term on the rhs of Eq. (25) reduces to an expression obtained by Blawzdziewicz and Szamel [13] for $\gamma_0 = 0$.

Although the expression (25) for $\eta_N(\phi)$ has been derived for large $\phi (0.3 < \phi < 0.55)$, where cage diffusion is the dominant finite-time contribution to the viscosity [via Eqs. (13) and (14)], Eq. (25) nevertheless appears to describe the ϕ dependence of $\eta_N(\phi)$ for small and intermediate concentrations also, due to the presence of the $\eta_0 \chi(\phi)$ term (cf. Fig. 3). Figure 3 also shows that the cage diffusion describes the very rapid increase of $\eta_N(\phi)$ with ϕ for $0.40 < \phi < 0.55$ very well.

Equation (25) has been evaluated using the Henderson-Grundke correction [32] to the Percus-Yevick equation for the computation of the hard sphere $S_{\mathrm{eq}}(k;\phi)$ and $S'_{\mathrm{eq}}(k;\phi)$. A convenient Padé approximation of $\eta_N(\phi)$ for practical use for all $0 < \phi < 0.55$ is

$$\eta_N(\phi) = \eta_0 \chi(\phi) \left[1 + \frac{1.44\phi^2 \chi(\phi)^2}{1 - 0.1241\phi + 10.46\phi^2} \right] \tag{27}$$

within a relative accuracy of less than 0.25%. This approximation yields for $\eta_N(\phi)$ the correct Einstein coefficient $\frac{5}{2}\phi$ as well as the same coefficient of $O(\phi^2)$ as Eq. (25).

Cichocki and Felderhof have obtained, on the basis of the pair Smoluchowski equation, exact results for $\eta(\phi, \omega)$ to $O(\phi^2)$. Their result to $O(\phi^2)$ for $\eta_N(\phi)$ is, without Brownian motion contributions [33],

$$\eta_N(\phi) = 1 + \frac{5}{2}\phi + 5.00\phi^2, \tag{28a}$$

while with Brownian motion contributions they find [34]

$$\eta_N(\phi) = 1 + \frac{5}{2}\phi + 5.91\phi^2. \tag{28b}$$

This can be compared with the approximate result we obtain from Eq. (25),

$$\eta_N(\phi) = 1 + \frac{5}{2}\phi + 6.03\phi^2, \tag{28c}$$

where the term $6.03\phi^2$ contains a contribution $4.59\phi^2$ from $\eta_\infty(\phi)$ and a contribution $1.44\phi^2$ from the second (mode-mode coupling) term in the large square brackets on the rhs of Eq. (25). Since for $\phi < 0.25$ the cage-diffusion contribution to $\eta(\phi;\omega)$ can be neglected, Eq. (22b) then reduces to $\eta_N(\phi) = \eta_\infty(\phi) = \eta_0 \chi(\phi)$. Equations (28b) and (28c) both give then a good representation of the experimental values for $\eta_N(\phi)$.

V. VISCOELASTIC BEHAVIOR

For $\omega \neq 0$, $\eta(\phi, \omega)$ of Eq. (20) is complex, so that the viscoelastic behavior of the suspension can be written in the form

$$\eta(\phi, \omega) = \eta'(\phi, \omega) + i\eta''(\phi, \omega), \tag{29}$$

where $\eta'(\phi, \omega)$ and $\eta''(\phi, \omega)$ are the real and imaginary parts of $\eta(\phi, \omega)$, respectively. It is convenient and customary [5] to consider instead of $\eta'(\phi, \omega)$ and $\eta''(\phi, \omega)$ reduced quantities defined by

$$\eta_R^*(\phi, \omega) = \frac{\eta'(\phi, \omega) - \eta(\phi, \infty)}{\eta(\phi, 0) - \eta(\phi, \infty)} = \frac{\eta'(\phi, \omega) - \eta_\infty(\phi)}{\eta_N(\phi) - \eta_\infty(\phi)} \tag{30a}$$

and

$$\eta_I^*(\phi, \omega) = \frac{\eta''(\phi, \omega)}{\eta_N(\phi) - \eta_\infty(\phi)}, \tag{30b}$$

where the reduced real part $\eta_R^*(\phi, \omega)$ varies as a function of ω between 1 (for $\omega \to 0$) and 0 (for $\omega \to \infty$) for all ϕ and $\eta_I^*(\phi, \omega)$ vanishes for $\omega \to 0$ and $\omega \to \infty$, exhibiting a maximum in between. In Fig. 4, $\eta_R^*(\phi, \omega)$ and $\eta_I^*(\phi, \omega)$ are compared with the experimental data of van der Werff *et al.* as a function of a reduced ω for all available ϕ for $0.44 \leqslant \phi \leqslant 0.57$ [5]. As van der Werff *et al.* state, the values they find for the reduced quantities $\eta_R^*(\phi, \omega)$ and $\eta_I^*(\phi, \omega)$ are very weakly dependent on ϕ, which is consis-

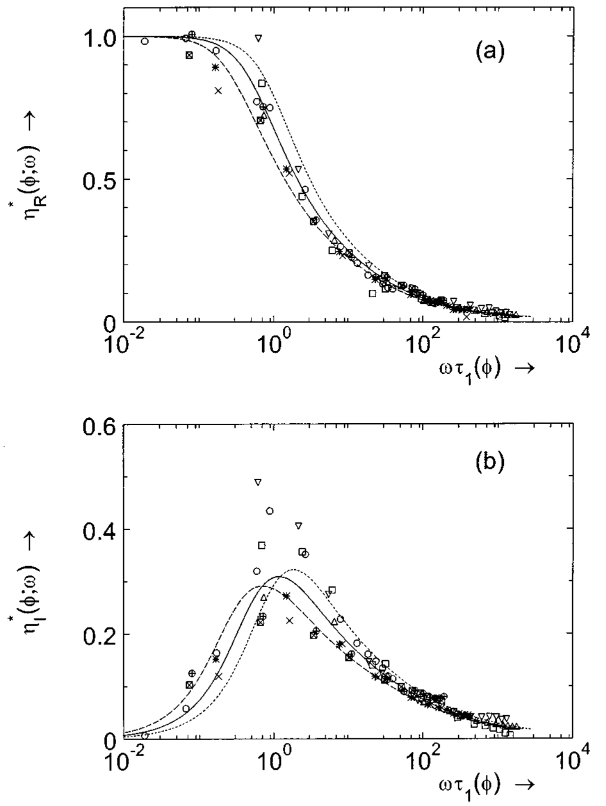

FIG. 4. (a) Real and (b) imaginary parts of the reduced viscosities $\eta_R^*(\phi,\omega)$ and $\eta_I^*(\phi,\omega)$, respectively as a function of $\omega\tau_1(\phi)$. Experimental points are from van der Werff *et al.* [5]: ⊕ for ϕ = 0.44, ○ for ϕ = 0.46, □ for ϕ = 0.47, □ for ϕ = 0.48, ▽ for ϕ = 0.51, ⋆ for ϕ = 0.52, × for ϕ = 0.54, and △ for ϕ = 0.57. Theory is from Eqs. (20), (25), and (30). Dashed line, ϕ=0.55; solid line, ϕ=0.50; dotted line, ϕ = 0.45. The cloud of points in (b) near $\omega\tau_1(\phi)=1$ should be discarded since they do not satisfy the Kramers-Kronig relation [12].

tent with the crowding of all experimental points around the theoretical curves, inside the experimental errors. The scaling of ω for the experimental data was performed in the same way as was done by van der Werff *et al.* by fitting the data for large ω by the expression (cf. Sec. VI)

$$\eta_R^*(\phi,\omega)=\eta_I^*(\phi,\omega)=\frac{3\sqrt{2}}{2\pi}\frac{1}{\sqrt{\omega\tau_1(\phi)}}, \tag{31}$$

where $\tau_1(\phi)$ is a phenomenological time for the experiments. The $\tau_1(\phi)$ used for the theoretical results is given in Sec. VI, Eq. (33).

Nevertheless, a more detailed comparison of $\eta_{R,I}^*(\phi,\omega)$ as a function of ϕ can be made, although the large experimental uncertainties of the data and the difference in the basic inputs in the theory (ϕ and η_0) and experiment (σ, c, and η_0, with c the weight concentration of the colloidal particles) complicate considerably a compelling detailed comparison of theory and experiment. Examples are given in Fig. 5. In the same figure the results of a general phenomenological description of the viscoelastic behavior of colloidal suspensions due to Cichocki and Felderhof are given [12]. This description is based on a three-pole approximation in the complex $\sqrt{\omega}$ plane, whose location is derived from the experimentally measured values $\eta_N^{\text{expt}}(\phi)$, $\eta_\infty^{\text{expt}}(\phi)$ and three additional parameters, one of them being a relaxation time. From these three poles the $\eta'(\phi,\omega)$ and $\eta''(\phi,\omega)$ as a function of ω can be derived. For the three concentrations $\phi=0.44$, 0.46, and 0.53, for which their procedure could be implemented, $\eta'(\phi,\omega)$ and $\eta''(\phi,\omega)$ are consistent with our results within the experimental errors. As was shown by Cichocki and Felderhof, the strongly deviating cloud of points near $\omega\tau_1(\phi)\approx 1$ in the imaginary part of the reduced viscosity $\eta_I^*(\phi,\omega)$ [cf. Fig. 4(b)] can be disgarded since they violate the Kramers-Kronig relations between the real and the imaginary part of $\eta(\phi,\omega)$ and must therefore be erroneous [12].

VI. LARGE-ω BEHAVIOR

For large ω, Eq. (20) for $\eta(\phi,\omega)$ can be written as

$$\eta(\phi,\omega)=\eta_\infty(\phi)+\frac{9}{5}\phi^2\chi^{5/2}\eta_0\frac{1}{\sqrt{\omega\tau_P}}(1+i)+O\left(\frac{1}{\omega}\right), \tag{32}$$

where the square-root singularity for $\omega\to\infty$ is induced by the large-k behavior of the integrand on the rhs of Eq. (20), as given by Eq. (21). We note that the correction $O(1/\omega)$ is an exact result for low concentrations to $O(\phi^2)$ (cf. Appendix A) and is consistent with what is found in the mode-mode coupling approximation.

Using Eq. (32) in Eq. (30) and comparing with Eq. (31) gives, for $\tau_1(\phi)$ the theoretical expression,

$$\tau_1(\phi)=\frac{25}{18\pi^2\phi^4\chi(\phi)^5}\left[\frac{\eta_N(\phi)}{\eta_0}-\chi(\phi)\right]^2\tau_P, \tag{33}$$

which is plotted in Fig. 6 and is consistent with the experimentally used $\tau_1(\phi)$ up to about $\phi\approx 0.55$, averaging at a value of about $\tau_P/4$ (cf. Sec. IV B in Ref. [5]). The systematically too low theoretical value of $\tau_1(\phi)$ corresponds to the systematically too high theoretical value of the coefficient of the $\omega^{-1/2}$ singularity in Eq. (32) as compared to the exact value given in Eq. (41) below.

In fact, in order to investigate this behavior further, an independent evaluation of $\eta(\phi,\omega)$ for large ω was made, starting from a Green-Kubo-like formula for $\eta(\phi,\omega)$ rather than from Eq. (8):

$$\eta(\phi,\omega)=\eta_\infty(\phi)+\frac{\beta}{V}\int_0^\infty dt\,\rho_\eta(t;\phi)e^{i\omega t}. \tag{34}$$

Here the stress-stress autocorrelation function $\rho_\eta(t)$ is defined by

$$\rho_\eta(t;\phi)=\langle\Sigma_{xy}^\eta e^{\Omega t}\Sigma_{xy}^\eta\rangle_{\text{eq}}, \tag{35}$$

where the angular brackets denote an equilibrium ensemble average. Here, instead of using the microscopic pressure tensor (the expression in the angular brackets of Eq. (3) in Sec. II), we use in this context the more customary microscopic stress tensor Σ_{xy}^η, which is equal but opposite in sign and can be written as

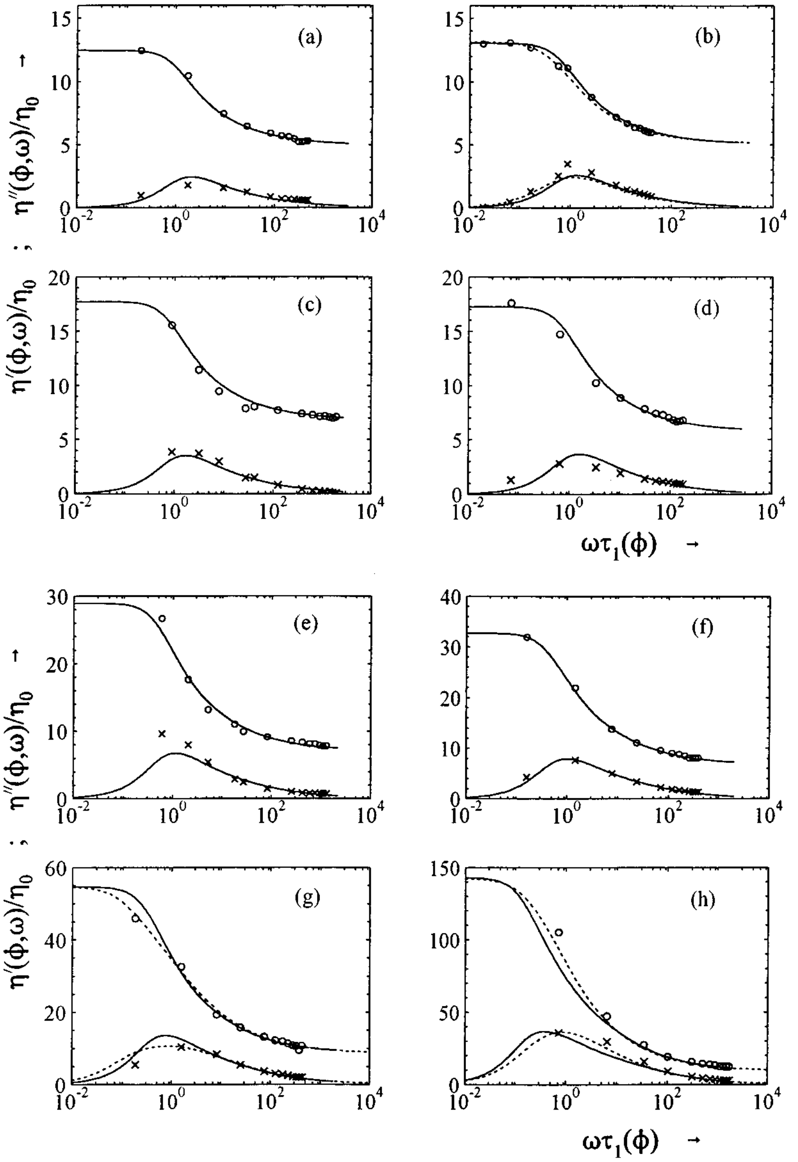

FIG. 5. Relative real and imaginary parts of the viscoelastic viscosity, respectively: $\eta'(\phi,\omega)/\eta_0$ (○) and $\eta''(\phi,\omega)/\eta_0$ (×), as a function of $\omega\tau_1(\phi)$, for eight suspensions studied experimentally by van der Werff *et al.* [5] from $\phi=0.44$ up to $\phi=0.57$ (cf. Table II). In order to make a fair and realistic comparison of the theory with experiment, keeping in mind the 4% uncertainty in the determination of ϕ [58] and the extreme sensitivity of the denominator of $\eta^*_{R,I}(\phi,\omega)$, as already pointed out by van der Werff *et al.* [5], we assign to the experimental data an effective volume fraction ϕ^* such that $\eta_N^{\text{theor}}(\phi^*)-\eta_\infty^{\text{theor}}(\phi^*)\equiv\eta_N^{\text{expt}}(\phi)-\eta_\infty^{\text{expt}}(\phi)$, within the experimental uncertainty of ϕ. Dotted line, phenomenological results by Cichocki and Felderhof [12] (only available for ϕ = 0.46, 0.54, and 0.57); solid line, theory from Eqs. (20) and (29) using $\phi=\phi^*$ (cf. Table II).

$$\Sigma_{xy}^{\eta}=\sum_{i=1}^{N} r_{i,x}F_{i,y}, \tag{36}$$

with $\mathbf{F}_i=-\boldsymbol{\nabla}_i\Phi(r^N)$ the force on particle i ($\boldsymbol{\nabla}_i=\partial/\partial\mathbf{r}_i$), $\Phi(r^N)=\Sigma_{i<j=1}^{N}V(r_{ij})$ the total potential energy of the colloidal particles, and

$$\Omega=D_s\sum_{i=1}^{N}[\boldsymbol{\nabla}_i+\beta F_i]\cdot\boldsymbol{\nabla}_i \tag{37}$$

the N-particle Smoluchowski operator [21,35] with D_0 replaced by the short-time self-diffusion coefficient $D_s(\phi)$ to make Eq. (34) applicable to all fluid densities. This is further discussed below. For $N=2$ and $\chi(\phi)=1$ the adjoint operator occurs in the pair Smoluchowski equation [Eq. (9)].

The short-time behavior of $\rho_\eta(t;\phi)$ determines the large-ω behavior of $\eta(\phi,\omega)$. Since for hard spheres the interparticle potential is singular, one determines the short-time behavior of $\rho_\eta(t;\phi)$ by first using a soft potential $V_l(r)=\epsilon(\sigma/r)^l$, where ϵ is the two-particle interaction en-

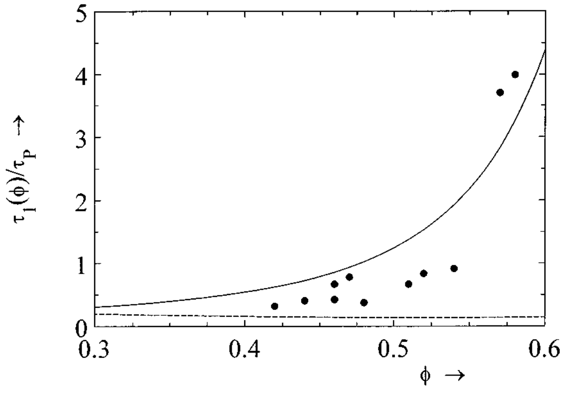

FIG. 6. Ratio of $\tau_1(\phi)$ and τ_P as a function of the volume fraction ϕ. Experimental points are from van der Werff *et al.* [5] (cf. Table II). Dashed line, theory from Eq. (33); solid line, theory using Eq. (41) instead of Eq. (32) in Eq. (30) in order to get the correct coefficient of the square-root singularity at large frequencies (cf. Sec. VI and Fig. 7).

ergy for $r=\sigma$, and then letting $l\rightarrow\infty$, so that $V_l(r)$ approaches a potential between two hard spheres of diameter σ. For $l\rightarrow\infty$, one can then derive for $\rho_\eta(t,\phi)$ the expression [36]

$$\rho_\eta(t;\phi)=\frac{2\pi n^2 V\sigma^3\chi(\phi)l}{15\beta^2}r(t^*), \tag{38a}$$

with

$$r(t^*)=\int_0^\infty ds\, e^{-s}\exp\left\{t^*\left[\left(s^2\frac{\partial}{\partial s}+s-s^2\right)\frac{\partial}{\partial s}\right]\right\}s, \tag{38b}$$

where

$$t^*=\frac{2D_s t l^2}{\sigma^2}. \tag{38c}$$

The leading term of $r(t^*)$ for $\lim_{t\rightarrow 0}\lim_{l\rightarrow\infty}$, i.e., $t^*\sim tl^2\rightarrow\infty$, which determines the short time behavior of $\rho_\eta(t;\phi)$ for a hard-sphere potential, reads [36]

$$r(t^*)=\frac{1}{\sqrt{\pi t^*}}. \tag{39}$$

Using Eqs. (34), (38), and (39) and the Stokes-Einstein relation (26), one obtains for $\eta(\phi,\omega)$ for large ω and for a hard-sphere potential for all ϕ the exact expression

$$\eta(\phi,\omega)\sim\eta_\infty(\phi)+\frac{18}{5}\phi^2\chi(\phi)\eta_0\left[\frac{D_0}{D_s(\phi)}\right]^{1/2}\frac{1+i}{\sqrt{\omega\tau_P}}. \tag{40}$$

Using then that $D_s(\phi)=D_0/\chi(\phi)$ (cf. Sec. VIII) one has

$$\eta(\phi,\omega)\sim\eta_\infty(\phi)+\frac{18}{5}\phi^2\chi(\phi)^{3/2}\eta_0\frac{1}{\sqrt{\omega\tau_P}}(1+i). \tag{41}$$

Equations (32) and (41) are both compared with the experimental data for large ω and for most experimental values of ϕ in Fig. 7. We emphasize that in order to get agreement with experiment it is necessary to replace the low-density Stokes-Einstein diffusion coefficient D_0 by the self-diffusion coefficent $D_s(\phi)$ in the basic Smoluchowski operator [cf. Eq. (37) and Fig. 7] [36]. We also emphasize that the exact result of Eq. (41) constitutes a generalization of Cichocki and Felderhof's low-concentration result to all concentrations in the fluid range. A detailed derivation of Eq. (41) will be given elsewhere [36].

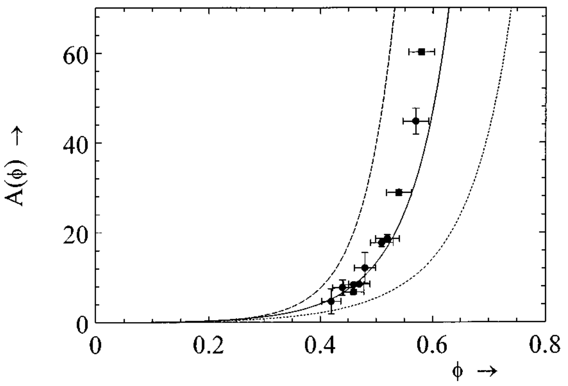

FIG. 7. Coefficient of the square-root singularity at large frequencies $A(\phi)$ as a function of the volume fraction ϕ. Experimental points are from van der Werff *et al.* [5] (cf. Table II). Dashed line, mode-mode coupling theory [Eq. (32)]; solid line, exact result starting from the Green-Kubo relation [Eq. (41)]; dotted line, the theoretical result with $D_s(\phi)=D_0$ [cf. Sec. VI, Eq. (40)].

It is clear that the experiments agree very well with Eq. (41) and not with Eq. (32), consistent with the systematically lower theoretical values of $\tau_1(\phi)$ in Fig. 6. This could well be related to the approximations made to obtain Eq. (32): (i) the use of the complete $S_{\mathrm{eq}}(k;\phi)$ (i.e. for all ϕ) in the two-particle equation (15) and the use of $\omega_H(k;\phi)$ as the only basic relaxation time, (ii) the replacement of the potential $V(r)$ in Eq. (8) by the direct correlation function $C_{\mathrm{eq}}(r;\phi)$, and (iii) the neglect of the force term on the lhs of Eq. (10) and consequenly the correct boundary condition of hard-sphere impenetrability incurred by the Fourier transform from Eq. (10) to Eq. (12) (cf. Appendix A). The first approximation was intended to incorporate the calculation of $\eta(\phi,\omega)$ contributions due to more than two isolated particles, i.e., correcting for the neglect of the three-particle distribution function in the equation (9) for $g(r;\phi,\omega,\gamma_0,t)$.

As pointed out before, the second approximation is necessary to perform a Fourier transform of Eq. (8). It also corrects partly for the unphysical contributions from overlapping particle configurations due to the neglect of the proper hard-sphere boundary condition (cf. Appendix A). We remark that the Fourier transform of Eq. (8) was due to the necessity of introducing the relaxation times $\tau_c(k;\phi)$ related to the cage diffusion for concentrated colloidal suspensions, which have only been determined for periodic particle arrangements, characterized by a wave number k. However, neither of these two approximations seems to be responsible for the incorrect asymptotic ω behavior of $\eta(\phi,\omega)$.

As for the third approximation, if we compare Eq. (32) for low densities, i.e., $\chi(\phi)=1$, with the exact solution for $\eta(\phi,\omega)$ obtained by Cichocki and Felderhof [11] to $O(\phi^2)$, we see that the second term on the rhs of Eq. (32) is smaller by a factor 2. Cichocki and Felderhof considered Eq. (10) with the correct hard-sphere boundary condition in $\mathbf{r}$ space and solved it exactly. If we solve Eq. (10) in the same manner but neglect the force term on the lhs (cf. Appendix A), we obtain, however, Eq. (32) in the limit of large ω with $\chi(\phi)=1$. This suggests that the third approximation, the neglect of the force term on the lhs of Eq. (10), and the ensuing violation of the proper hard-sphere boundary condition in real space in making the Fourier transform from Eq. (10) to Eq. (12) are the main reason for the erroneous expression (32).

We note that Eqs. (32) and (41) show that the difference between the exact and the mode coupling result for the coefficient of $\omega^{-1/2}$ is a constant factor $2/\chi(\phi)$. This only affects the approach to $\omega=\infty$, not $\eta_\infty(\phi)$ itself, and is of no influence if one plots the mode coupling theory on the phenomenological time scale $\omega\tau_1(\phi)$ using Eq. (33) (cf. Fig. 5). This may be of practical importance for predicting the viscoelastic behavior of concentrated colloidal suspensions since the scaling in time does not affect the Newtonian behavior of the viscosity [37].

VII. SMALL-ω BEHAVIOR

For low densities to $O(\phi^2)$ the small-ω behavior of $\eta(\phi,\omega)$ follows from Eqs. (20), (21), and (29) to be

$$\frac{\eta'(\phi,\omega)-\eta_\infty(\phi)}{\eta_0}=\left\{\frac{36}{25}-\frac{32}{175}(\omega\tau_P)^2\right\}\phi^2+\cdots, \tag{42a}$$

$$\frac{\eta''(\phi,\omega)}{\eta_0}=\frac{48}{175}(\omega\tau_P)\phi^2+\cdots. \tag{42b}$$

This can be compared with the exact results of Cichocki and Felderhof [11] to $O(\phi^2)$ for $\omega\rightarrow 0$:

$$\frac{\eta'(\phi,\omega)-\eta_\infty(\phi)}{\eta_0}=\left\{\frac{12}{5}-\frac{16}{81}(\omega\tau_P)^2\right\}\phi^2+\cdots, \tag{43a}$$

$$\frac{\eta''(\phi,\omega)}{\eta_0}=\frac{8}{15}\phi^2(\omega\tau_P)+\cdots. \tag{43b}$$

The agreement of Eqs. (42a) and (42b) with Eqs. (43a) and (43b) for small ω and low concentrations, in particular of the coefficient of $(\omega\tau_P)^2$ in the real parts, is better than that of Eqs. (32) and (41) for large ω. This is probably due to the fact that the neglect of the proper hard-sphere boundary condition in the mode-mode coupling theory is more serious for a description of the short-time behavior than the long-time behavior of the suspension. We remark, however, that the difference in the first terms on the rhs of Eqs. (42a) and (43a), i.e., 36/25 and 12/5, respectively, is a direct consequence of the violation of the proper hard-sphere boundary condition [cf. Appendix A, in particular Eq. (A25)].

VIII. DISCUSSION AND CONCLUSIONS

The ω dependence of $\eta(\phi,\omega)$ is well represented by Eq. (20) for all ϕ on the phenomenological time scale $\tau_1(\phi)$ or if plotted as a function of $\omega\tau_P$, when an overall shift to the theoretical curves of $2/\chi(\phi)$ is applied [37]. The latter is due to the fact that the asymptotic mode-mode coupling result (32) for the large-ω behavior of $\eta(\phi,\omega)$ is not correct because of the incomplete incorporation of the hard-sphere impenetrability in the theory. The mode-mode coupling contribution to $\eta(\phi,\omega)$ should be best for values of ω around $\omega\tau_1(\phi)\approx 1$, where there are rather few experimental points. It would be interesting therefore if a more detailed comparison between theory and experiment could be made in this ω regime to obtain a more appropriate test for the validity of the mode-mode coupling theory used here.

The result (20) for $\eta(\phi,\omega)$ is based exclusively on the instantaneous time behavior of $\eta_\infty(\phi)$ and the cage-diffusion relaxation mechanism. From the agreement of $\eta(\phi,\omega)$ and $\eta_N(\phi)$ with experiment, it would seem that these two physical processes essentially suffice to understand the Newtonian as well as the viscoelastic behavior in the entire fluid range of hard-sphere colloidal suspensions. That this agreement occurs without considering explicitly any hydrodynamical interactions between the colloidal particles in the theory presented here may appear rather puzzling. We do not have an explanation for this, other than that at high concentrations, where $0.3<\phi<0.55$, the surface to surface distance between the hard spheres is so small that a ‘‘quenching’’ of hydrodynamical effects is not unthinkable.

There may, however, be a deeper justification for the neglect of the usual hydrodynamical interactions in our theory. It seems that in a number of cases the same concentration dependence of a physical quantity of the suspension can be obtained by theories with and without hydrodynamical interactions between the Brownian particles. In this respect the following two observations are relevant.

(i) The concentration dependence of the infinite frequency viscosity $\eta_\infty(\phi)$ as well as of the Newtonian viscosity $\eta_N(\phi)$ for low and intermediate concentrations $0\leqslant\phi\leqslant 0.25$ is described by our relations [cf. Eqs. (22b) and (25)]

$$\begin{aligned}\eta_\infty(\phi)&=\eta_0\chi(\phi)\\&=\eta_0[1+\tfrac{5}{2}\phi+4.59\phi^2+O(\phi^3)]\end{aligned} \tag{44a}$$

and

$$\begin{aligned}\eta_N(\phi)&=\eta_0\chi(\phi)\left[1+\frac{1}{40\pi}\int_0^\infty d\kappa\,\kappa^2\frac{[S'_{\mathrm{eq}}(\kappa;\phi)]^2}{S_{\mathrm{eq}}(\kappa;\phi)d(\kappa)}\right]\\&=\eta_0[1+\tfrac{5}{2}\phi+6.03\phi^2+O(\phi^3)],\end{aligned} \tag{44b}$$

respectively. The rhs of Eqs. (44a) and (44b) can be compared with Beenakker's expression [38]

$$\begin{aligned}\eta^{\mathrm{eff}}(\phi)&=\lim_{k\rightarrow 0}[\eta(k;\phi)]\\&=\eta_0[1+\tfrac{5}{2}\phi+4.84\phi^2+O(\phi^3)]\end{aligned} \tag{44c}$$

for what he calls the effective viscosity. Beenakker's $\eta^{\mathrm{eff}}(\phi)$ is derived from a wave-vector-dependent viscosity $\eta(k;\phi)$, a complicated function of k, by using the quasistatic Stokes equation to describe the motion of the fluid, neglecting inertial effects. This implies, as he points out, that his equation is valid for $\tau_B<t<\tau_P$. Our relations (44a) and (44b), however, are valid for $t<\tau_B$ and $t>\tau_P$, respectively. Thus his result [Eq. (44c)] can be regarded as between Eqs. (44a) and (44b) [cf. Fig. 8(a)]. While for low concentrations the difference between the three expressions [as well as Eqs. (28a) and (28b)] is marginal since it does not appear to be relevant for comparison with experiment, we emphasize that the strong experimental increase of the Newtonian viscosity for higher concentrations $\phi>0.3$ can only be described by the integral on the rhs of Eq. (44b) [cf. Figs. 2 and 8(a)].

(ii) Also, the concentration dependence of the short-time self-diffusion coefficient $D_s(\phi)$ for low and intermediate concentrations $0\leqslant\phi\leqslant 0.45$ can be equally well described, within the experimental uncertainties, by our relation

$$D_s(\phi)=\frac{D_0}{\chi(\phi)} \tag{45a}$$

as by the Beenakker and Mazur expression [39]

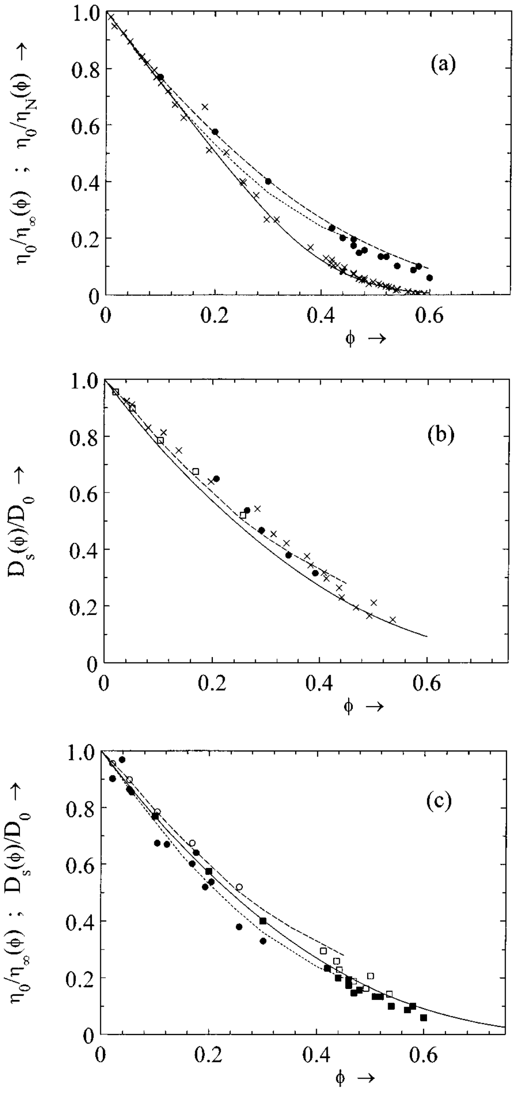

FIG. 8. (a) Inverse relative infinite frequency viscosity $\eta_0/\eta_\infty(\phi)$ [●, experimental points from van der Werff *et al.* [5]; dashed line, theory from Eq. (24)] and inverse relative Newtonian viscosity $\eta_0/\eta_N(\phi)$ [×, experimental points from van der Werff *et al.* [5,6]; solid line, theory from Eq. (25)] as a function of the volume fraction ϕ. Dotted line, Beenakker's expression (44c) [38] [cf. Sec. VIII, observation (i)]. (b) Relative short-time self-diffusion coefficient $D_s(\phi)/D_0$ as a function of the volume fraction ϕ. □, Zhu *et al.* [31]; ×, van Megen *et al.* [40]; ●, Pusey and van Megen [41]. The solid line corresponds to Eq. (45a) and the dashed line to the Beenakker and Mazur expression (45b) [39]. (c) Inverse relative infinite frequency viscosity $\eta_0/\eta_\infty(\phi)$ (●, Zhu *et al.* [31]; ■, van der Werff *et al.* [5]) and relative short-time self-diffusion coefficient $D_s(\phi)/D_0$ (○, Zhu *et al.* [31]; □, van Megen *et al.* [40] as a function of the volume fraction ϕ. Solid line, theory from Eq. (47b); dotted line, Beenakker [38]; dashed line, Beenakker and Mazur [39].

$$D_s(\phi)=\lim_{k\to\infty} D(k;\phi), \tag{45b}$$

where $D(k;\phi)$ is a wave-vector-dependent collective diffusion coefficient, which is, like $\eta(k;\phi)$, a complicated function of k. While our relation (45a) for $D_s(\phi)$ is valid for $t<\tau_B$, Beenakker and Mazur's expression (45b) is, like their viscosity, valid for $\tau_B<t<\tau_P$. On this larger time scale $D_s(\phi)$ will contain extra, in their case hydrodynamic, contributions in addition to our instantaneous contributions, leading to slightly larger values for the short-time self-diffusion coefficient. The same obtains for the experiments of van Megen *et al.* [40] and Pusey and van Megen [41] [cf. Fig. 8(b)].

Beenakker and Mazur consider only purely hydrodynamic interactions between the particles in that they study the hydrodynamical effect of a number of stationary particles on the motion of one moving particle. In our case no hydrodynamics enters explicitly at all; essentially only molecular considerations are used. For short times the (static) equilibrium radial distribution at contact $\chi(\phi)$, derived from the canonical distribution of the colloidal particles in equilibrium, occurs, yet a comparable agreement with experiment is obtained. It appears therefore that our $\chi(\phi)$ replaces effectively the hydrodynamic interactions considered elsewhere. For long times there is an extra (dynamic) contribution due to the increasing difficulty for a particle to diffuse out of the cage formed by its neighbors.

We believe that for a complex system such as a colloidal suspension there could be apparently very different alternate descriptions of the same phenomena. Perhaps the simplest and most striking example of this is the observation that Einstein's low concentration result for the viscosity of a colloidal suspension, derived from Stokes hydrodynamics [42]

$$\frac{\eta_\infty(\phi)}{\eta_0}=1+\frac{5}{2}\phi+O(\phi^2), \tag{46a}$$

can also be obtained, using an Einstein relation [cf. Eqs. (44a) and (45a)]

$$\frac{\eta_\infty(\phi)}{\eta_0}=\frac{D_0}{D_s(\phi)}=1+\frac{5}{2}\phi+O(\phi^2). \tag{46b}$$

Although these equivalent alternate descriptions of colloidal suspension properties, and especially Eq. (46b), could well be a fluke, a deeper origin cannot be ruled out in our opinion either.

In fact, for the equivalence of Einstein's expression (46a) and our (46b) the following physical argument can be given. Felderhof has shown [43], and it also follows from the Green-Kubo expression (34), that $\eta(\phi,\omega)=\eta_0[1+\frac{5}{2}\phi+\eta_2(\omega)\phi^2]$. Therefore, the first two terms in the expansion of $\eta(\phi,\omega)$ in powers of ϕ are independent of ω. This implies that when computed for any ω they should give the same answer: $\eta_0[1+\frac{5}{2}\phi]$. Einstein, as represented in Landau and Lifshitz [44], did the computation for $\omega=0$, i.e., he used a long-time stationary state hydrodynamic calculation to obtain the extra resistance of the suspension to shear from the change of the velocity field of the fluid due to a single Stokesian hard-sphere particle placed in it.

We propose to do a computation at $\omega=\infty$, i.e., for a very short (in fact, instantaneous) time. Then the placing of one particle, or even many mutually separated particles, in the solvent will not have any effect on the viscous resistance of the suspension. The only way the presence of the particles can produce an extra flow resistance is from pairs of particles (already) in contact, where an ''instantaneous'' collision takes place adding to the viscous dissipation in the suspension. Therefore, for $\omega=\infty$ the increase in the effective fluid viscosity as a function of ϕ will be given by the relative increase in the number of particle pairs at contact in equilibrium as a function of ϕ, which is $\chi(\phi)$. On the basis of this argument one would conjecture that for $\omega=\infty$, the increase in suspension viscosity, when compared to that of the pure solvent, would be $\chi(\phi)$ for all ϕ, not just $1+\frac{5}{2}\phi$ to $O(\phi)$. This conjecture is consistent with experiment (as shown in Fig. 2) and should be derivable from kinetic theory [45].

We also remark that the Einstein relation

$$D_0=\frac{k_BT}{3\pi\eta_0\sigma} \tag{47a}$$

appears to hold not only for infinitely dilute suspensions, but for all concentrations in the form [4]

$$D_s(\phi)=\frac{D_0}{\chi(\phi)}=\frac{k_BT}{3\pi\eta_\infty(\phi)\sigma}, \tag{47b}$$

as can be seen in Fig. 8(c). The physical reason for this seems to be that as long as the times of observation are sufficiently short (or the frequencies sufficiently high), so that no significant motion of the colloidal particles can take place, no hydrodynamical effects will occur and only the instantaneous effects due to particles at contact, which does not require any time to occur, i.e., $\chi(\phi)$, will be relevant. Therefore, in considering Fig. 8(c) one should bear in mind that most measurements are not made at $\omega=0$ (or, equivalently, for very short times), when $1/\chi(\phi)$ obtains, and also that there are considerable experimental uncertainties, as can be seen by the spread of the data at the same ϕ.

Recently Brady [10] has published a different model for the Newtonian as well as the frequency-dependent viscosity. His results can be obtained from the low-density result of Cichocki and Felderhof [11] (cf. Appendix A) with only two modifications: (i) a scaling of their exact solution [Eqs. (A2) and (A6)] for the low-density two-particle Smoluchowski equation (10) [Eq. (A1)] by replacing the Stokes-Einstein diffusion coefficient D_0 by the short-time self-diffusion coefficient $D_s(\phi)$ and (ii) the addition of a factor $g_{\rm eq}(r=\sigma;\phi)=\chi(\phi)$ to the low-density expression for the potential contribution of the viscosity in terms of the pair distribution function [cf. the second term on the rhs of Eq. (8)]. This leads directly to Brady's expression for $\eta(\phi,\omega)$ [cf. Eqs. (A11) and (A12)], which in our notation reads

$$\eta(\phi,\omega)=\eta_\infty(\phi)+\eta_0\phi^2\alpha_V(\omega)g_{\rm eq}(\sigma;\phi)\frac{D_0}{D_s(\phi)} \tag{48}$$

and reduces for $\omega=0$ [with Eq. (A12)] to his expression for the Newtonian viscosity $\eta_N(\phi)$,

$$\eta_N(\phi)=\eta_\infty(\phi)+\frac{12}{5}\eta_0\phi^2 g_{\rm eq}(\sigma;\phi)\frac{D_0}{D_s(\phi)}. \tag{49}$$

However, in his calculations Brady determines the three basic ingredients of his theory empirically: $\eta_\infty(\phi)$ is derived from measurements and Stokesian dynamics [46,47], while $g_{\rm eq}(\sigma;\phi)$ is taken to be given by the Carnahan-Starling approximation (24) for $0<\phi<0.5$ and by $1.2(1-\phi/\phi_m)^{-1}$ for $\phi>0.5$ [10], where $\phi_m=0.63$ is the volume fraction of random close packing of hard spheres. Furthermore, the relative short-time self-diffusion coefficient $D_s(\phi)/D_0$ is taken from Ladd's computer simulations for $0<\phi<0.45$ [47] and from Phung's Stokesian dynamics simulations for $\phi>0.45$ [48]. This leads to a curve for $\eta_N(\phi)$, as given by Eq. (49), that is virtually indistinguishable from our $\eta_N(\phi)$ based on Eq. (25) for $0<\phi<0.55$. We remark that Eq. (49), with the just-mentioned determination of $\eta_\infty(\phi)$, $g_{\rm eq}(\sigma;\phi)$, and $D_s(\phi)/D_0$, also describes very well the experimental data for $\eta_N(\phi)$ [5,6,49,50] for $0.55<\phi<0.60$, where the precise thermodynamic state of the suspension is not clear, while Eq. (25) gives then too low values for $\eta_N(\phi)$. Virtually the same result as Brady's description of $\eta_N(\phi)$ for $0<\phi<0.60$ can be obtained by using in his Eq. (49) for all ϕ our Eqs. (22b) and (45a) for $\eta_\infty(\phi)$ and $D_s(\phi)/D_0$, respectively, as well as his representation of $g_{\rm eq}(\sigma;\phi)$. It is clear that the precipitous increase of $\eta_N(\phi)$ for $\phi>0.55$ is then a direct consequence of the pole in $g_{\rm eq}(\sigma;\phi)$ at $\phi=\phi_m$.

However, for the viscoelastic behavior, when plotted as a function of $\omega\tau_1(\phi)$, Brady's results do not agree well with the experiments of van der Werff *et al.* [10,51]. This may well be related to the fact that the basic ingredient of Brady's theory that causes the increase of $\eta_N(\phi)$ for large ϕ is a static one, related to the behavior of $g_{\rm eq}(\sigma;\phi)\sim(1-\phi/\phi_m)^{-1}$ as random close packing is approached, while in our theory it is a dynamic one: the increasing difficulty of diffusion of a particle out of the cage formed by its neighbors. It appears that only the latter one is able to account for the frequency behavior of $\eta(\phi;\omega)$. The underlying physics of the two processes is therefore very different: while we use the typical high-density mechanism of cage diffusion, Brady upgrades the low-density physics by effectively scaling with $g_{\rm eq}(\sigma;\phi)$ and $D_s(\phi)$.

Very recently Liu *et al.* [52,53] have succesfully adapted the Newtonian viscosity equation (25) to charged and neutral micelles. This indicates that the physics contained in Eq. (25) is applicable to a wider class of suspensions than considered in this paper. Finally, we note that essentially the same mode-mode coupling term as in Eq. (25) gives the steep viscosity rise at high densities for atomic liquids since the atoms, like the colloidal particles, find themselves in cages, out of which they can only escape with increasing difficulty with increasing density [29,30].

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APPENDIX A

Here we compare for low densities $\phi\rightarrow 0$ and hard spheres the exact dynamic viscosity $\eta(\phi,\omega)$ as obtained from Eqs. (8) and (10) by Cichocki and Felderhof [11] with the mode-mode coupling approximation $\eta_{\rm MC}(\phi,\omega)$ given by Eq. (20). We first give the exact solution of Eq. (10) for $\delta g(\mathbf{r};\phi,\omega)$ as obtained by Cichocki and Felderhof. For $\phi\rightarrow 0$, $g_{\rm eq}(r;\phi)=\exp[-\beta V(r)]$, so that Eq. (10) reads

$$[-i\omega+2D_0\boldsymbol{\nabla}\cdot\{\beta\mathbf{F}(\mathbf{r})-\boldsymbol{\nabla}\}]\,\delta g(\mathbf{r};\phi,\omega) =\beta\frac{xy}{r}V'(r)e^{-\beta V(r)}, \tag{A1}$$

with $V'(r)=\partial V(r)/\partial r$. The solution of Eq. (A1) can be written as

$$\delta g(\mathbf{r};\phi,\omega)=\frac{xy}{r^2}f\left(\frac{r}{\sigma};\omega\right)e^{-\beta V(r)}. \tag{A2}$$

Substitution of Eq. (A2) into Eq. (A1) and using that

$$\{\beta\mathbf{F}(\mathbf{r})-\boldsymbol{\nabla}\}e^{-\beta V(r)}=0, \tag{A3}$$

one obtains in the hard-sphere limit $V(r)=\lim_{l\to\infty}V_l(r)=\lim_{l\to\infty}\epsilon(r/\sigma)^l$ the following equation for $f(u;\omega)$, with $u=r/\sigma$:

$$\left[\frac{\partial}{\partial u}u^2\frac{\partial}{\partial u}-6+\frac{i\omega\sigma^2}{2D_0}u^2\right]f(u;\omega)=0, \tag{A4}$$

with the boundary condition

$$f'(1;\omega)=\frac{\sigma^2}{2D_0}, \tag{A5}$$

where $f'(u;\omega)=\partial f(u;\omega)/\partial u$. This boundary condition ensures that the rhs of Eq. (A1), which diverges at $r=\sigma$ for hard spheres, cancels exactly a similar divergent term arising from $\mathbf{F}(\mathbf{r})$ on the lhs. The solution of Eq. (A4) with Eq. (A5) is, for $r\geqslant\sigma$ $(u\geqslant 1)$,

$$f(u;\omega)=\frac{\sigma^2}{2D_0}\frac{k_2(\alpha u)}{\alpha k_2'(\alpha)}, \tag{A6}$$

with $k_2(x)$ the modified spherical Bessel function [26] of the third kind,

$$k_2(x)=e^{-x}\{x^{-1}+3x^{-2}+3x^{-3}\}, \tag{A7}$$

and

$$\alpha=\alpha(\omega)=(1-i)\sqrt{\frac{\omega\sigma^2}{4D_0}}. \tag{A8}$$

We note that for hard spheres $f(r/\sigma;\omega)$ is continuous at $r=\sigma$ so that $\delta g(\mathbf{r};\phi,\omega)$ in Eq. (A2) shows a jump at $r=\sigma$ due to the factor $\exp[-\beta V(r)]=\Theta(r-\sigma)$ with $\Theta(x)$ the Heaviside step function. In particular, $\delta g(\mathbf{r};\phi,\omega)=0$ for $r<\sigma$, reflecting the inpenetrability of two hard spheres. Next we substitute (A2) for $\delta g(\mathbf{r};\phi,\omega)$ in Eq. (8) for $\eta(\phi;\omega)$. Using that for hard spheres

$$V'(r)e^{-\beta V(r)}=-k_BT\delta(r-\sigma), \tag{A9}$$

one obtains straightforwardly

$$\eta(\phi;\omega)=\eta_\infty(\phi)-\frac{2\pi}{15}k_BTn^2\sigma^3f(1;\omega). \tag{A10}$$

Substitution of Eqs. (A6) and (A7) leads to the final result for $\phi\to 0$,

$$\eta(\phi;\omega)=\eta_\infty(\phi)+\eta_0\phi^2\alpha_V(\omega) \tag{A11}$$

with

$$\alpha_V(\omega)=\frac{36}{5}\frac{\alpha^2+3\alpha+3}{\alpha^3+4\alpha^2+9\alpha+9} \tag{A12}$$

and $\alpha=\alpha(\omega)$ given by Eq. (A8).

In the mode-mode coupling theory, on the other hand, one neglects the force $\mathbf{F}(\mathbf{r})$ on the lhs of Eq. (A1), so that $\delta g_{\mathrm{MC}}(\mathbf{r};\phi,\omega)$ satifies

$$[-i\omega-2D_0\nabla^2]\,\delta g_{\mathrm{MC}}(\mathbf{r};\phi,\omega)=\beta\frac{xy}{r}V'(r)e^{-\beta V(r)}. \tag{A13}$$

The solution of this equation can be written in the form

$$\delta g_{\mathrm{MC}}(\mathbf{r};\phi,\omega)=\frac{xy}{r^2}f_{\mathrm{MC}}\left(\frac{r}{\sigma};\omega\right). \tag{A14}$$

Substitution of Eq. (A14) into Eq. (A13) yields the following equation for $f_{\mathrm{MC}}(u;\omega)$:

$$\left[\frac{\partial}{\partial u}u^2\frac{\partial}{\partial u}-6+\frac{i\omega\sigma^2}{2D_0}u^2\right]f_{\mathrm{MC}}(u;\omega)=0, \tag{A15}$$

with boundary condition $(\epsilon\to 0)$

$$f'_{\mathrm{MC}}(1+\epsilon;\omega)-f'_{\mathrm{MC}}(1-\epsilon;\omega)=\frac{\sigma^2}{2D_0}, \tag{A16}$$

which follows from the rhs of Eq. (A13) in the hard-sphere limit, using Eq. (A9). Thus $f_{\mathrm{MC}}(r/\sigma;\omega)$ is continuous for all r with a jump in its derivative at $r=\sigma$ given by Eq. (A16). The solution of Eqs. (A15) and (A16) is, for $u\leqslant 1$,

$$f_{\mathrm{MC}}(u;\omega)=\frac{\sigma^2}{2D_0}\frac{-K(\alpha)}{1+K(\alpha)}\frac{i_2(\alpha u)}{\alpha i_2'(\alpha)} \tag{A17}$$

and for $u\geqslant 1$,

$$f_{\mathrm{MC}}(u;\omega)=\frac{\sigma^2}{2D_0}\frac{1}{1+K(\alpha)}\frac{k_2(\alpha u)}{\alpha k_2'(\alpha)}, \tag{A18}$$

where $\alpha=\alpha(\omega)$ is defined in Eq. (A8), $k_2(x)$ in Eq. (A7), $i_2(x)$ is the modified spherical Bessel function of the second kind [26],

$$i_2(x)=\left(\frac{3}{x^3}+\frac{1}{x}\right)\sinh x-\frac{3}{x^2}\cosh x, \tag{A19}$$

and

$$K(\alpha)=-\frac{k_2(\alpha)i_2'(\alpha)}{k_2'(\alpha)i_2(\alpha)}. \tag{A20}$$

Thus $\delta g_{\mathrm{MC}}(\mathbf{r};\phi,\omega)$ given by Eqs. (A14), (A17), and (A18) is continuous for all r and nonvanishing for $r<\sigma$, allowing two spheres to overlap. To exclude such unphysical configurations in Eq. (8) for the viscosity $\eta(\phi,\omega)$ we replace $V(r)$ by $-k_BTC_{\mathrm{eq}}(r;\phi)$ [Eq. (17)]. Using that $C_{\mathrm{eq}}(r;\phi)=\exp[-\beta V(r)]-1$ for $\phi\rightarrow 0$, $\partial V(r)/\partial x$ in Eq. (8) is then replaced by

$$\frac{\partial V(r)}{\partial x}\rightarrow e^{-\beta V(r)}\frac{\partial V(r)}{\partial x} \tag{A21}$$

and the factor $\exp[-\beta V(r)]$ so obtained excludes the unphysical contributions in $\delta g_{\mathrm{MC}}(\mathbf{r};\phi,\omega)$ for $r<0$ and thus partially compensates for the error made in the boundary condition of Eq. (A13) as far as $\eta(\phi,\omega)$ is concerned. Substitution of Eq. (A14) in Eq. (8) with the replacement (A21) and using Eq. (A9) leads to

$$\eta_{\mathrm{MC}}(\phi,\omega)=\eta_\infty(\phi)-\frac{2\pi}{15}k_BTn^2\sigma^3 f_{\mathrm{MC}}(1;\omega), \tag{A22}$$

which is completely similar to Eq. (A10) for $\eta(\phi,\omega)$. Using Eq. (A18) for $f_{\mathrm{MC}}(1;\omega)$ yields the final result

$$\eta_{\mathrm{MC}}(\phi,\omega)=\eta_\infty(\phi)+\eta_0\phi^2\alpha_V(\omega)\frac{1}{1+K(\alpha)}, \tag{A23}$$

with $\alpha_V(\omega)$ given by Eq. (A12), $K(\alpha)$ by Eq. (A20), and $\alpha=\alpha(\omega)$ by Eq. (A8).

The result (A23) for $\eta_{\mathrm{MC}}(\phi,\omega)$ follows from Eq. (20) provided one uses there the low-density expression for $S_{\mathrm{eq}}(k;\phi)$ and $\omega_H(k)=D_0k^2$. To compare the exact expression (A11) for $\eta(\phi,\omega)$ with Eq. (A23) for $\eta_{\mathrm{MC}}(\phi,\omega)$ we note that for large frequencies $\omega\rightarrow\infty$, $\alpha\rightarrow\infty$ [cf. Eq. (A8)], and $K(\infty)=1$ [cf. Eqs. (A7), (A19), and (A20)], so that then

$$\eta_{\mathrm{MC}}(\phi,\omega)-\eta_\infty(\phi)=\frac{1}{2}[\eta(\phi,\omega)-\eta_\infty(\phi)]. \tag{A24}$$

For $\omega\rightarrow 0$, $\alpha\rightarrow 0$ [cf. Eq. (A8)] and $K(0)=2/3$, so that then

$$\eta_{\mathrm{MC}}(\phi,\omega)-\eta_\infty(\phi)=\frac{3}{5}[\eta(\phi,\omega)-\eta_\infty(\phi)]. \tag{A25}$$

Thus it appears that the mode coupling theory underestimates the two-particle Smoluchowski contribution to $\eta(\phi,\omega)$ by a factor 2 at high frequencies and 5/3 at low frequencies. The relevance of these factors is limited in practice since for low concentrations the main contribution to $\eta(\phi,\omega)$ comes from $\eta_\infty(\phi)$. For high concentrations the factor 2 is reduced by a factor $\chi(\phi)$ due to the replacement of D_0 by $D_s(\phi)$ in the two-particle Smoluchowski equation (6) (cf. Sec. VI).

APPENDIX B

Here we derive Eq. (20) for $\eta(\phi,\omega)$ directly, using the mode-mode coupling approximation (MMCA) for concentrated suspensions $0.3\leqslant\phi\leqslant 0.55$, in analogy with what is done for atomic liquids [29]. The basic idea behind the MMCA is that fluctuations (or ''excitations'') of a given dynamical variable decay predominantly into pairs of modes associated with conserved single-particle or collective dynamical variables [54]. If we restrict ourselves to the overdamped case without hydrodynamic interactions, the only important mode is the cage diffusion mode, i.e., the Fourier transform of the single-particle density fluctuations

$$n(\mathbf{k})=\sum_{i=1}^{N}\left(e^{i\mathbf{k}\cdot\mathbf{r}_i}-\langle e^{i\mathbf{k}\cdot\mathbf{r}_i}\rangle_{\mathrm{eq}}\right). \tag{B1}$$

In this case the lowest-order MMCA takes into account bilinear products of cage-diffusion modes: $n(\mathbf{k})n(-\mathbf{k})$ [55].

We start from the Green-Kubo expression (34) for $\eta(\phi,\omega)$ and Eq. (35) for the stress-stress autocorrelation function $\rho_\eta(t;\phi)$. The first approximation of the MMCA corresponds to the replacement of the full evolution operator $e^{\Omega t}$ by its projection onto the subspace of the product variables $n(\mathbf{k})n(-\mathbf{k})$,

$$e^{\Omega t}\approx Pe^{\Omega t}P. \tag{B2}$$

Here Ω is the N-particle Smoluchowski operator [cf. Eqs. (35) and (37)] and P the normalized projector operator defined by

$$P=\sum_{\mathbf{k}}\frac{|n(\mathbf{k})n(-\mathbf{k})\rangle_{\mathrm{eq}}\langle n(\mathbf{k})n(-\mathbf{k})|}{2N^2S_{\mathrm{eq}}^2(k;\phi)}, \tag{B3}$$

where $S_{\mathrm{eq}}(k;\phi)=(1/N)\langle n(\mathbf{k})n(-\mathbf{k})\rangle_{\mathrm{eq}}$ is the equilibrium static structure factor and $\mathbf{k}$ runs over the reciprocal lattice. From Eqs. (35), (B2), and (B3) we find for the stress-stress autocorrelation function

$$\rho_\eta(t;\phi)=\sum_{\mathbf{k},\mathbf{k}'}\frac{\langle\Sigma_{xy}^{\eta}n(\mathbf{k})n(-\mathbf{k})\rangle_{\mathrm{eq}}\langle n(\mathbf{k})n(-\mathbf{k})e^{\Omega t}n(\mathbf{k}')n(-\mathbf{k}')\rangle_{\mathrm{eq}}\langle n(\mathbf{k}')n(-\mathbf{k}')\Sigma_{xy}^{\eta}\rangle_{\mathrm{eq}}}{4N^4S_{\mathrm{eq}}^2(k;\phi)S_{\mathrm{eq}}^2(k';\phi)}. \tag{B4}$$

The second approximation is to assume that the two modes appearing in the product variables propagate independently from each other. This means that the four-variable correlation function $\langle n(\mathbf{k})n(-\mathbf{k})e^{\Omega t}n(\mathbf{k}')n(-\mathbf{k}')\rangle_{\mathrm{eq}}$ in Eq. (B4) can be factorized into products of two-variable correlation functions (as already used in the normalization of P [Eq. (B3)]), giving

$$\begin{aligned}\langle n(\mathbf{k})&n(-\mathbf{k})e^{\Omega t}n(\mathbf{k}')n(-\mathbf{k}')\rangle_{\mathrm{eq}}\\&=\langle n(\mathbf{k})e^{\Omega t}n(-\mathbf{k}')\rangle_{\mathrm{eq}}\langle n(-\mathbf{k})e^{\Omega t}n(\mathbf{k}')\rangle_{\mathrm{eq}}\\&\quad+\langle n(\mathbf{k})e^{\Omega t}n(\mathbf{k}')\rangle_{\mathrm{eq}}\langle n(-\mathbf{k})e^{\Omega t}n(-\mathbf{k}')\rangle_{\mathrm{eq}}\\&=N^2F_{\mathrm{eq}}^2(\mathbf{k};t)(\delta_{\mathbf{k},\mathbf{k}'}+\delta_{\mathbf{k},-\mathbf{k}'}),\end{aligned} \tag{B5}$$

with $F_{\rm eq}(\mathbf{k};t)=(1/N)\langle n(\mathbf{k})e^{\Omega t}n(-\mathbf{k})\rangle_{\rm eq}$ the equilibrium intermediate scattering function. As outlined in Sec. II the main diffusion process at long times and high concentrations $0.3\leqslant\phi\leqslant 0.55$ is the cage-diffusion process rather than free diffusion. Thus the long-time decay of the equilibrium intermediate scattering function is determined by $\omega_H(k;\phi)$, the lowest eigenvalue, given by Eqs. (13) and (14), corresponding to the eigenfunction $n(\mathbf{k})$ of a kinetic operator defined elsewhere [18–20]. This gives

$$F_{\rm eq}(\mathbf{k};t)=S_{\rm eq}(k;\phi)e^{-\omega_H(k;\phi)t}. \tag{B6}$$

Performing the summation over $\mathbf{k}'$ and changing the summation over $\mathbf{k}$ to an integral over $\mathbf{k}$ in the limit of large volume V, we find from Eqs. (B4)–(B6)

$$\rho_\eta(t;\phi)=\frac{V}{16\pi^3}\int d\mathbf{k}\left[\frac{V_\eta(\mathbf{k})}{S_{\rm eq}(k,\phi)}\right]^2 e^{-2\omega_H(k;\phi)t}, \tag{B7}$$

where

$$V_\eta(\mathbf{k})=\frac{1}{N}\langle\Sigma^{\eta}_{xy}n(\mathbf{k})n(-\mathbf{k})\rangle_{\rm eq} \tag{B8}$$

is the strength of the coupling between the microscopic stress tensor Σ^{η}_{xy} [Eq. (36)] and two microscopic densities. To evaluate $V(\mathbf{k})$ we use that for an arbitrary function $f(r^N)$ one has

$$\langle\mathbf{F}_i f(r^N)\rangle_{\rm eq}=-k_BT\langle\nabla_i f(r^N)\rangle_{\rm eq}, \tag{B9}$$

where $r^N=\mathbf{r}_1,\dots,\mathbf{r}_N$. Equation (B9) follows from partial integration and using the explicit form of the equilibrium distribution function. Substituting Eq. (36) for Σ^{η}_{xy} in Eq. (B8) and using Eq. (B9) yields

$$V_\eta(\mathbf{k})=-\frac{k_BT}{N}\sum_{i=1}^{N}\left\langle r_{i,x}\frac{\partial}{\partial r_{i,y}}n(\mathbf{k})n(-\mathbf{k})\right\rangle_{\rm eq}. \tag{B10}$$

From Eq. (B1) for $n(\mathbf{k})$ and the expression below (B3) for $S_{\rm eq}(k;\phi)$ it follows straightforwardly that

$$V_\eta(\mathbf{k})=-k_BTk_y\frac{\partial}{\partial k_x}S_{\rm eq}(k;\phi) \tag{B11}$$

or, equivalently,

$$V_\eta(\mathbf{k})=-k_BT\frac{k_xk_y}{k}S'_{\rm eq}(k;\phi). \tag{B12}$$

Substitution in Eq. (B7) and performing angular integrations in $\mathbf{k}$ space leads to the final result for $\rho_\eta(t;\phi)$, i.e.,

$$\rho_\eta(t;\phi)=\frac{(k_BT)^2V}{60\pi^2}\int_0^\infty dk\,k^4\left[\frac{S'_{\rm eq}(k,\phi)}{S_{\rm eq}(k,\phi)}\right]^2 e^{-2\omega_H(k;\phi)t}. \tag{B13}$$

Then Eq. (20) for $\eta(\phi,\omega)$ follows immediately from Eqs. (34) and (B13).

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