Long-time tails in the solid-body motion of a sphere immersed in a suspension

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Long-time tails in the translational and rotational motion of a sphere immersed in a suspension of spherical particles are discussed on the basis of the linear, time-dependent Stokes equations of hydrodynamics. It is argued that the coefficient of the $t^{-3/2}$ long-time tail of translational motion depends only on the effective mass density and shear viscosity of the suspension. A similar expression holds for the coefficient of the $t^{-5/2}$ long-time tail of rotational motion. In particular, the long-time tails are independent of the sphere radius, and therefore the expressions hold also for a particle of the suspension. On account of the fluctuation-dissipation theorem the long-time tails of the velocity autocorrelation function and the angular velocity autocorrelation function of interacting Brownian particles are also given by these expressions.

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I. INTRODUCTION

The coefficient of the $t^{-3/2}$ long-time tail of the velocity autocorrelation function of a single Brownian particle immersed in a fluid depends only on the temperature, shear viscosity, and mass density of the fluid. It is independent of the mass of the Brownian particle, its size, and the nature of the hydrodynamic boundary condition coupling it to the fluid motion. A similar simple expression holds for the coefficient of the $t^{-5/2}$ long-time tail of the angular velocity autocorrelation function. The coefficients follow by use of the fluctuation-dissipation theorem from expressions for the frequency-dependent translational and rotational mobilities derived in linear hydrodynamics, as shown by Zwanzig and Bixon [1] and others [2–5]. A similar long-time tail of the velocity autocorrelation function of a molecule was found by Alder and Wainwright [6] in a computer simulation of a hard-sphere fluid.

It was conjectured by Milner and Liu [7] that for a suspension of interacting Brownian particles the coefficient of the long-time tail of the velocity autocorrelation function differs from that for the pure solvent only in the replacement of the solvent mass density and shear viscosity by the suspension mass density and shear viscosity. The conjecture was based on arguments proposed by Alder and Wainwright [6] for the hard-sphere fluid, as well as on a calculation of the long-time coefficient to first order in volume fraction. The calculation requires analysis of the frequency-dependent mobility of two spheres in retarded hydrodynamic interaction.

Recently, Hagen, Frenkel, and Lowe [8] extended the conjecture of Milner and Liu to the angular velocity autocorrelation function. They used the same effective fluid picture in which it suffices to replace the solvent viscosity and mass density occurring in the coefficient of the long-time tail by the suspension viscosity and mass density. Their computer simulation data support the conjecture. Recently, we have analyzed some of the data by the method of Padé approximants applied to the Laplace transform of the autocorrelation function [9,10].

Some time ago we derived a theorem in linear hydrodynamics [11] which shows that a finite number of spheres, set in motion in a viscous fluid, eventually move with the same velocity. The coefficient of the long-time tail of the velocity of any of the spheres takes the same universal value as for a single sphere. We argued on the basis of the cluster expansion of the average hydrodynamic admittance in a suspension that therefore the velocity autocorrelation function of interacting Brownian particles has the same universal long-time tail as that for a single Brownian particle [12]. In the following we conclude that our argument was wrong, and that the conjecture of Milner and Liu [7] is correct.

We base our conclusion on a detailed analysis of the Green function of linear hydrodynamics and its relation to the motion of a single sphere immersed in an unbounded solvent. The hydrodynamic analysis shows that in the last stage of motion the solid-body motion of a suspended sphere becomes equal to the flow velocity of the surrounding fluid, which varies on a length scale much larger than the sphere diameter. In this last stage of motion the exchange of momentum and angular momentum is negligible. The argument can be extended to a suspension. Since the spatial variation of the final flow is on the macroscopic length scale, macroscopic average equations can be used in the calculation.

II. GREEN FUNCTION

We consider first an incompressible fluid of mass density ρ and shear viscosity η in infinite space without any suspended particles. The fluid is assumed to be at rest in the absence of applied forces. If a time-dependent force density $\mathbf{F}_0(\mathbf{r},t)$ of small amplitude is applied to the fluid, then a flow velocity $\mathbf{v}(\mathbf{r},t)$ and a pressure $p(\mathbf{r},t)$ are generated. We assume that these satisfy the linearized Navier-Stokes equations

$$\rho \frac{\partial \mathbf{v}}{\partial t} = \eta \nabla^2 \mathbf{v} - \nabla p + \mathbf{F}_0, \quad \nabla \cdot \mathbf{v} = 0. \tag{2.1}$$

After a Fourier analysis in time we find that the equations for the Fourier components with time factor $\exp(-i\omega t)$ are

$$-i\omega\rho\mathbf{v}_\omega=\eta\nabla^2\mathbf{v}_\omega-\nabla p_\omega+\mathbf{F}_{0\omega},\quad \nabla\cdot\mathbf{v}_\omega=0. \tag{2.2}$$

The solution in integral form is given by

$$\mathbf{v}_\omega(\mathbf{r})=\frac{1}{4\pi\eta}\int \mathsf{T}_\alpha(\mathbf{r}-\mathbf{r}')\cdot\mathbf{F}_{0\omega}(\mathbf{r}')d\mathbf{r}',$$

$$p_\omega(\mathbf{r})=\frac{1}{4\pi}\int \mathbf{Q}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{F}_{0\omega}(\mathbf{r}')d\mathbf{r}', \tag{2.3}$$

with propagators [13]

$$\mathsf{T}_\alpha(\mathbf{r})=\mathbf{1}G_\alpha(r)+\alpha^{-2}\nabla\nabla[G_0(r)-G_\alpha(r)],$$

$$G_\alpha(r)=\exp(-\alpha r)/r,\quad \mathbf{Q}(\mathbf{r})=\hat{\mathbf{r}}/r^2. \tag{2.4}$$

We have used the abbreviation

$$\alpha=(-i\omega\rho/\eta)^{1/2},\quad \mathrm{Re}\,\alpha>0. \tag{2.5}$$

We consider in particular a force density

$$\mathbf{F}_0(\mathbf{r},t)=\mathbf{P}\delta(\mathbf{r})\delta(t) \tag{2.6}$$

corresponding to a sudden impulse applied at the origin. Inverting the Fourier transform one finds that the generated flow velocity for $t>0$ is given by

$$\mathbf{v}(\mathbf{r},t)=\frac{1}{4\pi\eta}\mathsf{T}(\mathbf{r},\mathbf{t})\cdot\mathbf{P}, \tag{2.7}$$

with the tensor

$$\mathsf{T}(\mathbf{r},t)=\mathbf{1}\frac{1}{\sqrt{4\pi\nu t}^{3/2}}\exp\left(-\frac{r^2}{4\nu t}\right)+\nu\nabla\nabla\frac{\mathrm{erf}(r/\sqrt{4\nu t})}{r}, \tag{2.8}$$

where $\nu=\eta/\rho$ is the kinematic viscosity. More explicitly,

$$\mathsf{T}(\mathbf{r},t)=\frac{\exp(-r^2/4\nu t)}{\sqrt{4\pi\nu t}^{3/2}}\left[\left(1+2\frac{\nu t}{r^2}\right)\mathbf{1}-\left(1+6\frac{\nu t}{r^2}\right)\hat{\mathbf{r}}\hat{\mathbf{r}}\right]$$
$$+\nu\frac{-\mathbf{1}+3\hat{\mathbf{r}}\hat{\mathbf{r}}}{r^3}\mathrm{erf}\left(\frac{r}{\sqrt{4\nu t}}\right). \tag{2.9}$$

The relation to the tensor in Eq. (2.4) is

$$\mathsf{T}_\alpha(\mathbf{r})=\int_0^\infty e^{i\omega t}\mathsf{T}(\mathbf{r},t)dt. \tag{2.10}$$

A different derivation of the fundamental solution Eq. (2.9) was presented by Oseen [14].

The pressure generated by the impulse is

$$p(\mathbf{r},t)=\frac{1}{4\pi}\frac{\hat{\mathbf{r}}\cdot\mathbf{P}}{r^2}\delta(t). \tag{2.11}$$

The long-range pressure field is established instantaneously, because the fluid is incompressible. This corresponds to an infinite velocity of sound. There is a corresponding long-range dipolar flow field, as is evident from the limit $t\to 0+$ in Eq. (2.9),

$$\mathsf{T}(\mathbf{r},0+)=4\pi\nu\mathbf{1}\delta(\mathbf{r})+\nu\frac{-\mathbf{1}+3\hat{\mathbf{r}}\hat{\mathbf{r}}}{r^3}. \tag{2.12}$$

This shows that hydrodynamic interactions between suspended particles have an instantaneous long range.

At small distance from the origin the flow is uniform. By Taylor expansion in Eq. (2.9),

$$\mathsf{T}(\mathbf{r},t)=\frac{1}{\sqrt{4\pi\nu}}\left[\left(\frac{2}{3t^{3/2}}-\frac{r^2}{5\nu t^{5/2}}\right)\mathbf{1}+\frac{r^2}{10\nu t^{5/2}}\hat{\mathbf{r}}\hat{\mathbf{r}}\right]+O(r^3). \tag{2.13}$$

This holds for all $t>0$. The flow is uniform over the viscous length scale $l_v(t)=\sqrt{\nu t}$.

The total momentum imparted to the fluid by the force density $\mathbf{F}_0(\mathbf{r},t)$ in Eq. (2.6) amounts to $\mathbf{P}$. From Eq. (2.8) one finds

$$\int \mathsf{T}(\mathbf{r},t)d\mathbf{r}=\frac{8\pi\nu}{3}\mathbf{1}, \tag{2.14}$$

so that the total momentum of the fluid for $t>0$ is

$$\rho\int \mathbf{v}(\mathbf{r},t)d\mathbf{r}=\tfrac{2}{3}\mathbf{P}. \tag{2.15}$$

Hence at $t=0$ one-third of the imparted momentum is transported to infinity by sound waves.

We also consider a force density

$$\mathbf{F}_0(\mathbf{r},t)=-\tfrac{1}{2}\mathbf{L}\times\nabla\delta(\mathbf{r})\delta(t) \tag{2.16}$$

corresponding to a sudden twist applied at the origin. The twist imparts an angular momentum $\mathbf{L}$ to the fluid. From Eq. (2.8) one finds for the corresponding flow for $t>0$

$$\mathbf{v}(\mathbf{r},t)=\mathbf{L}\times\mathbf{r}\frac{\exp(-r^2/4\nu t)}{\pi^{3/2}\rho(4\nu t)^{5/2}}. \tag{2.17}$$

The pressure remains constant. The angular momentum of the fluid is for $t>0$

$$\rho\int \mathbf{r}\times\mathbf{v}(\mathbf{r},t)d\mathbf{r}=\mathbf{L}. \tag{2.18}$$

Hence no angular momentum is transferred to infinity. Near the origin the flow is a solid-body rotation decaying as $t^{-5/2}$.

III. SINGLE SPHERE

Next we consider a single sphere of radius a immersed in the fluid and centered at the origin. We assume mixed slip-stick boundary conditions at the sphere-fluid interface. For $t<0$ both sphere and fluid are at rest. At $t=0$ we suddenly apply a force or torque to the sphere, causing both sphere and fluid to move. Both motions eventually decay in time due to viscous dissipation. In the linear regime the displacement of the sphere may be neglected. We shall show that at long times the motion of sphere and fluid is quite simple and independent of the size of the sphere and the nature of the boundary conditions.

We consider a force

$$\mathbf{E}(t)=\mathbf{P}\delta(t) \tag{3.1}$$

applied to the sphere. After Fourier transform the equation of motion for the sphere reads

$$-i\omega m_p\mathbf{U}_\omega=\mathbf{K}_\omega+\mathbf{P}, \tag{3.2}$$

where m_p is the mass of the sphere, $\mathbf{U}(t)$ is its velocity, and $\mathbf{K}(t)$ is the force exerted by the fluid on the sphere, as given by a surface integral of the fluid stress tensor. The solution of the flow problem yields

$$[-i\omega(m_p+\tfrac{1}{2}m_f)+\zeta_t(\omega)]\mathbf{U}_\omega=\mathbf{P}, \tag{3.3}$$

where $m_f=(4\pi/3)a^3\rho$ is the mass of fluid displaced by the sphere and $\zeta_t(\omega)$ is the translational friction coefficient. For mixed slip-stick boundary conditions with slip parameter ξ taking values between 0 for stick and $\frac{1}{3}$ for pure slip the friction coefficient is given by [15]

$$\zeta_t(\omega)=6\pi\eta a(1-\xi)\frac{1+\alpha a}{1+\xi\alpha a}. \tag{3.4}$$

The initial value of the velocity is $\mathbf{U}(0+)=\mathbf{P}/m^*$, where $m^*=m_p+\frac{1}{2}m_f$ is the effective mass. This is less than $\mathbf{P}/m_p$ due to the loss of momentum to infinity via longitudinal sound waves [16]. From Eq. (3.3) one defines the translational admittance $\mathcal{Y}_t(\omega)$ as

$$\mathcal{Y}_t(\omega)=[-i\omega m^*+\zeta_t(\omega)]^{-1}. \tag{3.5}$$

At low frequency this has the expansion

$$\mathcal{Y}_t(\omega)=\mu_t(0)-\frac{1}{6\pi\eta}\left(\frac{-i\omega}{\nu}\right)^{1/2}+O(\omega), \tag{3.6}$$

where $\mu_t(0)=1/[6\pi\eta a(1-\xi)]$ is the steady-state mobility. The second term gives rise to the long-time behavior of the velocity,

$$\mathbf{U}(t)\approx\frac{1}{12\rho(\pi\nu t)^{3/2}}\mathbf{P} \quad \text{as} \quad t\to\infty. \tag{3.7}$$

It is remarkable that the coefficient is independent of sphere radius and slip coefficient, and depends only on the properties of the fluid. Comparing with Eq. (2.13) we see that the long-time tail is identical to that corresponding to the sudden impulse in Eq. (2.6). This suggests that in the last stage of motion the flow pattern can be identified with that given by the Green function, as in Eq. (2.7). The complete flow pattern is given by Eq. (7.6) of Ref. [17]. In the notation of Felderhof and Jones [17],

$$\mathsf{T}_\alpha(\mathbf{r})\cdot\mathbf{e}_z=\sqrt{4\pi/3}[2\mathbf{v}^-_{10N}(\mathbf{r})+3\mathbf{v}^-_{10P}(\mathbf{r})]. \tag{3.8}$$

The two contributions are

$$\mathbf{v}^-_{10N}(\mathbf{r})=\frac{\alpha}{3\pi}[2k_0(\alpha r)\mathbf{A}_{10}+k_2(\alpha r)\mathbf{B}_{10}],$$

$$\mathbf{v}^-_{10P}(\mathbf{r})=\frac{-1}{3\alpha^2r^3}\mathbf{B}_{10}, \tag{3.9}$$

with modified spherical Bessel functions $k_l(z)=(\frac{1}{2}\pi/z)^{1/2}K_{l+1/2}(z)$ and vector spherical harmonics

$$\mathbf{A}_{10}=\sqrt{3/4\pi}\mathbf{e}_z, \quad \mathbf{B}_{10}=\sqrt{3/4\pi}(\mathbf{1}-3\hat{\mathbf{r}}\hat{\mathbf{r}})\cdot\mathbf{e}_z. \tag{3.10}$$

One can check that at low frequency Eq. (3.8) is identical with the flow pattern of the sphere.

The momentum transfer from sphere to fluid at time t is given by the force $\mathbf{K}(t)$. From Eqs. (3.2) and (3.3) one finds for its Fourier transform

$$\mathbf{K}_\omega=[\tfrac{1}{2}i\omega m_f-\zeta_t(\omega)]\mathcal{Y}_t(\omega)\mathbf{P}. \tag{3.11}$$

Expanding this at low frequency one finds

$$\mathbf{K}_\omega=-\left(1-\frac{2}{9}\frac{m_p}{m_f(1-\xi)}(\alpha a)^2+\frac{2}{9}\frac{m_p}{m_f}(\alpha a)^3\right)\mathbf{P}+O(\omega^2). \tag{3.12}$$

Therefore the long-time behavior of the force is

$$\mathbf{K}(t)\approx-\frac{1}{6\sqrt{\pi}}\frac{m_p}{m_f}\frac{a^3}{\nu^{3/2}t^{5/2}}\mathbf{P} \quad \text{as} \quad t\to\infty. \tag{3.13}$$

This decays faster than the velocity $\mathbf{U}(t)$. Hence in the last stage of motion sphere and fluid move together with negligible momentum transfer.

Similar considerations hold when a torque

$$\mathbf{N}(t)=\mathbf{L}\delta(t) \tag{3.14}$$

is applied to the sphere. After Fourier transform the equation of motion for the sphere reads

$$-i\omega I\mathbf{\Omega}_\omega=\mathbf{T}_\omega+\mathbf{L}, \tag{3.15}$$

where I is the moment of inertia of the sphere, $\mathbf{\Omega}(t)$ is its rotational velocity, and $\mathbf{T}_\omega$ is the torque exerted by the fluid on the sphere, as given by a surface integral of the fluid stress tensor. The solution of the flow problem yields

$$[-i\omega I+\zeta_r(\omega)]\mathbf{\Omega}_\omega=\mathbf{L}, \tag{3.16}$$

where $\zeta_r(\omega)$ is the rotational friction coefficient given by [15]

$$\zeta_r(\omega)=8\pi\eta a^3(1-3\xi)\frac{1+\alpha a+\frac{1}{3}(\alpha a)^2}{1+\alpha a+\xi(\alpha a)^2}. \tag{3.17}$$

The initial value of the rotational velocity is $\mathbf{\Omega}(0+)=\mathbf{L}/I$. From Eq. (3.16) one defines the rotational admittance $\mathcal{Y}_r(\omega)$ as

$$\mathcal{Y}_r(\omega)=[-i\omega I+\zeta_r(\omega)]^{-1}. \tag{3.18}$$

At low frequency this has the expansion

$$\mathcal{Y}_r(\omega)=\mu_r(0)+i\left(I\mu_r(0)^2+\frac{1}{24\pi a\rho\nu^2}\right)\omega+\frac{1}{24\pi\eta}\left(\frac{-i\omega}{\nu}\right)^{3/2}+O(\omega^2), \tag{3.19}$$

where $\mu_r(0)=1/[8\pi\eta a^3(1-3\xi)]$ is the steady-state rotational mobility. The third term gives rise to the long-time behavior of the rotational velocity,

$$\mathbf{\Omega}(t)\approx\frac{1}{\pi^{3/2}\rho(4\nu t)^{5/2}}\mathbf{L}\quad\text{as}\quad t\to\infty. \tag{3.20}$$

Comparing with Eq. (2.17) we see that the long-time tail is identical with the solid-body rotation corresponding to the sudden twist in Eq. (2.16). This suggests that in the last stage of motion the flow pattern can be identified with that given by the Green function, as given by Eq. (2.17). The complete flow pattern is given by Eq. (7.9) of Ref. [17]. One can check that at low frequency the flow pattern agrees with Eq. (2.17).

The transfer of angular momentum from sphere to fluid at time t is given by the torque $\mathbf{T}(t)$. From Eqs. (3.15) and (3.16) one finds for its Fourier transform

$$\mathbf{T}_\omega=-\zeta_r(\omega)\mathcal{Y}_r(\omega)\mathbf{L}. \tag{3.21}$$

Expanding this at low frequency one finds

$$\mathbf{T}_\omega=-\left[1+I\mu_r(0)\omega-I\mu_r(0)\left(I\mu_r(0)+\frac{a^2}{3\nu}(1-3\xi)\right)\omega^2\right.$$
$$\left.-\frac{I}{24\pi\rho}\left(\frac{-i\omega}{\nu}\right)^{5/2}\right]\mathbf{L}+O(\omega^3). \tag{3.22}$$

Therefore the long-time behavior of the torque is

$$\mathbf{T}(t)\approx-\frac{5I}{64\pi^{3/2}\rho\nu^{5/2}}\frac{1}{t^{7/2}}\mathbf{L}\quad\text{as}\quad t\to\infty. \tag{3.23}$$

This decays faster than the angular velocity $\mathbf{\Omega}(t)$. Hence in the last stage of motion sphere and fluid move together with negligible transfer of angular momentum.

IV. SUSPENSION

After these preparations we consider the velocity autocorrelation function of a selected particle in a suspension of spherical Brownian particles at temperature T. The translational velocity autocorrelation function $C_t(t)$ of the selected particle is defined by

$$C_t(t)=\tfrac{1}{3}\langle\mathbf{U}(0)\cdot\mathbf{U}(t)\rangle, \tag{4.1}$$

where the angular brackets indicate a thermal average in the thermodynamic limit. According to the fluctuation-dissipation theorem [3,18,19] its one-sided Fourier transform $\hat{C}_t(\omega)$, defined as in Eq. (2.10), is given by

$$\hat{C}_t(\omega)=k_BT\langle\mathcal{Y}_t(\omega;X)\rangle, \tag{4.2}$$

where $\mathcal{Y}_t(\omega;X)$ is the translational admittance of the selected particle, which depends parametrically on the configuration X of all Brownian particles. If the particles are sufficiently large compared with the molecules of the solvent, then the admittance can by calculated from linear hydrodynamics. Similar expressions hold for the rotational velocity autocorrelation function.

In earlier work [11] we have shown that the long-time translational motion of an arbitrary number of bodies of arbitrary shape, interacting via arbitrary boundary conditions with an infinite incompressible fluid of mass density ρ and shear viscosity η, is identical to that of a single sphere, as given by Eq. (2.7). It does not matter how the momentum $\mathbf{P}$ is initially distributed over the bodies. Eventually all bodies move with the same velocity, identical to that of the interstitial fluid. After a time much longer than $l/\sqrt{\nu}$, where l is the size of the swarm of bodies, the flow pattern is given by Eq. (2.7). The total amount of diffusing momentum is $\frac{2}{3}\mathbf{P}$. One-third of the initial momentum is transported to infinity at $t=0$ by sound waves.

This general theorem [11] can be applied to the calculation of the average admittance in Eq. (4.2). We take the selected spherical particle of radius a to be centered at the origin. On the time scale under consideration the displacement of particles may be neglected. We assume that the remaining $N-1$ Brownian particles fill a volume V of simple shape surrounding the selected one, and that the solvent extends to infinity. The boundary of the volume V is assumed to have no influence on the flow of solvent. The probability distribution of particle centers $W(\mathbf{R}_1,\ldots,\mathbf{R}_N)$ is assumed known. We are interested in the low-frequency behavior of the translational admittance $\mathcal{Y}_t(\omega;X)$ of the selected particle, labeled 1, for fixed configuration $X=(\mathbf{R}_1,\ldots,\mathbf{R}_N)$, and the corresponding behavior of its conditional average over the probability distribution $W(X)$, keeping $\mathbf{R}_1$ fixed at the origin.

We shall argue that, although for each configuration X the coefficient of the $\sqrt{\omega}$ term in the low-frequency expansion of $\mathcal{Y}_t(\omega;X)$ has the universal value given by Eq. (3.6), nonetheless this has no relevance in the thermodynamic limit $N\to\infty, V\to\infty$ at constant density $n=N/V$. At finite N and V the coefficient is determined by the mass density and shear viscosity of the solvent. The corresponding long-time tail starts to be dominant at times much longer than $R/\sqrt{\nu}$, where R is the size of the volume V. However, in the thermodynamic limit the characteristic time $R/\sqrt{\nu}$ tends to infinity. The long-time tail of the central particle, as observed in experiment or computer simulation, will be dominated by the effective mass density and the effective viscosity of the suspension inside the volume V.

It remains to discuss the motion of the suspension. On the macroscopic length scale, and on a time scale on which diffusion of particles can be neglected, the average flow of the suspension is governed by macroscopic equations of the form [20,21]

$$-i\omega\rho_{\text{eff}}(\omega)\langle\mathbf{v}_\omega\rangle=\eta_{\text{eff}}(\omega)\nabla^2\langle\mathbf{v}_\omega\rangle-\nabla\langle p_\omega\rangle$$
$$+(1-\phi)\mathbf{F}_{0\omega}+n\gamma_t(\omega)\mathbf{E}_\omega,$$
$$\nabla\cdot\langle\mathbf{v}_\omega\rangle=0. \tag{4.3}$$

We have assumed for simplicity that no external torques act on the particles. The average flow velocity $\langle\mathbf{v}_\omega\rangle$ incorporates both fluid flow and solid-body motion of the particles. The effective coefficients $\rho_{\text{eff}}(\omega)$ and $\eta_{\text{eff}}(\omega)$ vary with frequency, but in the long-time limit only the zero-frequency values $\rho_{\text{eff}}(0)$ and $\eta_{\text{eff}}(0)$ are relevant. The zero-frequency mass density is simply

$$\rho_{\text{eff}}(0)=(1-\phi)\rho+\phi\rho_p, \tag{4.4}$$

where $\phi=4\pi na^3/3$ is the volume fraction and ρ_p is the mass density of the solid particles. On the relevant time scale, where particle displacements may be neglected, the effective viscosity $\eta_{\rm eff}(\omega)$ follows from an average over configurations X of a solution of the linearized Navier-Stokes equations. In the zero-frequency limit this becomes an average of the steady-state Stokes equations [22]. Numerical values of the effective viscosity $\eta_{\rm eff}(0)$ have been determined by computer simulation for a range of volume fraction [23]. Note that the zero-frequency limit is applied here on the time scale where particle displacements are neglected. The effect of Brownian motion on the distribution function is not taken into account. Thus the effective viscosity $\eta_{\rm eff}(0)$ considered above is a high-frequency viscosity on the diffusion time scale.

In Eq. (4.3) it has been assumed that the force density $\mathbf{F}_0(\mathbf{r},t)$ acting on the fluid and the force $\mathbf{E}(t)$ acting on the particles vary slowly in space, as compared with the interparticle distance. The convection coefficient $\gamma_t(\omega)$ is given by [20,21,24]

$$\gamma_t(\omega)=1+i\omega(m_p-m_f)\mathcal{Y}_t(\omega), \tag{4.5}$$

where $\mathcal{Y}_t(\omega)$ is the admittance of a single particle in infinite solvent. The convection coefficient $\gamma_t(\omega)$ incorporates the single-particle equation of motion and expresses how momentum is transferred to the fluid after a force is applied to the particle. Clearly, in the zero-frequency limit the convection coefficient may be replaced by unity, and its expansion in powers of frequency has no term of order $\sqrt{\omega}$. This shows that for the long-time motion of the suspension it is immaterial whether the initial momentum is imparted to the fluid or to the particles. In either case the suspension flow is described by the same average Green function. The long-time common motion of fluid and particles may be calculated from the macroscopic equation Eq. (4.3) with coefficients replaced by their zero-frequency values. The calculation is identical to that of Secs. II and III. The long-time tail of the local suspension velocity after an initial momentum $\mathbf{P}$ or angular momentum $\mathbf{L}$ is imparted at time $t=0$ in spherically symmetric fashion in a region of finite extent is given by Eqs. (3.7) and (3.20), respectively, with ρ replaced by $\rho_{\rm eff}(0)$ and ν replaced by $\nu_{\rm eff}(0)=\eta_{\rm eff}(0)/\rho_{\rm eff}(0)$.

In earlier work [12] we conjectured that the Fourier-Laplace transform of the velocity autocorrelation function of Brownian motion may be approximated by a simple expression based on its behavior at low and high frequencies. For the low-frequency behavior we used the theorem [11] mentioned at the beginning of this section. The theorem implies that the low-frequency expansion of any of the cluster integrals in the exact expression for the average admittance $\langle\mathcal{Y}_t(\omega;X)\rangle$ has the same $\sqrt{\omega}$ term as the one for a single sphere, given by Eq. (3.6). This implies that for fixed N and V the velocity of the sphere after an impulse at $t=0$ has the long-time behavior given by Eq. (3.7). The arguments presented in this section show that in the thermodynamic limit $N\to\infty, V\to\infty$ the $\sqrt{\omega}$ term in the expansion of the average admittance attains a different value. A similar mechanism is operative for the average rotational admittance. For long times the flow pattern becomes smooth and is described nearly precisely by the macroscopic equations. The microstructure appears only in the value of the effective viscosity. Thus the long-time behavior of the velocity autocorrelation function $C_t(t)$ is

$$C_t(t)\approx\frac{k_BT}{12\rho_{\rm eff}(0)[\pi\nu_{\rm eff}(0)t]^{3/2}} \quad \text{as} \quad t\to\infty. \tag{4.6}$$

Similarly, the long-time behavior of the rotational velocity autocorrelation function $C_r(t)$ is

$$C_r(t)\approx\frac{k_BT}{\pi^{3/2}\rho_{\rm eff}(0)[4\nu_{\rm eff}(0)t]^{5/2}} \quad \text{as} \quad t\to\infty. \tag{4.7}$$

In experiment and computer simulation the thermodynamic limit value of the long-time coefficient is the relevant one. The situation is somewhat similar to that for the equilibrium radial distribution function of a simple fluid. In experiment and simulation the relevant value of the integral of the radial distribution function of a closed system is the one given by the compressibility theorem, not the exact value derived for the canonical ensemble [25].

It will be clear that the conclusions of this section are independent of the choice of macroscopic geometry and of the nature of the suspension. In particular, the conclusions hold for any simple shape of the volume V. Also, the suspension may be polydisperse.

V. DISCUSSION

An analysis of the Green function of linear hydrodynamics and of the flow pattern caused by a single sphere moving and rotating in a viscous fluid yields illuminating insight into the nature of the long-time tails of translational and rotational motion. The same physical mechanism is operative for a sphere immersed in a suspension of spherical particles, and also for each of the particles of the suspension. We conclude that the conjecture of Milner and Liu [7] concerning the coefficient of the long-time tail of the velocity autocorrelation function of Brownian motion in a dense suspension, and its extension to rotational motion by Hagen, Frenkel, and Lowe [8], are correct. Of course, the same conclusion holds in two dimensions.

Milner and Liu [7] supported their conjecture by a calculation of the first virial correction to the coefficient of the long-time tail of the velocity autocorrelation function. In earlier work [12] we argued on the basis of the cluster expansion of the average hydrodynamic admittance in a suspension that their calculation must be incorrect. We derived a theorem [11] showing that the term linear in the square root of frequency in the integrand of the pair cluster integral vanishes, and concluded that the coefficient of the long-time tail is given by the first, single-sphere, term of the cluster expansion. However, in the thermodynamic limit the pair cluster integral has infinite range, and as a consequence the integral does obtain a term linear in the square root of frequency. Milner and Liu [7] have shown how this happens. We have performed a complete analysis of the pair cluster integral [26] and agree with their conclusion.

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