Velocity autocorrelation function of interacting Brownian particles

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We study the velocity correlation function of a selected particle in a suspension of interacting Brownian particles. Experimentally, the velocity correlation function can be observed with diffusing wave spectroscopy. The function has also been determined in computer simulation. We assume a wide separation of time scales between momentum relaxation and diffusive motion. The correlation function is found from linear hydrodynamics by use of the fluctuation-dissipation theorem. We propose a simple approximation based on the single particle result that is valid for a dilute suspension. The approximation is fully determined by the short-time self-diffusion coefficient and the effective mass of the selected particle. We discuss the concept of scaling within the framework of the approximation. We find that the amplitude of the $t^{-3/2}$ long-time tail is independent of the concentration of the suspension.

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I. INTRODUCTION

Recently it has become possible to measure the velocity correlation function of a Brownian particle on the fast time scale of momentum relaxation, by the method of diffusing wave spectroscopy [1–5]. The correlation function has also been studied in computer simulation, either via a fluctuating lattice Boltzmann equation [6], or by molecular dynamics simulation of a mixture [7]. The time scale under consideration is sufficiently short that retardation of hydrodynamic interactions due to fluid inertia must be taken into account.

In this paper, we analyze the velocity correlation function of a selected particle in a suspension of interacting Brownian particles on the basis of the fluctuation-dissipation theorem. It is assumed that the time scale of average momentum relaxation is sufficiently short, that diffusive motion may be neglected. As a consequence, it suffices to find the hydrodynamic admittance matrix at nonzero frequency for fixed configuration, and average this over the equilibrium distribution of particle configurations. The method of cluster expansion allows one to reduce the average to a sum of cluster integrals, each involving a hydrodynamic problem for a relatively small number of particles. For a semidilute suspension it suffices to solve the hydrodynamic two-sphere problem. However, even this is fairly complicated, and we do not attempt its complete solution here.

Rather, we conjecture that the Laplace transform of the velocity correlation function may be approximated by a simple expression based on its behavior at low and high frequency. The expression is characterized by two poles

in the square root of frequency plane. This generalizes the exact single particle result to higher density. We show that the parameters of the two-pole approximation may be calculated from the short-time self-diffusion coefficient, and the effective mass of the selected particle. The latter may be calculated from potential flow theory.

It has been proposed that the velocity autocorrelation function shows scaling behavior, and that the data for different systems may be collapsed onto a universal curve by suitable scaling of time [4–7]. Our analysis suggests that such scaling has only limited validity, at least for semidilute suspensions.

II. SINGLE PARTICLE BROWNIAN MOTION

In this section, we review well-known results for the velocity correlation function of a single Brownian particle. We consider the Brownian motion of a single spherical particle of radius a, mass m_p, immersed in an incompressible fluid of mass density ρ, shear viscosity η, at temperature T. The velocity correlation function of the Brownian particle is defined by

$$C(t) = \tfrac{1}{3} \langle \mathbf{U}_1(t) \cdot \mathbf{U}_1(0) \rangle , \tag{1}$$

where $\mathbf{U}_1$ is the translational velocity of the particle, the time evolution is governed by the Liouville equation of the whole system, and the angle brackets denote the equilibrium ensemble average. We attach the label 1, because later we shall discuss systems with many Brownian particles. We define the one-sided Fourier transform as

$$\hat{C}(\omega) = \int_0^\infty e^{i\omega t} C(t) dt . \tag{2}$$

According to the fluctuation-dissipation theorem [8–10] the Fourier transform is given by

$$\hat{C}(\omega) = k_B T \mathcal{Y}_t(\omega) , \tag{3}$$

where $\mathcal{Y}_t(\omega)$ is the translational admittance of the particle, defined from the linear response to a periodic applied

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force $\mathbf{E}_1(t) = \mathrm{Re}\mathbf{E}_{1\omega}\exp(-i\omega t)$,

$$\bar{\mathbf{U}}_{1\omega} = \mathcal{Y}_t(\omega)\mathbf{E}_{1\omega} .\tag{4}$$

The overhead bar is a reminder that we are considering the macroscopic linear response. On the macroscopic level the linear response may be calculated from the linearized Stokes equations for the fluid

$$\rho\frac{\partial\mathbf{v}}{\partial t} = \eta\nabla^2\mathbf{v} - \nabla p, \quad \nabla\cdot\mathbf{v} = 0 ,\tag{5}$$

where $\mathbf{v}(\mathbf{r},t)$ is the flow velocity, and $p(\mathbf{r},t)$ is the pressure, which follows from the condition of incompressibility. We shall assume stick boundary conditions at the particle surface. For small oscillations the boundary conditions may be applied at the undisplaced spherical surface. The equation of motion for the sphere is given by

$$m_p\frac{d\mathbf{U}_1}{dt} = \mathbf{K}_1 + \mathbf{E}_1 ,\tag{6}$$

where $\mathbf{K}_1$ is the force exerted by the fluid, which may be calculated from the fluid stress tensor. For periodic oscillations

$$-i\omega m_p\mathbf{U}_{1\omega} = \mathbf{K}_{1\omega} + \mathbf{E}_{1\omega} .\tag{7}$$

It was shown by Stokes [11] that the translational admittance is given by

$$\mathcal{Y}_t(\omega) = \frac{1}{-i\omega(m_p + \frac{1}{2}m_f) + \zeta_t(\omega)} ,\tag{8}$$

with $m_f = (4\pi/3)\rho a^3$ the fluid mass displaced by the sphere, and with friction coefficient

$$\zeta_t(\omega) = 6\pi\eta[1 + \alpha a] ,\tag{9}$$

where $\alpha = \sqrt{-i\omega\rho/\eta}$, $\mathrm{Re}\alpha > 0$. The added mass $\frac{1}{2}m_f$ is due to the inertia of the surrounding fluid. The frequency dependence of the friction coefficient is characterized by the viscous relaxation time $\tau_v = a^2\rho/\eta$. The square root branch cut in the frequency plane is taken along the negative imaginary axis. The square root singularity causes a long-time tail proportional to $t^{-3/2}$ in the velocity correlation function [12,13].

It follows from Eqs. (3) and (8) that the initial value of the correlation function is

$$C(0+) = \frac{k_B T}{m^*} ,\tag{10}$$

with the effective mass $m^* = m_p + \frac{1}{2}m_f$. From equipartition it follows that $C(0) = k_B T/m_p$. As explained by Zwanzig and Bixon [14], the difference is due to a rapid initial decrease of the correlation function on the time scale $\tau_s = a/s$, where s is the velocity of sound. Due to our assumption of fluid incompressibility the time scale τ_s is taken to be infinitesimal. The actual value of τ_s must be compared with the Brownian time scale $\tau_B = m_p/6\pi\eta a$. In practical situations τ_B and τ_v are of the same order of magnitude, and the time τ_s is much smaller.

We write the correlation function $C(t)$ in the form

$$C(t) = \frac{k_B T}{m^*}\gamma(t/\tau_M)\tag{11}$$

with a relaxation function $\gamma(\tau)$ that decays to zero starting from the initial value $\gamma(0+) = 1$, and with a mean relaxation time τ_M defined by

$$\tau_M = \frac{1}{C(0+)}\int_0^\infty C(t)dt .\tag{12}$$

From Eqs. (3), (8), and (10) we find

$$\tau_M = \frac{m^*}{6\pi\eta a} ,\tag{13}$$

so that $\tau_M = (m^*/m_p)\tau_B$. The Laplace transform of the relaxation function is defined as

$$\Gamma(z) = \int_0^\infty e^{-z\tau}\gamma(\tau)d\tau .\tag{14}$$

It is given by

$$\Gamma(z) = 6\pi\eta a\,\mathcal{Y}_t(\omega), \quad z = -i\omega\tau_M .\tag{15}$$

From Eqs. (8) and (9) we find the explicit expression

$$\Gamma(z) = \frac{1}{1 + \sigma\sqrt{z} + z} ,\tag{16}$$

with the parameter σ given by

$$\sigma = \left[\frac{9m_f}{2m^*}\right]^{1/2} .\tag{17}$$

It is evident that the function $\Gamma(z)$ has a square root branch cut along the negative real axis. The discontinuity of the imaginary part determines the spectral density $p(u)$ according to

$$p(u) = -\frac{1}{\pi}\mathrm{Im}\Gamma(z = -u + i0) .\tag{18}$$

The inverse Laplace transform shows that the relaxation function $\gamma(\tau)$ is given by a superposition of purely decaying exponentials

$$\gamma(\tau) = \int_0^\infty p(u)e^{-u\tau}du .\tag{19}$$

The spectral density has been normalized such that

$$\int_0^\infty p(u)du = 1, \quad \int_0^\infty \frac{p(u)}{u}du = 1 .\tag{20}$$

The function $\Gamma(z)$ has the Stieltjes representation

$$\Gamma(z) = \int_0^\infty \frac{p(u)}{u+z}du .\tag{21}$$

From Eqs. (16) and (18) one finds explicitly [15]

$$p(u) = \frac{1}{\pi}\frac{\sigma\sqrt{u}}{1 + (\sigma^2 - 2)u + u^2} .\tag{22}$$

This tends to a δ function at $u = 1$ for $\sigma \to 0$. The spectrum broadens as the parameter σ increases. The relaxation function is given explicitly by [16–19]

$$\gamma(\tau) = \frac{1}{\sqrt{\sigma^2 - 4}}[y_+w(-iy_+\sqrt{\tau}) - y_-w(-iy_-\sqrt{\tau})] ,\tag{23}$$

where $w(z)$ is related to the error function of complex argument [20]. The values $y_\pm$ correspond to the roots $z_\pm$ of the denominator in Eq. (16) as $y_\pm = \sqrt{z_\pm}$, and are given by

$$y_\pm = -\tfrac{1}{2}\sigma \pm \tfrac{1}{2}\sqrt{\sigma^2 - 4} \ . \tag{24}$$

The relaxation function has the long-time behavior

$$\gamma(\tau) \approx \frac{\sigma}{2\sqrt{\pi}} \tau^{-3/2} \quad \text{as } \tau \to \infty \ . \tag{25}$$

The corresponding long-time behavior of the velocity correlation function is

$$C(t) \approx \tfrac{1}{12} k_B T \sqrt{\rho} (\pi \eta t)^{-3/2} \quad \text{as } t \to \infty \ . \tag{26}$$

It is interesting to note that this is independent of the mass or size of the Brownian particle. A similar long-time tail was observed by Alder and Wainwright [21] in the velocity correlation function of a single molecule in a hard sphere fluid.

III. INTERACTING BROWNIAN PARTICLES

In nondilute colloidal suspensions one can observe the effects of interaction between Brownian particles. There are direct interactions, e.g., of van der Waals type, and hydrodynamic interactions caused by the flow of solvent fluid. In diffusing wave spectroscopy one observes the Brownian motion of individual particles, as modified by the interactions. The relevant time scale in such experiments is of the order of the Brownian relaxation time τ_B. Typically the experiments cover the range $0.1\tau_B - 1000\tau_B$. We must study the velocity correlation function of a selected particle, labeled 1, as defined in Eq. (1).

More generally we consider the Brownian motion of the whole set of N particles enclosed in the volume V. The configuration at any time, as specified by the positions of the particle centers, is denoted as $\mathbf{X} = (\mathbf{R}_1, \ldots, \mathbf{R}_N)$. Besides the translational velocities $\mathbf{U} = (\mathbf{U}_1, \ldots, \mathbf{U}_N)$, we must also consider the rotational velocities $(\boldsymbol{\Omega}_1, \ldots, \boldsymbol{\Omega}_N)$. The dynamics of the system of Brownian particles is characterized by the $6N \times 6N$ correlation matrix

$$\mathbf{C}(t) = \begin{bmatrix} \mathbf{C}_{UU}(t) & \mathbf{C}_{U\Omega}(t) \\ \mathbf{C}_{\Omega U}(t) & \mathbf{C}_{\Omega\Omega}(t) \end{bmatrix} . \tag{27}$$

The one-sided Fourier transform of the correlation matrix, defined as in Eq. (2), will be related to the admittance matrix in analogy to Eq. (3). The admittance matrix of the system $\mathbf{Y}(\mathbf{X},\omega)$ is defined for each configuration $\mathbf{X}$ from the linear response to periodic applied forces $\mathbf{E}_\omega = (\mathbf{E}_{1\omega}, \ldots, \mathbf{E}_{N\omega})$ and torques $\mathbf{N}_\omega = (\mathbf{N}_{1\omega}, \ldots, \mathbf{N}_{N\omega})$,

$$\begin{bmatrix} \overline{\mathbf{U}}_\omega \\ \overline{\boldsymbol{\Omega}}_\omega \end{bmatrix} = \begin{bmatrix} \mathbf{Y}_{UU}(\mathbf{X},\omega) & \mathbf{Y}_{U\Omega}(\mathbf{X},\omega) \\ \mathbf{Y}_{\Omega U}(\mathbf{X},\omega) & \mathbf{Y}_{\Omega\Omega}(\mathbf{X},\omega) \end{bmatrix} \begin{bmatrix} \mathbf{E}_\omega \\ \mathbf{N}_\omega \end{bmatrix} . \tag{28}$$

Again the overhead bar indicates that we are considering the macroscopic linear response. The admittance matrix $\mathbf{Y}(\mathbf{X},\omega)$ may in principle be calculated from the linearized Stokes equations Eq. (5).

For a typical system of Brownian particles the Brownian relaxation time τ_B is much smaller than the diffusion time $\tau_0 = a^2/D_0$, where $D_0 = k_B T/6\pi\eta a$ is the bare diffusion coefficient of a single sphere. This implies that the mean square displacement of a sphere after a time τ_B is much smaller than the radius squared of the sphere. Hence the correlation matrix for the subensemble with fixed configuration $\mathbf{X}$ may be related to the admittance matrix $\mathbf{Y}(\mathbf{X},\omega)$ by

$$\hat{\mathbf{C}}(\mathbf{X},\omega) = k_B T \mathbf{Y}(\mathbf{X},\omega) \ , \tag{29}$$

in analogy to Eq. (3). The desired correlation matrix $\hat{\mathbf{C}}(\omega)$ is given by the average over the equilibrium distribution $P_{\text{eq}}(\mathbf{X})$ of configurations $\mathbf{X}$,

$$\hat{\mathbf{C}}(\omega) = k_B T \int \mathbf{Y}(\mathbf{X},\omega) P_{\text{eq}}(\mathbf{X}) d\mathbf{X}$$
$$= k_B T \langle \mathbf{Y}(\mathbf{X},\omega) \rangle_X \ . \tag{30}$$

Finally, we take the thermodynamic limit $N \to \infty$, $V \to \infty$ at constant density $n = N/V$. The velocity correlation function of the selected particle, labeled 1, is given by

$$\hat{C}(\omega) = k_B T \mathcal{Y}_t^*(\omega) \ , \tag{31}$$

with the effective admittance $\mathcal{Y}_t^*(\omega)$ defined by

$$\mathcal{Y}_t^*(\omega) = \lim_{\substack{N \to \infty \\ V \to \infty}} \tfrac{1}{3} \text{tr} \langle \mathbf{Y}_{U_1 U_1}(\mathbf{X},\omega) \rangle_X \ . \tag{32}$$

We repeat that the conditions for the validity of Eq. (30) are the inequalities $\tau_s \ll \tau_B \approx \tau_v \ll \tau_0$. The fluctuation-dissipation theorem in the form Eq. (29) has been derived from fluctuating hydrodynamics by Hauge and Martin-Löf [22], by Bedeaux and Mazur [23], and by Hinch [19].

IV. EFFECTIVE ADMITTANCE

In this section, we study the effective admittance $\mathcal{Y}_t^*(\omega)$, defined in Eq. (32). The average may be evaluated by the technique of cluster expansion. This allows one to express the effective admittance in terms of the solution of a set of hydrodynamic problems, each involving a relatively small number of particles. The expression in Eq. (32) is transformed to

$$\mathcal{Y}_t^*(\omega) = \frac{1}{n} \sum_{s=1}^{\infty} \frac{1}{(s-1)!} \int d2 \cdots ds \, n(1, \ldots, s)$$
$$\times M(1; 2, \ldots, s, \omega) \ , \tag{33}$$

where $n(1, \ldots, s)$ is the s-particle equilibrium distribution function, as calculated in the thermodynamic limit, and the function $M(1; 2, \ldots, s, \omega)$ is related to the s-particle admittance matrix $\mathbf{Y}(1, \ldots, s; \omega)$ by a rooted cluster expansion [24]. The s-particle admittance matrix is to be calculated for infinite volume. The first few terms of the rooted cluster expansion read

$$M(1) = \tfrac{1}{3} \text{tr} \mathbf{Y}_{U_1 U_1}(1; \omega) = \mathcal{Y}_t(\omega) \ ,$$

$$M(1; 2) = \tfrac{1}{3} \text{tr} \mathbf{Y}_{U_1 U_1}(1, 2; \omega) - M(1) \ ,$$

$$M(1; 2, 3) = \tfrac{1}{3} \text{tr} \mathbf{Y}_{U_1 U_1}(1, 2, 3; \omega) - M(1; 2)$$
$$- M(1; 3) + M(1) \ . \tag{34}$$

Successive terms in Eq. (33) describe many-body hydrodynamic effects of increasing complexity. The term of order s involves at least the power n^{s-1} in density. If we limit attention to at most the two-body term, we approximate Eq. (33) by

$$\mathcal{Y}_t^*(\omega) \approx \mathcal{Y}_t(\omega) + n \int g(R) M(1;\mathbf{R},\omega)|_{\mathbf{R}_1=0} d\mathbf{R} , \qquad (35)$$

where $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$ is the relative distance vector of the pair (1,2), and $g(R)$ is the radial distribution function. Particle 1 may be taken to be centered at the origin. To first order in density the effective admittance is

$$\mathcal{Y}_t^*(\omega) = \mathcal{Y}_t(\omega) + n \int \exp[-\beta v(R)] M(1;\mathbf{R},\omega)|_{\mathbf{R}_1=0} d\mathbf{R}$$
$$+ O(n^2) , \qquad (36)$$

where $v(R)$ is the effective direct interaction between two Brownian particles.

Explicit calculations based on Eq. (35) or (36) would require a complete solution of the hydrodynamic two-body problem at frequency ω. A first attempt was made by Clercx and Schram [25]. However, their solution of the hydrodynamic problem involves only multipoles of low order. We show in the appendix that their solution leads to unphysical behavior of the velocity correlation function in some cases. A complete solution can be obtained on the basis of the solution of the two-sphere problem at zero frequency of Cichocki, Felderhof, and Schmitz [26], in combination with the linear response formulation of Ref. [27] and the addition theorem quoted by Felderhof and Jones [28]. However, this solution is technically demanding, and we shall not embark on it here. Rather, we shall construct an approximate expression for the velocity correlation function, based on exact results at low and high frequency.

V. TWO-POLE APPROXIMATION

The analytic behavior of the trace of the admittance tensor $\text{tr} Y_{U_1 U_1}(\mathbf{X},\omega)$ as a function of frequency, and consequently that of the effective admittance $\mathcal{Y}_t^*(\omega)$, is strongly limited by an exact theorem that shows that both functions may be represented as Stieltjes integrals with a positive spectral density on the negative imaginary ω axis. We prove the theorem in the appendix. It follows from the theorem that the velocity correlation function is a completely monotone function [29]. A good approximation may be found on the basis of an approximation to the spectral density. The effective admittance is studied conveniently by transformation to the square root of frequency plane [30]. A useful approximation is obtained if a small, but sufficient number of poles nearest the origin are taken into account. We conjecture that in the present problem two poles are sufficient, at least for low density.

The approximate analytic expression for the effective admittance takes a form analogous to Eqs. (8) and (9) for a single particle. Explicitly we write

$$\mathcal{Y}_t^*(\omega) \approx \frac{\mu_S^{tt}(\phi)}{1 + \sigma(\phi)\sqrt{z} + z} , \qquad (37)$$

where $\mu_S^{tt}(\phi)$ is the zero-frequency self-mobility of a single

sphere at volume fraction $\phi = (4\pi/3)na^3$, as found from low Reynolds number hydrodynamics. The coefficient $\sigma(\phi)$ is a generalization of the parameter σ in Eq. (16). It is defined from the exact low-frequency expansion of the effective admittance

$$\mathcal{Y}_t^*(\omega) = \mu_S^{tt}(\phi)[1 - \sigma(\phi)\sqrt{z} + O(z)] , \qquad (38)$$

where the variable z is defined by

$$z = -i\omega\tau_M(\phi) , \qquad (39)$$

with the density-dependent mean relaxation time $\tau_M(\phi)$. The latter is defined from the exact velocity correlation function as in Eq. (12). This requires determination of the effective mass $m^*(\phi)$ from the high-frequency behavior

$$\mathcal{Y}_t^*(\omega) \approx \frac{1}{-i\omega m^*(\phi)} \quad \text{as} \quad \omega \to \infty . \qquad (40)$$

The mean relaxation time is given by

$$\tau_M(\phi) = m^*(\phi)\mu_S^{tt}(\phi) , \qquad (41)$$

in analogy to Eq. (13). Thus determination of the two-pole approximation Eq. (37) requires calculation of the three transport coefficients $\mu_S^{tt}(\phi)$, $\sigma(\phi)$, and $m^*(\phi)$. We expect that Eq. (37) provides an accurate approximation to the exact function, at least for low density.

The mobility $\mu_S^{tt}(\phi)$ is known exactly at low density from the solution of the two-body Stokes problem [31,32]. For a system of hard spheres it is given to first order in volume fraction by

$$\mu_S^{tt}(\phi) = \frac{1}{6\pi\eta a}[1 - 1.8315\phi + O(\phi^2)] . \qquad (42)$$

In earlier work we have derived an approximate value for high density [33]. For systems with different direct interactions the corresponding equilibrium distribution function must be used [34]. Alternatively, the mobility may be found from the experimental value for the short-time self-diffusion coefficient $D_S^S(\phi)$ by use of the Einstein relation $D_S^S(\phi) = k_B T \mu_S^{tt}(\phi)$. The self-diffusion coefficient for short times, in the usual sense of Brownian motion theory based on the Smoluchowski equation [31,32], is relevant here, since on the time scale τ_B we neglect the change of configuration.

Milner and Liu have attempted to calculate the parameter $\sigma(\phi)$ to first order in volume fraction [35]. Unfortunately, their analysis is incorrect. Their result is in conflict with an exact relation. It may be shown that for any number of spheres the low-frequency expansion of the translational admittance tensor is given by

$$Y_{U_1 U_1}(\mathbf{X};\omega) = \mu_{11}^{tt}(\mathbf{X}) - \frac{1}{6\pi\eta}\left[\frac{-i\omega\rho}{\eta}\right]^{1/2} 1 + O(\omega) , \qquad (43)$$

where $\mu_{11}^{tt}(\mathbf{X})$ is the zero-frequency mobility tensor for configuration $\mathbf{X}$. The $\sqrt{\omega}$ term shows that the long-time tail in the velocity is independent of the presence of the other spheres. The proof of this simple relation is somewhat elaborate, and is presented elsewhere [36]. As a

consequence of Eq. (43) the parameter $\sigma(\phi)$ is given exactly by

$$\sigma(\phi) = \frac{1}{6\pi} \left[\frac{\rho}{m^*(\phi)} \right]^{1/2} [\eta \mu_S''(\phi)]^{-3/2} \ . \tag{44}$$

It remains to determine the effective mass $m^*(\phi)$. This follows from the response to an applied force on particle 1 at high frequency. In the low density limit it is given by $m^* = m_p + \frac{1}{2} m_f$. At higher density the effective mass is modified by instantaneous hydrodynamic interactions. If a δ-function force $\mathbf{E}_1(t) = \mathbf{S}\delta(t)$ is applied to a single sphere in infinite incompressible fluid, then instantaneously the potential flow pattern

$$\mathbf{v}(r,0+) = \frac{1}{2} \frac{a^3}{m^*} \frac{-1+3\hat{\mathbf{r}}\hat{\mathbf{r}}}{r^3} \cdot \mathbf{S}, \quad r > a \ , \tag{45}$$

is established [37]. Subsequently the flow pattern changes and decays due to viscous dissipation. The relation (45) shows that for many spheres there are instantaneous hydrodynamic interactions, which may be calculated from potential flow theory [38]. The theory of high-frequency response of a suspension is closely related to the theory of the dielectric constant of a system of electrically polarizable particles [37]. In the present case we need to calculate the self-mass, rather than the collective effective mass of the suspension. The latter is relevant for collective particle motion. The technique for calculating the effective self-mass $m^*(\phi)$ is well known. Numerical results for a dense suspension of hard spheres will be presented elsewhere. We write

$$m^*(\phi) = m^* + \delta m^*(\phi) \ , \tag{46}$$

where $m^* = m_p + \frac{1}{2} m_f$ is the single particle term, and $\delta m^*(\phi)$ is the correction due to hydrodynamic interactions.

Here we consider the effective self-mass for a semidilute suspension. Then the correction $\delta m^*(\phi)$ may be calculated analytically, apart from a simple quadrature. It suffices to consider the potential flow problem for a pair of spheres. To first order in volume fraction we write

$$\delta m^*(\phi) = k_m \phi + O(\phi^2) \ , \tag{47}$$

with a coefficient k_m which depends on the ratio m_f/m_p. The coefficient may be calculated by the method explained in Refs. [37] and [39]. It is convenient to write it as a sum of dipole and higher order multipole contributions,

$$k_m = k_m^D + k_m^M \ . \tag{48}$$

Both contributions are given by an integral over the low density radial distribution function $g_0(R) = \exp[-\beta v(R)]$. The integrand of the dipolar term may be evaluated analytically. The coefficient k_m^D is given by

$$k_m^D = - \frac{m_f}{m_f + 2m_p} \int_2^\infty \left[\frac{2\hat{\beta}}{x^6 - 4\hat{\beta}^2} + \frac{\hat{\beta}}{x^6 - \hat{\beta}^2} \right]$$

$$\times g_0(xa)x^2 dx \ , \tag{49}$$

where

$$\hat{\beta} = \frac{m_f - m_p}{m_f + 2m_p} \ , \tag{50}$$

and where we have used the dimensionless variable $x = R/a$. The integrand for the coefficient k_m^M is more complicated. In Table I we list the values of the coefficients k_m^D, k_m^M, and k_m, for several ratios m_f/m_p, as calculated for a system of hard spheres, i.e., with $g_0(R) = \theta(R - 2a)$. It is worth noting that multipolar effects are quite important, and that the coefficient k_m can take positive as well as negative values. The numerical value of the coefficient is quite small.

VI. SCALING

Several authors have observed scaling behavior of the velocity correlation function [4,5], in the sense that the data for different concentrations are collapsed onto a single master curve by suitable scaling of time. The scaling has also been studied in computer simulations [6,7]. We argue here that the scaling concept has only limited validity.

First, we note that the proper time scale for scaling, if applicable, is provided by the mean relaxation time $\tau_M(\phi)$, as defined in Eq. (12), generalized to volume fraction ϕ. Second, we remark that the exact result Eq. (43), together with Eq. (31), shows that the long-time behavior of the velocity correlation function is given by Eq. (26) for any concentration, provided the conditions for the validity of Eq. (31) are satisfied. This surprising result shows that the long-time behavior is independent not only of mass and size of the spheres, but of concentration as well. It also implies that the scaling cannot be com-

TABLE I. Values of the coefficients k_m^D, k_m^M, and k_m, defined in Eqs. (48) and (49), for different values of the mass ratio $r_m = m_f/m_p$. The dipole contribution k_m^D is calculated from the explicit expression Eq. (49) with the radial distribution function for hard spheres $g_0(R) = \theta(R - 2a)$. The multipole contribution k_m^M is calculated numerically from a truncated system of equations. The largest multipole order used to achieve the quoted accuracy is $l_{max} = 12$ for $r_m \leq 1.8$, $l_{max} = 13$ for $2 \leq r_m \leq 10$, and $l_{max} = 14$ for $r_{max} = 100$.

m_f/m_p	k_m^D	k_m^M	k_m
0.1	0.0077	0.0068	0.0145
0.2	0.0124	0.0130	0.0254
0.4	0.0156	0.0240	0.0397
0.6	0.0133	0.0335	0.0469
0.8	0.0077	0.0418	0.0495
1.0	0	0.0491	0.0491
1.2	−0.0088	0.0566	0.0468
1.4	−0.0182	0.0614	0.0433
1.6	−0.0278	0.0667	0.0389
1.8	−0.0374	0.0714	0.0340
2	−0.0469	0.0758	0.0289
4	−0.1255	0.1047	−0.0209
6	−0.1769	0.1202	−0.0567
8	−0.2116	0.1299	−0.0817
10	−0.2365	0.1366	−0.0999
100	−0.3623	0.1681	−0.1942

plete, since it does not apply to the long-time tail. It is quite possible that the range of time over which the long-time tail provides a good approximation to the actual correlation function varies with concentration.

The discussion in preceding sections shows that the initial value of the velocity correlation function must be scaled with the effective mass according to

$$C(0+) = \frac{k_B T}{m^*(\phi)} \ . \tag{51}$$

The numerical values presented in Table I show that the dependence on volume fraction is weak, at least for small ϕ.

If the two-pole approximation discussed in Sec. V is valid, then the relaxation function takes the form Eq. (23) with the value $\sigma(\phi)$ given in Eq. (44), and with the mean relaxation time $\tau_M(\phi)$ given by Eq. (41). Thus we predict that the relaxation function scales approximately with the time scale $\tau_M(\phi)$, but with a shape parameter $\sigma(\phi)$ that depends on volume fraction, predominantly via the mobility $\mu_S^{tt}(\phi)$. Accordingly, we expect broadening of the relaxation spectrum $p(u)$ with increasing volume fraction.

It would be of interest to analyze experimental data, as well as computer simulation data, on the basis of the two-pole approximation. We have shown elsewhere [40] that N-point Padé approximants provide a convenient tool. More generally the Laplace transform of the relaxation function is approximated by a ratio of two polynomials in $\sqrt{z}$. The zeros of the denominator determine the poles, and their relative importance is determined by the residues. The exact single particle result Eq. (16) suggests that at least at low volume fraction the two-pole approximation should be adequate. At higher volume fraction a third pole may be necessary to describe the data. The exact solution of the hydrodynamic two-sphere problem at finite frequency ω would allow one to check the validity of the two-pole approximation for semidilute suspensions.

At very long times the time-dependence of the mean square displacement, as found by computer simulation of a system of diffusing hard spheres, is well described by a two-pole approximation [41]. This shows that the description of the exact velocity correlation function requires at least a four-pole approximation. This becomes relevant when the Brownian time scale τ_B and the diffusion time scale τ_0 are not well separated.

VII. CONCLUSIONS

We have discussed the velocity correlation function of a selected particle in a suspension of interacting Brownian particles. On the assumption that the time scale of average momentum relaxation is much shorter than the time scale of diffusive motion, we have derived an expression for the velocity correlation function on the basis of the fluctuation-dissipation theorem. The expression is valid at any density.

The result Eq. (43) for the low-frequency behavior suggests that scaling of the correlation function with just the mean relaxation time has limited validity. The shape parameter $\sigma(\phi)$, which determines the width of the relaxa-

tion spectrum and hence the shape of the correlation function, depends on volume fraction and particle mass. It would be of interest to investigate the variation of shape in experiment or computer simulation.

A generalization of the single particle expression for the Laplace transform of the velocity autocorrelation function leads to a two-pole approximation. The parameters of the approximation may be found from the short-time diffusion coefficient and the effective mass of the Brownian particle. We expect the two-pole approximation to be valid at least for low density. It may be that at higher density the higher order terms in Eq. (43) will become important. That would imply that an approximation involving at least three poles would be required.

APPENDIX

In this appendix we prove that the trace of the admittance tensor $\mathrm{tr}Y_{U_1 U_1}(\mathbf{X}, \omega)$ has a Stieltjes representation as a function of frequency, with positive spectral density on the negative imaginary ω axis. We consider the linearized Navier-Stokes equations for the fluid, as given by Eq. (5), together with the equations of motion for the particles

$$m_{pj} \frac{d\mathbf{U}_j}{dt} = \mathbf{K}_j + \mathbf{E}_j \ ,$$

$$I_{pj} \frac{d\mathbf{\Omega}_j}{dt} = \mathbf{T}_j + \mathbf{N}_j, \quad j = 1, \ldots, N \ , \tag{A1}$$

where $\mathbf{K}_j$ and $\mathbf{T}_j$ are the force and torque exerted by the fluid on particle j. Furthermore, $\mathbf{E}_j$ and $\mathbf{N}_j$ are the externally applied force and torque, m_{pj} is the mass of particle j, and I_{pj} is its moment of inertia.

We consider a small perturbation from the situation in which particles and fluid are at rest. If the applied forces and torques are small, then the force $\mathbf{K}_j$ and the torque $\mathbf{T}_j$ may be calculated from the fluid stress tensor at the undisplaced particle surface. In this limit the whole problem is linear and may be summarized as [19]

$$\mathcal{M} \cdot \frac{\partial \mathbf{V}}{\partial t} = -\mathcal{H} \cdot \mathbf{V} + \mathbf{E} \ , \tag{A2}$$

where the generalized vector $\mathbf{V} = [\mathbf{v}(\mathbf{r}), \{\mathbf{U}_j\}, \{\mathbf{\Omega}_j\}]$ comprises the solenoidal flow field $\mathbf{v}(\mathbf{r})$ and the particle translational and rotational velocities, and the generalized force is given by $\mathbf{E} = [0, \{\mathbf{E}_j\}, \{\mathbf{N}_j\}]$. The mass operator $\mathcal{M}$ is diagonal with elements $[\rho\delta(\mathbf{r} - \mathbf{r}'), \{m_{pj}\}, \{I_{pj}\}]$, and the force operator $\mathcal{H}$ represents the momentum transfer, as given by the Stokes equation and integrals of the fluid stress tensor. The equations (A2), together with the boundary conditions, determine the time evolution of the system. The configuration $\mathbf{X} = (\mathbf{R}_1, \ldots, \mathbf{R}_N)$ appears parametrically, and may be regarded as fixed. The trace of the translational admittance tensor for particle 1 may be expressed as

$$\mathrm{tr}Y_{U_1 U_1}(\mathbf{X},\omega)= \sum_{\alpha} \left[e_{U_{1\alpha}} \left| \frac{1}{-i\omega\mathcal{M}+\mathcal{H}} \right| e_{U_{1\alpha}} \right] \qquad (A3)$$

in obvious notation.

We introduce the scalar product between two generalized vectors $\mathbf{V}$ and $\mathbf{V}'$ as

$$(\mathbf{V}|\mathbf{V}')= \int \mathbf{v}(\mathbf{r})\cdot\mathbf{v}'(\mathbf{r})d\mathbf{r}+ \sum_{j=1}^{N} [\mathbf{U}_j\cdot\mathbf{U}_j'+\mathbf{\Omega}_j\cdot\mathbf{\Omega}_j'] \ . \qquad (A4)$$

The mass operator $\mathcal{M}$ is clearly real, symmetric, and positive definite in this scalar product. It is easily shown that for stick boundary conditions the matrix element of the force operator $\mathcal{H}$ for the vectors $\mathbf{V}$ and $\mathbf{V}'$ is given by

$$(\mathbf{V}|\mathcal{H}\mathbf{V}')=\eta \int \sum_{\alpha\beta} \frac{\partial v_\alpha}{\partial x_\beta} \frac{\partial v_\alpha'}{\partial x_\beta} d\mathbf{r} \ . \qquad (A5)$$

It follows that the operator $\mathcal{H}$ is also real, symmetric, and

positive definite. Hence the formal structure of Eq. (A2) is that encountered in the theory of small oscillations in classical mechanics [42], with the difference that the time differentiation is of first, rather than second, order. By expansion in terms of eigenfunctions one shows that the trace in Eq. (A3) has the Stieltjes representation

$$\mathrm{tr}Y_{U_1 U_1}(\mathbf{X},\omega)= \int_0^{\infty} \frac{w(\mathbf{X},\lambda)}{\lambda-i\omega}d\lambda \qquad (A6)$$

with positive weight function $w(\mathbf{X},\lambda)$. After averaging over configurations $\mathbf{X}$ we find the same type of representation for the effective admittance $\mathcal{Y}_t^*(\omega)$.

From the Stieltjes representation of the effective admittance it follows that the velocity correlation function is a completely monotone decreasing function of time [29]. The time-dependent diffusion coefficient shown in Fig. 3 of Ref. [25] clearly is in conflict with this property. The violation of the general rule must be due to approximations made by the authors.

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