Scaling of transient hydrodynamic interactions in hard sphere suspensions

H. J. H. Clercx

Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
(Received 24 March 1997)

Analyses of retarded hydrodynamic interactions between pairs of spheres, computed in Fourier space over the full frequency range, have been performed to investigate scaling of the time-dependent self-diffusion coefficient $D_s(t,\varphi)$. It appears that up to intermediate volume fractions ($\varphi \lesssim 0.15$) $D_s(t,\varphi)$ shows scaling behavior when both the characteristic time τ is appropriately rescaled and $D_s(t,\varphi)$ is normalized by the short-time self-diffusion coefficient of the suspension $D_s = D_0(1 - 1.83\varphi)$. The rescaled characteristic time is based on matching of the long-time tail of the velocity autocorrelation function with the single-particle result. Scaling is observed for a range of particle to fluid density ratios (for $0 \leq \sigma \leq 2$, $\sigma = \rho_s/\rho$, with ρ_s the particle density and ρ the fluid mass density). Scaling for higher volume fractions, which is already present when the characteristic time is computed by optimal fitting, might be improved by including three-particle hydrodynamic interactions. The present results support the conclusion that modification of correlation functions in hard sphere suspensions, in order to include effects of two-particle hydrodynamic interactions, is already sufficient to show the existence of scaling of $D_s(t,\varphi)$. [S1063-651X(97)02909-7]

PACS number(s): 47.15.Gf, 05.40.+j, 82.70.Kj

I. INTRODUCTION

A colloidal suspension is a system of small particles immersed in a fluid. The characteristic radius a of the suspended particles is generally much larger than the length scale associated with the solvent molecules. This allows the application of continuum theories to describe the fluid motion (usually the Navier-Stokes equations for incompressible flows) in order to study the hydrodynamic interactions among the suspended particles. On the other hand, the particle radius is still small enough so that the Reynolds number Re is negligible or, in terms of characteristic quantities as the average particle velocity U and the kinematic viscosity of the fluid (ν): Re$=Ua/\nu \ll 1$. When this condition is satisfied it is allowed to linearize the Navier-Stokes equations, which simplify analytical solution procedures substantially.

A better understanding of the rheological behavior of colloidal suspensions is of considerable practical interest, especially for industrial and engineering applications. Examples can be found in the food processing industry, paint industry, etc. Particular model suspensions of hard spheres or rodlike particles, immersed in a Newtonian fluid, with specific interaction characteristics among the particles are extremely suitable to carry out experiments aimed at fundamental research, such as investigations of phase transition phenomena or the short-time particle dynamics in the prediffusive regime. Experimental, numerical, and theoretical studies of the dynamical and structural behavior of suspensions are often based on such model systems. By means of light-scattering experiments the dynamics of the particles in the fluid and the structure of the suspension can be studied. Some important aspects of the study of suspension dynamics are measurements of the (short-time) diffusivity of the particles and elucidating the role of hydrodynamic interactions in modifying the self-diffusion of a tagged particle. The recent development of diffusing wave spectroscopy (DWS), a dynamic light-scattering technique that exploits the multiple-scattering characteristics of dense suspensions in order to approximate the transport of light through a suspension by means of a diffusive process [1], has opened the way to measurements of particle dynamics on very-short-time scales. On these time scales the particle dynamics is still nondiffusive. Probing particle dynamics on such short-time scales is particularly important because particle interactions are then dominated by transient hydrodynamics and it allows the study of long-time tails of velocity autocorrelation functions in mesoscopic hard sphere systems.

One of the most remarkable experimental observations on the short-time dynamics of colloidal suspensions in recent past is the scaling behavior of the time-dependent self-diffusion coefficient $D_s(t,\varphi)$, where φ denotes the volume fraction of dispersed particles. Zhu *et al.* [2] have reported experimentally measured time-dependent diffusion coefficients, in the regime where the hydrodynamic interactions are transient, by employing DWS techniques. They have shown, by introducing suitable scaling parameters, that all curves of $D_s(t,\varphi)$ could be collapsed onto a single master curve. The scaling procedure proposed by Zhu *et al.* is based on rescaling the characteristic time $\tau_0 = a^2\rho/\eta$ (with ρ the fluid mass density) by using the suspension shear viscosity $\eta(\varphi)$ instead of the fluid shear viscosity η [resulting in a new characteristic time $\tau_\varphi = a^2\rho/\eta(\varphi)$] and normalizing the time-dependent self-diffusion coefficient by its long-time limit $D_s = D_0(1 - 1.83\varphi)$ [3] (the long-time limit should be read here as time scales much longer than τ_0, but short enough to keep the particle configuration effectively unchanged). For $\eta(\varphi)$ they have used a theoretical result for the high-frequency viscosity of a suspension of hard spheres [4]. Such a scaling basically means that the dynamics of particles in the suspension is apparently the same as if the particles are moving like single particles in an effective fluid with the suspension viscosity.

Since the interesting observations by Zhu and co-workers some more experiments have been carried out [5–7]. Kao, Yodh, and Pine [5] introduced some more scaling recipes showing that the precise scaling scenario is not extremely

important; all experimental data could reasonably well be collapsed onto a master curve with three slightly different scaling procedures. They also claimed that scaling sets in on much smaller times ($t \simeq 0.1 \tau_0$) than expected on the basis of the propagation of hydrodynamic interactions, which is expected to occur on time scales comparable to τ_0 (the time scale associated with the diffusion of vorticity over a distance comparable with the particle radius). Evidence for scaling is also supported by results from numerical simulations. Investigations by means of molecular-dynamics techniques [8] and by lattice Boltzmann methods [7,9–11] have been carried out to measure the scaling properties of ideal hard sphere suspensions in more detail. Lowe and Frenkel [11] have reported numerical simulations in order to study the scaling behavior of the velocity autocorrelation function (VACF) $\psi(t, \varphi)$ of a tagged Brownian particle in a suspension. The conclusion of that investigation is that effective fluid behavior only occurs on a time scale slightly longer than τ_0 ($t \gtrsim 4 \tau_\varphi$), contradicting the observations by Kao, Yodh, and Pine. Theoretical results aimed at explaining the scaling of $D_s(t, \varphi)$ and $\psi(t, \varphi)$ or aimed at showing that scaling could be obtained on the basis of hydrodynamics are rare. Milner and Liu [12] have derived an expression for the concentration dependence of the long-time tail of the VACF. They have shown, by analyzing the low-frequency behavior of the hydrodynamic interactions, that the long-time tail of the VACF in suspensions looks like the long-time tail of a single particle in a fluid with the suspension viscosity. The expression obtained by Milner and Liu is, however, only valid for times much larger than the Brownian relaxation time $\tau_0 = a^2 \rho / \eta$. Clercx and Schram [13] have carried out a complete analysis of two-particle hydrodynamic interactions, based on a multipole expansion of the flow field in Fourier space (with respect to time) in terms of vector spherical harmonics, which is valid over the complete frequency domain. With this particular method it is possible to study the effects of retarded hydrodynamic interactions on particle dynamics for all times, thus also on the small- and intermediate-time scales probed during the experiments by Zhu *et al.* [2] and Kao, Yodh, and Pine [5]. The analytical results in Ref. [13] have been presented in terms of frequency-dependent components of the mobility matrix, and a few results of the time-dependent self-diffusion coefficient have been shown. No scaling analysis of $D_s(t, \varphi)$ and $\psi(t, \varphi)$ has been made in that study. Some other approaches have been reported in the literature [14,15], but have the disadvantage that they are only valid for some particular frequency range or time domain. An overview on the topic of scaling of the time-dependent self-diffusion coefficient can be found in the review paper by Español and Zúñiga [16].

In Sec. II an outline is given of the procedure to determine the velocity correlation functions, including the effects of hydrodynamic interactions on these correlation functions. Results for the time-dependent self-diffusion coefficient as a function of volume fraction are presented in Sec. III, including an analysis of scaling based on two scaling scenarios. We end this paper by summarizing the main results and giving a conclusion in Sec. IV.

II. DERIVATION OF THE VELOCITY CORRELATION MATRIX

It has already been known for a long time that the dynamics of a Brownian particle in a viscous fluid is more compli-cated than expected on the basis of the solution of the Langevin equation

$$m \frac{d\mathbf{U}(t)}{dt} = -\zeta \mathbf{U}(t) + \mathbf{R}(t), \tag{1}$$

with $\mathbf{U}(t)$ the velocity of the Brownian particle, m its mass, $\zeta = 6 \pi \eta a$ the friction coefficient for spherical particles, and $\mathbf{R}(t)$ a random force exerted by the fluid molecules during collisions with the Brownian particle. The random force is assumed to be Gaussian, i.e., $\langle \mathbf{R}(t) \rangle = 0$, where $\langle \ \rangle$ denotes an ensemble average. Furthermore, white-noise statistics is assumed, i.e., $\langle R_i(t) R_j(t + t_0) \rangle = 2 \zeta k_B T \delta_{ij} \delta(t_0)$, with k_B the Boltzmann constant and T the absolute temperature. The assumption of white-noise statistics means that successive collisions of fluid molecules with the Brownian particle are uncorrelated. From Eq. (1) it is possible to derive in a straightforward manner an explicit relation for the VACF. The result is $\psi(t_0) = \langle U(t) U(t + t_0) \rangle = (k_B T / m) \exp(-\zeta t_0 / m)$.

The classical Langevin approach described above appears to be sufficient when the behavior of Brownian particles is studied on long-time scales, i.e., on time scales where the VACF has already decayed. On shorter time scales a more adequate description of hydrodynamics has to be used. This insight started to grow some 30 years ago with the advent of computer simulations of the behavior of fluids at the molecular level. Alder and Wainwright [17,18] found in computer experiments, where they simulated the motion of a tagged particle in a hard sphere fluid, that the VACF of that tagged particle has a long-time tail resulting in a surprisingly slow decay of the VACF, viz., $\psi(t_0) \simeq t_0^{-3/2}$ when $t_0 \gg \tau_0$, instead of showing an exponential decay. Alder and Wainwright were also able to explain the long-time tail for three-dimensional hard sphere fluids by considering the cooperative effect from the surrounding fluid molecules, which can be described by macroscopic hydrodynamics [17,18] (see also the works of Zwanzig and Bixon [19] and Case [20]). The dynamics of a Brownian particle is in fact governed by a combination of forces and is appropriately described by the so-called Stokes-Boussinesq equation

$$M \frac{d\mathbf{U}(t)}{dt} = -\zeta \mathbf{U}(t) - 6a^2 \sqrt{\pi \rho \eta} \int_0^t \frac{1}{\sqrt{t - \tau}} \frac{d\mathbf{U}(\tau)}{d\tau} \, d\tau$$
$$+ \mathbf{R}(t), \tag{2}$$

with $M = m + \frac{1}{2} m_0$, the effective mass associated with both the particle mass and the mass m_0 of the displaced fluid during particle motion. The second term on the right-hand side of Eq. (2) is the memory term and is associated with a retarded viscous force. This contribution is also known as the Basset history force. The feedback on the particle of the surrounding unsteady flow field, which contains information of the particle velocity at previous times (the momentum that is transferred from particle to fluid cannot simply disappear and is also not completely carried off by propagation of sound waves), is ''felt'' by the particle as an additional push in its original direction of motion. This results in the persistence of the velocity of the Brownian particle and gives a rough explanation of the long-time tail of the VACF. The

random force in Eq. (2) is still Gaussian, but not uncorrelated for different times due to cooperative effects of fluid motion. By applying Laplace transform techniques the VACF is found; it has the form

$$\psi(\tau) = k_B T \{\beta \exp(\beta^2 \tau)\text{erfc}(\beta\sqrt{\tau})$$
$$- \alpha \exp(\alpha^2 \tau)\text{erfc}(\alpha\sqrt{\tau})\}/[M(\beta-\alpha)],$$

with

$$\alpha = \frac{9}{4\sigma+2}(1+\tfrac{1}{3}\sqrt{5-8\sigma}),$$

$$\beta = \frac{9}{4\sigma+2}(1-\tfrac{1}{3}\sqrt{5-8\sigma}). \qquad (3)$$

The coefficient $\sigma = \rho s/\rho$ is the ratio between the particle density ρ_s and the fluid mass density ρ. The dimensionless time τ is defined as $\tau = \eta t/\rho a^2 \equiv t/\tau_0$. This result has been obtained by several authors, e.g., Widom [21] and Hinch [22]. From Eq. (3) it can directly be concluded that the equipartition of energy is not satisfied: $\psi(0) = k_B T/M$ instead of $k_B T/m$. By including compressibility it can be shown that on time scales $\tau_c \simeq a/c \ll \tau_0$ (with c the speed of sound) required for sound waves to travel a distance of the order of the particle radius, the VACF decreases from the equipartition value $k_B T/m$ to $k_B T/M$ [23]. The long-time tail is easily found by considering the limit $\tau \to \infty$,

$$\psi(\tau \to \infty) = (k_B T/M)\frac{4\sigma+2}{36\sqrt{\pi}}\frac{1}{\tau\sqrt{\tau}}. \qquad (4)$$

A different behavior of long-time tails of correlation functions is found for the angular velocity autocorrelation function ($\simeq \tau^{-5/2}$) [24] and for the VACF of Brownian particles in a harmonic potential ($\simeq \tau^{-7/2}$), which is of interest for particles in, for example, colloidal crystals [25]. The problem of long-time tails is also studied from the point of view of fractional calculus (see the work of Mainardi and Tampieri [26] and references therein).

A more suitable quantity from an experimental point of view is the time-dependent self-diffusion coefficient, with which the motion of Brownian particles can be characterized. Two slightly different but closely related definitions of the time-dependent self-diffusion coefficient exist, viz.,

$$D_s(t,\varphi) \equiv \frac{1}{6}\frac{d}{dt}\langle\Delta\mathbf{r}^2(t,\varphi)\rangle = \int_0^t \psi(t_0,\varphi)dt_0 \qquad (5)$$

and

$$D_s(t,\varphi) \equiv \frac{\langle\Delta\mathbf{r}^2(t,\varphi)\rangle}{6t}$$

$$= \int_0^t \psi(t_0,\varphi)dt_0 - \frac{1}{t}\int_0^t t_0\psi(t_0,\varphi)dt_0, \qquad (6)$$

with $\langle\Delta\mathbf{r}^2(t,\varphi)\rangle$ the mean-square displacement, which is a function of the concentration of dispersed particles. The results reported in Ref. [13] are based on Eq. (5). In this paper

only the second definition will be used to investigate the appearance of scaling. This expression is also the definition that is employed in experimental measurements of $D_s(t,\varphi)$ and in numerical simulations [8,9,11]. It is noteworthy that when Eq. (6) shows scaling, then also Eq. (5) should show scaling. The short-time self-diffusion coefficient can be recovered by considering the long-time limit $D_s(t \to \infty) = D_0(1-1.83\varphi)$.

The analytical calculation of the VACF for hydrodynamically interacting Brownian particles is much more complicated. As a first step time-dependent hydrodynamic interactions between spherical particles have to be analyzed in order to calculate particle velocities. This can be accomplished by solving the Fourier transformed (with respect to time) Navier-Stokes equations for the flow field surrounding two spherical particles [13]. No-slip boundary conditions are assumed. Subsequently, an analytical relation is necessary for the precise form of the VACF, including the effects of hydrodynamic interactions on the time-dependent velocities of the respective particles. We start with the definition of the correlation matrix

$$\boldsymbol{\psi}(\omega,\omega') = \begin{bmatrix} \boldsymbol{\psi}^{tt}(\omega,\omega') & \boldsymbol{\psi}^{tr}(\omega,\omega') \\ \boldsymbol{\psi}^{rt}(\omega,\omega') & \boldsymbol{\psi}^{rr}(\omega,\omega') \end{bmatrix}, \qquad (7)$$

where t and r denote translational and rotational, respectively. The submatrices represent $\boldsymbol{\psi}^{tt}(\omega,\omega') = \langle\mathbf{U}(\omega)\mathbf{U}^*(\omega')\rangle$, $\boldsymbol{\psi}^{rr}(\omega,\omega') = \langle\boldsymbol{\Omega}(\omega)\boldsymbol{\Omega}^*(\omega')\rangle$, and $\boldsymbol{\psi}^{tr}(\omega,\omega') = \langle\mathbf{U}(\omega)\boldsymbol{\Omega}^*(\omega')\rangle = \boldsymbol{\psi}^{rt\dagger}(\omega,\omega')$, where the dagger stands for Hermitian conjugation. $\mathbf{U}(\omega)$ and $\boldsymbol{\Omega}(\omega)$ are the Fourier transforms of the velocity and angular velocity, respectively. The correlation matrix shown in Eq. (7) could suggest decoupling of translational and rotational motions in each of the four submatrices when looked at superficially. However, due to hydrodynamic interactions, strong coupling can exist between translational and rotational motions. Consider a pair of spherical particles labeled 1 and 2. When particle 1 has a velocity parallel to the interparticle axis, only a force parallel to the interparticle axis is exerted on particle 2 and no torque. However, when particle 1 has a velocity perpendicular to the interparticle axis, a force parallel to the velocity of particle 1 and a torque perpendicular to both the interparticle axis and the velocity of particle 1 is exerted on particle 2. It is not surprising then that the full hydrodynamic problem has to be solved in order to determine, for example, velocity correlation functions. It has been shown by Clercx and Schram [13], on the basis of a generalization of a fluctuation-dissipation theorem derived by Bedeaux and Mazur [27], that the following relation exists between the Fourier transform of the correlation matrix $\boldsymbol{\psi}(\omega,\omega')$ and the frequency-dependent friction matrix $\boldsymbol{\zeta}(\omega)$, which contains the full hydrodynamics:

$$\boldsymbol{\psi}(\omega,\omega') = 4\pi k_B T\delta(\omega-\omega')\text{Re}\{[\boldsymbol{\zeta}(\omega)-i\omega\mathbf{S}]^{-1}\}, \quad (8)$$

with i the imaginary unit $\text{Re}\{[\boldsymbol{\zeta}(\omega)-i\omega\mathbf{S}]^{-1}\}$ denoting the real part of $[\boldsymbol{\zeta}(\omega)-i\omega\mathbf{S}]^{-1}$, and $\mathbf{S}$ a so-called mass-inertia matrix, which has for a spherical particle the form $\mathbf{S}^{tt} = m\mathbf{I}$, $\mathbf{S}^{tr} = \mathbf{S}^{rt} = 0$, and $\mathbf{S}^{rr} = \frac{2}{5}ma^2\mathbf{I}$ (see [13]). A relatively simple expression for the Fourier transform of $\boldsymbol{\psi}(\omega,\omega')$ is obtained by substituting Eq. (8) into the expression
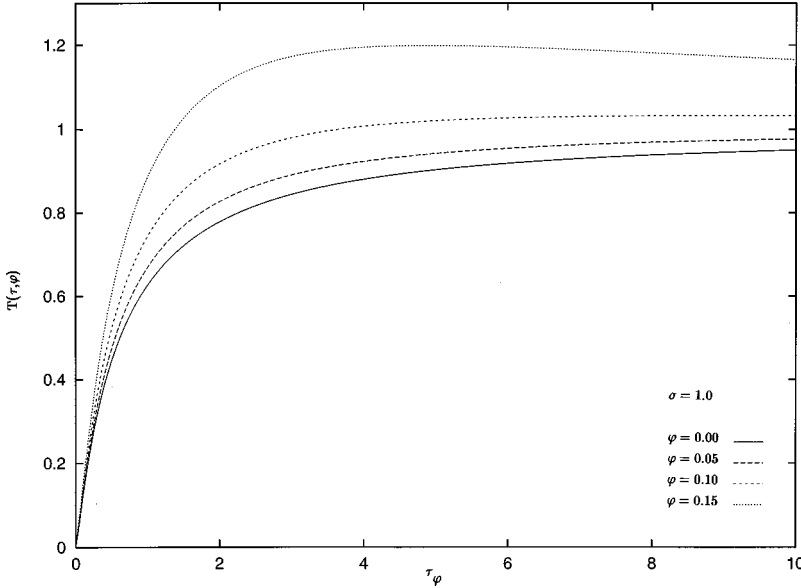
FIG. 1. Velocity autocorrelation function $\phi(t/\tau_\varphi)$ divided by its long-time decay $\phi(t/\tau_\varphi \to \infty)$ for $\sigma = 1$ and several volume fractions. The characteristic time is defined as $\tau_\varphi = (1 - 3.77\varphi)^{2/3}\tau_0$.

$$\psi(t, t+t_0) = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-i\omega t} e^{i\omega'(t+t_0)} \psi(\omega, \omega')$$

$$\times d\omega \, d\omega'$$

$$= (k_B T/\pi) \int_{-\infty}^{+\infty} e^{i\omega t_0} \mathrm{Re}\{[\boldsymbol{\zeta}(\omega) - i\omega \mathbf{S}]^{-1}\} d\omega$$

$$\equiv \psi(t_0). \tag{9}$$

When we introduce a dimensionless frequency $\omega_0 = a^2 \rho \omega/\eta$ and use the dimensionless time τ, which was introduced previously, Eq. (9) is simplified to

$$\psi(\tau) = 6\pi\eta a(k_B T/M) \frac{4\sigma+2}{9\pi} \int_0^\infty \cos(\omega_0 \tau)$$

$$\times \mathrm{Re}\{[\boldsymbol{\zeta}(\omega_0) - i\omega_0 \widetilde{\mathbf{S}}]^{-1}\} d\omega_0, \tag{10}$$

where it is already anticipated, by introducing the factor $6\pi\eta a(k_B T/M)$, that only velocity autocorrelation functions are investigated. The mass-inertia matrix $\mathbf{S}$ is slightly modified; we now use $\widetilde{\mathbf{S}}^{tt} = \frac{4}{3}\pi\eta a\sigma\mathbf{I}$ and $\widetilde{\mathbf{S}}^{rr} = \frac{8}{15}\pi\eta a^3\sigma\mathbf{I}$. The matrices $\widetilde{\mathbf{S}}^{tr}$ and $\widetilde{\mathbf{S}}^{rt}$ remain zero. In obtaining Eq. (10) we have used $\mathrm{Re}\{[\boldsymbol{\zeta}(\omega_0) - i\omega_0\widetilde{\mathbf{S}}]^{-1}\} = \mathrm{Re}\{[\boldsymbol{\zeta}(-\omega_0) + i\omega_0\widetilde{\mathbf{S}}]^{-1}\}$. The single-particle result for the VACF [Eq. (3)] follows directly from Eq. (10) by observing that for this particular situation the matrix $\boldsymbol{\zeta}(\omega_0) - i\omega_0\widetilde{\mathbf{S}}$ is diagonal and by using

$$\zeta^{tt}(\omega_0) = 6\pi\eta a[1 + \tfrac{1}{2}(1-i)\sqrt{2\omega_0} - \tfrac{1}{9}i\omega_0]. \tag{11}$$

Translational motions of a single-spherical particle are completely decoupled from rotational motions. This is not the case when particle interactions are considered as explained before.

We have studied the behavior of the correlation matrix for dilute suspensions where the volume fraction $\varphi \ll 1$. In this case we have to take into account two-particle hydrodynamic interactions only. Using the simplest form of the pair distribution function, $g(\mathbf{R}) = 0$ for $|\mathbf{R}| < 2a$ and $g(\mathbf{R}) = 1$ for $|\mathbf{R}| \geq 2a$ with $\mathbf{R}$ the interparticle distance vector and a the particle radius, we can determine an expression for the ensemble average of the correlation matrix. Actually, it is a configuration average, and up to order φ it can be written as $\langle \psi(\tau) \rangle_c = \boldsymbol{\phi}_0(\tau) + \varphi\boldsymbol{\phi}_1(\tau)$, where $\langle \ \rangle_c$ denotes an average over all configurations of the N particles. $\boldsymbol{\phi}_0(\tau)$ is the correlation matrix for a Brownian particle in the limit of an infinitely diluted suspension and $\varphi\boldsymbol{\phi}_1(\tau)$ is the correction due to the two-particle hydrodynamic interactions. The VACF is now some particular component of $\langle \psi(\tau) \rangle_c$,

$$\langle \psi_{ii}^{tt}(t_0) \rangle_c = \langle\langle U_i(t) U_i(t+t_0) \rangle\rangle_c \equiv \phi(t_0). \tag{12}$$

For convenience we finally write for the VACF [see Eq. (9)]

$$\phi(\tau) = \phi_0(\tau) + \varphi\phi_1(\tau)$$

$$= (k_B T/M) \frac{4\sigma+2}{9\pi} \{\psi_0(\tau) + \varphi\psi_1(\tau)\}. \tag{13}$$

For $\tau \to \infty$ we expect that the following relation should exist (see also [12]):

$$\phi(\tau \to \infty) = (k_B T/M) \frac{4\sigma+2}{36\sqrt{\pi}} \frac{1}{\tau\sqrt{\tau}} (1 + C\varphi), \tag{14}$$

where C, which is a function of $\sigma = \rho_s/\rho$, has to be determined numerically. One of the scaling scenarios employed in this study is based on scaling of the VACF with this expression of the long-time tail.

The approach to determine the friction matrix is outlined in detail in Ref. [13]. Employing this method in order to find the lowest-order modification of the long-time tail results in $C = -3.77 \pm 0.04$ when $\sigma = 1$. More generally, it appears that for $0 \leq \sigma \leq 2$, $C = -3.77 + 0.48(\sigma - 1)$ with an error margin of approximately 1%, which is due to errors in extrapolation. It agrees reasonably well with the analytical result obtained by Milner and Liu [12], $C = -3.75 + 0.5(\sigma - 1)$, and is consistent with their argument that higher-order multipolar corrections do not lead to corrections of the value based on a second-order reflection calculation. It is an open question how three- and many-body interactions will modify the
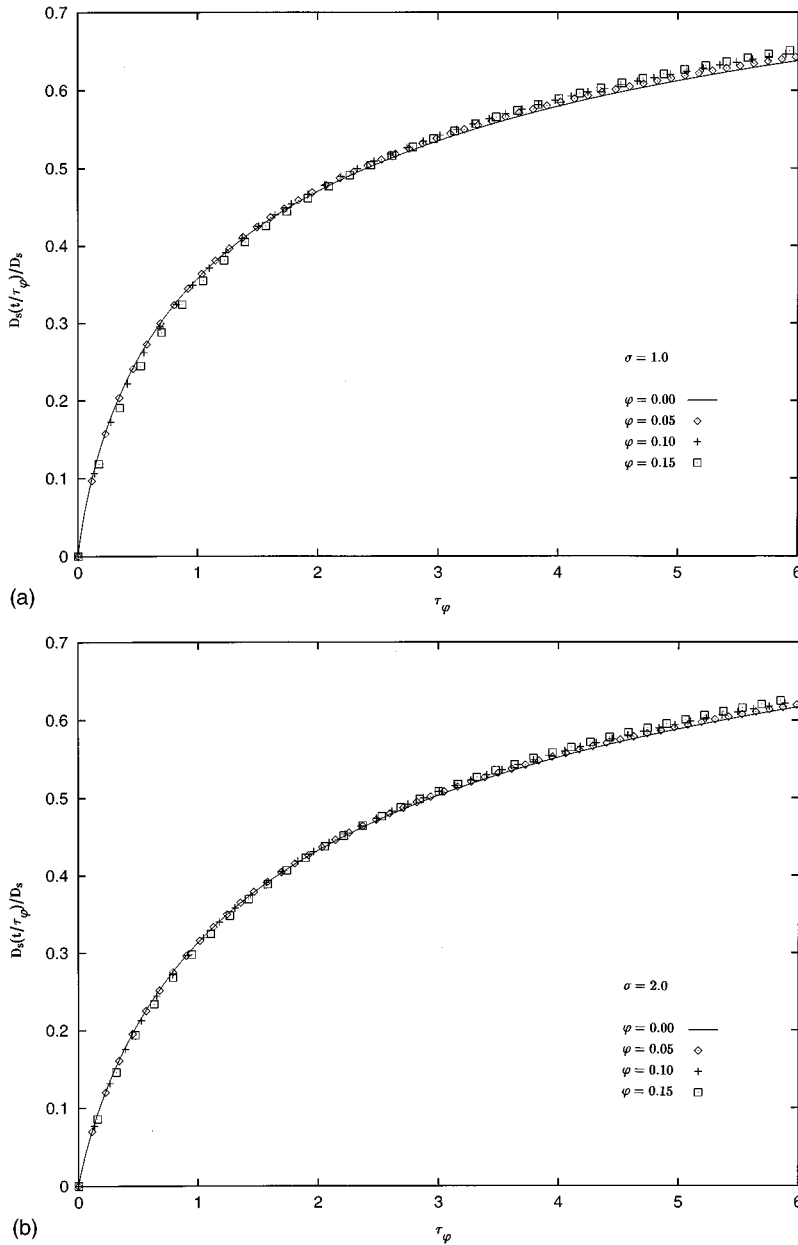
FIG. 2. (a) Time-dependent self-diffusion co-efficient divided by its asymptotic limit $D_s(t/\tau_\varphi)/D_s$ for $\sigma=1$. The short-time self-diffusion coefficient is $D_s=D_0(1-1.83\varphi)$. The characteristic time is defined as $\tau_\varphi=(1-3.77\varphi)^{2/3}\tau_0$. The drawn line is the single-particle result. (b) Time-dependent self-diffusion coefficient divided by its asymptotic limit $D_s(t/\tau_\varphi)/D_s$ for $\sigma=2$. The short-time self-diffusion coefficient is $D_s=D_0(1-1.83\varphi)$. The characteristic time is defined as $\tau_\varphi=(1-3.31\varphi)^{2/3}\tau_0$. The drawn line is the single-particle result.

VACF and its long-time tail. Such an analysis is in principle possible when the method presented in Ref. [13] is combined with a method to calculate three-particle hydrodynamic interactions. For the quasistatic case such an analysis has been carried out [28], but it might be expected that for transient hydrodynamic interactions a numerical analysis of the theoretical results is quite expensive.

III. SCALING OF THE TIME-DEPENDENT SELF-DIFFUSION COEFFICIENT

Following both the theoretical approach by Milner and Liu [12] and the numerical study by Lowe and Frenkel [11], we have calculated the VACF $\phi(\tau)$ [Eq. (13)] divided by the theoretical one-particle long-time result [$\psi(\tau\rightarrow\infty)$, Eq. (4)], i.e., we have defined a function $T(\tau,\varphi)$ by

$$T(\tau,\varphi)=(4/\sqrt{\pi})\,\tau\sqrt{\tau}\{\psi_0(\tau)+\varphi\psi_1(\tau)\}. \qquad (15)$$

In the limit $\tau\rightarrow\infty$ we obtain $T(\tau\rightarrow\infty,\varphi)=1+C\varphi$, with $C=-3.77+0.48(\sigma-1)$. By introducing a new characteristic time instead of τ_0, viz., $\tau_\varphi=(1+C\varphi)^{2/3}\tau_0$, it is possible to show some amount of scaling of the VACF for short and intermediate times and small volume fractions (see Fig. 1). Scaling for large times is implicitly satisfied due to the definition of τ_φ. For small volume fractions ($\varphi\lesssim0.1$) scaling is comparable with the numerical results presented by Lowe and Frenkel, but for higher volume fractions the discrepancy with their results, which implicitly include many-particle interactions, starts to grow, which is an indication that three- and many-particle interactions will also give a significant contribution to the VACF on small- and intermediate-time scales. From the present calculations it is not possible yet to indicate a time scale beyond which effective fluid behavior will occur. Large deviations from scaling for $\varphi\gtrsim0.15$ always occur on time scales of order τ_0. Although it is not clear to what amount these results are changed by including three-
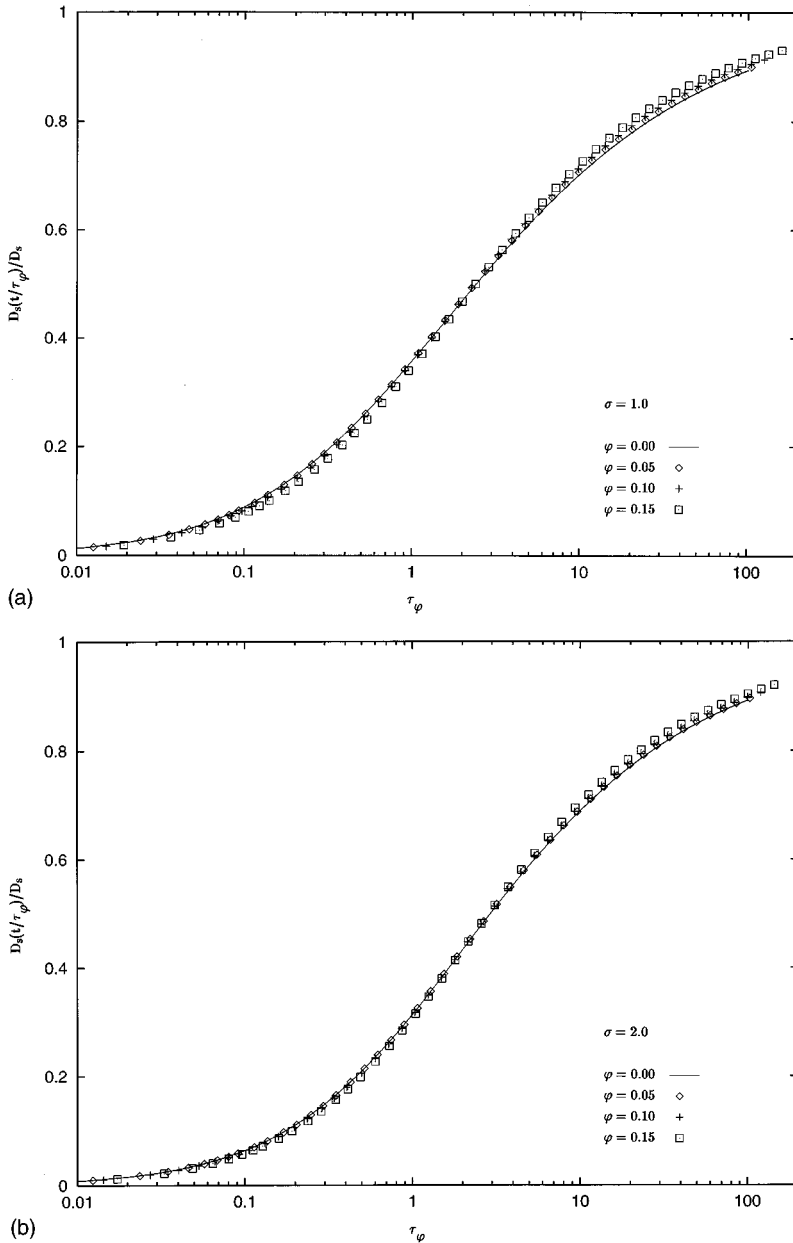
FIG. 3. (a) Scaling of the time-dependent self-diffusion coefficient divided by its asymptotic limit $D_s(t/\tau_\varphi)/D_s$ for $\sigma = 1$. The short-time self-diffusion coefficient is $D_s = D_0(1 - 1.83\varphi)$. The characteristic time is defined as $\tau_\varphi = (1 - 3.77\varphi)^{2/3}\tau_0$. The drawn line is the single-particle result. (b) Scaling of the time-dependent self-diffusion coefficient divided by its asymptotic limit $D_s(t/\tau_\varphi)/D_s$ for $\sigma = 2$. The short-time self-diffusion coefficient is $D_s = D_0(1 - 1.83\varphi)$. The characteristic time is defined as $\tau_\varphi = (1 - 3.31\varphi)^{2/3}\tau_0$. The drawn line is the single-particle result.

particle interactions, it seems that this observation supports the conclusion by Lowe and Frenkel quoted earlier that no effective fluid behavior exists at time scales of order τ_0.

The scaling scenario for the time-dependent self-diffusion coefficient is based on τ_φ and normalization is carried out with the Batchelor result for the short-time self-diffusion coefficient $D_s = D_0(1 - 1.83\varphi)$. In Fig. 2 the results of $D(t/\tau_\varphi)/D_s$ on short- and intermediate-time scales $(0 \leqslant \tau_\varphi \leqslant 6)$ are shown for two values of σ: in Fig. 2(a) for $\sigma = 1$ and in Fig. 2(b) for $\sigma = 2$ (the particle density is twice as large as the fluid density). This particular choice of time scale in the figures is motivated by the possibility to compare the scaled curves with those obtained numerically by Lowe and Frenkel [11] and the experimental data by Kao, Yodh, and Pine [5]. The small deviation from perfect scaling for $\tau_\varphi \simeq 6$ is due to the fact that the rescaled time is chosen such that the velocity autocorrelation functions collapse asymptotically for all φ, resulting in a small deviation from scaling of the VACFs for short and intermediate times. This effect is

also found and discussed by Lowe and Frenkel. As a consequence, a small vertical shift in $D(t/\tau_\varphi)/D_s$ for large τ_φ will occur for the present calculations due to a difference of the integrals when calculating $D(t/\tau_\varphi)/D_s$ by using Eq. (6) [see Fig. 1, where $T(t,\varphi) \geqslant T(t,\varphi=0)$]. Despite this small discrepancy, reasonable scaling is observed over a large-time interval. This is shown in Fig. 3, where $D(t/\tau_\varphi)/D_s$ for $\sigma = 1$ [Fig. 3(a)] and $\sigma = 2$ [Fig. 3(b)] is plotted for $0.01 \leqslant \tau_\varphi \leqslant 200$. The logaritmic scale for τ_φ facilitates a comparison with numerical data by Ladd [9] and experimental results reported by Zhu et al. [2]. Up to volume fractions $\varphi = 0.15$, the scaling is comparable with the other numerically and experimentally obtained curves. The time-dependent self-diffusion coefficient has been calculated for several values of σ ranging from 0 to 2. All data obtained by the proposed analytical procedure can be collapsed onto a master curve with a comparable accuracy as shown for $\sigma = 1$ and 2, and scaling seems to be better when σ increases. In the limit $\sigma \to 0$ scaling is not perfect, but the observed lack of scaling
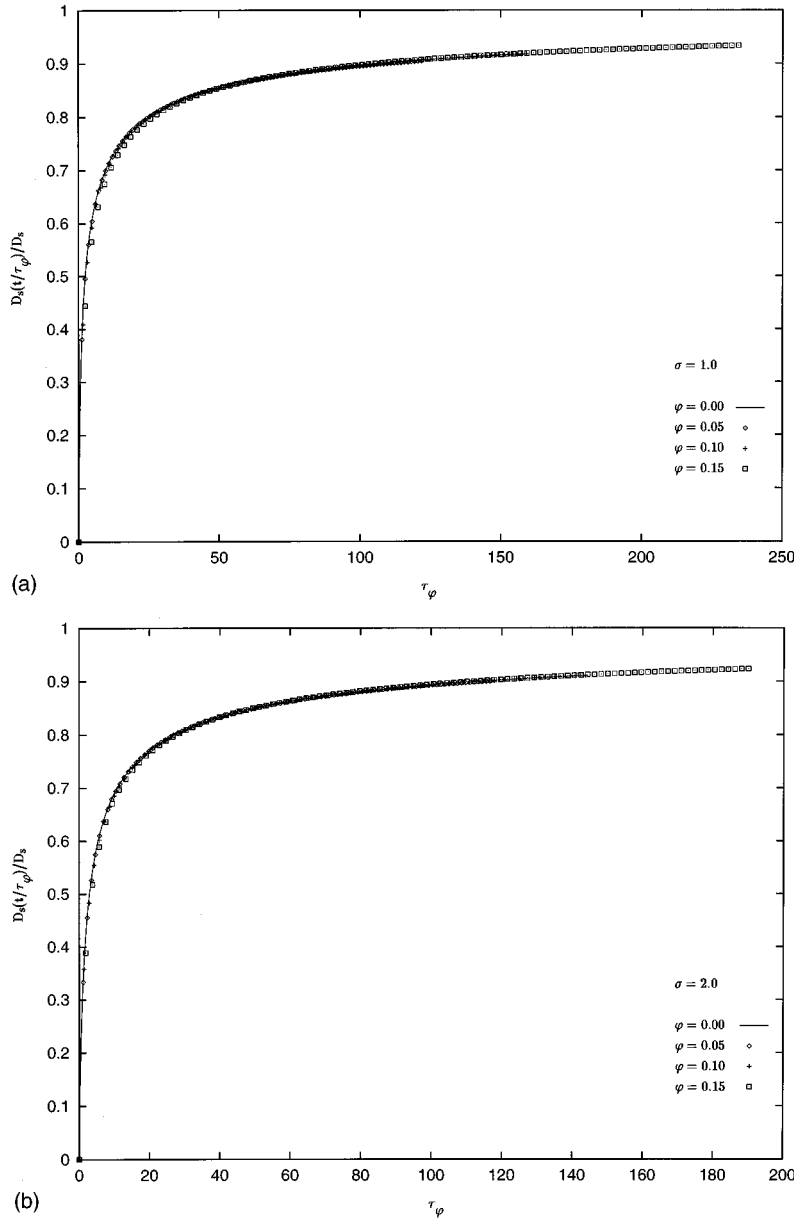
FIG. 4. (a) Scaling based on a best-fit procedure of the time-dependent self-diffusion coefficient divided by its asymptotic limit $D_s(t/\tau_\varphi)/D_s$ for $\sigma = 1$. The short-time self-diffusion coefficient is $D_s = D_0(1 - 1.83\varphi)$. The drawn line is the single-particle result. (b) Scaling based on a best-fit procedure of the time-dependent self-diffusion coefficient divided by its asymptotic limit $D_s(t/\tau_\varphi)/D_s$ for $\sigma = 2$. The short-time self-diffusion coefficient is $D_s = D_0(1 - 1.83\varphi)$. The drawn line is the single-particle result.

is not large. This slight discrepancy is possibly due to inaccuracies in the underlying calculations to obtain $\psi(\omega,\omega')$ [Eq. (8)] and in performing Fourier transforms that apparently require a higher resolution and accuracy. However, it should not be ruled out beforehand that some physical explanation exists for this observation.

On the other hand, a best-fit procedure, necessary because a small vertical shift was observed in calculating $D(t/\tau_\varphi)/D_s$ from Eq. (6), has been used to find an optimal rescaled time in order that the long-time part of the time-dependent diffusion coefficients for the different volume fractions collapse onto one curve. Scaling in the long-time limit is achieved by introducing a larger effective viscosity (or, equivalently, a smaller value for τ_φ) than in the case where we match the long-time tail of the VACF with the single-particle result. As a consequence, scaling for small times is not perfect but still satisfactory. In Figs. 4(a) and 4(b) we have plotted the time-dependent diffusion coefficient for this alternative scaling scenario for $\sigma = 1$ and 2, respectively. From these results it can be concluded that scaling is

present for small and intermediate volume fractions. For higher volume fractions ($\varphi \gtrsim 0.2$) the theoretical analysis of transient hydrodynamic interactions should be extended in order to include three- and probably many-particle interactions.

IV. CONCLUSION

Based on a calculation of retarded hydrodynamic interactions between pairs of particles, it has been shown that volume-fraction-dependent corrections to the single-particle correlation functions can be determined. An important result is the calculation of the volume-fraction-dependent modification of the long-time tail from a calculation based on the method expounded in Ref. [13]. The result is consistent with the expression obtained by Milner and Liu [12]. It has also been shown that it is possible to collapse the curves of the time-dependent diffusion coefficients onto the single-particle curve for volume fractions up to $\varphi = 0.15$. For higher volume fractions scaling is not perfect but still present (up to φ

=0.25). However, it might be expected that additional corrections to the correlation functions, due to three-particle hydrodynamic interactions, will improve scaling; for that reason a discussion of results for $\varphi \geq 0.2$ is postponed until three-particle contributions can be included. In this context it is worthwhile to mention that the apparent lack of scaling in the results of the time-dependent self-diffusion coefficient for $\varphi \geq 0.25$, which are shown in Ref. [13], is partly due to the assumption that corrections of $O(\varphi^2)$ would not be very important. This appears to be, however, an incorrect conclusion. For $\sigma = 1$ the present theoretical results support the experimental data and simulation results reported in recent years [2,5,7,9,11]. The results for other values of σ between 0 and 2 support the idea that scaling also exists for systems where the density of the particles is not the same as the fluid density. It is not clear if scaling remains important in the case of a high particle to fluid density mismatch ($\sigma \gg 1$). The higher σ, the more expensive (from a computational point of view) the calculations are to obtain the VACF and time-dependent diffusion coefficients. Finally, it is interesting to note that this full theoretical analysis, where sufficient multipoles are taken into account to obtain computationally converged values for the time-dependent diffusion coefficients

and VACFs (including long-time tails), disagrees with an analysis presented by Cichocki and Felderhof [29]. They claimed that the long-time tail of the VACF of a particle in a colloidal suspension should be independent of volume fraction. Our analysis strongly supports the conclusion from recent experiments and numerical simulations that in addition to the time-dependent diffusion coefficients also the long-time tails of the VACF of colloidal particles depend on the volume fraction. Furthermore, the present results are consistent with the analysis of the volume-fraction-dependent modification of the long-time tail of the VACF of colloidal particles reported by Milner and Liu [12].

An important conclusion of this work is that the theoretically obtained time-dependent diffusion coefficient shows already scaling for $0 \leq \sigma \leq 2$ when two-particle hydrodynamic interactions, in combination with the simplest pair distribution function for obtaining configurational averages, are included in the calculation of the VACF.

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