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Translational Brownian motion in a fluid with internal degrees of freedom

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The friction coefficient for a smooth hard sphere (Brownian particle) moving through a fluid composed of finite-sized particles with internal rotational degrees of freedom is computed. Inertial effects are included. The long-time limit of the velocity-autocorrelation function is obtained. We find that the velocity-autocorrelation function decays as $t^{-3/2}$ but with a coefficient that is altered from the usual Navier-Stokes results to include contributions from transport processes involving internal rotational degrees of freedom of the fluid.

I. INTRODUCTION

The Navier-Stokes equations, which describe the hydrodynamic behavior of fluids, assume that the particles comprising the fluid are point particles or smooth spheres and therefore are unable to exert a torque on one another. The Navier-Stokes equations describe the low frequency, long-wavelength behavior of such fluids, and result from the conservation of mass, linear momentum, and energy during collision processes. However, if the particles in the fluid have a nonspherical shape or are not smooth, they can be set into rotation during collisions and energy can be transferred from translational motion to rotational motion. During these collisions, the total angular momentum of colliding particles must be conserved. The requirement that angular momentum be conserved leads to an additional set of hydrodynamic equations which must be coupled to the Navier-Stokes equations if one wishes to have a complete hydrodynamic description of the fluid.

The simplest theory of Brownian motion for a spherical particle moving through a fluid assumes that the friction on the particle due to the surrounding medium (composed of point particles) is constant and is given by Stokes's formula. This in turn implies that the random noise exerted on the particle by the background medium is white.[1] This "simple" theory of Brownian motion is only applicable for an extremely massive Brownian particle which experiences negligible acceleration. When one is dealing with a Brownian particle which is small enough to experience sizable accelerations due to fluctuating forces from the medium or a fluctuating external force, then inertial effects must be retained in computing the friction due to the medium. Inertial effects cause the friction force to become memory dependent and cause the random noise on the Brownian particle to become colored.

It is our purpose in this and a subsequent paper to investigate the effect of the internal rotational degrees of freedom of a fluid on the Brownian motion of a spherical particle embedded in that fluid. We shall assume that the Brownian particle is small enough that inertial effects must be retained. In this paper we shall consider the translational motion of the particle. In a subsequent paper, we shall consider rotational motion. We shall begin in Sec. II, with a discussion of the hydrodynamic equations which describe a fluid with internal rotational degrees of freedom. The dispersion relations for the hydrodynamic modes in such a fluid are obtained in Sec. III. In Sec. IV solutions of the hydrodynamic equations for a fluid at constant temperature are obtained for the case when a hard sphere is immersed in it, and in Sec. V we obtain the force on a smooth hard sphere which translates through the fluid. As we shall see, internal degrees of freedom in the fluid can alter the friction force on the Brownian particle. Finally, in Sec. VI we obtain an expression for the velocity-autocorrelation function after long times. We find that the velocity-autocorrelation function decays as $t^{-3/2}$ but with a coefficient which is changed from the usual Navier-Stokes results by terms which depend on transport processes involving internal rotational degrees of freedom of the fluid.

II. HYDRODYNAMIC EQUATIONS FOR A FLUID WITH ROTATIONAL DEGREES OF FREEDOM

The hydrodynamic equations for a fluid with internal rotational degrees of freedom[2,3] take the following form. The continuity equation, as usual, is written

$$\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x_k}(\rho v_k)=0\,, \tag{2.1}$$

where ρ is the mass density and v_k is the kth component of average velocity. The momentum balance equation can be written

$$\frac{\partial}{\partial t}(\rho v_i)+\frac{\partial}{\partial x_k}(\rho v_k v_i)=\frac{\partial}{\partial x_k}P_{ki}\,, \tag{2.2}$$

where P_{ki} is the pressure tensor and is defined in terms of the hydrostatic pressure P and the stress tensor Π_{ki} as

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$$P_{ki} = P\delta_{ki} + \Pi_{ki}. \tag{2.3}$$

The angular momentum balance equation can be written

$$\frac{\partial L_i}{\partial t} + \frac{\partial}{\partial x_k}(v_k L_i) = \frac{\partial}{\partial x_k}(P_{kj} x_\ell \epsilon_{i\ell j}) + \frac{\partial \tau_{ki}}{\partial x_k}, \tag{2.4}$$

where L_i is the ith component of the total angular momentum density for the fluid, $\epsilon_{i\ell j}$ is the Levi-Civita tensor and has the property that for even permutations of $(i\ell j)$, $\epsilon_{i\ell j} = +1$, for odd permutations $\epsilon_{i\ell j} = -1$, and $\epsilon_{i\ell j} = 0$ if any two indices are equal. The tensor τ_{ki} is the torque tensor and is defined so that $n_k \tau_{ki}$ is the ith component of torque on a surface with unit vector $\hat{n}$ due to mutual rotation of particles in the fluid. The quantity $n_k P_{kj} x_\ell \epsilon_{i\ell j}$ gives the ith component of torque on a surface with unit vector $\hat{n}$ due to the translational motion of the fluid. The total angular momentum density $\vec{L}$ can, in general, be written

$$\vec{L} = \rho \vec{r} \times \vec{v} + \vec{I} \cdot \vec{\Omega}, \tag{2.5}$$

where $\vec{I}$ is the tensor describing the moment of inertia of fluid particles per unit volume and $\vec{\Omega}$ is the average angular velocity of particles in a given region of fluid. In the following we shall assume that the molecules have a mass distribution which to first approximation is more or less spherical so that $I_{ij} \sim I\delta_{ij}$. If we write $I = \rho I_0$, we may think of $\sqrt{I_0}$ as an effective radius of gyration of the fluid particles. The angular momentum then becomes

$$\vec{L} = \rho \vec{r} \times \vec{v} + I\vec{\Omega}. \tag{2.6}$$

The equation for energy balance can be written

$$\frac{\partial}{\partial t}(\rho\epsilon) + \frac{\partial}{\partial x_k}(\rho v_k \mu' + \rho v_k s T) = \frac{\partial J_k^E}{\partial x_k}, \tag{2.7}$$

where $\vec{J}^E$ is a dissipative energy current, s is the local specific entropy, T is the local temperature,

$$\mu' = \mu + \frac{1}{2}\frac{I}{\rho}\vec{\Omega} \cdot \vec{\Omega} + \tfrac{1}{2}\vec{v} \cdot \vec{v}, \tag{2.8}$$

and μ is the chemical potential of the fluid.

It is also useful to write an equation for the entropy density ρs:

$$\frac{\partial}{\partial t}(\rho s) + \frac{\partial}{\partial x_k}(\rho s v_k) = \frac{\partial J_k^s}{\partial x_k} + \sigma_s, \tag{2.9}$$

where J_k^s is the dissipative entropy current

$$\vec{J}^s = \frac{1}{T}(\vec{J}^E + \vec{\tau} \cdot \vec{\Omega} - \vec{\pi} \cdot \vec{v}) \tag{2.10}$$

and σ_s is the entropy production per unit volume due to dissipative processes in the fluid

$$\sigma_s = \frac{1}{T} J_k^s \frac{\partial T}{\partial x_k} + \frac{1}{T}\tau_{jk}\frac{\partial \Omega_k}{\partial x_j} + \frac{1}{T}\pi_{jk}\frac{\partial v_k}{\partial x_j} - \frac{1}{T}\epsilon_{ikj}\Omega_i \pi_{kj}. \tag{2.11}$$

If we take the cross product of Eq. (2.2) with the position vector and combine it with Eq. (2.4), we obtain the following equation for the ith component of average internal angular velocity $\vec{\Omega}$

$$\frac{\partial}{\partial t}(I\Omega_i) + \frac{\partial}{\partial x_k}(v_k I\Omega_i) = \epsilon_{ikj} P_{kj} + \frac{\partial \tau_{ki}}{\partial x_k}. \tag{2.12}$$

If we assume a linear relation exists between forces and fluxes in the fluid, the dissipative currents take the following form. The dissipative entropy current is written

$$\vec{J}_s = \frac{K}{T}\vec{\nabla} T, \tag{2.13}$$

where K is the coefficient of thermal conductivity. The stress tensor becomes

$$\pi_{ij} = \eta_2(\vec{\nabla} \cdot \vec{v})\delta_{ij} + \eta_1\left(\frac{\partial v_j}{\partial x_i} + \frac{\partial v_i}{\partial x_j} - \tfrac{2}{3}\delta_{ij}(\vec{\nabla} \cdot \vec{v})\right) - \eta_3\left(\frac{\partial v_j}{\partial x_i} - \frac{\partial v_i}{\partial x_j} - 2\epsilon_{ijk}\Omega_k\right), \tag{2.14}$$

where η_1 and η_2 are the coefficients of shear and bulk viscosity, respectively, and η_3 is a new viscous transport coefficient which couples rotational motion of fluid particles to translational flow. The torque tensor takes the form

$$\tau_{ij} = \xi_2(\vec{\nabla} \cdot \vec{\Omega})\delta_{ij} + \xi_1\left(\frac{\partial \Omega_j}{\partial x_i} + \frac{\partial \Omega_i}{\partial x_j} - \tfrac{2}{3}\delta_{ij}(\vec{\nabla} \cdot \vec{\Omega})\right) + \xi_3\left(\frac{\partial \Omega_j}{\partial x_i} - \frac{\partial \Omega_i}{\partial x_j}\right), \tag{2.15}$$

where ξ_1, ξ_2, ξ_3 are three new transport coefficients describing dissipation of the average internal angular velocity of particles due to mutual friction between particles. Equation (2.1) completely determines the hydrodynamic behavior for a fluid of particles which have rotational motion in addition to translational motion.

III. DISPERSION RELATIONS

We will now linearize these equations about absolute equilibrium and find the dispersion relations for the hydrodynamic modes.[1] Let ρ_0, s_0, and $\rho_0 I_0$ denote the equilibrium values of the mass density, specific entropy, and moment of inertia density, respectively. At equilibrium $\vec{\Omega} = 0$ and we assume $\vec{v} = 0$. After linearization, Eqs. (2.1), (2.2), (2.9), and (2.12) together with (2.13)–(2.15) take the form

$$\frac{\partial \rho}{\partial t} + \rho_0 \vec{\nabla} \cdot \vec{v} = 0, \tag{3.1}$$

$$\rho_0 \frac{\partial v}{\partial t} = -\vec{\nabla} P + (\eta_2 + \tfrac{4}{3}\eta_1)\vec{\nabla}(\vec{\nabla} \cdot \vec{v}) - (\eta_1 + \eta_3)\vec{\nabla} \times \vec{\nabla} \times \vec{v} + 2\eta_3 \vec{\nabla} \times \vec{\Omega}, \tag{3.2}$$

$$\rho_0 \frac{\partial s}{\partial t} = \frac{K}{T_0} \nabla^2 T , \tag{3.3}$$

$$\rho_0 I_0 \frac{\partial \vec{\Omega}}{\partial t} = 2\eta_3(\vec{\nabla}\times\vec{v} - 2\vec{\Omega}) + (\xi_2 + \tfrac{4}{3}\xi_1)\vec{\nabla}(\vec{\nabla}\cdot\vec{\Omega}) - (\xi_1+\xi_3)\vec{\nabla}\times\vec{\nabla}\times\vec{\Omega} . \tag{3.4}$$

We can simplify these equations if we divide the average velocity $\vec{v}$ and average angular velocity $\vec{\Omega}$ into their longitudinal and transverse parts

$$\vec{v} = \vec{v}_l + \vec{v}_t \tag{3.5}$$

and

$$\vec{\Omega} = \vec{\Omega}_l + \vec{\Omega}_t , \tag{3.6}$$

where by definition the longitudinal parts $\vec{v}_l$, and $\vec{\Omega}_l$ have the properties $\vec{\nabla}\times\vec{v}_l = 0$ and $\vec{\nabla}\times\vec{\Omega}_l = 0$ and the transverse parts $\vec{v}_t$ and $\vec{\Omega}_t$ have the property $\vec{\nabla}\cdot\vec{v}_t = 0$ and $\vec{\nabla}\cdot\vec{\Omega}_t = 0$. For a plane wave disturbance, $\vec{v}_l$ and $\vec{\Omega}_l$ are parallel to the direction of propagation of the wave and $\vec{v}_t$ and $\vec{\Omega}_t$ are perpendicular to it. The hydrodynamic equations now decouple into the following sets. For the coupled longitudinal sound and heat modes we have the usual equations

$$\frac{\partial \rho}{\partial t} + \rho_0 \vec{\nabla}\cdot\vec{v}_l = 0 , \tag{3.7}$$

$$\rho_0 \frac{\partial \vec{v}_l}{\partial t} = \vec{\nabla} P + (\eta_2 + \tfrac{4}{3}\eta_1)\vec{\nabla}(\vec{\nabla}\cdot\vec{v}_l) , \tag{3.8}$$

$$\rho_0 \frac{\partial s}{\partial t} = \frac{K}{T_0} \nabla^2 T . \tag{3.9}$$

The transverse part of the average velocity becomes coupled to the transverse part of the average angular velocity,

$$\rho_0 \frac{\partial \vec{v}_t}{\partial t} = -(\eta_1 + \eta_3)\vec{\nabla}\times\vec{\nabla}\times\vec{v}_t + 2\eta_3 \vec{\nabla}\times\vec{\Omega}_t , \tag{3.10}$$

$$\rho_0 I_0 \frac{\partial \vec{\Omega}_t}{\partial t} = 2\eta_3 \vec{\nabla}\times\vec{v}_t - 4\eta_3 \vec{\Omega}_t - (\xi_1+\xi_3)\vec{\nabla}\times\vec{\nabla}\times\vec{\Omega}_t , \tag{3.11}$$

and the longitudinal part of the average angular velocity obeys the equation

$$\rho_0 I_0 \frac{\partial \vec{\Omega}_l}{\partial t} = -4\eta_3 \vec{\Omega}_l + (\xi_2 + \tfrac{4}{3}\xi_1)\vec{\nabla}(\vec{\nabla}\cdot\vec{\Omega}_l) . \tag{3.12}$$

We can now find the dispersion relations for the normal modes of this system. We first must Fourier transform the space and time dependence of these equations. We use the convention that

$$\vec{v}(\vec{r}, t) \sim \vec{v}(\vec{k}, \omega)\, e^{i(\vec{k}\cdot\vec{r} - \omega t)} \tag{3.13}$$

with similar expressions for other quantities. We also choose the entropy and pressure as our independent thermodynamic variables. We then find the following dispersion relations. From Eqs. (3.7)–(3.9) we find the usual dispersion relations for heat and sound modes. For the heat mode we find

$$\omega = -i \frac{K k^2}{\rho_0 c_p} , \tag{3.14}$$

where c_p is the specific heat at constant pressure. For the sound modes we obtain

$$\omega = \pm c_0 k - \frac{i k^2}{2\rho_0}\left[\eta_2 + \tfrac{4}{3}\eta_1 + K\left(\frac{1}{c_v} - \frac{1}{c_p}\right)\right] , \tag{3.15}$$

where c_0 is the speed of sound, $c_0^2 = (\partial P/\partial \rho)_s^0$, and c_v is the specific heat at constant volume. The coupled transverse velocity and angular velocity modes yield the dispersion relations

$$\omega = \frac{-i[4\eta_3 + (I_0\eta + \xi)k^2]}{2\rho_0 I_0} \pm \frac{i}{2\rho_0 I_0}\{[4\eta_3 + (I_0\eta + \xi)k^2]^2 - 4I_0(4\eta_1\eta_3 + \eta\xi)k^2\}^{1/2} . \tag{3.16}$$

In Eq. (3.16), we have let $\eta = \eta_1 + \eta_3$ and $\xi = \xi_1 + \xi_3$. Let us note that in the limit $k \to 0$ the dispersion relations for the transverse modes reduce to $\omega = 0$ and $\omega = -4\eta_3 i/(\rho_0 I_0)$. Thus, one of the transverse normal modes ($\omega = 0$) is hydrodynamic and the other, $\omega = -4\eta_3 i/(\rho_0 I_0)$, is not.[4] This is a consequence of the fact that the average velocity is a conserved quantity while the transverse angular velocity is not. The longitudinal angular velocity mode is also not hydrodynamic. It has a dispersion relation

$$\omega = \frac{-4\eta_3 i}{\rho_0 I_0} - \frac{i(\xi_2 + \tfrac{4}{3}\xi_1)k^2}{\rho_0 I_0} . \tag{3.17}$$

Notice that if we set $\eta_3 = 0$ then the internal angular velocity decouples from the translational motion and both the transverse and longitudinal average angular velocity modes become hydrodynamic.

IV. SOLUTIONS TO THE HYDRODYNAMIC EQUATIONS

Let us now solve the hydrodynamic equations for the case when the system has uniform temperature.[5] Then pressure gradients can be expressed in terms of density gradients

$$\vec{\nabla} P = \left(\frac{\partial P}{\partial \rho}\right)_T^0 \vec{\nabla}\rho , \tag{4.1}$$

where

$$\left(\frac{\partial P}{\partial \rho}\right)_T^0 = \left(\frac{\partial P}{\partial \rho}\right)_s^0 \frac{c_p}{c_v} \equiv c_0^2 \frac{c_p}{c_v}$$

is the isothermal compressibility. We can now Fourier transform the time dependence of Eqs. (3.1), (3.2), and (3.4), and using (4.1) we can write them in the form

$$-i\omega\rho_0\vec{v}_\omega=\left(\eta_2+\tfrac{4}{3}\eta_1-\frac{\rho_0c^2}{i\omega}\right)\vec{\nabla}(\vec{\nabla}\cdot\vec{v}_\omega)-(\eta_1+\eta_3)\vec{\nabla}\times\vec{\nabla}\times\vec{v}_\omega+2\eta_3\vec{\nabla}\times\vec{\Omega}_\omega \tag{4.2}$$

and

$$-i\omega\rho_0I_0\vec{\Omega}_\omega=2\eta_3(\vec{\nabla}\times\vec{v}_\omega-2\vec{\Omega}_\omega)+(\xi_2+\tfrac{4}{3}\xi_1)\vec{\nabla}(\vec{\nabla}\cdot\vec{\Omega}_\omega)-(\xi_1+\xi_3)\vec{\nabla}\times\vec{\nabla}\times\vec{\Omega}_\omega, \tag{4.3}$$

where $c^2=c_0^2c_p/c_v$ and

$$\vec{v}_\omega\equiv\vec{v}_\omega(\vec{r})=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\,\vec{v}(\vec{r},t) \tag{4.4}$$

with a similar expression for $\vec{\Omega}_\omega=\vec{\Omega}_\omega(\vec{r})$.

Let us now decouple Eqs. (4.2) and (4.3) into their transverse and longitudinal parts. We obtain for the longitudinal velocity

$$-i\omega\rho_0\vec{v}_\omega^{\,l}=\left(\zeta-\frac{\rho_0c^2}{i\omega}\right)\vec{\nabla}(\vec{\nabla}\cdot\vec{v}_\omega^{\,l})=\left(\zeta-\frac{\rho_0c^2}{i\omega}\right)\nabla^2\vec{v}_\omega^{\,l}, \tag{4.5}$$

where $\zeta=\eta_2+\frac{4}{3}\eta_1$. For the transverse velocity and angular velocity we obtain

$$-i\omega\rho_0\vec{v}_\omega^{\,t}=-\eta\vec{\nabla}\times\vec{\nabla}\times\vec{v}_\omega^{\,t}+2\eta_3\vec{\nabla}\times\vec{\Omega}_\omega^{t} \tag{4.6}$$

and

$$(-i\omega\rho_0I_0+4\eta_3)\vec{\Omega}_\omega^{t}=2\eta_3\vec{\nabla}\times\vec{v}_\omega^{\,t}-\xi\vec{\nabla}\times\vec{\nabla}\times\vec{\Omega}_\omega^{t}, \tag{4.7}$$

where $\eta=\eta_1+\eta_3$ and $\xi=\xi_1+\xi_3$. Finally, the equation for the longitudinal angular velocity takes the form

$$(-i\omega\rho_0I_0+4\eta_3)\vec{\Omega}_\omega^{l}=\delta\vec{\nabla}(\vec{\nabla}\cdot\vec{\Omega}_\omega^{l})=\delta\nabla^2\vec{\Omega}_\omega^{l}, \tag{4.8}$$

where $\delta=\xi_2+\frac{4}{3}\xi_1$.

We now wish to find the force exerted on a hard sphere as it moves through an infinite medium whose motion is governed by Eqs. (4.5)–(4.8). If we assume that the disturbances created by the motion of the sphere either propagate outward or decay to zero as one moves far from the sphere, we can immediately write the solutions to Eqs. (4.5) and (4.8). Equation (4.5) can be written in the form

$$\nabla^2\vec{v}_\omega^{\,l}+\mathscr{k}_l^2\vec{v}_\omega^{\,l}=0, \tag{4.9}$$

where

$$\mathscr{k}_l^2=\frac{i\omega\rho_0}{\left(\zeta-\dfrac{\rho_0c^2}{i\omega}\right)} \tag{4.10}$$

Its solution in spherical coordinates is

$$\vec{v}_\omega^{\,l}(\vec{r})=\vec{\nabla}\,\Gamma_v(\vec{r},\mathscr{k}_l), \tag{4.11}$$

where

$$\Gamma_v(\vec{r},\mathscr{k}_l)=\sum_{n=0}^{\infty}\mathfrak{L}_n^v h_n(\mathscr{k}_l r)P_n(\cos\theta). \tag{4.12}$$

In Eq. (4.12), the functions $h_n(\mathscr{k}r)$ are spherical Hankel functions, the functions $P_n(\cos\theta)$ are Legendre polynomials, and $\mathfrak{L}_n^v$ are constants to be determined by the boundary conditions on the sphere. Equation (4.8) can be written

$$\nabla^2\vec{\Omega}_\omega^{l}+k_l^2\vec{\Omega}_\omega^{l}=0, \tag{4.13}$$

where

$$k_l^2=\frac{i\omega\rho_0I_0-4\eta_3}{\delta}. \tag{4.14}$$

Its solution has the form

$$\vec{\Omega}_\omega^{l}(\vec{r})=\vec{\nabla}\,\Gamma_\Omega(\vec{r},k_l), \tag{4.15}$$

where

$$\Gamma_\Omega(\vec{r},k_l)=\sum_{n=0}^{\infty}\mathfrak{L}_n^\Omega h_n(k_l r)P_n(\cos\theta) \tag{4.16}$$

and the constants $\mathfrak{L}_n^\Omega$ are also determined by boundary conditions on the sphere.

The equations for the transverse velocity and angular velocity are slightly more complicated. If we combine Eqs. (4.6) and (4.7) we obtain

$$\xi\eta\nabla^4\vec{v}_\omega^{\,t}+(\eta\theta_\omega+i\omega\rho_0\xi+4\eta_3^2)\nabla^2\vec{v}_\omega^{\,t}+i\omega\rho_0\theta_\omega\vec{v}_\omega^{\,t}=0 \tag{4.17}$$

and

$$\xi\eta\nabla^4\vec{\Omega}_\omega^{t}+(\eta\theta_\omega+i\omega\rho_0\xi+4\eta_3^2)\nabla^2\vec{\Omega}_\omega^{t}+i\omega\rho_0\theta_\omega\vec{\Omega}_\omega^{t}=0, \tag{4.18}$$

where

$$\theta_\omega=i\omega\rho_0I_0-4\eta_3. \tag{4.19}$$

The solution to Eq. (4.17) can be written

$$\vec{v}_\omega^{\,t}(\vec{r})=\vec{\nabla}\times(\vec{r}\psi_v^{+}+\vec{r}\psi_v^{-})+\frac{1}{k_+}\vec{\nabla}\times\vec{\nabla}\times(\vec{r}\chi_v^{+})+\frac{1}{k_-}\vec{\nabla}\times\vec{\nabla}\times(\vec{r}\chi_v^{-}), \tag{4.20}$$

where

$$\psi_v^{\pm}(\vec{r})=\sum_{n=0}^{\infty}M_n^{\pm}h_n(k_\pm r)P_n(\cos\theta) \tag{4.21}$$

and

$$\chi_v^{\pm}(\vec{r})=\sum_{n=0}^{\infty}N_n^{\pm}h_n(k_\pm r)P_n(\cos\theta). \tag{4.22}$$

The solution for (4.18) can be written

$$\vec{\Omega}_\omega^{t}(\vec{r})=\vec{\nabla}\times(\vec{r}\psi_\Omega^{+}+\vec{r}\psi_\Omega^{-})+\frac{1}{k_+}\vec{\nabla}\times\vec{\nabla}\times(\vec{r}\chi_\Omega^{+})+\frac{1}{k_-}\vec{\nabla}\times\vec{\nabla}\times(\vec{r}\chi_\Omega^{-}), \tag{4.23}$$

where

$$\psi_{\Omega}^{\pm}(\vec{r}) = \sum_{n=0}^{\infty} \mathfrak{M}_n^{\pm} h_n(k_{\pm} r) P_n(\cos\theta) \tag{4.24}$$

and

$$\chi_{\Omega}^{\pm}(\vec{r}) = \sum_{n=0}^{\infty} \mathfrak{N}_n^{\pm} h_n(k_{\pm} r) P_n(\cos\theta) . \tag{4.25}$$

The constants $M_n^{\pm}$, $\mathfrak{M}_n^{\pm}$, $N_n^{\pm}$, and $\mathfrak{N}_n^{\pm}$ are determined by boundary conditions on the sphere and are interrelated through Eqs. (4.2) and (4.3). The wave vectors $k_{\pm}$ obey the equation

$$\xi\eta k_{\pm}^4 - (\eta\theta_{\omega} + i\omega\rho_0\xi + 4\eta_3^2) k_{\pm}^2 + i\omega\rho_0\theta_{\omega} = 0 . \tag{4.26}$$

Thus,

$$k_{\pm}^2 = \left(\frac{1}{2\xi\eta}\right)(\eta\theta_{\omega} + i\omega\rho_0\xi + 4\eta_3^2) \pm \left(\frac{1}{2\xi\eta}\right) \times [(\eta\theta_{\omega} + i\omega\rho_0\xi + 4\eta_3^2)^2 - 4\xi\eta i\omega\rho_0\theta_{\omega}]^{1/2} . \tag{4.27}$$

If we remember that

$$\vec{v}_{\omega} = \vec{v}_{\omega}^l + \vec{v}_{\omega}^t \tag{4.28}$$

and

$$\vec{\Omega}_{\omega} = \vec{\Omega}_{\omega}^l + \vec{\Omega}_{\omega}^t , \tag{4.29}$$

we obtain the full solutions to Eqs. (4.2) and (4.3).

V. FORCE ON A SMOOTH HARD SPHERE

Let us now consider a smooth hard sphere which moves through the fluid with velocity $\vec{u}(t) = u(t)\hat{\vec{z}}$. The fact that it is smooth means that no torques and no force directed tangent to its surface can be exerted on it. The only force on the sphere will be normal to the surface. Since for a sphere all normal forces are directed through the center of mass, there is no way that the fluid can excite or damp rotational motion in the sphere. Therefore, the only motion of interest is translational motion. Because the sphere is hard, we must also require that the normal component of velocity of the fluid at the surface of the sphere is equal to the normal component of velocity of the sphere. Then no fluid can flow into or out of the sphere. The boundary conditions at the surface of the sphere thus take the form

$$\hat{\vec{r}} \cdot \vec{v}(R, \theta) = \hat{\vec{r}} \cdot \vec{u}(t) , \tag{5.1}$$

$$\hat{\vec{r}} \cdot \vec{\tau}(R, \theta) = 0 , \tag{5.2}$$

and

$$\hat{\vec{r}} \times [\hat{\vec{r}} \cdot \vec{\pi}(R, \theta)] = 0 , \tag{5.3}$$

where R is the radius of the sphere. The boundary condition in Eq. (5.1) together with Eqs. (5.2) and (5.3) and (3.10) and (3.11) ensure that only the terms for which $n = 1$ in Eqs. (4.12), (4.24), and (4.25) contribute to the motion of the fluid.

If we now require that $\vec{\Omega}_{\omega}^t$ and $\vec{v}_{\omega}^t$ be related through Eqs. (4.6) and (4.7) and if we impose boundary conditions (5.1)–(5.3), we obtain the following expression for transverse velocity

$$\vec{v}_{\omega}^t(r, \theta) = \cos\theta\, \hat{\vec{r}} \left(\mathfrak{L} \frac{\partial h^l}{\partial r} + \frac{N_+}{k_+} \frac{2h^+}{r} + \frac{N_-}{k_-} \frac{2h^-}{r}\right) - \sin\theta\hat{\theta}\left[\mathfrak{L} \frac{h^l}{r} + \frac{N_+}{k_+}\left(\frac{h^+}{r} + \frac{\partial h^+}{\partial r}\right) + \frac{N_-}{k_-}\left(\frac{h^-}{r} + \frac{\partial h^-}{\partial r}\right)\right] . \tag{5.4}$$

The Hankel functions in Eq. (5.4) are defined

$$h^l = -\frac{e^{i\textit{k}_l r}}{\textit{k}_l^2 r^2}(\textit{k}_l r + i) \tag{5.5}$$

and

$$h^{\pm} = -\frac{e^{ik_{\pm} r}}{k_{\pm}^2 r^2}(k_{\pm} r + i) . \tag{5.6}$$

The constants $\mathfrak{L}$ and $N_{\pm}$ are defined

$$\mathfrak{L} = \frac{u_{\omega}^0 \textit{k}_l^2 R^3}{\Delta} e^{-i\textit{k}_l R}\left[X_+A_+\left(C_- + \frac{4\eta_1 D_-}{R}\right) - X_-A_-\left(C_+ + \frac{4\eta_1 D_+}{R}\right)\right] \tag{5.7}$$

and

$$\frac{N_{\pm}}{k_{\pm}} = \mp \frac{u_{\omega}^0 k_{\pm}^2 R^3}{\Delta} e^{-ik_{\pm} R}\left(\frac{2\eta_1}{R}\right) X_{\mp} A_{\mp}[3D_l - i\textit{k}_l^2 R^2] , \tag{5.8}$$

where u_{ω}^0 is the Fourier transform of the Brownian-particle velocity,

$$X_{\pm} = (\eta k_{\pm}^2 - i\omega\rho_0) , \tag{5.9}$$

$$D_l = (\textit{k}_l R + i) , \tag{5.10}$$

$$D_{\pm} = (k_{\pm} R + i) , \tag{5.11}$$

$$C_{\pm} = \left[-\eta k_{\pm}^2 R D_{\pm} + \frac{2\eta_1}{R}(D_{\pm} - ik_{\pm}^2 R^2)\right] , \tag{5.12}$$

$$A_{\pm} = [\xi(D_{\pm} - ik_{\pm}^2 R^2) + 2\xi_1 D_{\pm}] , \tag{5.13}$$

and

$$\Delta = A_+X_+\left(B_l C_- - \frac{4\eta_1}{R} D_l D_-\right) - A_-X_-\left(B_l C_+ - \frac{4\eta_1}{R} D_l D_+\right) . \tag{5.14}$$

In Eq. (5.14),

$$B_l = 2D_l - i\textit{k}_l^2 R^2 . \tag{5.15}$$

It is interesting to note that only the transverse components of the average angular velocity contribute to the friction on the Brownian particle.

Let us now compute the total force exerted by the medium on the sphere

$$\vec{F}_{\omega} = \int d\vec{S} \cdot \vec{P}_{\omega} = R^2 \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta P_{rr}(\omega)\hat{r} , \tag{5.16}$$

where $d\vec{S}$ is an infinitesimal area element on the surface and is directed along the outward normal to the surface. Since no tangential force can be exerted on the sphere, only component $P_{rr}(\omega)$ of the pressure tensor contributes. From Eq. (5.16), we obtain

$$\vec{F}_\omega = \frac{4\pi}{3}\frac{R^2 u_\omega^0 \hat{z}}{\Delta}\left\{(i\omega\rho_0)RD_l\left[X_+A_+\left(C_- + \frac{4\eta_1}{R}D_-\right) - X_-A_-\left(C_+ + \frac{4\eta_1}{R}D_+\right)\right] - 4\eta_1\eta(3D_l - i{\not k}_l^2R^2)[k_+^2D_+A_-X_- - k_-^2D_-A_+X_+]\right\}. \tag{5.17}$$

Equation (5.17) gives the friction force on a smooth sphere moving in a fluid composed of particles which have rotational degrees of freedom, when inertial effects are included.

As a check on Eq. (5.17), it is useful to consider various limiting cases. In the limit $\eta_3 \to 0$, the rotational modes decouple from the translational modes and we obtain

$$\vec{F}_\omega = \frac{\frac{4\pi}{3}u_\omega^0\eta_1 k_-^2 R\hat{z}\{D_l[18D_- - k_-^2R^2(k_-R + 3i)] - 4i{\not k}_l^2 D_- R^2\}}{[(k_-R + 3i)(i{\not k}_l^2 k_-^2 R^2 - 2D_l k_-^2) - 2i{\not k}_l^2 D_-]}, \tag{5.18}$$

where now

$$k_-^2 = \frac{i\omega\rho_0}{\eta_1}. \tag{5.19}$$

Thus, all information relating to rotational motion has cancelled out as it should. This expression for the frictional force has been obtained by Zwanzig and Bixon.[6] The limit of an incompressible fluid is found by setting ${\not k}_l \to 0$. Then we obtain

$$\vec{F}_\omega = -4\pi\eta_1 R u_\omega^0 \hat{z}\left(1 + \frac{2k_-R}{k_-R + 3i} - \frac{k_-^2R^2}{6}\right). \tag{5.20}$$

Finally, let us take the static limit ($\omega \to 0$). In that case, the friction force reduces to the well known result obtained by Stokes

$$\vec{F}_0 = -4\pi\eta_1 R u_0^0 \hat{z}. \tag{5.21}$$

It is also of interest to find the friction force in the static limit when the rotational modes are allowed to contribute. If we let $\omega \to 0$ in Eq. (5.18), we find

$$\vec{F}_0 = \frac{-4\pi\eta_1 R u_0^0 \hat{z}\left[3\eta_1 D_+^0(\xi + 2\xi_1) - (\eta_1 + 2\eta)iR^2\left(\frac{4\eta_1\eta_3}{\eta}\right)\right]}{(\eta + 2\eta_1)\left(D_+^0(\xi + 2\xi_1) + \frac{\eta_3}{\eta}i[4\eta_1R^2 - (\xi + 2\xi_1)]\right)}, \tag{5.22}$$

where

$$D_+^0 = i\left[R\left(\frac{4\eta_1\eta_3}{\eta\xi}\right)^{1/2} + 1\right]. \tag{5.23}$$

Thus, we see that even for a smooth hard sphere, rotational modes in the fluid can substantially change the friction. Corrections to the static friction which result from rotational modes go to zero as $\eta_3 \to 0$.

VI. VELOCITY AUTOCORRELATION FOR THE BROWNIAN PARTICLE

Now that we have determined the friction force on the hard sphere, we can focus on the motion of sphere. The equation of motion for the sphere can be written

$$m\frac{du(t)}{dt} + \int_{-\infty}^{\infty}\alpha(t - t')u(t')\,dt' = F_{ex}(t) + F_{rand}(t), \tag{6.1}$$

where $\alpha(t)$ is a memory-dependent friction force whose Fourier transform $\tilde{\alpha}(\omega)$ is just

$$\tilde{\alpha}(\omega) = -\frac{F_\omega}{u_\omega^0} \tag{6.2}$$

[cf. Eq. (5.17)]. The friction force is assumed to be causal [$\alpha(t) = 0$ for $t < 0$ and $\alpha(t) \neq 0$ for $t > 0$]. On the right hand side of Eq. (6.1), $F_{ex}(t)$ is an external force which couples to the hard sphere and $F_{rand}(t)$ represents the effect of random fluctuating forces on the sphere due to the medium in which it is embedded. We shall assume that

$$\langle F_{rand}(t)\rangle = 0 \text{ and } \langle F_{rand}(t')u(t)\rangle = 0. \tag{6.3}$$

The average is taken with respect to the probability distribution for $F_{rand}(t)$. We expect that temporal variations in the velocity of the sphere will be much slower than those of the random force, so the average of the product of $F_{rand}(t)$ and $u(t)$ is zero. The autocorrelation function for the random force $\langle F_{rand}(t)F_{rand}(t')\rangle$ is determined from the friction force through use of the fluctuation-dissipation theorem.[7-11]

The linear response of the sphere to an external field is most easily determined by first finding the response function $\phi(t)$ which is defined through the equation

$$\langle u(t)\rangle = \int_{-\infty}^{\infty} \phi(t-t')F_{ex}(t')\,dt' . \tag{6.4}$$

$\phi(t)$ is assumed to be causal. Let us now take the average of Eq. (6.1)

$$m\frac{d}{dt}\langle u(t)\rangle + \int_{-\infty}^{\infty} \alpha(t-t')\langle u(t')\rangle dt' = F_{ex}(t) . \tag{6.5}$$

Then we can substitute Eq. (6.4) into Eq. (6.5), take the Fourier transform, and we obtain

$$\phi(\omega) = \frac{1}{-im\omega + \tilde{\alpha}(\omega)} , \tag{6.6}$$

where

$$\phi(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\,\tilde{\phi}(\omega) . \tag{6.7}$$

From Eq. (6.6) we can find the linear response of the system to any external force;

$$\langle u(t)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\,\tilde{\phi}(\omega)\tilde{F}_{ex}(\omega) , \tag{6.8}$$

where $\tilde{F}_{ex}(\omega)$ is the Fourier transform of the external force.

We next obtain the velocity-autocorrelation function of the hard sphere. If we multiply Eq. (6.1) by $u(t'')$ and take the average we find

$$m\frac{d}{dt}\langle u(t)u(t'')\rangle + \int_{-\infty}^{\infty} \alpha(t-t')\langle u(t')u(t'')\rangle dt' = 0 \tag{6.9}$$

[we have assumed that $F_{ex}(t)=0$]. From this equation we can readily show that the Fourier transform of the autocorrelation function is given by

$$\langle \tilde{u}(\omega)\tilde{u}(\omega')\rangle = 2\pi k_B T\delta(\omega+\omega')[\tilde{\phi}(\omega)+\tilde{\phi}^*(\omega)] , \tag{6.10}$$

where the asterisk denotes complex conjugation and k_B is Boltzmann's constant. To obtain Eq. (6.10) we use the equipartition theorem to write $\langle u^2(0)\rangle = k_B T/m$. From the fluctuation-dissipation theorem the correlation function for the random force can be written

$$\langle \tilde{F}_{rand}(\omega)\tilde{F}_{rand}(\omega')\rangle = \frac{\langle \tilde{u}(\omega)\tilde{u}(\omega')\rangle}{\tilde{\phi}(\omega)\tilde{\phi}^*(\omega)} . \tag{6.11}$$

As a rule the noise on the sphere will not be "white" when the friction force includes frequency-dependent effects.

We can now simplify the expression for the velocity-autocorrelation function and find its long time behavior. The velocity-autocorrelation function can be written

$$\langle u(t)u(0)\rangle = \frac{k_B T}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\left(\frac{1}{-i\omega m+\tilde{\alpha}(\omega)} + \frac{1}{i\omega m+\tilde{\alpha}^*(\omega)}\right) . \tag{6.12}$$

Since the response function $\phi(t)$ is causal, $\tilde{\phi}(\omega)$ will have no poles in the upper half complex-frequency plane. Furthermore, because $\alpha(t)$ is real, $\tilde{\alpha}^*(\omega)=\tilde{\alpha}(-\omega)$ [one can show this explicitly in Eq. (5.17)]. Thus by letting $\omega \to -\omega$ in the second term, we obtain an integral involving $\tilde{\phi}(\omega)$ which must be closed in the upper half complex-frequency plane and we get no contribution. Then we find

$$\langle u(t)u(0)\rangle = \frac{k_B T}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\left(\frac{1}{-i\omega m+\tilde{\alpha}(\omega)}\right) . \tag{6.13}$$

We can evaluate Eq. (6.13) by finding an appropriate contour in the lower half plane.

Before attempting to evaluate Eq. (6.13), we must find the branch points of $\tilde{\alpha}(z)$, where z is now a complex frequency. This is the same as finding the branch points of $k_\pm(z)$ [cf. Eq. (4.27)]. One can easily show that $k_+(z)$ has branch points at $z=0$ and $z=-i\{(a-b)\pm[(a-b)^2-a^2]^{-1/2}\}/\rho_0$, where $a=4\eta_1\eta_3/(I_0\eta-\xi)$ and $b=8\eta_3^2\xi/(I_0\eta-\xi)^2$; and $k_-(z)$ has branch points for $z=-4\eta_3 i/\rho_0 I_0$ and $z=-i\{(a-b)\pm[(a-b)^2-a^2]^{1/2}\}/\rho_0$. Thus Eq. (6.13) may be evaluated using the contour in Fig. 1. However, if we note that the function $\tilde{\alpha}(\omega)$ remains unchanged under the interchange $k_+ \leftrightarrow k_-$, we find that the contributions from branch cuts associated to the branch points $-i\{(a-b)\pm[(a-b)^2-a^2]^{1/2}\}/\rho_0$ cancel and we obtain the following expression for the correlation function

$$\begin{aligned}\langle u(t)u(0)\rangle = {} & \frac{k_B T i}{2\pi}\int_0^{\infty} dr\, e^{-rt}\left[\left(\frac{1}{-mr+\tilde{\alpha}(re^{3\pi i/2})} - \frac{1}{-mr+\tilde{\alpha}(re^{-\pi i/2})}\right)\right] \\ & + \frac{k_B T i}{2\pi}e^{-ct}\int_0^{\infty} dr\, e^{-rt}\left[\left(\frac{1}{-m(C+r)+\tilde{\alpha}(-ic+re^{3\pi i/2})}\right) - \left(\frac{1}{-m(C+r)+\tilde{\alpha}(-iC+re^{-\pi i/2})}\right)\right] \\ & + (\text{contribution from poles within contour}) ,\end{aligned} \tag{6.14}$$

where $C=4\eta_3/\rho_0 I_0$. The expression for $\tilde{\alpha}(\omega)$ is too complicated for us to search for poles within the contour analytically. If explicit values for the transport coefficients are used, they can be found numerically. However, in the limit $\eta_3 \to 0$ no poles exist within the contour, so it is unlikely that they will be found for $\eta_3 \pm 0$.

The long-time contribution to the correlation

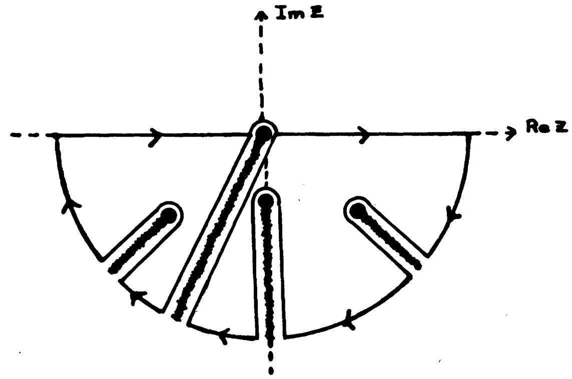

FIG. 1. Integration contour in the lower half complex-frequency plane for the velocity-autocorrelation function. Contributions from the two complex branch points in the lower half plane cancel.

function[7] comes from the first integral in Eq. (6.14) (the branch point at $z=0$). The second integral dies away exponentially. The long time behavior of the correlation function comes from small values of r since contributions for large r are exponentially small. Thus we can obtain the long-time limit by expanding the integral in powers of $\sqrt{r}$. This is straightforward but tedious. Let us first note that

$$\tilde{\alpha}(\omega)=a+ab\sqrt{\omega}(1-i)\,, \tag{6.15}$$

where

$$a=\frac{4\pi R\eta_1[(\eta_1+2\eta)a_+-2\eta_3 d_+(\xi+2\xi_1)]}{\left[(\eta+2\eta_1)a_+-\eta_3(\xi+2\xi_1)\left(d_++\frac{2\eta_1}{\eta}\right)\right]} \tag{6.16}$$

and

$$b=\frac{\sqrt{2}\,\eta_1 R a_+\left(\frac{\rho_0}{\eta_1}\right)^{1/2}}{\left[(\eta+2\eta_1)a_+-\eta_3(\xi+2\xi_1)\left(d_++\frac{2\eta_1}{\eta}\right)\right]} \tag{6.17}$$

In Eqs. (6.16) and (6.17)

$$d_+=1+R\left(\frac{4\eta_1\eta_3}{\eta\xi}\right)^{1/2} \tag{6.18}$$

and

$$a_+=(\xi+2\xi_1)\left[1+R\left(\frac{4\eta_1\eta_3}{\eta\xi}\right)^{1/2}\right]+\frac{4\eta_1\eta_3}{\eta}R^2\,. \tag{6.19}$$

We thus find that

$$\alpha(re^{3\pi i/2})=a+\sqrt{2}\,ab\sqrt{r}\,i \tag{6.20}$$

and

$$\alpha(re^{-\pi i/2})=a-\sqrt{2}\,ab\sqrt{r}\,i\,, \tag{6.21}$$

and the long-time limit of the velocity-autocorrelation function becomes

$$\langle u(t)u(0)\rangle=\frac{2k_BT}{\rho_0}\left(\frac{\rho_0}{4\pi\eta_1 t}\right)^{3/2}\left(\frac{\eta_1 a_+}{(\eta_1+2\eta)a_+-2\eta_3 d_+(\xi+2\xi_1)}\right)\xrightarrow[\eta_3\to 0]{}\frac{2k_BT}{3\rho_0}\left(\frac{\rho_0}{4\pi\eta_1 t}\right)^{3/2}. \tag{6.22}$$

Thus we obtain a $t^{-3/2}$ tail but with a coefficient which is altered by the transport processes associated with the internal degrees of freedom.

Contributions from transport processes associated with internal degrees of freedom cancel out of Eq. (6.22) when $\eta_3\to 0$. Grad[3] estimates the size of η_3 for gases to be

$$\eta_3\sim\frac{I_0}{\lambda^2}\eta_1\,, \tag{6.23}$$

where λ is the mean free path and $\sqrt{I_0}$ is the effective radius of gyration of the particles in the fluid. Thus for gases, effects of internal degrees of freedom can be neglected. However, for dense gases or liquids where internal and translational degrees of freedom are more strongly coupled, the effects might be quite large.

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