# Dynamical orientation correlations in solution[a)]

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A many particle coupled translation–rotation diffusion model is analyzed in regard to single particle and collective orientational correlation functions. This model contains a hydrodynamic mechanism which gives rise to dynamical orientation correlations in solution. An approximate expression for the dynamical correlation factor $\dot{g}$ is derived in terms of the static pair distribution function. In contradiction to recent arguments, $\dot{g}$ does not vanish for this model. We also show that in the case where the pair potential of the solute particles is spherically symmetric, the Debye relaxation law is unmodified by the long-range hydrodynamic interaction.

## I. INTRODUCTION

A complete understanding of the dynamics of a fluid requires both a knowledge of the motion of individual particles and also a knowledge of the way in which motions of different molecules are correlated. There is much interest in understanding reorientational motions in complex liquids and solutions. Many experiments, such as NMR relaxation, Raman line shapes, and incoherent neutron scattering, are sensitive only to the single particle motion. Other experiments, such as dielectric relaxation, depolarized Rayleigh light scattering, and coherent neutron scattering, measure collective reorientational motions. A comparison of these two types of measurements can then lead to information about the degree of correlation of the motion of different molecules in the fluid. An example of such a comparison is the work of Alms, Bauer, Brauman, and Pecora on chloroform and nitrobenzene using a combination of $^{13}$C relaxation measurements and depolarized Rayleigh light scattering[1] and the work of Rosenthal and Strauss on chloroform using Raman scattering, infrared spectra, and depolarized Rayleigh scattering.[2] Information on the correlation of orientational motions can also be obtained more indirectly by measuring a collective reorientational property as a function of concentration in solution. Examples of such studies include the light scattering work of Pecora and co-workers on solutions of aromatic molecules[3] and Gierke and Flygare on MBBA solutions.[4]

These light scattering studies are often interpreted with the aid of the theory due to Keyes and Kivelson.[5] In the "diffusion" limit this theory indicates that both the single particle and collective orientational correlation functions decay as single exponentials. In this limit the Keyes–Kivelson theory indicates that the ratio of the decay times for these correlation functions depends on a static correlation function, analogous to the Kirkwood $g$ factor, and on a dynamic factor related to the time-correlation functions of the angular momenta of different molecules.

In order to improve our understanding of the correlation effects on rotational motion, we examine in this paper a particular model of the coupled motion of molecules in solution. In the model we consider the coupled Brownian diffusion of solute particles interacting with anisotropic potentials in a continuum solvent, the motion of which may be described hydrodynamically. Such a model is most appropriate for macromolecular solutions, but it may also contain many features relevant to the more extensively studied solutions of small anisotropic molecules. In this regard the success of hydrodynamic theories in explaining single particle rotational motions is encouraging.[6]

This model contains a hydrodynamic mechanism which gives rise to dynamical orientation correlation. This is manifest in the appearance of long-range off-diagonal coupled diffusion constants in the $N$-particle translational–rotational diffusion equation describing the system. These diffusion constants are related to the correlation functions of angular momenta of different solute molecules.

The long-range character of this type of correlation does not emerge directly in the light scattering experiment. The present model does, however, exhibit a nonvanishing dynamical orientation pair correlation factor for solutions of symmetric top molecules, in contradiction to recent arguments of Gierke.[7] A somewhat more startling result is that if the potential of interaction of the solute particles is isotropic, the rotational hydrodynamic coupling has no effect on the usual two-point correlation functions measured in linear response experiments. This result is of some significance with respect to recent hypotheses concerning deviations from simple Debye relaxation observed in magnetic resonance studies by Koenig *et al.* on aqueous protein solutions.[8] There is, however, an effect on the four-point and higher order correlation functions which are related to nonlinear response phenomena such as the Kerr effect.

In Sec. II of this paper, we discuss the derivation of the $N$-particle coupled rotational–translation diffusion equation. The hydrodynamic theory of the diffusion tensors in this theory is also presented in Sec. II. In

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Sec. III an approximate treatment of the $N$-particle diffusion equation is given which leads to an expression for the dynamic correlation factor for collective orientational motion in terms of the equilibrium correlations of the system. The case of isotropic interaction potentials is further developed in Sec. IV. Section V presents a discussion of the results of this work and possible further implications of this approach for the dynamics of solutions of anisotropic molecules.

## II. COUPLED ROTATIONAL-TRANSLATIONAL DIFFUSION EQUATION

Consider a collection of $N$ Brownian solute molecules labeled with positional coordinates $\mathbf{X}_i$, $i=1, \ldots N$ and orientational coordinates $\boldsymbol{\Omega}_i$, $i=1,\ldots N$. For infinitesimal step Brownian motion, the configurational probability density $P(\{X_i, \Omega_i\}=\{Q\})$ is locally conserved and therefore satisfies the equation

$$\frac{\partial P}{\partial t}=-\sum_i[\nabla_{\mathbf{X}_i}\cdot\mathbf{J}_{\mathbf{X}_i}+\mathrm{L}(i)\cdot\mathrm{J}_{\Omega_i}]\ , \tag{2.1}$$

where $\mathbf{J}_{X_i}$ and $\mathrm{J}_{\Omega_i}$ are the probability current densities along the positional and orientational coordinates of the $i$th particle; $\mathrm{L}(i)$ is the operator $\mathbf{u}_i\times\nabla_{\mathbf{u}_i}$ where $\mathbf{u}_i$ is a unit vector fixed on the molecule.

For Brownian particles the probability current densities are linearly related to the deviation of the configurational probability density from its equilibrium value

$$\begin{aligned}\mathrm{J}_{\mathbf{X}_i}=-\sum_j&[\mathbf{D}_{ij}^{xx}(Q)\cdot(\nabla_{\mathbf{X}_j}P+\beta P\nabla_{\mathbf{X}_j}U)\\&+\mathbf{D}_{ij}^{X\Omega}(Q)\cdot(\mathrm{L}_jP+\beta P\mathrm{L}_jU)]\ ,\end{aligned} \tag{2.2}$$

$$\begin{aligned}\mathrm{J}_{\Omega_i}=-\sum_j&[\mathbf{D}_{ij}^{\Omega X}(Q)\cdot(\nabla_{\mathbf{X}_j}P+\beta P\nabla_{\mathbf{X}_j}U)\\&+\mathbf{D}_{ij}^{\Omega\Omega}(Q)\cdot(\mathrm{L}_jP+\beta P\mathrm{L}_jU)]\ ,\end{aligned} \tag{2.3}$$

where $U(Q)$ is the potential of mean force of the system. The equilibrium probability distribution $P_{\mathrm{eq}}(Q)$ is related to $U(Q)$ according to

$$P_{\mathrm{eq}}(Q)=\mathrm{const}\exp[-\beta U(Q)]\ . \tag{2.4}$$

The diffusion coefficients are a function of the Brownian particle system's configuration. Because of the separation of time scales of momentum relaxation and configurational change in a dense fluid, these diffusion coefficients can be expressed as integrals of the time-correlation functions of the velocity $\mathbf{v}_j$ and angular velocities $\omega_j$

$$\begin{aligned}\mathbf{D}_{ij}^{XX}(Q)&=\int_0^\infty\langle\mathbf{v}_i(0)\,\mathbf{v}_j(t)\rangle_Q\,dt\ ,\\ \mathbf{D}_{ij}^{X\Omega}(Q)&=\int_0^\infty\langle\mathbf{v}_i(0)\,\omega_j(t)\rangle_Q\,dt\ ,\\ \mathbf{D}_{ij}^{\Omega X}(Q)&=\int_0^\infty\langle\omega_i(0)\,\mathbf{v}_j(t)\rangle_Q\,dt\ ,\\ \mathbf{D}_{ij}^{\Omega\Omega}(Q)&=\int_0^\infty\langle\omega_i(0)\,\omega_j(t)\rangle_Q\,dt\ .\end{aligned} \tag{2.5}$$

The average $\langle\cdots\rangle_Q$ is taken over an ensemble with initial configuration $Q$. The separation of configurational and momentum relaxation time scales is only approximately valid. However, if the forces are not too large and when the behavior at extremely short distances (less than a mean free path) is neglected, the error incurred should not be too severe. A more accurate theory of many particle diffusion equations would lead to a non-Markovian form of the diffusion equation and the expressions for the memory kernels would involve projected time correlation functions.[9]

In a hydrodynamic fluctuation model the velocity and angular velocity correlations can be obtained from the Langevin equation for the fluctuating velocity and angular velocity:

$$m_i\frac{d\mathbf{v}_i}{dt}=-\sum_j[\boldsymbol{\zeta}_{ij}^{XX}\cdot\mathbf{v}_j+\boldsymbol{\zeta}_{ij}^{X\Omega}\cdot\omega_j]+\mathbf{F}_i(t)_{\mathrm{random}} \tag{2.6}$$

$$I_i\frac{d\omega_i}{dt}=-\sum_j[\boldsymbol{\zeta}_{ij}^{\Omega X}\cdot\mathbf{v}_j+\boldsymbol{\zeta}_{ij}^{\Omega\Omega}\circ\omega_j]+\mathrm{T}_i(t)_{\mathrm{random}}\ . \tag{2.7}$$

The drag coefficients in this Langevin equation depend on the configuration of the solute molecules. The solution of these Langevin equations and integration of the resulting correlation functions lead to a generalized Einstein relation between the drag coefficients $\boldsymbol{\zeta}_{ij}^{\alpha\beta}$ and the diffusion constants:

$$\mathbf{D}_{ij}^{\alpha\beta}=k_BT(\boldsymbol{\zeta}^{-1})_{ij}^{\alpha\beta}\ . \tag{2.8}$$

where the matrix inverse is defined by

$$\sum_{\gamma,k}(\boldsymbol{\zeta}^{-1})_{ik}^{\alpha\gamma}\cdot(\boldsymbol{\zeta})_{kj}^{\gamma\beta}=\mathbf{1}\,\delta_{\alpha\beta}\,\delta_{ij}\ . \tag{2.9}$$

Here $\mathbf{D}_{ij}^{\alpha\beta}$ and $\boldsymbol{\zeta}_{ij}^{\alpha\beta}$ are $3\times3$ matrices for each $(i,j)$ pair. The labels $\alpha$, $\beta$ refer to translation $(X)$ and rotation $(\Omega)$.

We can understand the origin of the coupled drag coefficients with a hydrodynamic picture. The translational or rotational motion of one Brownian particle causes a flow in the surrounding solvent. The moving solvent then exerts forces and torques on the other solute molecules. The theory of this effect for translational motion is quite advanced in polymer dynamics[10]; this theory can be extended to include rotational motion. The exact treatment of hydrodynamic interaction for any arbitrary configuration of finite-sized bodies is extremely difficult,[11] but it is possible to develop a theory which is accurate when the Brownian particles are well separated. For simple geometries of two particles, exact hydrodynamic calculations indicate that this approximate theory can be quite accurate.[12]

When the Brownian particles are far apart, they can be thought of as point centers of drag force and point centers of drag torque acting on the fluid. In general it is possible to treat the flow due to each solute particle by a multipole expansion of the force exerted by its surface on the solvent.[13]

The velocity field induced in a viscous incompressible fluid at point $\mathbf{R}$ by a steady point force $\mathbf{F}$ applied at point $\mathbf{R}'$ is

$$\mathbf{u}(\mathbf{R})=\mathbf{T}^{XX}(\mathbf{R}-\mathbf{R}')\cdot\mathbf{F}\ , \tag{2.10}$$

where $\mathbf{T}^{XX}$ is the Oseen tensor

$$\mathbf{T}^{XX}(\mathbf{R}) = (8\pi\eta_0 R)^{-1}[\mathbf{I} + \hat{\mathbf{R}}\hat{\mathbf{R}}] . \tag{2.11}$$

The Oseen tensor is familiar as the Green's function of the steady state linearized incompressible fluid Navier–Stokes equations.

The velocity field induced by a steady torque $\tau$ applied at a point in the fluid is not so familiar. It is, however, directly related to the velocity field induced by a sphere with stick boundary conditions rotating at angular velocity $\omega$

$$\mathbf{u}(\mathbf{R}) = a^3\, \omega \mathbf{x} \mathbf{R}/R^3 , \tag{2.12}$$

where $a$ is the radius of the sphere. The torque exerted by the rotating sphere on the fluid is $\tau = -8\pi a^3 \eta_0 \omega$. Thus the velocity field due to an applied torque is

$$\mathbf{u}(\mathbf{R}) = -(8\pi\eta_0 R^3)^{-1}\, \mathbf{R} \mathbf{x} \tau \equiv \mathbf{T}^{X\Omega}(\mathbf{R}) \cdot \tau . \tag{2.13}$$

Note that this result is independent of the radius of the sphere—as expected, since the sphere was introduced as a ficticious point source. This relation therefore defines a "translation–rotation Oseen tensor," $\mathbf{T}^{X\Omega}(\mathbf{R})$. This tensor decays in space as $1/R^2$, more rapidly than the usual translational Oseen tensor.

The force on particle $i$ moving with velocity $\mathbf{v}_i$ is

$$\mathbf{F}_i = -\zeta_0^{XX} \cdot [\mathbf{v}_i - \mathbf{u}(\mathbf{r}_i)] , \tag{2.14}$$

where $\zeta_0^{XX}$ is the drag tensor for the particle and $\mathbf{u}(r_i)$ is the velocity field which would be present in the absence of the $i$th particle. This velocity field is related to the forces and torques exerted by the other Brownian particles

$$\mathbf{u}(\mathbf{r}_i) = -\sum_{j(\neq i)} [\mathbf{T}^{XX}(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_j + \mathbf{T}^{X\Omega}(\mathbf{r}_i - \mathbf{r}_j) \cdot \tau_j] . \tag{2.15}$$

Equations (2.14) and (2.15) combine to give a set of relations relating the linear velocities of the Brownian particles to the forces and torques on them:

$$\mathbf{F}_i = -\zeta_0^{XX} \cdot \left[ \mathbf{v}_i + \sum_{j(\neq i)} (\mathbf{T}_{ij}^{XX} \cdot \mathbf{F}_j + \mathbf{T}_{ij}^{X\Omega} \cdot \tau_j) \right] , \tag{2.16}$$

where

$$\mathbf{T}_{ij}^{XX} = \mathbf{T}^{XX}(\mathbf{r}_i - \mathbf{r}_j) \text{ and } \mathbf{T}_{ij}^{X\Omega}(\mathbf{r}_i - \mathbf{r}_j) . \tag{2.17}$$

In a similar fashion, the torque on a particle is determined by its angular velocity and by the velocity field which would be present in the absence of that particle. Indeed, if a particle is immersed in a solvent with an inhomogeneous velocity field it will feel a torque. The degree of inhomogeneity is determined by the vorticity $\psi = \frac{1}{2} \nabla \times \mathbf{u}$, and the torque on a particle is

$$\tau_i = -\zeta_0^{\Omega\Omega} \cdot (\omega_i - \psi(\mathbf{r}_i)) . \tag{2.18}$$

The vorticity field is given by

$$\psi(\mathbf{r}_i) = -\frac{1}{2} \sum_{j(\neq i)} [\nabla_{\mathbf{r}_i} \times \mathbf{T}^{XX}(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_j + \nabla_{\mathbf{r}_i} \times \mathbf{T}^{X\Omega}(\mathbf{r}_i - \mathbf{r}_j) \cdot \tau_j] \tag{2.19}$$

We can define in this way new tensors $\mathbf{T}^{\Omega X} = \frac{1}{2} \nabla \times \mathbf{T}^{XX}(\mathbf{r}_i - \mathbf{r}_j) = \mathbf{T}^{X\Omega}$ and $\mathbf{T}^{\Omega\Omega} = \frac{1}{2} \nabla \times \mathbf{T}^{X\Omega}$. Therefore

$$\tau_i = -\zeta_0^{\Omega\Omega} \cdot \left[ \omega_i + \sum_{j(\neq i)} (\mathbf{T}_{ij}^{\Omega X} \cdot \mathbf{F}_j + \mathbf{T}_{ij}^{\Omega\Omega} \cdot \tau_j) \right] . \tag{2.20}$$

The "rotation–rotation Oseen tensor" $\mathbf{T}^{\Omega\Omega}$, which we will use explicitly later, is particularly simple

$$\mathbf{T}^{\Omega\Omega}(\mathbf{r}) = \frac{1}{2} \nabla \times \mathbf{T}^{X\Omega} = \frac{(-1)}{16\pi\eta_0} \frac{1}{r^3} \left( \mathbf{I} - \frac{3\mathbf{r}\mathbf{r}}{r^2} \right) . \tag{2.21}$$

This tensor has just the same form as the tensorial interaction between dipoles in a fluid.[14]

The relationship between these hydrodynamic tensors and the drag coefficients in Eq. (2.5) is made clear by rewriting Eqs. (2.15) and (2.20) in the form

$$\begin{aligned} \mathbf{v}_i &= -\zeta_0^{XX-1} \cdot \mathbf{F}_i - \sum_{j(\neq i)} (\mathbf{T}_{ij}^{XX} \cdot \mathbf{F}_j + \mathbf{T}_{ij}^{X\Omega} \cdot \tau_j) \\ &= -\sum_j [(\zeta^{-1})_{ij}^{XX} \cdot \mathbf{F}_j + (\zeta^{-1})_{ij}^{X\Omega} \cdot \tau_j] , \end{aligned} \tag{2.22}$$

$$\begin{aligned} \omega_i &= -\zeta_0^{\Omega\Omega-1} \cdot \tau_i - \sum_{j(\neq i)} (\mathbf{T}_{ij}^{\Omega X} \cdot \mathbf{F}_j + \mathbf{T}_{ij}^{\Omega\Omega} \cdot \tau_j) \\ &= -\sum_j [(\zeta^{-1})_{ij}^{\Omega X} \cdot \mathbf{F}_j + (\zeta^{-1})_{ij}^{\Omega\Omega} \cdot \tau_j] . \end{aligned} \tag{2.23}$$

Therefore, combining these equations with the generalized Einstein relation Eq. (2.8), we see that the diffusion coefficients in the many particle diffusion equation are directly related to the hydrodynamic interaction tensors

$$\mathbf{D}_{ij}^{XX} = k_B T[(\zeta_0^{XX})^{-1} \delta_{ij} + (1 - \delta_{ij}) \mathbf{T}_{ij}^{XX}] , \tag{2.24}$$

$$\mathbf{D}_{ij}^{\Omega X} = k_B T(1 - \delta_{ij}) \mathbf{T}_{ij}^{X\Omega} , \tag{2.25}$$

$$\mathbf{D}_{ij}^{\Omega X} = k_B T(1 - \delta_{ij}) \mathbf{T}_{ij}^{\Omega X} , \tag{2.26}$$

$$\mathbf{D}_{ij}^{\Omega\Omega} = k_B T[\zeta_0^{\Omega\Omega})^{-1} \delta_{ij} + (1 - \delta_{ij}) \mathbf{T}_{ij}^{\Omega\Omega}] . \tag{2.27}$$

The long-range character of $\mathbf{T}^{\Omega\Omega}$ indicates that collective hydrodynamic effects lead to a correlation of the angular velocities of distant solute particles. The other diffusion coefficients $\mathbf{D}^{X\Omega}$ and $\mathbf{D}^{\Omega X}$ reflect the presence of long-range correlations of the rotation and translation of different solute particles.

## III. SINGLE AND MANY PARTICLE MOTION IN THE COUPLED DIFFUSION MODEL

In this section we are primarily interested in determining for the coupled diffusion model introduced in Sec. II the relationship of correlation functions for single particle variables $A_i\,[= Y_{lm}(\Omega_i)$, for example] to corresponding correlation functions for collective variables of the form $A_c = \sum_{i=1}^N A_i$.

In linear response theory, a correlation function of the form $\langle A(0)A(t)\rangle$ can be written as the average of $A(0)$ over a time dependent ensemble density $P(t)$[15]:

$$\langle A(0)A\,|\,t)\rangle = \int A(0)P(t)\,dQ . \tag{3.1}$$

This density $P(t)$ is a solution of the many particle diffusion Eq. (2.1) and has the initial value $P(t=0) = A(0)P_{\text{eq}}(Q)$. Thus we may write

$$P(t) = \exp(t\hat{\mathcal{L}})\,[A(0)P_{\text{eq}}(Q)] ; \tag{3.2}$$

where $\hat{\mathcal{L}}$ is the diffusion operator

$$\hat{\mathcal{L}} = \sum_{i,j} \{\nabla_{\mathbf{X}_i} \cdot [\mathbf{D}_{ij}^{XX} \cdot (\nabla_{\mathbf{X}_j} + \beta(\nabla_{\mathbf{X}_j} U)) + \mathbf{D}_{ij}^{X\Omega}(\mathbf{L}_j + \beta(\mathbf{L}_j U))]$$
$$+ \mathbf{L}_i \cdot [\mathbf{D}_{ij}^{\Omega X} \cdot (\nabla_{\mathbf{X}_j} + \beta(\nabla_{\mathbf{X}_j} U)) + \mathbf{D}_{ij}^{\Omega\Omega} \cdot (\mathbf{L}_j U))]\} . \tag{3.3}$$

The correlation function is

$$\langle A(0)A(t)\rangle = \int A(0)\exp(t\hat{\mathcal{L}})[A(0)P_{\mathrm{eq}}(Q)]\,dQ . \tag{3.4}$$

It is convenient for our calculations to introduce the operator $\mathcal{L}$ which is adjoint to $\hat{\mathcal{L}}$, so that Eq. (3.4) becomes

$$\langle A(0)A(t)\rangle = \int P_{\mathrm{eq}} A(0)[\exp(t\mathcal{L})A(0)]\,dQ$$
$$\equiv \langle A|\exp(t\mathcal{L})|A\rangle = \langle A|A(t)\rangle . \tag{3.5}$$

Here we have introduced bra–ket notation for the scalar product with respect to the equilibrium probability density $P_{\mathrm{eq}}$. The adjoint diffusion operator $\mathcal{L}$ is explicitly

$$\mathcal{L} = \mathcal{L}_{\mathrm{TT}} + \mathcal{L}_{\mathrm{TR}} + \mathcal{L}_{\mathrm{RR}} , \tag{3.6}$$

with

$$\mathcal{L}_{\mathrm{TT}} = \sum_{i,j} [\nabla_i \cdot \mathbf{D}_{ij}^{XX} \cdot \nabla_j - \beta(\nabla_i U) \cdot \mathbf{D}_{ij}^{XX} \cdot \nabla_j] , \tag{3.7}$$

$$\mathcal{L}_{\mathrm{TR}} = \sum_{i,j} [\mathbf{L}_i \cdot \mathbf{D}_{ij}^{\Omega X} \cdot \nabla_j - \beta(\mathbf{L}_i U) \cdot \mathbf{D}_{ij}^{\Omega X} \cdot \nabla_j$$
$$+ \nabla_i \cdot \mathbf{D}_{ij}^{X\Omega} \cdot \mathbf{L}_j - \beta(\nabla_i U) \cdot \mathbf{D}_{ij}^{X\Omega} \cdot \mathbf{L}_j] , \tag{3.8}$$

$$\mathcal{L}_{\mathrm{RR}} = \sum_{i,j} [\mathbf{L}_i \cdot \mathbf{D}_{ij}^{\Omega\Omega} \cdot \mathbf{L}_j - \beta(\mathbf{L}_i U) \cdot \mathbf{D}_{ij}^{\Omega\Omega} \cdot \mathbf{L}_j] . \tag{3.9}$$

In terms of this operator, the variable $A$ satisfies the equation

$$\frac{\partial}{\partial t}|A(t)\rangle = \mathcal{L}|A(t)\rangle . \tag{3.10}$$

In general it is not possible, for an arbitrary potential of mean force $U$, to exactly evaluate $\langle A|\exp(t\mathcal{L})|A\rangle$ or, equivalently, to solve Eq. (3.10).

In order to gain some understanding of the effect of dynamical correlations on the relationship of single particle and collective correlation functions, therefore, we must resort to an approximate solution of the many particle diffusion equation. The approach we use is a projection operator technique similar to that used in the formal theory of Keyes and Kivelson.[5,16]

We select as variables in this projection operator scheme $A_s$, the single particle variable, and the collective variable

$$A_\perp = A_c - \langle A_c|A_s\rangle\langle A_s|A_s\rangle^{-1}A_s . \tag{3.11}$$

These variables are chosen so as to be orthogonal, $\langle A_\perp|A_s\rangle = 0$. The projection operator onto this set of two variables therefore has a very simple form

$$P = |A_s\rangle\langle A_s|A_s\rangle^{-1}\langle A_s| + |A_\perp\rangle\langle A_\perp|A_\perp\rangle^{-1}\langle A_\perp| . \tag{3.12}$$

We introduce also the orthogonal projector $Q = 1 - P$. In order to obtain relaxation equations for $A_s$ and $A_\perp$, we operate on Eq. (3.10) with the projection operators $P$, $Q$, to obtain the equations

$$\frac{\partial}{\partial t}P|A(t)\rangle = (P\mathcal{L}P)P|A(t)\rangle + (P\mathcal{L}Q)Q|A(t)\rangle , \tag{3.13a}$$

$$\frac{\partial}{\partial t}Q|A(t)\rangle = (Q\mathcal{L}Q)Q|A(t)\rangle + (Q\mathcal{L}P)P|A(t)\rangle . \tag{3.13b}$$

We solve Eq. (3.13b) for $Q|A(t)\rangle$ and substitute this into (3.13a)

$$\frac{\partial}{\partial t}P|A(t)\rangle = (P\mathcal{L}P)P|A(t)\rangle$$
$$+ \int_0^t ds\, P\mathcal{L}Q\exp[Q\mathcal{L}Q(t-s)]Q\mathcal{L}PP|A(t)\rangle . \tag{3.14}$$

where we have assumed the initial condition $Q|A(0)\rangle = 0$. Equation (3.14) is exact.

The approximation we introduce is to neglect the memory term. Thus we will be concerned with the dynamical equation

$$\frac{\partial}{\partial t}P|A(t)\rangle = (P\mathcal{L}P)P|A(t)\rangle . \tag{3.15}$$

This approximation is identical to the approximation used by Bixon[17] and by Zwanzig[18] in deriving the Rouse–Zimm theory of polymer chain dynamics from a many particle diffusion equation. We also note that the neglect of the memory term in Eq. (3.14) is exact at short times. This approximation is therefore also equivalent to the moment theory approximation made by Ackerson *et al.*,[19] and to a decoupling approximation of Altenberger and Deutch[20] in their theories of the concentration dependence of the diffusion coefficient and light scattering from polymer solutions. Neglected in this short-time approximation are correlations with other variables which would build up on the time scale of the diffusion process. The inclusion of this memory term would lead to nonexponential decay of the time correlation functions.

The operator Eq. (3.15) leads to a relaxation equation for the correlation functions of $A_s$ and $A_\perp$, which in terms of the components $A_\alpha = (A_s, A_\perp)$, has the form

$$\frac{\partial}{\partial t}\langle A_\alpha|PA(t)\rangle = \sum_\beta \Gamma_{\alpha\beta}\langle A_\beta|PA(t)\rangle . \tag{3.16}$$

The relaxation matrix is

$$\mathbf{\Gamma} = \begin{bmatrix} \langle A_s|\mathcal{L}|A_s\rangle & \langle A_s|\mathcal{L}|A_\perp\rangle \\ \langle A_\perp|\mathcal{L}|A_s\rangle & \langle A_\perp|\mathcal{L}|A_\perp\rangle \end{bmatrix} \cdot \begin{bmatrix} \langle A_s|A_s\rangle^{-1} & 0 \\ 0 & \langle A_\perp|A_\perp\rangle^{-1} \end{bmatrix} . \tag{3.17}$$

The matrix elements exhibited in Eq. (3.17) can be written as averages of one and two particle properties. We shall use the notation

$$g = \langle A_2|A_1\rangle\langle A_1|A_1\rangle^{-1} , \tag{3.18}$$

$$\dot{g} = \langle A_2|\mathcal{L}|A_1\rangle\langle A_1|\mathcal{L}|A_1\rangle^{-1} . \tag{3.19}$$

In terms of these two expressions the relaxation matrix is

$$\mathbf{\Gamma} = \frac{\langle A_1 | \mathfrak{L} | A_1 \rangle}{\langle A_1 | A_1 \rangle} \begin{bmatrix} 1 & \left(\dfrac{\dot{g}-g}{1+Ng}\right) \\ N(\dot{g}-g) & \left(\dfrac{1+N\dot{g}}{1+Ng}\right) \end{bmatrix} . \tag{3.20}$$

This matrix is of the same form as that appearing in the Keyes–Kivelson theory. The solution of the relaxation equation therefore leads to the same conclusion as in the Keyes–Kivelson theory, i.e., the single particle and collective correlation functions both decay as single exponentials with correlation times $\tau_s$ and $\tau_c$, respectively, and the correlation times satisfy the relation

$$\tau_s/\tau_c = [(1+N\dot{g})/(1+Ng)] . \tag{3.21}$$

In the Keyes–Kivelson theory and in the application discussed here the single particle functions $A_i$ are chosen to be spherical harmonics of the orientation angles of the $i$th particle.

The quantity $g$, a quantity of order $1/N$, is identical to the static orientation factor, analogous to the Kirkwood $g$ factor, used by Keyes and Kivelson. The quantity $\dot{g}$, also of order $1/N$, is an approximate expression for the dynamical orientation correlation factor introduced by Keyes and Kivelson. While in the formal theory of Keyes and Kivelson the dynamical orientation correlation is undetermined, our approximation expression Eq. (3.19) may be evaluated in terms of static correlation functions.

We leave the tedious but straightforward evaluation of the matrix elements involved in $\dot{g}$ to the Appendix. The result is

$$N\dot{g} = -\frac{1}{2}\left[\frac{\zeta_0^{\Omega\Omega}}{8\pi\eta_0 a^3}\right]\frac{\rho a^3}{4\pi} K(l) \int_0^\infty \frac{f(l, l, 2; r)}{r} dr , \tag{3.22}$$

where $K(l)$ is a (nonzero) constant factor dependent only on the $l$ value appropriate to the orientational property considered ($l = 2$ for light scattering, $l = 1$ for dielectric relaxation, etc.) and $f(l, l, 2; r_{12})$ is related to the invariant expansion of the two particle distribution function[21] often used in equilibrium statistical mechanics of complex fluids. The invariant expansion of the two particle distribution is written

$$g(\mathbf{r}_1, \mathbf{\Omega}_1, \mathbf{r}_2, \mathbf{\Omega}_2) = \sum_{l_1 l_2 l_3} f(l_1 l_2 l_3; r_{12})\, \phi_{l_1 l_2 l_3}(\mathbf{\Omega}_1, \mathbf{\Omega}_2, \mathbf{\Omega}_{12}) \tag{3.23}$$

where $r_{12}$, $\mathbf{\Omega}_{12}$ are the spherical coordinates of the vector $\mathbf{r}_2 - \mathbf{r}_1$. The spherical invariant $\phi_{l_1 l_2 l_3}(\mathbf{\Omega}_1, \mathbf{\Omega}_2, \mathbf{\Omega}_{12})$ is

$$\phi_{l_1 l_2 l_3}(\mathbf{\Omega}_1, \mathbf{\Omega}_2, \mathbf{\Omega}_{12}) = \sum_{m_1 m_2 m_3} \left[ (-1)^{m_2} \begin{pmatrix} l_2 & l_1 & l_3 \\ -m_2 & m_1 & m_3 \end{pmatrix} \times \mathbf{Y}_{l_1 m_1}(\mathbf{\Omega}_1) \mathbf{Y}_{l_2 m_2}(\mathbf{\Omega}_2) \mathbf{Y}_{l_3 m_3}(\mathbf{\Omega}_{12}) \right]. \tag{3.24}$$

The coefficient $f(l, l, 2; r_{12})$ is involved in $\dot{g}$ because of the tensorial character of the rotation–rotation Oseen tensor. For comparison we note that the static correlation factor $g$ is dependent on the coefficient $f(l, l, 0; r_{12})$

$$Ng = \frac{\rho}{4\pi} \int_0^\infty f(l, l, 0; r)\, r^2 dr . \tag{3.25}$$

Expression (3.22) for $\dot{g}$ is the primary result of this section. Its numerical evaluation involves a knowledge of the pair distribution function of the fluid, but several qualitative conclusions can be drawn from this expression. These will be discussed in Sec. V.

## IV. NONINTERACTING COUPLED ROTATIONAL DIFFUSION MODEL

In this section we explore the consequences of the rotational hydrodynamic interaction for a different model system: spherical macroparticles in an isotropic fluid where direct interaction between the particles is absent and, accordingly, equilibrium angular correlations are not present. In this model the appropriate diffusion equation includes both translational and rotational diffusion with hydrodynamic interaction. For simplicity we shall ignore translational diffusion and focus on the crossrotational effects. Since we neglect the effect of direct interaction, our model should be restricted to dilute systems. This restricted model is described by the diffusion equation

$$\frac{\partial P(t)}{\partial t} = (\mathfrak{L}_0 + \mathfrak{L}_1) P(t) = \mathfrak{L}_{\mathrm{RR}} P(t) , \tag{4.1}$$

where $\mathfrak{L}_0$ is the rotational diffusion operator for the individual particles

$$\mathfrak{L}_0 = \sum_{i=0}^{N} D_0 L^2(i) \tag{4.2}$$

with $D_0 = (kT/8\pi\eta a^3)$ equal to the rotational diffusion coefficient as given by the Debye Law, for independent particles, and

$$L^2(i) = \nabla^2_{\mathbf{\Omega}_i} \tag{4.3}$$

is the angular Laplacian operator. In the diffusion equation, Eq. (4.1), the operator $\mathfrak{L}_1$ describes the hydrodynamic interaction between the particles; from Eq. (2.27) one has

$$\mathfrak{L}_1 = \sum_{i,j(i\neq j)} \mathbf{L}(i) \cdot \mathbf{D}_{ij}^{\Omega\Omega} \cdot \mathbf{L}(j) , \tag{4.4}$$

where

$$\mathbf{D}_{ij}^{\Omega\Omega} = k_B T\, \mathbf{T}_{ij}^{\Omega\Omega} . \tag{4.5}$$

We are interested in evaluating correlation functions of the form

$$C_{A,B}(t) = \langle\langle A_n(t)\, B_m(0) \rangle\rangle , \tag{4.6}$$

where $A_n(t)$ denotes a function of the orientation of $n$ particles at time $t$. The double angular bracket signifies an average over interparticle positions and over particle orientation. Since the equilibrium distribution for this $N$-particle disordered system is

$$P_{\mathrm{eq}}(\mathbf{\Omega}^N) = (4\pi)^{-N} , \tag{4.7}$$

the correlation function $C_{A,B}(t)$ may be expressed as

$$C_{A,B}(t)=\int d\Omega^N P_{\mathrm{eq}}(\Omega^N)\, B_m^*(\Omega^m)\, \langle \exp(\mathcal{L}t)\rangle\, A_m(\Omega^n)\ . \qquad (4.8)$$

The angular bracket in Eq. (4.8) denotes an average over the positions of the particles; the distribution of the center of mass of the particles is considered to be independent of particle orientation, consistent with neglecting direct particle interactions in Eq. (4.1).

We shall evaluate correlation functions of several cases of interest. Before proceeding, it is important to note that the diffusion operators $\mathcal{L}_0$ and $\mathcal{L}_1$ commute since

$$[L^2(i),\ \mathbf{L}(i)]=[L^2(i),\ \mathbf{L}(j)]=0\ . \qquad (4.9)$$

Accordingly, Eq. (4.8) may be expressed as

$$C_{A,B}(t)=\int d\Omega^N P_{\mathrm{eq}}(\Omega^N)\, B_m^*(\Omega^m) \times[\langle \exp(\mathcal{L}_1 t)\rangle \exp(\mathcal{L}_0 t)\, A_n(\Omega^n)]\ . \qquad (4.10)$$

This simplification greatly facilitates evaluation of the correlation functions of interest.

### A. Two-point correlations

For this case, the dynamical functions $A$ and $B$ each depend upon the coordinates of a single particle,

$$A=\mathbf{Y}_{lm}(\Omega_i)\ ;\quad B=\mathbf{Y}_{l'm'}(\Omega_j)\ . \qquad (4.11)$$

Since

$$\mathcal{L}_0\, \mathbf{Y}_{lm}(\Omega_i)=-D_0 l(l+1)\, \mathbf{Y}_{lm}(\Omega_i)\ ,$$

one finds

$$C_{i,j}(t)=\exp[-D_0 l(l+1)t] \times \int d\Omega^N P_{\mathrm{eq}}(\Omega^N)\, \mathbf{Y}_{l'm'}(\Omega_j)\, \langle \exp(\mathcal{L}_1 t)\rangle\, \mathbf{Y}_{lm}(\Omega_i)\ . \qquad (4.12)$$

However, $\mathcal{L}_1$ vanishes when it operates on any function which depends upon the orientation of just one particle, since this operator always contains products of the angular momentum operators of two particles. Thus

$$C_{ij}(t)=\exp[-D_0 l(l+1)t] \times \int d\Omega^N P_{\mathrm{eq}}(l^N)\, \mathbf{Y}^*_{l'm'}(\Omega_j)\, \mathbf{Y}_{lm}(\Omega_i) =\exp[-D_0 l(l+1)t]\, \delta_{ij}\, \delta_{ll'}\, \delta_{mm'}\ . \qquad (4.13)$$

This result is identical to the result of the independent particle Debye rotational diffusion model; self-correlations decay exponentially and crosscorrelations are not present. We may conclude that the rotational hydrodynamic interaction that exists in the fluid is not manifest in the two-point correlation functions when translational motion is ignored and the rotational diffusion coefficient is given by the longrange asymptotic form discussed in Sec. II and explicitly displayed in Eq. (2.27).

### B. Four-point correlations

In this section we demonstrate that four-point correlation functions are influenced by crossdiffusional effects in the simplified model where $D_{ij}$ is given by Eq. (4.5), when translational effects are ignored. The four-point correlation function

$$C_4(t)=\langle\langle \mathbf{Y}^*_{l_1'm_1'}(\Omega_1)\, \mathbf{Y}^*_{l_2'm_2'}(\Omega_2) \times \mathbf{Y}_{l_1m_1}[\Omega_1(t)]\, \mathbf{Y}_{l_2m_2}[\Omega_2(t)]\rangle\rangle\ , \qquad (4.14)$$

when expressed in terms of its Laplace transform

$$\hat{C}_4(Z)=\int_0^\infty \exp[-zt]\, C_4(t)\, dt\ , \qquad (4.15)$$

takes the form

$$\hat{C}_4(Z)=\hat{C}_0(Z)+\Delta\hat{C}(Z)\,. \qquad (4.16)$$

We shall show that in contrast to the case of two-point correlations, the hydrodynamic interaction introduced through $\mathcal{L}_1$ influences $\hat{C}_4(Z)$. An exact evaluation is not possible, so we shall employ perturbation theory.

From Eqs. (4.14) and (4.15) one has

$$\hat{C}_4(Z)=\langle\langle \mathbf{Y}^*_{l_1'm_1'}\, \mathbf{Y}^*_{l_2'm_2'}[Z-\mathcal{L}_0-\mathcal{L}_1]^{-1}\, \mathbf{Y}_{l_1m_1}\, \mathbf{Y}_{l_2m_2}\rangle\rangle\ . \qquad (4.17)$$

We employ the operator identity

$$[Z-\mathcal{L}_0-\mathcal{L}_1]^{-1}=[Z-\mathcal{L}_0]^{-1}\,[1+\mathcal{L}_1(Z-\mathcal{L}_0-\mathcal{L}_1)^{-1}] \qquad (4.18)$$

to obtain an expression for the propogator to second order in $\mathcal{L}_1$:

$$(Z-\mathcal{L}_0-\mathcal{L}_1)^{-1}=(Z-\mathcal{L}_0)^{-1}+(Z-\mathcal{L}_0)^{-1}\mathcal{L}_1(Z-\mathcal{L}_0)^{-1} +(Z-\mathcal{L}_0)^{-1}\mathcal{L}_1(Z-\mathcal{L}_0)^{-1}\mathcal{L}_1(Z-\mathcal{L}_0)^{-1}+\dots\ . \qquad (4.19)$$

When this expression is substituted into Eq. (4.17), one finds

$$\hat{C}_0(Z)=\langle\langle \mathbf{Y}^*_{l_1'm_1'}\mathbf{Y}^*_{l_2'm_2'}(Z-\mathcal{L}_0)^{-1}\mathbf{Y}_{l_1m_1}\, \mathbf{Y}_{l_2m_2}\rangle\rangle =\{Z-D_0[l_1(l_1+1)+l_2(l_2+1)]\}^{-1}\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{m_1m_1'}\delta_{m_2m_2'} \qquad (4.20)$$

and

$$\Delta\hat{C}(Z)=\{Z-D_0[l_1(l_1+1)+l_2(l_2+1)]\}^{-3} \times\langle \mathbf{Y}^*_{l_1'm_1'}\, \mathbf{Y}^*_{l_2'm_2'}\, \langle\mathcal{L}_1\mathcal{L}_1\rangle\, \mathbf{Y}_{l_1m_1}\, \mathbf{Y}_{l_2m_2}\rangle \qquad (4.21)$$

where use has been made of the fact that $\mathcal{L}_0$ and $\mathcal{L}_1$ commute. In Eq. (4.21) the inner angular bracket denotes an average over particle positions and the outer angular bracket denotes an average over particle orientations. The linear term in $\mathcal{L}_1$ from Eq. (4.19) does not contribute to $\Delta\hat{C}(Z)$ because it vanishes when isotropically averaged over particle positions.

The onlyterms in $\langle\mathcal{L}_1\mathcal{L}_1\rangle$ that make a nonvanishing contribution to $\Delta\hat{C}(Z)$, Eq. (4.21), are those that depend upon the orientations of particles 1 and 2. Thus we may take

$$\langle\mathcal{L}_1\mathcal{L}_1\rangle=(k_BT)^2\,\langle[\mathbf{L}(1)\cdot\mathbf{T}_{12}^{\Omega\Omega}\cdot\mathbf{L}(2)]^2\rangle\ . \qquad (4.22)$$

A tedious but straightforward calculation leads to

$$\langle\mathcal{L}_1\mathcal{L}_1\rangle=\left[\frac{k_BT}{16\pi\eta_0}\right]^2\left\langle\frac{1}{r_{12}^6}\right\rangle\{\tfrac{3}{5}\,[L(1)^2L(2)^2]+\tfrac{1}{5}\,[\mathbf{L}(1)\cdot\mathbf{L}(2)]^2\}\ . \qquad (4.23)$$

Accordingly, the correction term in Eq. (4.21) is equal to

$$\Delta\hat{C}(Z)=[k_BT/(16\pi\eta_0)]^2\left\langle\frac{1}{r_{12}^6}\right\rangle\{Z+D_0[l_1(l_1+1)+l_2(l_2+1)]\}^{-3}$$
$$\times\{\tfrac{3}{5}\,l_1(l_1+1)l_2(l_2+1)\,\delta_{l_1l_1'}\delta_{l_2l_2'}\delta_{m_1m_1'}\delta_{m_2m_2'}$$
$$+\tfrac{1}{5}\,\langle l_1'm_1';\,l_2'm_2'|[\mathbf{L}(1)\cdot\mathbf{L}(2)]^2|\,l_1m_1;\,l_2m_2\rangle\} \qquad (4.24)$$

where we have introduced a Dirac notation for the remaining angular integrations.

The matrix element in Eq. (4.24) can be evaluated using angular momenta coupling $\mathbf{F}=\mathbf{L}(1)+\mathbf{L}(2)$ and angular momenta coupling coefficients

$$\langle l_1l_2F,M|\,l_1m_1;\,l_2m_2\rangle\ . \qquad (4.25)$$

The result is simplest for the symmetric case $l_1=l_1'$, $m_1=m_1'$, $l_2=l_2'$, $m_2=m_2'$

$$\Delta C(Z)=[k_BT/(16\pi\eta_0)]^2\left\langle\frac{1}{r_{12}^6}\right\rangle\{Z+D_0[l_1(l_1+1)+l_2(l_2+1)]\}^{-3}$$
$$\times\left\{\tfrac{3}{5}\,l_1(l_1+1)\,l_2(l_2+1)+\frac{1}{20}\sum_{M,F}\{[F(F+1)-l_1(l_1+1)-l_2(l_2+1)]^2\,|\,\langle l_1m_1;\,l_2m_2|\,l_1l_2F,M\rangle|^2\}\right\}. \qquad (4.26)$$

Thus for the symmetric four-point correlation function one finds that the simple exponential decay expected on the basis of independent rotational diffusion,

$$C_0(t)=\exp\{-D_0[l_1(l_1+1)+l_2(l_2+1)]\,t\}\ , \qquad (4.27)$$

is modified by a time-dependent correction factor that includes the effects of hydrodynamic interactions

$$\Delta C(t)=(\text{const})\int_0^t d\tau\int_0^\tau ds\,f(t-\tau)\,f(\tau-s)\,f(s)\ , \qquad (4.28)$$

where

$$f(t)=\exp\{-D_0[l_1(l_1+1)+l_2(l_2+1)]\,t\} \qquad (4.29)$$

and the positive constant equals

$$(\text{const})=\left[\frac{k_BT}{16\pi\eta_0}\right]^2\left\langle\frac{1}{r_{12}^6}\right\rangle\left\{\tfrac{3}{5}\,l_1(l_1+1)\,l_2(l_2+1)\right.$$
$$+\frac{1}{20}\sum_{F,M}[F(F+1)-l_1(l_1+1)-l_2(l_2+1)]^2$$
$$\left.\times|\,\langle l_1m_1;\,l_2m_2|\,l_1l_2F,M\rangle|^2\right\}. \qquad (4.30)$$

In summary, we find that in this simple model where translation is neglected, anisotropic forces are ignored and only the longrange part of the hydrodynamic interaction is retained, the interparticle correlations in the fluid will be manifest in the four-point correlation functions but not in either the "self" or "cross" two-point correlation functions. It is just these two-point correlation functions that arise in depolarized light scattering or magnetic and dielectric relaxation experiments. Thus for systems which conform to the rather stringent conditions of this idealized model, we would expect to see no effect from the rotational hydrodynamic interaction which is present between the particles. It is amusing to note, however, that four-point functions of angular position arise in mode–mode coupling theories[22] of the two-point orientational correlation function. We expect that the hydrodynamically induced correlations discussed here will be physically present in the systems considered by these investigators.

### C. Relaxing the assumptions of the model

The startling result of this simplified noninteracting coupled rotational diffusion model is that the two-point correlation function is unmodified from the independent particle Debye rotational diffusion model [see Eq. (4.13)]. This will not be the case if some of the assumptions of the model are relaxed.

At first glance one might well assume that if the dynamics of translation ($\mathcal{L}_{TT}+\mathcal{L}_{TR}$) were included explicitly in Eq. (4.1) in addition to $\mathcal{L}_{RR}$, that a different outcome would be reached. However, this is not the case for two-point correlation functions where the dynamical variable of interest $A$ is a spherical harmonic of the orientation of a single particle. *The reason for this* $\mathbf{Y}_{lm}(\mathbf{\Omega}_i)$ *is an eigenfunction of the coupled noninteracting diffusion operator.* Thus[23]

$$[\mathcal{L}_{TT}+\mathcal{L}_{TR}+\mathcal{L}_{RR}]\,\mathbf{Y}_{lm}(\mathbf{\Omega}_i)=-D_0l(l+1)\,\mathbf{Y}_{lm}(\mathbf{\Omega}_i) \qquad (4.31)$$

and

$$\exp[(\mathcal{L}_{TT}+\mathcal{L}_{TR}+\mathcal{L}_{RR})\,t]\,\mathbf{Y}_{lm}=\exp[-D_0l(l+1)\,t]\,\mathbf{Y}_{lm}\ , \qquad (4.32)$$

where the operators are defined in Eqs. (3.6)–(3.8) with $U=0$ for this noninteracting case. Accordingly we may conclude that the results of Sec. IV. A, in particular Eq. (4.13), will not be modified by including translational diffusion.

One might well inquire about what will cause a deviation from the independent Debye rotational diffusion result in this model. In Sec. III it has been demonstrated that the presence of anisotropic interparticle forces will cause deviation. However, there is another possibility. Our derivation of the coupled diffusion coefficients $\mathbf{D}_{ij}^{X\Omega}$, $\mathbf{D}_{ij}^{XX}$, $\mathbf{D}_{ij}^{\Omega\Omega}$, is based on an approximate hydrodynamic treatment where the particles are considered as point disturbances that give rise to point sources of force and torque in the fluid. Such a picture can only be correct when the particles are separated by a distance much greater than their size. In this limiting case one finds $\mathbf{D}_{ii}^{\Omega\Omega}=D_0$ (rotational) for isotropic particles; the "self" diffusion coefficient is unmodified from the Debye value $D_0=[kT/8\pi\eta_0a^3]$ by the presence of the other particles. However, in a more complete hydrodynamic calculation of the interaction between particles [see, e.g., Refs. (11) and (12)] valid for closer interparticle separations, one would find, even with $U=0$, the result that $\mathbf{D}_{ii}^{\Omega\Omega}$ is an explicit function of particle separation. This will have two important consequences. First, $Y_{lm}(\Omega_i)$ need no longer be an eigenfunction of $\mathcal{L}_{RR}$

and second, the "self" two-particle correlation function $C_{ii}(t)$ [see Eqs. (4.6) and (4.11)] will no longer relax as a single exponential.

Finally we note that if the particles are not spherically symmetric and therefore are characterized by a tensor single particle rotational diffusion coefficient $\mathbf{D}_0$, then the analysis of the coupled, noninteracting diffusion model presented in this section must be modified.

## V. DISCUSSION

The hydrodynamic mechanism developed in this paper provides a concrete model for which previous conceptions of dynamical orientation correlations can be tested. The model is realistic for macromolecular solutions but it should be applied to molecular solutions with caution, because of the use of hydrodynamics at a microscopic level.

Several experimental determinations of the dynamical orientation correlation factor $\dot{g}$ have concluded that $\dot{g}$ is much smaller than the static correlation factor $g$. In order to explain this observation, Gierke has recently put forward an argument based on symmetry principles which concludes that $\dot{g}$ vanishes for symmetric tops.[7] This is not the case for the present model, because Gierke's assumption that the correlation of the angular velocities of two different molecules is not related to their relative positions and orientations, does not hold.

The present calculation immediately suggests one explanation for why $\dot{g}$ usually is less than $g$. The static correlation factor $g$ can become quite large if there is incipient long-range order in a fluid. It diverges for a fluid approaching a liquid crystal transition point, such as MBBA in the studies of Gierke and Flygare.[4] Our expression for $\dot{g}$ shows that this quantity is only weakly influenced by long-range correlations because the hydrodynamic interaction between two molecules decreases with increasing separation.

In Sec. IV we have specialized the coupled diffusion model to the case where hydrodynamic interactions are present for both rotation and translation, but where no direct interaction is present between the particles. The somewhat surprising conclusion of the analysis is that the Debye law for two-particle orientation correlation functions is not modified by the hydrodynamic mechanism. This result is pertinent to some recent NMR relaxation experiments and their interpretation by Koenig on aqueous protein solutions.[8] One qualitative explanation put forward to explain observed deviations from the Debye law for the water molecules involved long-range hydrodynamic interaction between the spherical protein and the water.[8] This explanation is not in accord with the present model, but of course, the diffusional model may not be totally adequate since the orientational relaxation time of the water molecules can be comparable to the angular momentum relaxation time of the protein molecules.

While for the isotropic case the two-point functions, related to linear response measurements, are unchanged by the hydrodynamic effect, four-point functions, related to nonlinear response experiments, are modified. This illustrates the difficulty in inferring details about microscopic motions from comparisons of nonlinear and linear response measurements.[24] It also illustrates a potential weakness in simple decoupling schemes often used in mode-mode coupling theories to relate multipoint correlation functions to simpler correlation functions.

Finally we wish to point out that the many particle coupled diffusion-rotation model which we have discussed in this paper is a reasonable starting point in the examination of many other problems where the effect of rotational motion on transport phenomena is of interest.

## APPENDIX

The matrix elements that interest us are of the form

$$M_{11}(l, m \mid l', m') = \int dQ\, \mathbf{Y}^*_{lm}(\Omega_1)[\mathcal{L}\mathbf{Y}_{l'm'}(\Omega_1)]P_{\text{eq}}(Q)\ , \tag{A1}$$

$$M_{12}(l, m \mid l', m') = \int dQ\, \mathbf{Y}^*_{lm}(\mathbf{\Omega}_1)[\mathcal{L}\mathbf{Y}_{l'm'}(\mathbf{\Omega}_2)]P_{\text{eq}}(Q)\ . \tag{A2}$$

In evaluating these matrix elements it is advantageous to perform some partial integrations to yield

$$M_{11}(l, m \mid l', m') = -\int dQ[\mathbf{L}(1)\mathbf{Y}^*_{lm}(\mathbf{\Omega}_1)] \cdot \mathbf{D}^{\Omega\Omega}_{11} \cdot [\mathbf{L}(1)\mathbf{Y}_{l'm'}(\mathbf{\Omega}_1)]P_{\text{eq}}(Q)\ , \tag{A3}$$

$$M_{12}(l, m \mid l'm') = -\int dQ[\mathbf{L}(1)\mathbf{Y}^*_{lm}(\mathbf{\Omega}_1)] \cdot \mathbf{D}^{\Omega\Omega}_{12} \cdot [\mathbf{L}(2)\mathbf{Y}_{l'm'}(\Omega_2)]P_{\text{eq}}(Q)\ . \tag{A4}$$

We have simplified these expressions by using the fact that the variables $\mathbf{Y}_{lm}(\mathbf{\Omega}_i)$ are independent of the positional coordinates $X_i$. It is very easy to evaluate the one particle matrix element $M_{11}$ when the fluid is isotropic:

$$M_{11}(l, m \mid l', m') = -\frac{l(l+1)}{4\pi} D^{\Omega\Omega}_0 \delta_{ll'} \delta_{mm'}\ . \tag{A5}$$

In order to evaluate the two particle matrix element $M_{12}$ we write the vector operator $\mathbf{L}$ in the basis

$\mathbf{e}_q : \mathbf{e}_0 = \mathbf{e}_z\ , \quad \mathbf{e}_\pm = \mp(\mathbf{e}_x \pm i\mathbf{e}_y)/\sqrt{2}\ .$

This gives

$$M_{12} = -\sum_{qq'} \langle [L_q(1)Y_{lm}(\Omega_1)]^* D_{12}(q \mid q')[L_{q'}(2)Y_{l'm'}(\Omega_2)]\rangle\ , \tag{A6}$$

where

$$D_{12}(q \mid q') = \mathbf{e}_q \cdot \mathbf{D}^{\Omega\Omega}_{12} \cdot \mathbf{e}^*_{q'}\ . \tag{A7}$$

Using well-known angular momentum algebra, $M_{12}$ can be written as

$$\begin{aligned} M_{12} = -\sum_{qq'} &(-1)^q(-1)^{q'} \sqrt{l(l+1)}\sqrt{l'(l'+1)} \\ &\times (l, m+q; 1, -q \mid l1l, m)^* (l', m'+q'; 1, -q' \mid l'1l', m') \\ &\times \langle \mathbf{Y}^*_{l,m+q}(\Omega_1) D_{12}(q \mid q')\mathbf{Y}_{l',m'+q'}(\Omega_2)\rangle\ . \end{aligned} \tag{A8}$$

We employ the notation and conventions of Edmonds.[24]

Using the explicit form Eqs. (2.21) and (2.27) for $\mathbf{D}_{12}^{\Omega\Omega}$, we find that $D_{12}(q|q')$ can be written as

$$D_{12}(q|q') = \frac{c}{r_{12}^3} \sum_p 3\sqrt{20\pi}\,(-1)^{q'} \times \begin{pmatrix} 1 & 1 & 2 \\ q & -q' & p \end{pmatrix} \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} \mathbf{Y}_{2p}^{*}(\Omega_{12}) \,, \tag{A9}$$

where $c = -(k_B T/16\pi\eta_0)$.

Thus $M_{12}$ involves equilibrium averages of the form

$$Z = \langle \mathbf{Y}_{l,m+q}^{*}(\Omega_1) \frac{1}{r_{12}^3}(\Omega_{12}) \mathbf{Y}_{l',m'+q'}(\Omega) \rangle \,. \tag{A10}$$

We can use the invariant expansion of the distribution function[21] to write this average as

$$Z = 4c\sqrt{(3\pi/2)}\,(-1)^{m'+1} \int_0^\infty \frac{f(l,l',2;r)}{r}\,dr \times \sum_p \begin{pmatrix} 1 & 1 & 2 \\ q & -q' & p \end{pmatrix} \begin{pmatrix} l' & l & 2 \\ -(m'+q') & (m+q) & p \end{pmatrix}. \tag{A11}$$

This expression, combined with Eqs. (A9) and (A8), yields an expression for $M_{12}$ as an integral over $f(l,l,2;r)$. When this result is specialized to the case $l=l'$, we obtain

$$M_{12}(l,m|l,m) = \langle A_2|\mathfrak{L}|A_1\rangle = -cl(l+1)K(l)\frac{P}{(4\pi)^2 N}\int_0^\infty \frac{f(l,l,2;r)}{r}\,dr \,. \tag{A12}$$

Since

$$M_{11}(l,m|l,m) = \langle A_1|\mathfrak{L}|A_1\rangle = -\frac{l(l+1)}{4\pi} D_0^{\Omega\Omega} \,, \tag{A13}$$

we then obtain Eq. (3.22) for $\dot{g}$ where the coefficient $K(l)$ is

$$K(l) = \frac{1}{(2l+1)(l+1)l} \begin{Bmatrix} l & l & 2 \\ 1 & 1 & l \end{Bmatrix}. \tag{A14}$$

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