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Translational and Rotational Diffusion of an Anisotropic Particle in a Molecular Liquid: Long-Time Tails and Brownian Limit

A. J. Masters[1] **and T. Keyes**[2]

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Formally exact equations are written down, describing the translational and rotational diffusion of an anisotropic tagged particle in a fluid of anisotropic particles. These equations are tractable in the long-time limit, and reduce to the solution of ordinary hydrodynamic equations supplemented by slip boundary conditions in the Brownian limit for a smooth tagged particle. No rotational viscosities or spin-diffusion constants appear in these results. The relation to other work is discussed.

KEY WORDS: Mode coupling; long time tails; Brownian, Stokes–Einstein law; rotational viscosity; spin field.

1. INTRODUCTION

When a tagged particle moves through a fluid, its collisions with the fluid molecules have the effect of setting up flow fields in the fluid which at later times react back upon the tagged particle. These flow fields are responsible for the famous long-time tail of the velocity correlation function (VCF), which is proportional to $t^{-3/2}$ in three dimensions,$^{(1,2)}$ where t is the time. When the tagged particle is very large and massive, the Brownian limit, these flow fields may be calculated by solving the fluid hydrodynamic equations subject to boundary conditions imposed at the particle's surface. This calculation gives rise to the Stokes–Einstein form for the diffusion constant, D, and yields an expression for the constant of proportionality multiplying the $t^{-3/2}$ tail. Away from this Brownian limit, though, there

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[1] RSRE, St. Andrews Road, Malvern, Worcs WR14 3PS United Kingdom.
[2] Department of Chemistry, Boston University, Boston, Massachusetts 02215.

would appear to be no justification for using the continuum hydrodynamic equations (although it must be noted that in practice they seem to give excellent results even for the case of self-diffusion,(3,4)) so a more fundamental, microscopic theory is then required. Many of the microscopic theories so far developed have considered the special case of a smooth, hard sphere moving in a fluid of smooth, hard spheres. In this situation it is natural to use the methods of kinetic theory. These techniques have given a microscopic justification for the hydrodynamic approach in the Brownian limit, in the cases when the fluid is a dilute gas,(5,7) a moderately dense gas,(8,9) and a fluid of any density.(10) For these smooth sphere interactions, the appropriate hydrodynamic boundary conditions turned out to be the "slip" ones. In addition, these theories were able to give a simple expression for the long-time behavior of the VCF for a particle of arbitrary mass and size(9–14)—a result that was in perfect agreement with earlier mode-coupling calculations.(15) If one were instead to consider a system of particles interacting via continuous, spherically symmetric potentials rather than hard sphere ones, then methods that might best be described as mode-coupling-like would appear to be the easiest to apply, and indeed, when some care is taken, the expected Brownian and long-time limits again emerge.(10,16,17)

Most real liquids, though, are not composed of spherical molecules. The particles instead interact via anisotropic potentials, and they also rotate. The tagged particle, even a spherical Brownian particle, is not normally a smooth sphere—there is generally some surface roughness and it may also possess some internal degrees of freedom, i.e., it might have its own, internal temperature. It would therefore be of interest to extend the above microscopic theories to take account of these extra effects, and one might also hope to calculate the rotational diffusion constant, D_r, and the angular momentum correlation function (AMCF). In the Brownian limit, one should again be able to calculate these quantities using the fluid hydrodynamic equations, but this time applying "stick" boundary conditions at the tagged particle's surface. For the case of a spherical Brownian particle, the Stokes–Einstein–Debye form for D_r is obtained, and the AMCF is predicted to have at $t^{-5/2}$ tail in three dimensions.(18,19) Turning now to microscopic theories, Mehaffey, Desai, and Kapral(20) derived a "ring" kinetic equation describing a rough-sphere tagged particle moving in a moderately dense rough sphere fluid, and obtained the long-time forms both of the VCF and the AMCF for a tagged particle of arbitrary mass and size. In the Brownian limit, these coefficients agreed perfectly with those obtained from the hydrodynamic calculation. Van Beijeren and Dorfman(5) have considered the flow of a dilute gas past a fixed sphere, with the gas consisting of nonrotating spheres which interacted with the fixed sphere via both a specular and a diffuse reflection mechanism. They showed that in the diffusely reflecting case it was the stick boundary conditions which were appropriate, and this led to the stick hydrodynamic results for the drag and the torque on the fixed sphere. Thus this constituted a microscopic justification of the stick boundary condition for this system. Their results, when combined with the Stokes and Stokes–Debye relations, yielded the usual expressions for the Brownian limits of the VCF and AMCF. A model system in which a gas molecule's velocity is reversed upon colliding with the fixed sphere also seems to lead to stick boundary conditions.(16,21) So far, however, there exists no general microscopic derivation of the stick boundary condition for fluids of arbitrary density, though further understanding is coming through the study of model systems.(22)

When the fluid contains rotating molecules, however, people have wondered whether the normal hydrodynamic equations gave an adequate description of the fluid, even in the Brownian limit. The normal equations reflect the conservation of the mass, momentum, and energy of the fluid. However the angular momentum is also a conserved variable, and taking this into account leads to an additional set of hydrodynamic equations involving the spin field of the fluid and new transport coefficients, such as η_r, the rotational viscosity.(23,24) A mode-coupling calculation by Keyes and Ladanyi(25) led to an expression for D_r in the Brownian limit that involved η_r. Hydrodynamical calculations for a spherical tagged particle have also been carried out by Hynes, Kapral, and Weinberg(26) and Reichl.(27) By assuming certain boundary conditions on the spin field at the tagged particle's surface, they obtained new expressions for D, D_r, and the long-time tails of the VCF and AMCF, both for smooth and rough spheres. Reichl was able to use her results in order to explain why the light-scattering experiments of Paul and Pusey(28a) yielded values for D and the long-time coefficient of the VCF at variance with the predictions of more conventional hydrodynamic theories, and was in fact able to extract estimates of the values of η_r and the spin-diffusion coefficient ξ. Later experimental work by Ohbayashi *et al.*,(28b) however, gave values for D and the long-time tail in good agreement with the predictions of "conventional" hydrodynamics. Thus, at present, there is no consensus as to what the true experimental results are, so it is not clear whether there is any need to hunt for effects above and beyond conventional hydrodynamics.

It would therefore seem, in the light of all this, that a complete microscopic theory would be highly desirable. Firstly one would like to more fully investigate the basis of the augmented hydrodynamic equations and boundary conditions used above. Secondly a microscopic theory might also be able to calculate the long-time behavior of the VCF and AVCF away from the Brownian limit, and not be restricted to having either a dilute fluid or spherical particles. Thus, in the following, we consider a tagged particle of arbitrary mass, size, and shape in a fluid of nonspherical, rotating molecules, and we take the potentials of interaction to be continuous, albeit harshly repulsive, as the particles get near each other. The methods to be used are simple extensions of those used to investigate the smooth sphere system.(10) We do not here consider the possible effects of other internal degrees of freedom—that is, our tagged particle does not possess an internal temperature. This could well be an effect very relevant for understanding the stick boundary condition(5,22)—it certainly must be important if one were dealing with problems involving heat transport. Our system, however, does at least formally include the effects of surface roughness. Thus in the following sections we consider the long-time and Brownian limits of the VCF and AMCF, comparing our results with those obtained by other means. The resolution of the problem of stick still eludes us, however, but this has not prevented us from offering some analysis and thoughts on the matter toward the end of the paper.

2. A BRIEF REVIEW OF HYDRODYNAMICS AND COLLECTIVE ANGULAR-MOMENTUM FLUCTUATIONS IN MOLECULAR FLUIDS

In this section we give a quick resumé of some of the results obtained by Ailawadi *et al.*(24) in their investigation of the hydrodynamics of a molecular fluid, as many of the results will be used later on. They chose as dynamical variables the Fourier components of the densities of the locally conserved variables of the fluid—that is, the number density, $n_{\mathbf{k}}$, the momentum density, $\mathbf{p}_{\mathbf{k}}$, and the energy density, $e_{\mathbf{k}}$—and in addition they included the spin density, $\mathbf{J}_{\mathbf{k}}$. The definitions are

$$n_{\mathbf{k}} = \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \tag{1a}$$

$$\mathbf{p}_{\mathbf{k}} = \sum_i \mathbf{p}_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \tag{1b}$$

$$e_{\mathbf{k}} = \sum_i e_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \tag{1c}$$

and

$$\mathbf{J}_{\mathbf{k}} = \sum_i \mathbf{J}_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \tag{1d}$$

where $\mathbf{r}_i$, $\mathbf{p}_i$, and e_i are the center-of-mass position, momentum, and total energy of particle i, and $\mathbf{J}_i$ is its angular momentum about its center of mass. Mori's generalized Langevin equation$^{(29)}$ was then used to write down expressions for the time correlation functions of these variables in the hydrodynamic limit—that is, for small **k** and long times. Defining the z direction to be parallel to **k**, they showed that symmetry considerations prevented any coupling between $J^z_{\mathbf{k}}$ and the other variables, to lowest order in **k**. Furthermore the transverse components of $\mathbf{J}_{\mathbf{k}}$ only coupled to the transverse momentum density. This meant that in addition to the normal hydrodynamic equations involving $n_{\mathbf{k}}$, $p^z_{\mathbf{k}}$ and $e_{\mathbf{k}}$, they obtained the additional results that

$$\langle J^z_{\mathbf{k}}(z)\, J^z_{-\mathbf{k}}\rangle = \frac{\rho V_{\text{tot}} I k_B T}{z + 4\eta_r/\rho m} \tag{2a}$$

$$\langle p^x_{\mathbf{k}}(z)\, p^x_{-\mathbf{k}}\rangle = \rho V_{\text{tot}} m k_B T \left\{\frac{1}{z + k^2\eta/\rho m} + \left(\frac{k^2 I}{4\rho}\right)\frac{1}{z + 4\eta_r/I\rho}\right\} \tag{2b}$$

$$\begin{aligned}\langle p^x_{\mathbf{k}}(z)\, J^y_{-\mathbf{k}}\rangle &= \langle J^y_{\mathbf{k}}(z)\, p^x_{-k}\rangle^* \\ &= \rho V_{\text{tot}} m k_B T \left\{\left(\frac{ik}{2}\right)\frac{1}{z + k^2\eta/\rho m} + \frac{1}{z + 4\eta_r/I\rho}\right\}\end{aligned} \tag{2c}$$

and

$$\langle J^y_{\mathbf{k}}(z)\, J^y_{-\mathbf{k}}\rangle = \rho V_{\text{tot}} I k_B T \left\{\left(\frac{k^2 I}{4m}\right)\frac{1}{z + k^2\eta/\rho m} + \frac{1}{z + 4\eta_r/I\rho}\right\} \tag{2d}$$

These expressions are the Laplace transforms of the time correlation functions with z being the transform variable. The notation is that ρ is the average number density of the fluid, V_{tot} the total volume of the system, k_B Boltzmann's constant, T the absolute temperature, m and I the mass and moment of inertia of a fluid molecule ($I = \frac{1}{3}\operatorname{Tr}\vec{I}$), and η and η_r the shear and rotational viscosities, respectively. We have only considered the low-k and small-z (long time) limit here—there will be higher-order terms in the numerators and denominators of these expressions, among which the spin diffusion constant, ξ, appears. The microscopic definitions of η and η_r, involving the Mori projected time evolution operator, are given in Ref. 24, along with a detailed discusion. With these results for the bulk fluid for reference, we now can turn to the problems of calculating the VCF and AMCF of a tagged particle in a molecular fluid.

3. THE TRANSLATIONAL DIFFUSION CONSTANT AND THE VCF

As was stated in the Introduction, it is via the mutual forces exerted by the fluid particles and tagged particle on each other that the tagged particle's motion gets coupled to flow fields in the fluid, which lead to the long-time tails and Stokes–Einstein behavior. Thus in this section we investigate the VCF using very similar methods to those used in Ref. 10 (henceforth to be called I)—that is, the VCF is firstly related to a force correlation function, and then the force correlation function is analyzed in terms of the hydrodynamic fluid variables, this analysis being conducted in real space, as opposed to **k** space, in order to allow greater physical insight into what the various manipulations mean.

The VCF, denoted by $C(t)$, is given by

$$C(t) = \langle \mathbf{V}_1(t) \cdot \mathbf{V}_1 \rangle \tag{3}$$

where $\mathbf{V}_1$ is the velocity of the tagged particle. By using Mori's generalized Langevin equation,(29) we may express the Laplace transform of the VCF, $C(z)$, as

$$\begin{aligned} C(z) &= \int_0^\infty dt\, e^{-zt} C(t) \\ &= \frac{3k_B T/m_1}{z + \nu(z)} \end{aligned} \tag{4a}$$

where $\nu(z)$, the friction coefficient, is given by

$$\nu(z) = (3m_1 k_B T)^{-1} \langle \{[Z - Q_1 i\mathscr{L}]^{-1}\, \mathbf{F}_1\} \cdot \mathbf{F}_1 \rangle \tag{4b}$$

Here m_1 is the mass of the tagged particle, $\mathbf{F}_1$ is the force exerted by the fluid upon the tagged particle, $i\mathscr{L}$ is the Liouville operator, Q_1 is the Mori projection operator that projects a dynamical variable orthogonal to $\mathbf{V}_1$, and we are working in three dimensions.

We now couple $\mathbf{F}_1$ to the local fluctuations of the fluid's number, momentum, energy, and spin density around the tagged particle. Thus we introduce the variables

$$\alpha'_n(\bar{1}, \bar{2}) = \sum_{i>1} \delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1i})\, \delta(\bar{\Omega}_1 - \Omega_1)\, \delta(\bar{\Omega}_2 - \Omega_i) \tag{5a}$$

$$\mathbf{a}_p(\bar{1}, \bar{2}) = \sum_{i>1} \mathbf{p}_i \delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1i})\, \delta(\bar{\Omega}_1 - \Omega_1)\, \delta(\bar{\Omega}_2 - \Omega_i) \tag{5b}$$

$$\mathbf{a}_J(\bar{1}, \bar{2}) = \sum_{i>1} \mathbf{J}_i \delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1i})\, \delta(\bar{\Omega}_1 - \Omega_1)\, \delta(\bar{\Omega}_2 - \Omega_i) \tag{5c}$$

and

$$a_e(\bar{1}, \bar{2}) = \sum_{i>1} e_i \delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1i})\, \delta(\bar{\Omega}_1 - \Omega_1)\, \delta(\bar{\Omega}_2 - \Omega_i) \tag{5d}$$

where the barred variables are field variables, the unbarred dynamical variables. Ω_1 and Ω_i denote the Euler angles of particles 1 and i, $\mathbf{J}_i$ is, as before, the angular momentum of particle i about its center of mass, and e_i is the energy of the ith fluid molecule, and is given by

$$e_i = \frac{p_i^2}{2m} + \frac{J_i^2}{2I} + U(1, i) + \frac{1}{2} \sum_{\substack{j \neq i \\ i,j > 1}} U(i, j) \tag{5e}$$

where $U(i, j)$ is the anisotropic, pair potential of interaction between molecules i and j. In the subsequent analysis these potentials are taken to be short ranged and continuous, being harshly repulsive when the particles get very close. As these potentials are taken to be finite everywhere, although extremely large in regions of overlap, there is always a finite probability of finding the molecules at any distance apart. Thus, unlike the case of hard particle interactions, $\mathbf{r}_{12}$ may take on all values in Eqs. (5a)–(5d). Furthermore, again as in I, it is convenient to work with orthogonal, fluctuating quantities, so we introduce $a_n(\bar{1}, \bar{2})$ and $a_T(\bar{1}, \bar{2})$, given by

$$a_n(\bar{1}, \bar{2}) = a_n'(\bar{1}, \bar{2}) - \langle a_n'(\bar{1}, \bar{2}) \rangle \tag{6a}$$

and schematically

$$a_T = a_e - \langle a_e \rangle - \langle a_e a_n \rangle \langle a_n a_n \rangle^{-1} a_n \tag{6b}$$

so that $a_T(\bar{1}, \bar{2})$ is orthogonal to a_n, for all values of the field variables. We called the variable a_T because it is closely related to the local temperature fluctuations in the fluid.

We now analyze $v(z)$ in terms of these variables for all values of the field variables. Firstly we note that $\mathbf{F}_1$ is given exactly as an integral over $a_n(1, 2)$, i.e.,

$$F_1 = \int d\bar{1}\, d\bar{2}\, \nabla_1 U(\bar{1}, \bar{2})\, a_n(\bar{1}, \bar{2}) \tag{7}$$

where $d\bar{1} \equiv d\bar{r}_1\, d\bar{\Omega}_1$ and $d\bar{2} \equiv d\bar{r}_2\, d\bar{\Omega}_2$. Alternatively we may write, schematically, that

$$\mathbf{F}_1 = \langle \mathbf{F}_1 a_n \rangle \langle a_n a_n \rangle^{-1} a_n \tag{8}$$

which simply stresses the point that $\mathbf{F}_1$ is simply a linear combination of the variable a_n at various field points. By using the continued fraction method of Mori theory we obtain the result

$$v(z) = (3m_1 k_B T)^{-1} \langle \mathbf{F}_1 a_n(12) \rangle * RR_{nn}(12; 1'2') * \langle a_n(1'2')\, \mathbf{F}_1 \rangle \tag{9}$$

where the asterisk means integrate over repeated variables (both angular and spatial), and the angled brackets denote a grand canonical ensemble average. For convenience we have dropped the bars over the field variables. The quantity RR_{nn} is given by the coupled integral equations

$$RR_{\alpha\beta}(12;1'2') * RR^{-1}_{\beta\gamma}(1'2';1''2'') = \delta_{\alpha\gamma}\delta(1-1'')\,\delta(2-2'') \tag{10a}$$

and

$$\begin{aligned} RR^{-1}_{\alpha\beta}(12;1'2') = {} & z\langle a_\alpha(12)\,a_\beta(1'2')\rangle - \langle (Q_1 i\mathscr{L} a_\alpha(12))\,a_\beta(1'2')\rangle \\ & + \langle \{[z - Qi\mathscr{L}]^{-1}\, Qi\mathscr{L} a_\alpha(12)\}\, Qi\mathscr{L} a_\beta(1'2')\rangle \end{aligned} \tag{10b}$$

In these equations the Greek suffixes assume the labels n, p, J, and T, and summation convention is used. Furthermore a repeated suffix also implies a scalar product when the suffix takes on the labels p or J. The Mori projection operator Q projects a dynamical variable orthogonal to $\mathbf{V}_1$ and also to $a_\alpha(12)$, for all values of α and field variables.

We now investigate the small-z limit of $v(z)$, which leads to the long-time tail in $C(t)$. As the ideas involved here are almost identical to those in I, we shall proceed fairly rapidly. We define the far-field form of RR^{-1} to be R^{-1}, so that

$$R^{-1}_{\alpha\beta}(12;1'2') = \lim_{|\mathbf{r}_{12}|\to\infty} RR^{-1}_{\alpha\beta}(12;1'2') \tag{11}$$

and thus

$$RR^{-1}_{\alpha\beta}(12;1'2') = R^{-1}_{\alpha\beta}(12;1'2') - S_{\alpha\beta}(12;1'2') \tag{12}$$

where $S_{\alpha\beta}$ contains all the near-field complexities. We use a frequency expansion, with the notation that a zero superscript means the $z=0$ value of the quantity, a superscript of 1, the first-order correction, and so on. In three dimensions we would expect $C^{(1)}(z) \propto z^{1/2}$. We can then show that

$$\begin{aligned} v^{(1)}(z) = {} & (3m_1 k_B T)^{-1} \langle \mathbf{F}_1 a_n\rangle * (1 + RR^{(0)} * S^{(0)})_{n\beta} * R^{(1)}_{\beta\gamma} \\ & * (1 + S^{(0)} * RR^{(0)})_{\gamma n} * \langle a_n \mathbf{F}_1\rangle \end{aligned} \tag{13}$$

We have left out here the field variable arguments, but hopefully the form of the full equation is still clear. The "1" represents the same product of delta functions and Kronecker deltas as is given on the right-hand side of Eq. (10a). In order to get this equation, we used the facts that the z dependence of the memory function in Eq. (10b) (the term involving Q), was irrelevant as far as $v^{(1)}$ is concerned, so that $S^{(1)}$ makes no appearance, and also that the Fourier transform of $S^{(0)}$ with respect to $\mathbf{k}_1$ and $\mathbf{k}_2$ contained no part proportional to $\delta(\mathbf{k}_1 - \mathbf{k}_2)$.

To proceed further we introduce the definition

$$T_{k;k'}^{l_1l_2;l_1'l_2'} = \int d1\, d2\, d1'\, d2'\, e^{i\mathbf{k}\cdot\mathbf{r}_{12}} D_{m_1n_1}^{l_1}(\Omega_1)\, D_{m_2n_2}^{l_2}(\Omega_2)$$
$$\times\, T(12;1'2')\, e^{-i\mathbf{k}\cdot\mathbf{r}_{12}'} D_{m_1'n_1'}^{l_1'}(\Omega_1')^*\, D_{m_2'n_2'}^{l_2'}(\Omega_2')^* \tag{14}$$

where $T(12; 1\,2)$ is an arbitrary function of the field points, and D_{mn}^{l} is a Wigner rotation matrix.$^{(30)}$ For convenience we have left out the m, n dependence of the quantity on the left-hand side of Eq. (14). In the following, for the sake of brevity, we use l as shorthand for (l, m, n), so a sum over l also implies a sum over m and n. By using the orthogonality properties of these D_{mn}^{l}s and by inverse Fourier transforming, it is straightforward to invert this definition and obtain $T(12; 1'2')$ in terms of $T_{k;k'}^{l_1l_2;l_1'l_2'}$. Because the potentials of interaction are taken to be short ranged, and because we also assume we are not near a critical point, $R_{\alpha\beta}(12; 1'2')$ describes pure fluid and pure tagged particle dynamics, with no correlation between the fluctuations as the processes are taking place far apart. We thus find that $R_{\mathbf{k};\mathbf{k}'}^{l_1l_2;l_1'l_2'}$ is diagonal—that is,

$$R_{\mathbf{k};\mathbf{k}'}^{l_1l_2;l_1'l_2'} = (2\pi)^3\, \delta(\mathbf{k}-\mathbf{k}')\, \delta_{l_1,l_1'}\delta_{l_2,l_2'} R_{\mathbf{k}}^{l_1l_2} \tag{15}$$

On inverting Eq. (14), and using Eq. (15), we obtain an expression for $R_{\alpha\beta}(12; 1'2')$ in terms of $R_{\alpha\beta;k;k'}^{l_1l_2;l_1'l_2'}$, which may be substituted into Eq. (13) to give

$$v^{(1)}(z) = (3m_1k_BT)^{-1}(2\pi)^3 \int d\mathbf{k}$$
$$\times \sum_{l_1,l_2} [\langle \mathbf{F}_1 a_n\rangle * (1 + RR^{(0)} * S^{(0)})_{n\alpha} * e^{-i\mathbf{k}\cdot\mathbf{r}_{12}} D_{m_1n_1}^{l_1^*}(\Omega_1)\, D_{m_2n_2}^{l_2^*}(\Omega_2)]$$
$$\times R_{\alpha\beta;\mathbf{k}}^{(1)l_1l_2} \cdot [e^{i\mathbf{k}\cdot\mathbf{r}_{12}'} D_{m_1n_1}^{l_1}(\Omega_1')\, D_{m_2n_2}^{l_2}(\Omega_2')(S^{(0)} * RR^{(0)} + 1)_{\beta n} * \langle a_n \mathbf{F}_1\rangle] \tag{16}$$

The long-time tail comes from the small $|\mathbf{k}|$ region of this integral ($k < k_c$, where k_c is a cut-off wave vector of the order of an inverse fluid correlation length). Let us therefore consider in detail the small-$|k|$ behavior of $R_{\alpha\beta;k}^{(l)l_1l_2}$. Firstly we note that only $l_1 = l_2 = 0$ terms can contribute to the long time tail. To see this consider the case when $l_2 = 0$ but $l_1 \neq 0$. Then one might conclude this term would give rise to an exponential long time decay, proportional to $\exp[-l_1(l_1 + l)\, D_r t]$ for $m_1 = n_1 = 0$, using the Debye formula for time correlation functions of the form $\langle D_{m_1n_1}^{l_1}(\Omega_1(t))\, D_{m_1n_1}^{l_1^*}(\Omega_1)\rangle$. A similar argument would also go through for terms for which $l_1 = 0$ but

$l_2 \neq 0$—again naively one might expect an exponential decay. Previous mode-coupling analysis,(31–34) however, has shown that these correlation functions have themselves got long time tails, and in general

$$\lim_{t \to \infty} \langle D^{l_1}_{m_1 n_1}(\Omega_1(t))\, e^{i\mathbf{k}\cdot\mathbf{r}_1(t)} D^{l_1^*}_{m_1 n_1}(\Omega_1)\, e^{-i\mathbf{k}\cdot\mathbf{r}_1}\rangle \propto t^{-(2c^{(l_1)}+3)/2} e^{-k^2\Gamma t} \tag{17}$$

where $c^{(l_1)} \geqslant 1$, and Γ is a constant. A similar form of long time behavior holds for collective fluid particle orientational decay. Furthermore some of these collective correlation functions contain terms proportional to $k^2 \exp[-k^2\Gamma' t]$ (Γ' a constant)—for example, for $l_2 = 2$, these terms arise from the coupling of the orientational variables to the fluid shear modes.(35a,b) In the formalism used here, all these effects are contained in the z dependence of the memory function in Eq. (10C), which we claimed had no influence on $v^{(1)}$. However, even if we use in Eq. (16) the z-dependent memory function form which corresponds to the above, we still find that the $l_1 = l_2 = 0$ term is the only contributor to the $t^{-3/2}$ long-time tail. The other terms only contribute to weaker power law behavior. A more formal justification of these statements may be given by conducting an analysis of the frequency-dependent memory function in Eq. (10C) in terms of trilinear variables. This is simply an extension of the analysis sketched out in the appendix of I.

Given that only $l_1 = l_2 = 0$ terms are important, it is further easy to show that, again as in *I*, the dominant long-time tail arises from the shear modes. That is, the long-time tail arises simply from $R^{(1),00}_{pp;\mathbf{k}}$ which is given by

$$R^{(1),00}_{pp;\mathbf{k}} = (\overleftrightarrow{1} - \hat{k}\hat{k}) \left\{ \frac{1}{z + k^2(\eta/\rho m + D)} - \frac{1}{k^2(\eta/\rho m + D)} \right\} (k_B T m \rho)^{-1}$$
$$+ \text{ longitudinal terms} \tag{18}$$

Here the caret denotes a unit vector, and $\overleftrightarrow{1}$ is the unit tensor. We have neglected higher-order terms in k or z in this expression, as they do not contribute to the long-time tail. Contributions from R_{JJ} and R_{pJ} are also of higher order in k than the term given above, so they also only give rise to a weaker power law long-time behavior. Thus, substitution of Eq. (18) into Eq. (16) and dropping all the other Rs in the sum, gives the result

$$v^{(1)}(z) = (3m_1 k_B T)^{-1}(2\pi)^{-3} \int_{|\mathbf{k}| < k_c} d\mathbf{k}\, f_1^{\mu\nu}(\mathbf{k})\, f_2^{\omega\mu}(\mathbf{k})\, R^{(1),00}_{p_\nu p_\omega;\mathbf{k}} \tag{19a}$$

where

$$f_1^{\mu\nu}(\mathbf{k}) = \int d1\, d2\, \langle \mathbf{F}_1^{\mu} a_n(1''2'')\rangle * RR^{(0)}_{n\alpha}(1''2''; 1'2')$$
$$* S^{(0)}_{\alpha p_\nu}(1'2'; 12)\, e^{-i\mathbf{k}\cdot\mathbf{r}_{12}} \tag{19b}$$

and

$$f_2^{\mu\nu}(\mathbf{k}) = \int d1\, d2\, e^{i\mathbf{k}\cdot\mathbf{r}_{12}} S_{p_\mu\alpha}^{(0)}(12;1'2') * RR_{\alpha n}^{(0)}(1'2';1''2'') \\ * \langle a_n(1''2'')\,\mathbf{F}_1^\nu\rangle \tag{19c}$$

where μ, ν, and ω are Cartesian components of the tensors. The long time tail comes from the $|\mathbf{k}| \to 0$ limits of $f_1(\mathbf{k})$ and $f_2(\mathbf{k})$, which are fortunately easily evaluated, because we have the results

$$\int d1\, d2\, S_{\alpha p}^{(0)}(1'2';12) = -\delta_{\alpha n}\langle \mathbf{F}_1 a_n(1'2')\rangle \tag{20a}$$

and

$$\int d1\, d2\, S_{p\alpha}^{(0)}(12;1'2') = +\delta_{\alpha n}\langle \mathbf{F}_1 a_n(1'2')\rangle \tag{20b}$$

The reason for the simplicity of this result is given in I. It is connected with the fact that the total momentum of the fluid can only change because of the forces exerted upon it by the tagged particle, whatever the complex fluid structure may be or whatever dynamical processes occur in the vicinity of this particle. Thus the integral over $S_{\alpha p}^{(0)}$ or $S_{p\alpha}^{(0)}$ simply reduces to terms involving the force exerted by the tagged particle on the bulk fluid, which by Newton's third law, is the negative of the force exerted on the tagged particle by the fluid. In our formalism this force only makes its appearance in the correlation function $\langle \mathbf{F}_1 a_n\rangle$. If now take the $z = 0$ limit of Eq. (9), giving

$$\nu^{(0)} = (3m_1 k_B T)^{-1}\langle \mathbf{F}_1^\mu a_n\rangle * RR_{nn}^{(0)} * \langle a_n \mathbf{F}_1^\mu\rangle \tag{21}$$

it is easy to see that

$$\begin{aligned} f_1^{\mu\nu}(0) &= -f_2^{\mu\nu}(0) \\ &= -m_1 k_B T \nu^{(0)} \delta_{\mu\nu} \end{aligned} \tag{22}$$

So all that is now needed to obtain the long-time tail of the VCF is to set $|k| = 0$ in $f_1(k)$ and $f_2(k)$ in Eq. (19a) and then substitute the expression for $\nu^{(1)}$ into the formula for $C^{(1)}$, which is

$$C^{(1)}(z) = -\frac{3k_B T}{m_1} \frac{\nu^{(1)}}{[\nu^{(0)}]^2} \tag{23}$$

which comes directly from Eq. (4a). Upon using Eq. (22) for $f_1(0)$ and

$f_1(0)$, we find that the $v^{(0)}$ terms in Eq. (23) cancel, and we are left, after inverse Laplace transforming and doing the k integral, with the final result.

$$\lim_{t \to \infty} C(t) = \frac{k_B T}{4m\rho} \left[\pi \left(\frac{\eta}{\rho m} + D \right) t \right]^{-3/2} \tag{24}$$

This is of the exact same form as that given by previous mode coupling methods and microscopic theories for the diffusion of spheres. There are several points of interest connected with this result. Firstly it should hold for arbitrary mass, shape, and size of the tagged particle. Secondly, the only point where the mass, shape, and size of the tagged particle enter the expression is via the translational diffusion constant D. If, as is often the case for self-diffusion, $D \ll \eta/\rho m$, then the long-time tail is determined almost entirely by fluid properties, irrespective of the nature of the diffusing particle. Thirdly we see that no rotational viscosity comes into the expression. We believe that this is quite reasonable, because although the angular momentum of the fluid is a conserved quantity, it is impossible to write down a local form for the angular momentum density—that is, it does not give rise to a true, hydrodynamic variable.(36) Thus as we expect the long-time behavior of $C(t)$ to be determined by the decay of true hydrodynamic fluctuations in the fluid, the absence of η_r does not surprise us. We do note, however, that this result differs from that given by Reichl,(27) whose tail coefficient does involve η_r, as well as ξ. Further calculations by Gegenmüller,(37) using the augmented hydrodynamical equations, seem to yield a long-time tail coefficient in agreement with Eq. (24) in the Brownian limit, and in agreement with the conventional hydrodynamic tail, for the case of a spherical particle with either slip or stick boundary conditions. We therefore are tempted to regard Eq. (24) as correct. Fourthly there is the problem of explaining the experimental results of Paul and Pusey,(28a) who found the tail coefficient to be only 75% of that given by conventional hydrodynamics or by Eq. (24). In our theory we have had to assume that the potentials of interaction were short ranged, and we also neglected internal degrees of freedom of the tagged particle. In the experimental work it would seem that the short-range potential criterion was satisfied. It is conceivable that the second assumption could have made all the difference, but this would seem to us to be very unlikely. Thus we have to admit that we have found no theoretical reason for the discrepancy and we live in hope that a more experimental reason for it can be found! The fact that Ohbayashi *et al.*(28b) obtained results in agreement with Eq. (24) suggests that "conventional" theory could well be entirely adequate.

We now turn to the Brownian limit. Again the development closely follows I, so we shall be brief. We introduce the functions, $f_\alpha(12)$, defined by

$$f_\alpha(12) = \langle \mathbf{F}_1 a_n(1'2') \rangle * RR_{n\alpha}(1'2'; 12) \tag{25}$$

so that $v(z)$ may be expressed in the form

$$v(z) = (3m_1 k_B T)^{-1}\, \mathbf{f}_n(12) * \langle a_n(12)\, \mathbf{F}_1 \rangle \tag{26}$$

where we have used Eq. (9). The functions $f_\alpha(12)$ obey the set of integral equations

$$f_\beta(12) * RR^{-1}_{\beta\gamma}(12; 1'2') = \langle \mathbf{F}_1 a_n(1'2') \rangle\, \delta_{n\gamma} \tag{27}$$

obtained from combining Eq. (25) with Eq. (10a). Because we are in the Brownian limit, we may completely ignore the tagged particle's translational and rotational motion in evaluating the correlation functions present in RR^{-1}. Although a completely rigorous proof of this statement is probably none too easy, it is almost certainly true, essentially coming about because in this limit $\eta/\rho m \gg D$ or D_r.

As in I, we now have to confront the difficulty that in order to calculate $v(z)$ from Eq. (26), we need to know $f_n(12)$ in the vicinity of the Brownian particle—that is, we need to know it in the boundary layer region. Unfortunately this is just the region in which we cannot simplify Eq. (27) by making use of a gradient expansion, because in this region $f_\alpha(12)$ varies on a molecular and not a Brownian length scale. Thus our strategy will be the following. We first use Eq. (27) to reexpress $v(z)$ simply in terms of the far-field forms of $f_\alpha(12)$. In fact it turns out that we do not even need the full functions $f_\alpha(12)$—all that we require are the functions $\bar{f}_\alpha(12)$, given by

$$\bar{f}_\alpha(12) = \int d\Omega_2\, f_\alpha(12) \tag{28}$$

Thus, for a given orientation of the Brownian particle, $\bar{f}_\alpha(12)$ only depends upon the vector $\mathbf{r}_{12}$. We then examine the large $|\mathbf{r}'_{12}|$ form of Eq. (27), which gives us hydrodynamic equations for the functions $\bar{f}_\alpha(12)$. Finally we use the full expression of Eq. (27) to attempt to find boundary conditions that these far-field functions have to obey at the edge of the boundary layer. Of course this has not yet given us an explicit expression for $v(z)$, but the object of this section is to investigate the microscopic basis of using hydrodynamic equations and boundary conditions. Once these have been accepted, then although solving the problem is in general very difficult, at least a well-defined starting point has been laid out.

To relate $v(z)$ to the far fields, consider Eq. (27) with $\gamma = p$. Let us integrate this equation over the angles Ω_2, and also over the volume V, where V is large enough so that outside of it the fluid properties may be considered to be unperturbed by the presence of the Brownian particle. Typically the surface, S, of this volume will lie on the order of several molecular correlation lengths (denoted by ξ) away from the "true" surface of the particle. If we let a typical dimension of the Brownian particle be R, then we have $\xi/R \ll 1$. In order to be a bit more definite about S and V, let us consider the quantity $\tilde{G}(12) = \int d\Omega_2 G(12)$ where $G(12)$ is the angular-dependent, two-particle distribution function, and let us, for a given orientation Ω_1, construct the contours of constant $\tilde{G}(12)$. We shall take S to be one of these contours, sufficiently far away from the tagged particle such that $\tilde{G}(12) \simeq 1$ to whatever accuracy we demand. We thus have the result

$$\int d\Omega_1\, d\Omega_2 \int_V d\mathbf{r}_{12}\, f_\alpha(1'2') * RR^{-1}_{\alpha p}(1'2'; 12) = 0 \qquad (29)$$

We now consider the sum term by term. For $\alpha = n$ and taking the trace of the tensors we have the result

$$\int_V d1'\, d2'\, \mathbf{f}_n(12) * RR^{-1}_{np}(12; 1'2')$$

$$= \rho k_B T \int d\Omega_1 \int_S d\hat{\sigma}\, \hat{\sigma} \cdot \tilde{\mathbf{f}}_n(12) - \mathbf{f}_n(12) * \langle a_n(12)\, \mathbf{F}_1 \rangle \qquad (30)$$

Here $\hat{\sigma}$ is the unit vector normal to the surface S. We see that the second term on the right-hand side is $(3m_1 k_B T)\, v(z)$, while the first term is a surface integral, which by definition means that on it the functions have their far-field forms.

We next set $\alpha = p$. Now the problem is a little more complicated, because we have to consider the dissipative term in Eq. (10b). As in I, however, we can make progress because the Mori projection operator Q projects out from $i\mathscr{L}\mathbf{a}_p(12)$ all terms involving the force exerted on the fluid by the tagged particle. Following the argument in I, it can be shown that the whole of the volume integral comes from regions near the surface S, and as the function takes on its far-field form out there and there is no correlation there between a fluid particles coordinates and those of the Brownian particle, then we may use a gradient expansion and express the original volume integral as a surface integral over S. The term proportional to z in Eq. (10b) makes a negligible contribution provided z is small and that the average value of f_p inside V is not of order (R/ξ) times its value on S. A similar argument goes through upon setting $\alpha = J$. In order to write down explicitly the contributions from these terms we need the result

$$\begin{aligned}(k_B T V_{\mathrm{tot}})^{-1} \langle \overleftrightarrow{\sigma}_{\alpha\beta}(z=0)\, \overleftrightarrow{\sigma}_{\mu\nu} \rangle = {} & (\eta_B - 2\eta/3)\, \delta_{\alpha\beta} \delta_{\mu\nu} \\ & + \eta(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}) \\ & + \eta_r(\delta_{\alpha\mu}\delta_{\beta\nu} - \delta_{\alpha\nu}\delta_{\beta\mu}) \end{aligned} \tag{31a}$$

where η_B is the bulk viscosity of the fluid, and $\overleftrightarrow{\sigma}$ is the microscopic stress tensor, given by

$$\overleftrightarrow{\sigma} = \sum_{i>1} \left\{ \frac{1}{m} \mathbf{p}_i \mathbf{p}_i + \frac{1}{2} \sum_{\substack{j \neq i \\ j > 1}} \mathbf{f}_{ij} \mathbf{r}_{ij} \right\} - \overleftrightarrow{1} P V_{\mathrm{tot}} \tag{31b}$$

where P is the pressure of the system. Unlike the case of an atomic fluid, $\overleftrightarrow{\sigma}$ is not a symmetric tensor.

Finally on setting $\alpha = T$, we find that only the Euler term contributes to $v(z)$—the contribution of the dissipative term is of $O(\xi/R)$ times smaller. Following the arguments in I, it is again possible to convert the volume integral into a surface integral simply involving the far-field form of $\tilde{\mathbf{f}}_T(12)$. Collecting these terms together, and using Eq. (26), we arrive at the new expression for $v(z)$, which is

$$\begin{aligned} v(z) = \frac{\rho}{3m_1} \int d\Omega_1 \int_S d\hat{\sigma} \Bigg\{ & \hat{\sigma} \cdot \tilde{\mathbf{f}}_n(12) + \left[\frac{(\gamma - 1)\, k_B T^2}{C_v S(0)} \right]^{1/2} \hat{\sigma} \cdot \tilde{\mathbf{f}}_T(12) \\ & - \frac{(\eta_B - 2\eta/3)}{\rho} \hat{\sigma}_\alpha \nabla_\beta \overleftrightarrow{\tilde{f}}{}_p^{\alpha\beta}(12) - \frac{(\eta + \eta_r)}{\rho} (\hat{\sigma} \cdot \nabla) \overleftrightarrow{\tilde{f}}{}_p^{\alpha\alpha}(12) \\ & - \frac{(\eta - \eta_r)}{\rho} \hat{\sigma}_\beta \nabla_\alpha \overleftrightarrow{\tilde{f}}{}_p^{\alpha\beta}(12) - \frac{2\eta_r}{\rho} \varepsilon_{\alpha\beta\gamma} \hat{\sigma}_\beta \overleftrightarrow{\tilde{f}}{}_J^{\alpha\gamma}(12) \Bigg\} \end{aligned} \tag{32}$$

Here $\varepsilon_{\alpha\beta\gamma}$ is the third rank isotropic tensor, C_v is the specific heat at constant volume, γ is the ratio of the specific heats, $S(0)$ is the zero-k limit of the structure factor of the fluid, and the Greek subscripts and superscripts here denote Cartesian components. This result is essentially relating $v(z)$ to the integral over the surface S of the normal component of the hydrodynamic stress tensor. Thus the first two terms in the curly brackets correspond to the pressure contribution, arising from density and temperature fluctuations, respectively, and the remaining terms correspond to the dissipative part of the hydrodynamic stress tensor. The extra terms involving η_r arise from the presence of the spin field. This expression is in full agreement with that of Hynes *et al.*,(26) and Reichl,(27) except they also kept terms of higher order in the gradient operator. These extra terms only make a contribution to $v(z)$ of $O(\xi/R)$ times that of the terms in Eq. (32). We discuss this more fully later on.

We now consider the equations obeyed by the far fields, by taking the large $|\mathbf{r}'_{12}|$ limit of Eq. (27), integrating over Ω'_2 and conducting a gradient expansion. We obtain once again the equations used in Refs. 26 and 27 except in a slightly disguised form. They are

$$zS(0)\,\tilde{\mathbf{f}}_n(12)+\rho k_B T\,\nabla_\beta\,\overleftrightarrow{\tilde{f}}{}_p^{\alpha\beta}(12)=0 \tag{33a}$$

$$\begin{aligned} &z\overleftrightarrow{\tilde{f}}{}_p^{\alpha\beta}(12)+\frac{1}{m}\nabla_\beta\tilde{\mathbf{f}}_n^\alpha(12)+\left[\frac{(\gamma-1)\,k_BT^2}{m^2C_vS(0)}\right]^{1/2}\nabla_\beta\tilde{\mathbf{f}}_T^\alpha(12)\\ &\quad-\frac{1}{\rho m}\left\{\left(\eta_B+\frac{\eta}{3}-\eta_r\right)\nabla_\beta\nabla_\gamma\overleftrightarrow{\tilde{f}}{}_p^{\alpha\gamma}(12)+(\eta+\eta_r)\,\nabla^2\overleftrightarrow{\tilde{f}}{}_p^{\alpha\beta}(12)\right.\\ &\quad\left.+\,2\eta_r\varepsilon_{\mu\gamma\beta}\nabla_\mu\overleftrightarrow{\tilde{f}}{}_J^{\alpha\gamma}(12)\right\}=0 \end{aligned} \tag{33b}$$

$$z\overleftrightarrow{\tilde{f}}{}_J^{\alpha\beta}(12)+\frac{\eta_r}{\rho I}\left\{4\overleftrightarrow{\tilde{f}}{}_J^{\alpha\beta}(12)+2\varepsilon_{\mu\gamma\beta}\nabla_\mu\overleftrightarrow{\tilde{f}}{}_p^{\alpha\gamma}(12)\right\}=0 \tag{33c}$$

and

$$zC_v\tilde{\mathbf{f}}_T^\alpha(12)+\left[\frac{(\gamma-1)\,k_B}{S(0)\,C_v}\right]^{1/2}\nabla_\beta\,\overleftrightarrow{\tilde{f}}{}_p^{\alpha\beta}(12)-\frac{\lambda}{\rho}\nabla^2\tilde{\mathbf{f}}_T^\alpha(12)=0 \tag{33d}$$

where λ is the thermal conductivity of the fluid. The equations used in Refs. 26 and 27 contained in them higher-order terms—for example, extra terms appeared in Eq. (33c) involving two gradient operators acting upon $\tilde{f}_J$, the transport coefficient multiplying it being a spin-diffusion constant. In our opinion, though, it is inconsistent to retain these terms, which are of a Burnett order, and not other terms of the same order, such as, for example, three gradient operators acting on $\tilde{f}_p$ in Eq. (33c). Let us note from these equations, before proceeding, that we would expect that $\tilde{f}_J \sim O(1/R)\,\tilde{f}_p$, by considering Eqs. (33b) or (33c).

It now remains to extract the boundary conditions that these functions obey on the surface S. We use similar methods to those used in I, and those used by Ronis *et al.*$^{(38)}$ We shall assume that the average values of $f_\alpha(12)$ within the volume V are not of $O(R/\xi)$ times their values on S, and we shall take z to be $O((k_BT/m)^{1/2}/a)$, where a is a molecular length, which is always a requirement on z in the Brownian limit. Firstly let us set $\gamma=n$ in Eq. (27). We note that $\tilde{\mathbf{f}}_n(12)$ is a vector. Its vector nature can only be constructed from the vector $\hat{r}_{12}$ and from the vectors describing the orientation of the Brownian particle, which we shall denote by $\hat{\Omega}_1$. We therefore take the scalar product of Eq. (27), having set $\gamma = n$, with $\hat{r}_{12}$ and $\hat{\Omega}_1$ in turn, and integrate over the volume V, and the angles Ω_2. As in I, the result is the equivalent of the normal velocity boundary condition on S, which states

$$\overset{\leftrightarrow}{\tilde{f}}_p(12) \cdot \hat{\sigma} = \hat{\sigma}, \qquad \mathbf{r}_{12} \text{ on } S \tag{34a}$$

—the result being correct to $O(\xi/R)$. A similar argument goes through upon setting $\gamma = T$ on Eq. (27)—we again obtain the equivalent of the zero temperature gradient condition,

$$\hat{\sigma} \cdot \nabla \tilde{\mathbf{f}}_T(12) = 0, \qquad \mathbf{r}_{12} \text{ on } S \tag{34b}$$

again correct to $O(\xi/R)$.

For $\gamma = p$ in Eq. (27), the situation is slightly more complicated than it was in I. In that situation the functions appearing in the equations only depended upon $\mathbf{r}_{12}$. Thus in order to investigate Eq. (27) for $\gamma = p$ for that problem, we took the scalar product of the equation with $(\overset{\leftrightarrow}{1} - \hat{r}_{12}\hat{r}_{12}) \cdot \langle \mathbf{F}_1 a_n(12) \rangle = 0$ as $\langle \mathbf{F}_1 a_n(12) \rangle \propto \hat{r}_{12}$, the zero tangential stress boundary condition emerged. If we repeat this calculation here, we find in general no such simple result. Thus let us take the scalar product of Eq. (27), $\gamma = p$, with $(\overset{\leftrightarrow}{1} - \hat{s}\hat{s})$, where $\hat{s}(12)$ is the unit vector normal to the contour of constant $G(12)$ at that point, so $\hat{s} \equiv \hat{s}(\Omega_1, \Omega_2, \mathbf{r}_{12})$. We then integrate over Ω_2 and the volume V and we use the result that

$$\langle \mathbf{F}_1 a_n(12) \rangle = \rho k_B T \nabla G(12) \tag{35}$$

so that $\hat{s}(12)$ is parallel to $\nabla G(12)$. If we can now assume that $|\nabla \hat{s}(12)| \sim O(1/R)$, in the volume V, then we regain the zero-tangential stress boundary condition, which says

$$(\eta + \eta_r)(\overset{\leftrightarrow}{1} - \hat{\sigma}\hat{\sigma})_{\beta\delta}\, \hat{\sigma}_\gamma \nabla_\gamma \overset{\leftrightarrow}{\tilde{f}}{}_p^{\alpha\beta}(12) + 2\eta_r \varepsilon_{\mu\gamma\beta}(\overset{\leftrightarrow}{1} - \hat{\sigma}\hat{\sigma})_{\beta\delta}\, \hat{\sigma}_\mu \overset{\leftrightarrow}{\tilde{f}}{}_J^{\alpha\gamma}(12) = 0 \tag{36}$$

for $\mathbf{r}_{12}$on S, to lowest order in (ξ/R).

If, however, $\hat{s}(12)$ is rapidly varying, such that $|\nabla \hat{s}(12)| \neq O(1/R)$, as would be the case for a microscopically rough surface, then the above condition does not hold true. Thus in order to get the slip condition we require the tagged particle to be microscopically smooth. It is probable that hydrodynamic stick boundary conditions apply for rough surfaces, but as yet, we do not see how to derive them from Eq. (27), which in this case seems to require explicit knowledge as to how $\hat{s}(12)$ and the other functions behave within the boundary layer region.

Lastly we consider the $\gamma = J$ equation in Eq. (27), concentrating in particular upon the $\beta = J$ term. To make the terms in the equation scalars, let us take the vector product with $\hat{s}(12)$, and then the scalar product with $(\overset{\leftrightarrow}{1} - \hat{s}\hat{s})$, and then integrate over Ω_2 and V. In the previous equations, we always had the result that $\int d\Omega_2\, Qi\mathscr{L}a_\alpha(12) = \nabla \cdot \mathbf{J}$, for $\alpha = n$, P, and T, where J was a flux. This was because the total number, momentum, and energy are conserved variables. It was also because of this result that the volume integral over V could be related to the surface integral of the far fields over S. For $\alpha = J$, though, this does not hold true because the internal angular momentum of the fluid molecules is not conserved. Thus, schematically $\int d\Omega_2\, Qi\mathscr{L}a_J(12) = J_0 + \nabla \cdot \mathbf{J}_1$. If we ignored the J_0 term, then we would regain Reichl's "slip" condition on the function $\tilde{f}_J$ on S, the transport coefficients appearing in this being the spin diffusion constants associated with the correlation function of the flux $\mathbf{J}_1$. However there is no justification for dropping the J_0 term—in fact it is likely that the volume integral involving the J_0 term is of $O(R/\xi)$ times the term involving $\mathbf{J}_1$. Thus we believe that it is impossible to extract a boundary condition on $\tilde{f}_J$ on S from a microscopic view point, even for a molecularly smooth particle.

It might be objected, however, that the reason for this failure was that we integrated the spin-density equation, whereas we should have integrated a true angular momentum equation. This, however, also fails. If we consider the identity

$$\int d\Omega_2 \int_V d\mathbf{r}_{12}\, f_\beta(1'2') * \{RR^{-1}_{\beta J}(1'2'; 12) + RR^{-1}_{\beta p}(1'2'; 12) \wedge \mathbf{r}_{12}\} = 0 \qquad (37)$$

where $\wedge$ denotes a vector product, then the $RR^{-1}_{\beta p}$ term does cancel out the J_0 flux arising from $Qi\mathscr{L}a_J(12)$. Then it is indeed possible to obtain boundary conditions on the surface S. The problem, however, is that because $|\mathbf{r}_{12}| \sim R$, then the second term in curly brackets is $O(R/\xi)$ times the first and is totally dominant when the resulting integrated expression is analyzed to lowest order in ξ/R. In fact the information one gets from doing this is identical to that obtained by considering Eq. (27) with $\gamma = p$ alone.

So, in conclusion, provided that the tagged particle's surface is microscopically smooth, we have obtained once again the usual slip boundary conditions, which arose from the equations of motion of the conserved variables. These conditions, though, are sufficient to solve Eqs. (33a)–(33d). If, for instance we take the $z = 0$ limit of these equations, then from Eq. (33c) we have

$$2\overset{\leftrightarrow}{\tilde{f}}{}^{\alpha\beta}_{J}(12) + \varepsilon_{\mu\gamma\beta} \nabla_\mu \overset{\leftrightarrow}{\tilde{f}}{}^{\alpha\gamma}_{p}(12) = 0 \qquad (38)$$

If this result is then substituted into Eqs. (32), (33c), and (36), we see that all the terms involving η_r or $\overleftrightarrow{\bar{\mathcal{J}}}_J^{\alpha\beta}$ cancel out—that is, we are once again left with the conventional hydrodynamic equations with slip boundary conditions, which lead to the usual Stokes–Einstein result for D.

As we mentioned before, the augmented hydrodynamic equations used in Refs. (26), (27) contained higher-order terms in the gradient operator than we have considered here, and they used a boundary condition on the spin field in order to fully determine the problem. The expressions then obtained for D are of the Stokes–Einstein form, with correction terms of $O(\xi/R)$ times smaller. In practice it could well be possible that these correction terms are accurate estimates of the true correction terms, but it must be pointed out that equally they need not be. The equations and boundary conditions used are not consistent to the next order in (ξ/R), which is the Burnett level of description—all manner of other effects, including boundary layer effects, come into their own at this level of description, and simply picking out certain contributions strikes us as being a dangerous procedure. We believe, therefore, that it is safest to stick to the normal hydrodynamic equations and boundary conditions, for simply augmenting the set by including a spin field does not form a systematic theory of corrections to hydrodynamics. Furthermore the boundary conditions required on the spin field in order to solve these higher-order equations do not seem to come out naturally from a microscopic treatment.

4. THE ROTATIONAL DIFFUSION CONSTANT AND THE AMCF

In this section we apply the techniques used in the previous section to investigate the long-time tail and Brownian limit of the angular momentum correlation function. We denote the AMCF by $C_R(t)$, and it is given by

$$C_R(t) = \langle \mathbf{J}_1(t) \cdot \mathbf{J}_1 \rangle \tag{39}$$

where $\mathbf{J}_1$ is the angular momentum of particle 1 about its center of mass. We use Mori's generalized Langevin equation$^{(29)}$ to write the Laplace transform of the AMCF, $C_R(z)$, in the form

$$\begin{aligned} C_R(z) &= \int_0^\infty dt\, e^{-zt} C(t) \\ &= \frac{3k_B T I_1}{z + \nu_R(z)} \end{aligned} \tag{40}$$

where $\nu_R(z)$, the rotational friction coefficient, is given by

$$\nu_R(z) = (3I_1 k_B T)^{-1} \langle \{ [z - Q_2 i\mathscr{L}]^{-1} \mathbf{N}_1 \} \cdot \mathbf{N}_1 \rangle \tag{41}$$

Here I_1 is the moment of inertia of particle 1 ($I_1 = \frac{1}{3}\,\mathrm{Tr}\,\overleftrightarrow{I}_1$), $\mathbf{N}_1$ is thr torque exerted by the fluid upon the tagged particle and Q_2 projects a variable orthogonal to $\mathbf{J}_1$. We can now couple $\mathbf{N}_1$ to the variables $a_\alpha(12)$ given in Eqs. (5) and (6), and again we have the exact result that $\mathbf{N}_1$ is simply an integral over $a_n(12)$, or

$$\mathbf{N}_1 = \langle \mathbf{N}_1 a_n \rangle \langle a_n a_n \rangle^{-1} a_n \tag{42}$$

We first consider the long-time limit, this time it being our suspicion that $C_R^{(1)}(z) \propto z^{3/2}$. Strictly speaking, according to our previous notation, $v_R^{(1)}(z) \sim z$, but for long-time behavior we are looking for nonanalytic behavior of z at the origin, so we shall continue to use the superscript (1) with that understanding. The arguments advanced in Section 3 still go through, and we obtain as the equivalent of Eq. (16) the result

$$\begin{aligned} v_R^{(1)}(z) = {} & (3I_1 k_B T)^{-1}(2\pi)^{-3} \int d\mathbf{k} \\ & \times \sum_{l_1, l_2} [\langle \mathbf{N}_1 a_n \rangle * (1 + RR^{(0)} * S^{(0)})_{n\alpha} * e^{-i\mathbf{k}\cdot\mathbf{r}_{12}} D^{l_1^*}_{m_1 n_1}(\Omega_1)\, D^{l_2^*}_{m_2 n_2}(\Omega_2)] \\ & \times R^{(1)l_1 l_2}_{\alpha\beta;\mathbf{k}} \cdot [e^{i\mathbf{k}\cdot\mathbf{r}'_{12}} D^{l_1}_{m_1 n_1}(\Omega'_1)\, D^{l_2}_{m_2 n_2}(\Omega'_2)(S^{(0)} * RR^{(0)} + 1)_{\beta n} * \langle a_n \mathbf{F}_1 \rangle] \end{aligned} \tag{43}$$

Once again it can be shown that the dominant long-time tail arises from the $l_1 = l_2 = 0$ term, and in particular for α, $\beta = p, J$. The expressions required are those for $R^{(1)00}_{pp;\mathbf{k}}$—given in Eq. (18), and

$$\begin{aligned} R^{(1)00}_{p_\alpha J_\beta;\mathbf{k}} &= -\varepsilon_{\alpha\beta\gamma} \frac{ik_\gamma}{2\rho m k_B T} \left\{ \frac{1}{z + k^2(\eta/\rho m + D)} - \frac{1}{k^2(\eta/\rho m + D)} \right\} \\ &= -R^{(1)00*}_{J_\beta p_\alpha;\mathbf{k}} \end{aligned} \tag{44a}$$

and

$$R^{(1)00}_{J_\alpha J_\beta;\mathbf{k}} = (\overleftrightarrow{1} - \hat{k}\hat{k})_{\alpha\beta} \cdot \left\{ \frac{1}{z + k^2(\eta/\rho m + D)} - \frac{1}{k^2(\eta/\rho m + D)} \right\} \tag{44b}$$

The long-time tail arises from the small-k limit of the terms in square brackets. For $\alpha = \beta = J$, these terms are nonzero when $|\mathbf{k}| \to 0$. For $\alpha = p$ the situation is different. $\mathbf{N}_1$ is a pseudovector, whereas $\int d1\, d2\, RR^{(0)}_{n\alpha}(1''2''; 1'2') * S^{(0)}_{\alpha p}(1'2'; 12)$ is an ordinary vector. Thus this time on setting $|\mathbf{k}| = 0$ in the first square bracketed term the expression must have value zero, on grounds of symmetry. The first nonvanishing term is $O(|\mathbf{k}|)$, obtained by expanding the exponential to first order in $\mathbf{k}$, and is of the form of an antisymmetric second-rank tensor $\propto \varepsilon_{\alpha\beta\gamma}\mathbf{k}_\gamma$. A similar argument applies for $\beta = p$. We thus see that all four terms, to lowest order in k, give rise to an integral over $\mathbf{k}$ of $k^2/(z + k^2(\eta/\rho m + D))$, which indeed corresponds to the expected $t^{-5/2}$ tail.

Collecting terms, we simplify Eq. (43) to

$$v_R^{(1)}(z) = \frac{g_1 g_2}{(3I_1 k_B T)(2\pi)^3(18m\rho k_B T)} \times \int_{|\mathbf{k}| < k_c} d\mathbf{k}\, k^2 \left\{ \frac{1}{z + k^2(\eta/\rho m + D)} - \frac{1}{k^2(\eta/\rho m + D)} \right\} \tag{45a}$$

where

$$g_1 = \int d1\, d2 \langle \mathbf{N}_1^\mu a_n(1''2'') \rangle * RR_{n\alpha}^{(0)}(1''2''; 1'2') * [S_{\alpha\mathbf{J}_\mu}^{(0)}(1'2'; 12) - S_{\alpha\mathbf{p}_\omega}^{(0)}(1'2'; 12) \cdot \mathbf{r}_{12}^\nu \cdot \varepsilon_{\nu\omega\mu}] \tag{45b}$$

and

$$g_2 = \int d1\, d2 [\varepsilon_{\nu\omega\mu} \mathbf{r}_{12}^\nu S_{\mathbf{p}_\omega\alpha}^{(0)}(12; 1'2') - S_{\mathbf{J}_\mu\alpha}^{(0)}(12; 1'2')] * RR_{\alpha n}^{(0)}(1'2'; 1''2'') * \langle a_n(1''2'')\, \mathbf{N}_1^\mu \rangle \tag{45c}$$

where the Greek letters μ, ν, and ω refer to Cartesian components of the vectors or tensors. Once again the expressions for g_1 and g_2 may be simplified, to give

$$g_1 = (3I_1 k_B T)\, v_R^{(0)} = -g_2 \tag{46a}$$

where we used the results

$$\mathbf{N}_1 = -\sum_{i \neq 1} (\dot{\mathbf{J}}_i - \mathbf{r}_{1i} \wedge \dot{\mathbf{p}}_i) \tag{46b}$$

a rewriting of the law of conservation of angular momentum, and

$$v_R^{(0)} = (3I_1 k_B T)^{-1} \langle \mathbf{N}_1 a_n \rangle * RR_{nn}^{(0)} * \langle a_n \mathbf{N}_1 \rangle \tag{46c}$$

the rotational version of Eq. (21). Finally to get the long-time tail of the AMCF we use

$$C_R^{(1)}(z) = -\frac{3I_1 k_B T v_R^{(1)}(z)}{[v_R^{(0)}]^2} \tag{47}$$

obtained from Eq. (40), and we substitute for $v_R^{(1)}(z)$ from Eq. (45a), using the values for g_1 and g_2 given in Eq. (45). Again the $v_R^{(0)}$ terms cancel, and after taking an inverse Laplace transform and doing the **k** integral, we obtain the result

$$\lim_{t \to \infty} C_R(t) = \frac{3k_B T I_1^2 \pi}{32 m\rho} [\pi(\eta/\rho m + D)t]^{-5/2} \tag{48}$$

Alternatively, if we had considered the angular velocity correlation function instead of the angular momentum correlation function, the factor of I_1^2 in Eq. (47) would be missing. Thus we again have obtained a remarkably simple expression for the long-time tail of the AMCF, for a tagged particle of arbitrary mass, size, and shape. This result agrees in the Brownian limit with the hydrodynamic result for a rough sphere and is in agreement with the ring kinetic theory results for rough spheres.(18) Once again no rotational viscosities appear in the tail coefficient.

Finally it is possible to consider the Brownian limit of the AMCF, following the methods given in Section 3 for the VCF. The results of doing this are once again that $v_R(z)$ is given by solving the normal equations of hydrodynamics subject to slip-boundary conditions on the surface S, provided the tagged particle is microscopically smooth, so that to lowest order in (ξ/R), $v_R(z)$ does not involve η_r or spin-diffusion constants. Corrections to $v_R(z)$ in (ξ/R) will involve these new effects, but they will also involve may other ones not included in the augmented set of hydrodynamic equations used in Refs. 26 and 27. Thus while the Brownian limit of those equations is the same as that of conventional hydrodynamics, the correction terms obtained could well not be trustworthy.

5. DISCUSSION

In the preceding sections we have examined the long-time tail and Brownian limits of the VCF and AMCF, for a particle of arbitrary mass, shape, and size moving in a fluid of nonspherical particles. We found the long-time tail coefficients to be of a remarkably simple form, which, on taking the Brownian limit and taking the tagged particle to be spherical, agreed with the conventional hydrodynamic results. These coefficients did not involve either the rotational viscosity or spin diffusion constants of the fluid. The reason that the anisotropy of the tagged particle had so little effect upon the long-time behavior, was that these effects were damped out at long times by the rotational diffusion of the particle—only an isotropic part [the $l_1 = l_2 = 0$ terms in Eqs. (16) and (43)] contributed to the asymptotic behavior. We note though, that in general this result would not agree with that obtained from the following calculation, in the high mass limit. In principle one could calculate a frequency dependent drag (or torque) coefficient on a fixed particle, and then average this quantity over all orientations of the particle. The Einstein (or Einstein–Debye) relation then would give the frequency-dependent VCF or AMCF, and hence the long-time behavior in the high mass limit. This disagreement would be due to the fact that the latter calculation does not take into account the self-motion of the tagged particle properly, except in the infinite mass limit. Thus, for a particle of finite mass, we believe that our results [Eqs. (24) and (47)] are correct at sufficiently long times. However, if we posed the question as to what would happen at long, but not infinitely long, times as we made the particle more and more massive, then the drag calculation would give the correct result for a sufficiently massive particle.

As for the Brownian limits, we believe that they may be obtained simply using the conventional equations of hydrodynamics. Augmenting the set by including a spin field will not alter the large-particle limit, but will introduce estimates for correction terms of $O(\xi/R)$ times smaller than the leading terms. However as the theory is not consistent to that order, these estimates could well be in error. If the tagged particle is microscopically smooth, the required hydrodynamic boundary conditions are the slip ones. If, however, the particle is not smooth, we would expect stick boundary conditions to apply, but we were unable to show this from a microscopic viewpoint. The basic problem is that, using the conservation laws, it is easy to obtain conditions upon the normal component of either the velocity, stress tensor, or temperature gradient on an outer surface. It is not easy, however, to obtain a boundary condition, on the outer surface, for the tangential component of the velocity, which is required for stick. It is interesting to note, though, that if we define the macroscopic stress tensor by $\overset{\rightrightarrows}{\pi}$, it is possible to obtain an expression for the ratio $\hat{\sigma}\cdot\overset{\rightrightarrows}{\pi}\cdot\hat{\sigma}/\hat{\sigma}\cdot\overset{\rightrightarrows}{\pi}\cdot\vec{t}$, where $\hat{\sigma}$ and $\vec{t}$ are normal and tangential vectors, respectively, on the outer surface, although the expression for the constant of proportionality is rather obscure. If we repeated the Stokes-law calculation for the drag on a sphere using the normal velocity boundary condition and the new boundary condition $\hat{\sigma}\cdot\overset{\rightrightarrows}{\pi}\cdot\vec{t}/\hat{\sigma}\cdot\overset{\rightrightarrows}{\pi}\cdot\hat{\sigma}=1$, then the usual stick result is again obtained. Of course this leaves us with two problems. The first is why, on microscopic grounds, should this ratio be unity, and the second is how, for a general system, can one relate a boundary condition on radial and tangential components of the stress tensor to the widely used and successful stick boundary condition.

So, in summary, we hope we have given a reasonably careful account of the derivation of long-time tail and Brownian limits in these anisotropic systems. Clearly much work remains to be done to understand the stick boundary condition, and the problems of obtaining a good theory for molecular diffusion from first principles also must soon be attacked. Nevertheless we hope that the results given here can help to give checks on possible future, approximate theories.

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