The effects of hydrodynamic interactions on translational and rotational relaxation[a]

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A theory of coupled translational and rotational relaxation in solution including the effects of hydrodynamic interaction is presented. The translational, translational–rotational, and rotational diffusion tensors are computed using the method of hydrodynamic reflections. The correlation functions $C_{lm}(t) = \langle Y_{lm}{}^{*}[\mathbf{u}(0)] \; Y_{lm}[\mathbf{u}(t)] \rangle$ and $C_{lm}(\mathbf{q}, t) = \langle \exp i\mathbf{q}\cdot[\mathbf{r}(t) - \mathbf{r}(0)] \; Y_{lm}{}^{*}[\mathbf{u}(0)] \; Y_{lm}[\mathbf{u}(t)] \rangle$ are found from a coupled translational–rotational diffusion equation. $C_{lm}(t)$ is shown to reduce to the Debye result under conditions relevant to magnetic resonance experiments. The concentration dependence of the rotational diffusion coefficient is calculated and compared with experiment. The failure of the results to account for the dynamical correlations seen in recent NMR studies of protein solutions by Koenig and co-workers is discussed.

INTRODUCTION

The use of hydrodynamic methods to theoretically describe dynamical and frictional properties of polymer solutions has been very fruitful. The methods of Kirkwood and Rieseman[1] for treating the hydrodynamic interactions between particles in solution using the Oseen tensor have become standard techniques in polymer theory. Their approach is based on the solution of the Navier–Stokes equation for point particles having no volume.

The calculation of hydrodynamic interactions between particles of finite size is much more difficult, but some progress has been made. Stimson and Jeffrey[2] have given an exact solution for two particles approaching each other along their line of centers, with stick boundary conditions. Translations along other directions as well as rotations have been considered by other authors.[3,4] Another approach is to construct approximate solutions in series, by a method of reflections. The translational self- and cross diffusion tensors have been found in this manner by Aguirre and Murphy,[5] Batchelor, Mou and Chang,[7] and Felderhof.[8] An approximate result for the translational cross-diffusion tensor has been found from a variational principle by Rotne and Prager.[9]

In this paper the translational, translational–rotational, and rotational diffusion tensors for two spherical particles of unequal size are found by extension of the treatments of Aguirre and Murphy[5] and Felderhof,[8] and compared with previous results. An N-particle coupled translational–rotational diffusion equation embodying our results can be applied to many problems. We apply these results in particular to find time correlation functions of interest in NMR and incoherent neutron scattering.

These results are compared with the experimental results of Koenig and co-workers,[10] who have observed dynamical correlations between the tumbling of protein and solvent molecules in NMR experiments on solutions of globular proteins. The reorientational correlation function of water molecules is found to decay on two vastly different time scales. The long time decay is

characterized by the reorientational time of the protein molecules, whereas the short decay typifies the usual time scale for water. We might ask why the water molecules retain memory of how the solute protein molecule reorients. Koenig *et al.* are able to exclude experimentally any mechanism which involves binding of solvent to protein molecules and suggest their results are due to long range hydrodynamic interactions. We find, however, only slight corrections to the usual Debye model results for the orientational correlation function. Some of our results are very similar to those recently given by Wolynes and Deutch[11] in another theoretical treatment of this problem.

HYDRODYNAMIC INTERACTIONS

We consider a model system consisting of N spherical Brownian particles executing translations and rotations in a viscous fluid. Our interest is in rotational relaxation, but the translational and rotational problems cannot be decoupled at the outset due to the existence of hydrodynamic translation–rotation coupling (which exists even between spheres when stick boundary conditions are applied), i.e., a sphere translating and rotating in a viscous fluid exerts both a force and a torque on a second sphere placed in its velocity field. Similarly, a rotating sphere exerts both a force and a torque on another particle. This point is discussed at greater length by Happel and Brenner.[4] The difficulties that appear when translational motion is completely disregarded will be discussed in a forthcoming note.[12]

In the limit that inertial effects may be neglected the translational and rotational relaxation of a system of N spherical Brownian particles is described by a coupled translational–rotational diffusion equation. The conditional probability distribution $P(\{\mathbf{r}_i\}, \{\mathbf{u}_i\}, t; \{\mathbf{r}_i'\}, \{\mathbf{u}_i'\})$ of the positions $\mathbf{r}_i$ and orientations $\mathbf{u}_i$ satisfies

$$\frac{\partial P}{\partial t} = \sum_{kl} [\nabla_k \cdot (\mathbf{D}_T)_{kl} \cdot (\nabla_l P - \beta P \nabla_l U) + \nabla_k \cdot (\mathbf{D}_{TR})_{kl}$$
$$\cdot (i\mathbf{L}_l P - i\beta P \mathbf{L}_l U) + i\mathbf{L}_k \cdot (\mathbf{D}_{RT})_{kl} \cdot (\nabla_l P - \beta P \nabla_l U)$$
$$+ i\mathbf{L}_k \cdot (\mathbf{D}_R)_{kl} \cdot (i\mathbf{L}_l P - i\beta P \mathbf{L}_l U)] . \tag{1}$$

$\mathbf{L}_k = -i\mathbf{u}_k \times \nabla_{\mathbf{u}_k}$ is the dimensionless angular momentum operator in the space of the kth particle, U is the inter-

molecular potential, and $\beta = (kT)^{-1}$. A derivation of this equation is given by Condiff and Dahler,[13] who prove that the matrix D of diffusion tensors is related to the matrix of friction tensors ζ (the "grand resistance matrix" of Happel and Brenner) by a generalized Einstein relation

$$D = kT\,\zeta^{-1}, \tag{2}$$

where

$$D = \begin{pmatrix} D_T & D_{TR} \\ D_{RT} & D_R \end{pmatrix} , \qquad \zeta = \begin{pmatrix} \zeta_T & \zeta_{TR} \\ \zeta_{RT} & \zeta_R \end{pmatrix} . \tag{3}$$

The submatrices D_T, D_R, D_{TR}, and D_{RT} are explicitly given in terms of the friction submatrices by

$$\begin{aligned}
D_T &= kT(\zeta_T - \zeta_{TR}\,\zeta_R^{-1}\zeta_{RT})^{-1} , \\
D_R &= kT(\zeta_R - \zeta_{RT}\,\zeta_T^{-1}\zeta_{TR})^{-1} , \\
D_{TR} &= kT(\zeta_{TR} - \zeta_R\zeta_{TR}^{-1}\zeta_T)^{-1} , \\
D_{RT} &= kT(\zeta_{TR} - \zeta_T\,\zeta_{RT}^{-1}\zeta_R)^{-1} .
\end{aligned} \tag{4}$$

The friction tensors relate the hydrodynamic forces and torques F and N to the particle velocities and angular velocities u and Ω by

$$\begin{pmatrix} F \\ N \end{pmatrix} = - \begin{pmatrix} \zeta_T & \zeta_{TR} \\ \zeta_{RT} & \zeta_R \end{pmatrix} \begin{pmatrix} u \\ \Omega \end{pmatrix} . \tag{5}$$

Note that F, N, u, and Ω, are column vectors containing N components and the matrices ζ_T, ζ_R, ζ_{TR}, and ζ_{RT} contain N^2 friction tensors. Happel and Brenner show $\zeta_{TR} = \zeta_{RT}^{\dagger}$ and consequently $D_{TR} = D_{RT}^{\dagger}$ (also shown by Condiff and Dahler). The operation $\dagger$ indicates transposition of both the matrix and the tensors which are its elements.

To proceed further the hydrodynamic friction tensors must be calculated for a system of N particles. This may in principle be obtained from a solution of the Navier–Stokes equation in the presence of N spheres. This has not yet proved possible in practice.

Our procedure will be to calculate the matrix of friction tensors for two particles in a viscous fluid from a solution of the Navier–Stokes equation. The two body results will then be generalized to the N body case by assuming the hydrodynamic interactions to be pairwise additive.

The two particle friction tensors may be obtained from the solution of the Navier–Stokes equation

$$\eta\nabla^2 v = \nabla p \tag{6}$$

for an incompressible, viscous fluid in the presence of two particles simultaneously translating and rotating. The solution is found in series, using a method of reflections. We use the method and notation of Aguirre and Murphy,[5] who have solved this problem for pure translational motion.

The velocity field v in the presence of two spheres, moving with velocities u_1 and u_2 and angular velocities Ω_1 and Ω_2, is constructed as

$$v = v_1 + v_2 + v_3 + \cdots . \tag{7}$$

Each term in this expansion is required to satisfy the Navier–Stokes equation. Stick boundary conditions are used, as they are appropriate for the description of Brownian motion of macromolecules. The total velocity field v must satisfy

$$\begin{aligned}
v &= u_1 + \Omega_1 \times r_1 , \quad \text{on } S_1 , \\
&= u_2 + \Omega_2 \times r_2 , \quad \text{on } S_2 ,
\end{aligned} \tag{8}$$

where r_k is the radius vector of particle k and S_k is the surface of particle k. v_1 is chosen to satisfy

$$v_1 = u_1 + \Omega_1 \times r_1 , \quad \text{on } S_1 . \tag{9}$$

Note that while v_1 satisfies the boundary conditions on S_1, it does not on S_2. Therefore, v_2 is required to satisfy

$$v_2 = u_2 + \Omega_2 \times r_2 - v_1 , \quad \text{on } S_2 . \tag{10}$$

Higher terms are required to satisfy

$$\begin{aligned}
v_3 &= -v_2 , \quad \text{on } S_1 , \\
v_4 &= -v_3 , \quad \text{on } S_2 ,
\end{aligned} \tag{11}$$

and so on. It is clear that by this method one can construct successive approximations to the desired solution of the Navier–Stokes equation.

The problem has now been reduced to one of solving the Navier–Stokes equation for one spherical particle with arbitrary boundary conditions on the surface. This problem has been solved by Brenner,[14] who finds

$$v = -\sum_{n=0}^{\infty} {}^{n+2}V[n+1](\nabla^n u_0)_0 , \tag{12}$$

with

$$v = u_0(r) , \quad \text{on } S .$$

The tensor ${}^{n+2}V$ contain the effects of spherical symmetry and stick boundary conditions; ${}^2V$ gives the usual Stokes solution. The tensors $(\nabla^n u_0)_0$ contain the boundary values on the surface of the sphere. The subscript $(\ )_0$ means that the enclosed quantity is evaluated at the center of the sphere. This result may be used to construct the approximation v_k to the solution of the Navier–Stokes equation in the presence of two translating and rotating particles. Note that $(\nabla^n u_k)_0 = 0$ unless $n = 0$, in which case we get u_k. Also $(\nabla^n \Omega_k \times r_k)_0 = 0$ unless $n = 1$, in which case $(\nabla \Omega_k \times r_k)_0 = \epsilon \cdot \Omega_k$, where ϵ is the completely antisymmetric triadic formed from the Levi–Civita tensor. However, $(\nabla^n v_k)_0$ is nonvanishing to all orders (unless, of course, $k = 1$). Using Eqs. (9), (10), and (12) we may write

$$v_1 = -{}^2V_1 \cdot u_1 - {}^3V_1 : \epsilon \cdot \Omega_1 \tag{13}$$

and

$$\begin{aligned}
v_2 = &-{}^2V_2 \cdot u_2 - {}^3V_2 : \epsilon \cdot \Omega_2 - \sum_{n=0}^{\infty} {}^{n+2}V_2[n+1](\nabla^{n\,2}V_1) \cdot u_1 \\
&- \sum_{n=0}^{\infty} {}^{n+2}V_2[n+1](\nabla^{n\,3}V_1) : \epsilon \cdot \Omega_1 .
\end{aligned} \tag{14}$$

v_3, v_4, etc. may be constructed in an analogous manner. Explicit results for the ${}^{n+2}V_k$ are given by Brenner[14] and by Aguirre and Murphy.[5]

To obtain the friction tensors the forces and torques

on the two particles must be found. This is conveniently done using Faxén's theorems[14,15]

$$F_1 = \zeta_{T1}\left[\left(1 + \frac{R_1^2}{6}\Delta\right)v\right]_0 - \zeta_{T1}u_1 \ , \quad \zeta_{T_k} = 6\pi\eta R_k$$

$$= -(\zeta_T)_{11} \cdot u_1 - (\zeta_T)_{12} \cdot u_2 - (\zeta_{TR})_{11} \cdot \Omega_1 - (\zeta_{TR})_{12} \cdot \Omega_2 \ ,$$

$$N_1 = -\tfrac{1}{2}\zeta_{R1}\boldsymbol{\epsilon} : (\nabla v)_0 - \zeta_{R1}\Omega_1 \ , \quad \zeta_{R_k} = 8\pi\eta R_k^3 \tag{15}$$

$$= -(\zeta_R)_{11} \cdot \Omega_1 - (\zeta_R)_{12} \cdot \Omega_2 - (\zeta_{RT})_{11} \cdot u_1 - (\zeta_{RT})_{12} \cdot u_2 \ .$$

Note that Δ is the scalar Laplacian operator, a different quantity than ∇^2, a dyadic operator. It is straightforward, although tedious, to obtain expressions for the friction tensors in terms of the polyadic velocity fields $^{n+2}V_k$.

As is shown later, the lowest order term of $(D_T)_{11}$ explicitly involving r_{12} is of fourth order, while for $(D_R)_{11}$ it is of sixth order. Therefore, we give the friction tensors ζ_T and ζ_{TR} to fourth order, and ζ_R to sixth order. Our results are

$$(\zeta_T)_{11} = \zeta_{T1}(I + {}^2V_2 \cdot {}^2V_1 + {}^3V_2 : \nabla^2 \ V_1 + {}^4V_2 \ \vdots \ \nabla^2 \ {}^2V_1 + {}^2V_2 \cdot {}^2V_1 \cdot {}^2V_2 \cdot {}^2V_1 + \tfrac{1}{6}R_1^2\Delta \ {}^2V_2 \cdot {}^2V_1)$$

$$= \zeta_{T1}\left[I + \left(\frac{3}{4}\right)^2 \frac{R_1R_2}{r_{12}^2}(I + 3\hat{r}_{12}^2) + \frac{3}{8}\frac{R_1R_2(R_1^2+R_2^2)}{r_{12}^4}(I - 5\hat{r}_{12}^2) + \left(\frac{3}{4}\right)^4 \frac{R_1^2R_2^2}{r_{12}^4}(I + 15\hat{r}_{12}^2) + \frac{3}{4}\frac{R_1R_2^3}{r_{12}^4}(I + 4\hat{r}_{12}^2)\right] + O(r_{12}^{-6}) \ ,$$

$$(\zeta_T)_{12} = \zeta_{T1}({}^2V_2 + {}^2V_2 \cdot {}^2V_1 \cdot {}^2V_2 + \tfrac{1}{6}R_1^2\Delta \ {}^2V_2)$$

$$= -\zeta_{T1}\left[\frac{3}{4}\frac{R_2}{r_{12}}(I + \hat{r}_{12}^2) + \frac{R_2(R_1^2+R_2^2)}{4r_{12}^3}(I - 3\hat{r}_{12}^2) + \left(\frac{3}{4}\right)^3\frac{R_1R_2^2}{r_{12}^3}(I + 7\hat{r}_{12}^2)\right] + O(r_{12}^{-5}) \ ,$$

$$(\zeta_{TR})_{11} = \zeta_{T1}{}^2V_2 \cdot {}^3V_1 : \boldsymbol{\epsilon} = \tfrac{9}{2}\pi\eta R_1 R_2 \frac{R_2^3}{r_{12}^4}\hat{r}_{12} \cdot \boldsymbol{\epsilon} + O(r_{12}^{-5}) \ , \tag{16}$$

$$(\zeta_{TR})_{12} = \zeta_{T1}({}^3V_2 : \boldsymbol{\epsilon} + {}^2V_2 \cdot {}^2V_1 \cdot {}^2V_2 : \boldsymbol{\epsilon} + \tfrac{1}{6}R_1^2\Delta \ {}^3V_2 : \boldsymbol{\epsilon}) = 6\pi\eta R_1 R_2\left[\frac{R_2^2}{r_{12}^2} + \left(\frac{3}{4}\right)^2\frac{R_1R_2^3}{r_{12}^4}\right]\hat{r}_{12} \cdot \boldsymbol{\epsilon} + O(r_{12}^{-6}) \ ,$$

$$(\zeta_R)_{11} = -\tfrac{1}{2}\zeta_{R1}\boldsymbol{\epsilon} : [\boldsymbol{\epsilon} + \nabla \ {}^2V_2 \cdot {}^3V_1 : \boldsymbol{\epsilon} + \nabla \ {}^3V_2 : \nabla \ {}^3V_1 : \boldsymbol{\epsilon} + \nabla \ {}^4V_2 \ \vdots \ \nabla^2 \ {}^3V_1 : \boldsymbol{\epsilon} + \nabla \ {}^2V_2 \cdot {}^2V_1 \cdot {}^2V_2 \cdot {}^3V_1 : \boldsymbol{\epsilon}]$$

$$= \zeta_{R1}\left[I + \frac{3R_1^3R_2}{4r_{12}^4}(I - \hat{r}_{12}^2) + \left(\frac{3}{4}\right)^3\frac{R_1^4R_2^2}{r_{12}^6}(I - \hat{r}_{12}^2) + \frac{4R_1^3R_2^3}{r_{12}^6}(I - \tfrac{3}{4}\hat{r}_{12}^2)\right] + O(r_{12}^{-8}) \ ,$$

$$(\zeta_R)_{12} = -\tfrac{1}{2}\zeta_{R1}\boldsymbol{\epsilon} : [\nabla \ {}^3V_2 : \boldsymbol{\epsilon} + \nabla \ {}^2V_2 \cdot {}^2V_1 \cdot {}^3V_2 : \boldsymbol{\epsilon}] = \zeta_{R1}\left[\frac{R_2^3}{2r_{12}^3}(I - 3\hat{r}_{12}^2) + \left(\frac{3}{4}\right)^2\frac{R_1R_2^4}{r_{12}^5}(I - \hat{r}_{12}^2)\right] + O(r_{12}^{-7}) \ .$$

Although Aguirre and Murphy[5] ignore rotational contributions, our result for ζ_T is the same as theirs, as expected. Our lowest order terms for $(\zeta_R)_{12}$ and ζ_{TR} give the "rotation–rotation" and "translation–rotation" Oseen tensors of Wolynes and Deutch."

Using the explicit expressions for $^{n+2}V_k$ given by Aguirre and Murphy[5] the diffusion tensors D_T, D_{TR}, and D_R may be found from the generalized Stokes–Einstein relations of Eq. (4). After a lengthy calculation we find

$$(D_T)_{11} = \frac{kT}{\zeta_{T1}}\left(I - \frac{15R_1R_2^3}{4r_{12}^4}\hat{r}_{12}^2\right) + O(r_{12}^{-6}) \ ,$$

$$(D_T)_{12} = \frac{kT}{\zeta_{T1}}\left[\frac{3R_1}{4r_{12}}(I + \hat{r}_{12}^2) + \frac{R_1(R_1^2+R_2^2)}{4r_{12}^3}(I - 3\hat{r}_{12}^2)\right] + O(r_{12}^{-7})$$

$$(D_{TR})_{11} = 0 + O(r_{12}^{-8}) \ ,$$

$$(D_{TR})_{12} = -\frac{kT}{8\pi\eta r_{12}^2}\hat{r}_{12} \cdot \boldsymbol{\epsilon} + O(r_{12}^{-8}) \ , \tag{17}$$

$$(D_R)_{11} = \frac{kT}{\zeta_{R1}}\left[I - \frac{15R_1^3R_2^3}{4r_{12}^6}(I - \hat{r}_{12}^2)\right] + O(r_{12}^{-12}) \ ,$$

$$(D_R)_{12} = -\frac{kT}{\zeta_{R1}}\left[\frac{R_1^3}{2r_{12}^3}(I - 3\hat{r}_{12}^2)\right] + O(r_{12}^{-9}) \ .$$

These are the unique components of D; the full matrix may be obtained by application of the symmetry relation $D_{RT} = D_{TR}^\dagger$ and by complete interchange of the labels 1 and 2 where appropriate.

Felderhof[8] has recently shown how the translational diffusion tensors may be calculated directly, rather than by inversion of the grand resistance matrix. In Appendix A this method is extended to the rotational problem and the expressions found for D_R and D_{TR} by this method are in agreement with Eq. (17) above. This method was used to determine the order of the neglected terms in Eq. (17).

It is of interest to note that our result for $(D_T)_{11}$ does not agree with Eq. (21) of Aguirre and Murphy,[5] the reason being that they have used $D_T = kT\zeta_T^{-1}$ instead of our Eq. (4). This points out an inconsistancy in their work. In a preceeding paper Murphy and Aguirre[16] derived their Einstein relation from a Fokker–Planck equation for translational motion only. A hydrodynamic calculation of D_T consistent with their derivation of the Einstein relation would therefore require *slip* boundary conditions, rather than stick, as in that case there are no hydrodynamic torques. Our result for $(D_T)_{11}$ agrees with results given by Batchelor,[6] Felderhof,[8] and Mou and Chang.[7] All authors agree that $(D_T)_{12}$ is given by Eq. (17) to third order.

Assuming the hydrodynamic interactions to be pairwise additive we suggest that the appropriate generalization of our self-diffusion tensors to the N-body case is given by

$$(D_T)_{ii} = \frac{kT}{\zeta_{Ti}} \left(I - \sum_{k \ne i} \frac{15 R_i R_k^3}{4 r_{ik}^4} \hat{r}_{ik}^2 \right) ,$$

$$(D_R)_{ii} = \frac{kT}{\zeta_{Ri}} \left[I - \sum_{k \ne i} \frac{15 R_i^3 R_k^3}{4 r_{ik}^6} (I - \hat{r}_{ik}^2) \right] . \qquad (18)$$

Alternatively, one might generalize the friction tensors to the N-body case by assuming pairwise additivity and obtain D from the Einstein relation. This procedure also gives Eqs. (18). These approximations should be good for dilute solutions (low concentrations of Brownian particles).

These results enable us to find the dependence of the rotational diffusion constant on the Brownian particle concentration, a result which will subsequently be compared with Koenig's measurements. For an isotropic solution of N identical Brownian particles of radius R_1

$$\langle D_R \rangle = \frac{kT}{\zeta_R} \frac{3}{4\pi R^3} \int_{2R_1}^{R} r^2 \, dr \, d\Omega \left[I - N \frac{15 R_1^6}{4 r^6} (I - \hat{r}^2) \right] \qquad (19)$$

$$= \frac{kT}{\zeta_R} \frac{3}{R^3} \int_{2R_1}^{R} r^2 \, dr \left(1 - \frac{5N}{2} \frac{R_1^6}{r^6} \right) I . \qquad (20)$$

Keeping only the largest terms as $R \to \infty$

$$\langle D \rangle = \frac{kT}{\zeta} \left(1 - \frac{5N}{16} \frac{R_1^3}{R^3} \right) I \qquad (21)$$

$$= \frac{kT}{\zeta} \left(1 - \frac{5}{16} \phi \right) I , \qquad (22)$$

where $\phi = N \frac{4}{3} \pi R_1^3 / V$ is the volume fraction of Brownian particles.

We note that higher order approximations to $(D_R)_{ii}$ will give corrections to the numerical coefficient of ϕ in Eq. (22). As we have shown the neglected term in $(D_R)_{ii}$ to be of order r_{ik}^{-12}, the corrections are expected to be small.

ORIENTATION CORRELATIONS

The coupled diffusion equation (1) may be used to calculate time correlation functions of position and orientation. In this section we consider the orientational correlation functions

$$C_{lm}(t) = \langle Y_{lm}^*[u(0)] \, Y_{lm}[u(t)] \rangle \qquad (23)$$

of interest in NMR. Appendix B discusses the related function

$$C_{lm}(q, t) = \langle \exp i q \cdot [r(t) - r(0)] \, Y_{lm}^*[u(0)] \, Y_{lm}[u(t)] \rangle . \qquad (24)$$

of interest in incoherent neutron scattering. If the diffusion equation (1) is written as

$$\partial P / \partial t = LP = (L_T + L_{TR} + L_R) P , \qquad (25)$$

then the correlation function $C_{lm}(t)$ may be written as

$$C_{lm}(t) = \langle Y_{lm}^*(u) \, e^{L_R^\dagger (r, u) t} \, Y_{lm}(u) \rangle , \qquad (26)$$

where the average is over an equilibrium distribution of orientations and, where necessary, an isotropic distribution of configurations. The operator $L_R^\dagger$ is the adjoint of the rotational diffusion operator and is given explicitly by

$$L_R^\dagger = - \sum_{ij} L_i \cdot D_{ij} \cdot L_j - \beta \sum_{ij} (L_i U) \cdot D_{ij} \cdot L_j . \qquad (27)$$

Here, and in the remainder of this section, D is taken to mean D_R, and we drop explicit use of the subscript R.

Wolynes and Deutch[11] have shown that the Debye result

$$C_{lm}(t) = e^{-l(l+1)Dt} \qquad (28)$$

is obtained from this analysis when the rotational self-diffusion tensor is given by the Stokes–Einstein result

$$D_{ii} = I \, kT / 8\pi\eta R_i^3 . \qquad (29)$$

We show below that our result (18) for D_{ii} gives non-exponential corrections to the Debye result.

The diffusion operator $L_R^\dagger$ is decomposed into a sum of one and two particle operators

$$L_R^\dagger = L_0^\dagger + L_1^\dagger , \qquad (30)$$

where

$$L_0^\dagger = - \sum_j L_j \cdot D_{jj} \cdot L_j ,$$

$$L_1^\dagger = - \sum_{i \ne j} L_i \cdot D_{ij} \cdot L_j . \qquad (31)$$

Here we have neglected the possible effects of the potential U. The correlation function $C_{lm}(t)$ may now be found using perturbation theory.

The Laplace transform of $C_{lm}(t)$ defined by

$$\tilde{C}_{lm}(p) = \int_0^\infty dt \, e^{-pt} \, C_{lm}(t) \qquad (32)$$

is given by

$$\tilde{C}_{lm}(p) = \left\langle Y_{lm}^*(u) \frac{1}{s - L^\dagger} Y_{lm}(u) \right\rangle . \qquad (33)$$

This result is expanded by perturbation theory to give

$$\tilde{C}_{lm}(p) = \left\langle Y_{lm}^*(u) \left(\frac{1}{p - L_0^\dagger} - \frac{1}{p - L_0^\dagger} L_1^\dagger \frac{1}{p - L_0^\dagger} \right. \right.$$
$$\left. \left. + \frac{1}{p - L_0^\dagger} L_1^\dagger \frac{1}{p - L_0} L_1^\dagger \frac{1}{p - L_0} \cdots \right) Y_{lm}(u) \right\rangle . \qquad (34)$$

Borrowing the language of quantum mechanics it is clear that $\tilde{C}_{lm}(p)$ is a one-particle matrix element and therefore all terms in the expansion involving the two particle operator $L_1^\dagger$ must vanish. Therefore,

$$\tilde{C}_{lm}(p) = \left\langle Y_{lm}^*(u) \frac{1}{p - L_0^\dagger} Y_{lm}(u) \right\rangle ,$$

$$C_{lm}(t) = \langle Y_{lm}^*(u) \, e^{L_0^\dagger t} \, Y_{lm}(u) \rangle . \qquad (35)$$

It is clear from the form of the self-diffusion tensor D_{ii} given in Eq. (18) that $C_{lm}(t)$ is no longer exponential.

For N identical isotropic Brownian particles of radius R the averages over angles and configurations may be performed analytically, giving a divergent result.[17]

This divergent behavior likely results from neglect of many-body hydrodynamic interactions. Summation of these terms in analogy to the summation of ring diagrams in kinetic theory would most likely remove the divergence and would probably introduce a term of order $\phi^n \ln \phi$ in

Eq. (22)—much like the terms found by Kawasaki and Oppenheim[18] in their study of the density expansion of transport coefficients. We have been able to evaluate the lowest order three-body hydrodynamic interactions and find that for some geometries they oppose the two-body interactions. These results are summarized in Appendix C.

At the short times probed by relaxation experiments (α finite) the Debye result is recovered. It is, therefore, of interest in connection with the magnetic relaxation experiments mentioned earlier to investigate the possibility of intermolecular coupling via long range potentials.

The effect of intermolecular potential may be conveniently examined by making a cumulant expansion of the correlation function

$$C_{lm}(t) = \exp \sum_{n=1}^{\infty} K_n \frac{t^n}{n!} \quad ,$$
$$K_1 = \langle Y_{lm}^*(\mathbf{u}) L_0^\dagger Y_{lm}(\mathbf{u}) \rangle \ ,$$
$$K_2 = \langle Y_{lm}^*(\mathbf{u}) L_0^{\dagger 2} Y_{lm}(\mathbf{u}) \rangle - \langle Y_{lm}^*(\mathbf{u}) L_0^\dagger Y_{lm}(\mathbf{u}) \rangle^2 \ , \tag{36}$$

etc.

It is easy to establish that the contribution to the first cumulant of $C_{lm}(t)$ due to the effects of an intermolecular potential U vanishes. In this case

$$K_1 = -\left\langle Y_{lm}^*(\mathbf{u}) \left(\mathbf{L}_i \cdot \mathbf{D}_{ii} \cdot \mathbf{L}_i - i\beta \sum_k \mathbf{N}_k \cdot \mathbf{D}_{ki} \cdot \mathbf{L}_i \right) Y_{lm}(\mathbf{u}) \right\rangle \ , \tag{37}$$

where the torque is $\mathbf{N}_k = i\mathbf{L}_k U$ in terms of the potential U. Breaking the average into an average $\langle \cdots \rangle_\mathbf{R}$ over configurations and an average $\langle \cdots \rangle_\Omega$ over orientations this becomes

$$K_1 = -\left\langle Y_{lm}^*(\mathbf{u}) \left(\mathbf{L}_i \cdot \langle \mathbf{D}_{ii} \rangle_\mathbf{R} \cdot \mathbf{L}_i - i\beta \right. \right.$$

$$\left. \left. \sum_k \langle \mathbf{N}_k \cdot \mathbf{D}_{ki} \rangle_\mathbf{R} \cdot \mathbf{L}_i \right) Y_{lm}(\mathbf{u}) \right\rangle_\Omega \ . \tag{38}$$

Note that $\mathbf{N}_k \cdot \mathbf{D}_{ki}$ is a pseudovector function of position and, therefore, its average over an isotropic distribution of positions is zero

$$\langle \mathbf{N}_k \cdot \mathbf{D}_{ki} \rangle_\mathbf{R} = 0 \tag{39}$$

and there is no contribution to K_1 from the intermolecular potential U.

DISCUSSION

Recently, Koenig and co-workers[10] have studied the magnetic relaxation of aqueous protons in biopolymer solutions, finding that the tumbling of the solvent apparently has a component due to interactions with the macromolecular solute particles. Their data is well described by a correlation function of the form

$$C_{lm}(t) = (1 - \alpha) e^{-l(l+1)D_s t} + \alpha e^{-l(l+1)D_B t} \ , \tag{40}$$

where D_B is the rotational diffusion coefficient of the Brownian (polymer) molecules, D_s the rotational diffusion coefficient of the solvent, and α a small positive coefficient of order 10^{-4}. They are also able to mea-

sure the dependence of the diffusion coefficient D_B on polymer concentration.[19]

Wolynes and Deutch show that no deviation from the Debye result is obtained treating the hydrodynamic interactions to lowest order. Using a higher order result for the self-diffusion tensor we have obtained a small deviation from the Debye result, but our result is not of the form observed by Koenig et al.

We assume the polymer particles form cages about each other of radius $R \sim O(n^{-1/3})$ expressed in terms of the number density n. The Stokes friction on a spherical particle in a spherical cavity of fluid has been given by Landau and Lifshitz.[20] It is

$$\zeta = 8\pi\eta \, \frac{R_1^3 R_2^3}{R_2^3 - R_1^3} \quad , \tag{41}$$

where R_1 is the radius of the test particle and R_2 is the radius of the cavity. The rotational diffusion coefficient is, therefore,

$$D = \frac{kT}{8\pi\eta R_1^3} \left(1 - \frac{R_1^3}{R_2^3} \right)$$
$$= \frac{kT}{8\pi\eta R_1^3} \left(1 - \frac{V_1}{V_2} \right) \tag{42}$$

in terms of the particle volume V_1 and cage volume V_2. The cage volume is taken to be $V_2 = 2/n$, where n is the protein number density. Therefore,

$$D = \frac{kT}{\zeta_1} \left(1 - \frac{\phi}{2} \right) \tag{43}$$

in terms of the volume fraction $\phi = \frac{4}{3}\pi R_1^3 n$. This argument gives a result of the same order of magnitude as our more detailed calculation, and again in serious disagreement with the observed data.

It is possible that our inability to account for Koenig's observations is an artifact of the perfect spherical symmetry of our model. Vastly enhanced effects in this case would likely require large geometric anisotropy. Since the proteins studied by Koenig are well known to be roughly spherical, it does not appear that hydrodynamic interactions are responsible for Koenig's observations and we suggest a review of the experimental data with this in mind.

ACKNOWLEDGMENTS

APPENDIX A: DIRECT HYDRODYNAMIC CALCULATION OF THE DIFFUSION TENSORS

Recently, Felderhof[8] has shown how the translational diffusion tensors may be directly calculated from hydrodynamics (i.e., without prior calculation of the friction matrix). In this Appendix the rotational and rotational–translational diffusion tensors are found by a similar calculation.

Rather than calculate the drag forces and torques on particles with specified velocities and angular velocities

Felderhof suggests the calculation of the velocities and angular velocities of particles subject to fixed forces and torques. It is convenient for our purpose to require

$$\mathbf{F}_1 = 0 , \quad \mathbf{N}_1 = \zeta_{R1}\mathbf{\Omega}_{10} \neq 0 , \tag{A1}$$

$$\mathbf{F}_2 = \mathbf{N}_2 = 0 .$$

The velocity field $\mathbf{v}$ is again found from a series expansion

$$\mathbf{v} = \mathbf{v}_1 + \mathbf{v}_2 + \mathbf{v}_3 + \cdots \tag{A2}$$

by a method of reflections. $\mathbf{v}_1$ is required to produce a constant torque $\mathbf{N}_1$ on particle 1, and therefore

$$\mathbf{v}_1 = \mathbf{\Omega}_{10} \times \mathbf{r}_1 , \quad \text{on } S_1 , \tag{A3}$$

and application of Eq. (12) gives

$$\mathbf{v}_1 = -{}^3\mathbf{V}_1 : \boldsymbol{\epsilon} \cdot \mathbf{\Omega}_{10} . \tag{A4}$$

Particle 2 is assumed initially stationary, as required by Eq. (A1). However, $\mathbf{v}_1$ will exert both a force and torque on particle 2, and we therefore require 2 to move with velocity $\mathbf{u}_{21}$ and angular velocity $\mathbf{\Omega}_{21}$, to be chosen in such a way that there is no net force or torque on 2 due to $\mathbf{v}_1$. This requires

$$\mathbf{F}_{21} = \zeta_{T2}\{[1 + (R_2^2/6)\Delta]\mathbf{v}_1 - \mathbf{u}_{21}\}_0 = 0 ,$$
$$\mathbf{N}_{21} = -\tfrac{1}{2}\zeta_{R2}\,\boldsymbol{\epsilon} : (\nabla\mathbf{v}_1)_0 - \zeta_{R2}\,\mathbf{\Omega}_{21} = 0 . \tag{A5}$$

Substituting Eq. (A4) into (A5) gives $\mathbf{u}_{21}$ and $\mathbf{\Omega}_{21}$ explicitly as

$$\mathbf{u}_{21} = -\frac{1}{8\pi\eta r_{12}^2}\,\hat{\mathbf{r}}_{21} \cdot \boldsymbol{\epsilon} \cdot \mathbf{N}_1$$

$$= \beta(\mathbf{D}_{TR})_{21} \cdot \mathbf{N}_1 ,$$

$$\mathbf{\Omega}_{21} = -\frac{R_1^3}{2r_{12}^3}\,(\mathbf{I} - 3\hat{\mathbf{r}}_{12}^2) \cdot \mathbf{N}_1$$

$$= \beta(\mathbf{D}_R)_{21} \cdot \mathbf{N}_1 .$$

The generalized Einstein relation (2) allows us to identify the diffusion coefficients $(\mathbf{D}_{TR})_{21}$ and $(\mathbf{D}_R)_{21}$.

Now the reflection back to particle 1 is made. $\mathbf{v}_2$ is required to satisfy

$$\mathbf{v}_2 = \mathbf{u}_{21} + \mathbf{\Omega}_{21} \times \mathbf{r}_2 - \mathbf{v}_1 , \quad \text{on } S_2 , \tag{A8}$$

and

$$\mathbf{v}_2 = -{}^3\mathbf{V}_2 : (\boldsymbol{\epsilon} \cdot \mathbf{\Omega}_{21} - \nabla\mathbf{v}_1) + O(r^{-6}) . \tag{A9}$$

As before $\mathbf{u}_{12}$ and $\mathbf{\Omega}_{21}$ may be found from the requirement that $\mathbf{v}_2$ exert no force on particle 1. Application of Faxen's theorems, as in Eq. (A5), gives

$$\mathbf{\Omega}_{12} = -\frac{1}{\zeta_{R1}}\,\frac{15R_1^3 R_2^3}{4r_{12}^6}\,(\mathbf{I} - \hat{\mathbf{r}}_{12}^2) \cdot \mathbf{N}_1 , \quad \mathbf{u}_{12} = 0 . \tag{A10}$$

The diffusion tensors found from these terms are

$$(\mathbf{D}_R)_{11} = \frac{kT}{\zeta_{R1}}\left[\mathbf{I} - \frac{15R_1^3 R_2^3}{4r_{12}^6}\,(\mathbf{I} - \hat{\mathbf{r}}_{12}^2)\right] , \tag{A11}$$

$$(\mathbf{D}_{RT})_{11} = 0 . \tag{A12}$$

Equations (A6), (A7), (A11), and (A12) are in agreement with Eqs. (17) of the main text, as expected.

APPENDIX B: TIME CORRELATIONS OF POSITION AND ORIENTATION

The coupled translational–rotational diffusion equation (1) may be used to calculate the self-spacetime correlation function

$$C_{lm}(q, t) = \langle e^{i\mathbf{q}\cdot[\mathbf{r}(t)-\mathbf{r}(0)]} Y_{lm}^*[\mathbf{u}(0)] Y_{lm}[\mathbf{u}(t)]\rangle \tag{B1}$$

relevant to incoherent neutron scattering. In terms of the adjoint diffusion operator $L^\dagger$, $C_{lm}(\mathbf{q}, t)$ may be written as

$$C_{lm}(q, t) = \langle e^{-i\mathbf{q}\cdot\mathbf{r}} Y_{lm}^*(\mathbf{u})\, e^{L^\dagger(\mathbf{r}_1\mathbf{u})t}\, e^{i\mathbf{q}\cdot\mathbf{r}} Y_{lm}[\mathbf{u}(t)]\rangle , \tag{B2}$$

where the average is over an isotropic distribution of positions and orientations. Neglecting the potential U the adjoint diffusion operator $L^\dagger$ may be written as

$$L^\dagger = \sum_{kl}\Bigl[\nabla_k \cdot (\mathbf{D}_T)_{kl} \cdot \nabla_l + i\nabla_k \cdot (\mathbf{D}_{TR})_{kl} \cdot \mathbf{L}_l$$
$$+ i\mathbf{L}_k \cdot (\mathbf{D}_{RT})_{kl} \cdot \nabla_l - \mathbf{L}_k \cdot (\mathbf{D}_R)_{kl} \cdot \mathbf{L}_l\Bigr] . \tag{B3}$$

There is considerable simplification due to the symmetries of the hydrodynamic diffusion tensor matrices. From the symmetry of the grand resistance matrix we have found that $\mathbf{D}_{RT} = \mathbf{D}_{TR}^\dagger$. Note that the adjoint of each matrix element is taken, as well as the adjoint of the matrix itself. Because $\mathbf{D}_{TR}$ couples vectors and pseudovectors (velocities and torques), each element $(\mathbf{D}_{TR})_{kl}$ must be a second rank pseudotensor. Its Cartesian components therefore obey

$$[(\mathbf{D}_{TR})_{kl}]_{ab}^\dagger = [(\mathbf{D}_{TR})_{kl}]_{ba}$$
$$= -[(\mathbf{D}_{TR})_{kl}]_{ab} \tag{B4}$$
$$= [(\mathbf{D}_{RT})_{lk}]_{ab} .$$

Note that the indices kl label a particular element of $\mathbf{D}_{TR}$ and the indices ab label the Cartesian components of $(\mathbf{D}_{TR})_{kl}$. From Eq. (B4) it follows that

$$i\mathbf{L}_k \cdot (\mathbf{D}_{RT})_{kl} \cdot \nabla_l = -i\mathbf{L}_k \cdot (\mathbf{D}_{TR})_{lk} \cdot \nabla_l$$
$$= -i\nabla_l \cdot (\mathbf{D}_{TR})_{lk} \cdot \mathbf{L}_k + i[\nabla_l \cdot (\mathbf{D}_{TR})_{lk}] \cdot \mathbf{L}_k , \tag{B5}$$

as, in general, $\mathbf{D}_{TR}$ need not have zero divergence. Therefore, by symmetry arguments alone $L^\dagger$ may be written as

$$L^\dagger = \sum_{kl}\{\nabla_k \cdot (\mathbf{D}_T)_{kl} \cdot \nabla_l - \mathbf{L}_k \cdot (\mathbf{D}_R)_{kl} \cdot \mathbf{L}_l$$
$$+ i[\nabla_l \cdot (\mathbf{D}_{TR})_{lk}] \cdot \mathbf{L}_l\} . \tag{B6}$$

Suppose only pairwise (two particle) hydrodynamic interactions are considered. Then, $(\mathbf{D}_{TR})_{kl}$ depends only on the vector $\mathbf{r}_{kl}$ and, by symmetry, must be of the form $(\mathbf{D}_{TR})_{kl} = f(r_{kl})\boldsymbol{\epsilon} \cdot \mathbf{r}_{kl}$. It is clear that in this case $\nabla \cdot (\mathbf{D}_{TR})_{kl} = 0$. In general, however, each element of $\mathbf{D}_{TR}$ will depend on all $\tfrac{1}{2}N(N-1)$ interparticle distances, and it is not clear that $\nabla \cdot \mathbf{D}_{TR}$ will still be zero.

As this paper only considers pairwise interactions $L^\dagger$ takes the form

$$L^\dagger = L_T^\dagger + L_R^\dagger , \tag{B7}$$

$$L_T^\dagger = \sum_{kl}\nabla_k \cdot (\mathbf{D}_T)_{kl} \cdot \nabla_l , \quad L_R^\dagger = -\sum_{kl}\mathbf{L}_k \cdot (\mathbf{D}_R)_{kl} \cdot \mathbf{L}_l ,$$

and similarly for L. Therefore, the joint probability distribution $P(\{r_i\}, \{u_i\}, t; \{r_i'\}, \{u_i'\})$ takes the uncoupled form $P_T(\{r_i\}, t; \{r_i'\}) P_R(\{u_i\}, t; \{u_i'\})$. $C_{lm}(q, t)$, however, is not uncoupled due to the position dependence of D_R and D_T. Rather, it may be written as

$$C_{lm}(q, t) = \langle (e^{-iq\cdot r} e^{L_T^\dagger(r)t} e^{iq\cdot r})[Y_{lm}^*(u) e^{L_R^\dagger(u,r)t} Y_{lm}(u)] \rangle \ . \tag{B8}$$

It is an interesting result that there are no explicit translational–rotation coupling terms in Eq. (B7). The weak coupling manifested in Eq. (B8) results from the effect of hydrodynamic interactions on the translational and rotational diffusion tensors. We note in passing that Eq. (B6) does not depend on the spherical symmetry of the particles; it is true for any system of orthotropic bodies.

APPENDIX C: THREE PARTICLE HYDRODYNAMIC INTERACTIONS

In general, the hydrodynamic diffusion tensors (translational and rotational) are of the form[7]

$$\mathbf{D}_{ii} = D^0 \mathbf{I} + \sum_{i \neq j} \mathbf{T}_{ii}^{(2)}(\mathbf{r}_{ij}) + \sum_{j, k \neq i} \mathbf{T}_{ii}^{(3)}(\mathbf{r}_{ij}, \mathbf{r}_{jk}, \mathbf{r}_{ki}) + \cdots \ , \tag{C1}$$

$$\mathbf{D}_{ij} = \mathbf{D}_{ij}^{(2)}(\mathbf{r}_{ij}) + \sum_{k \neq j} \mathbf{D}_{ij}^{(3)}(\mathbf{r}_{ik}, \mathbf{r}_{kj}) + \cdots \ , \tag{C2}$$

as a consequence of the nonadditivity of hydrodynamic interactions. $\mathbf{D}_{ij}^{(2)}$ and $\mathbf{T}_{ij}^{(2)}$ are the two body terms derived and discussed in the main text, $\mathbf{D}_{ij}^{(3)}$ and $\mathbf{T}_{ij}^{(3)}$ are the terms involving the nonadditive interaction of three particles, and so on. In this Appendix the lowest order (in interparticle separation) contributions to the diffusion tensors involving three particles are given and their effects discussed. A similar analysis could in principle be performed for interactions of any order.

The computation of the three-body hydrodynamic interactions is done by a straightforward extension of the method of Appendix A. The calculation is lengthy and will not be repeated here.[21] The results are

$$(\mathbf{D}_T^{(3)})_{11} = \frac{kT}{\zeta_{T1}} \frac{3R_1 R_2^3 R_3^3}{\mu^2 r^3 \rho^3} [\mathbf{A}(\rho, r, \mu) + \mathbf{A}(-\mu, -r, -\rho)] \ , \tag{C3}$$

$$(\mathbf{D}_T^{(3)})_{13} = \frac{kT}{\zeta_{T1}} \frac{15 R_1 R_2^3}{8\rho^2 r^2} [3(\hat{\rho} \cdot \hat{r})^2 - 1] \hat{r}\hat{\rho} \ , \tag{C4}$$

$$(\mathbf{D}_R^{(3)})_{11} = \frac{kT}{\zeta_{R1}} \frac{75 R_1^3 R_2^3 R_3^3}{8\rho^3 r^3 \mu^3} [\mathbf{B}(\rho, r, \mu) + \mathbf{B}(-\mu, -r, -\rho)] \ , \tag{C5}$$

$$(\mathbf{D}_R^{(3)})_{13} = -\frac{kT}{\zeta_{R1}} \frac{15 R_1^3 R_2^3}{4\rho^3 r^3} [(\hat{r} \times \hat{\rho})(\hat{\rho} \times \hat{r}) + (\hat{\rho} \cdot \hat{r})^2 \mathbf{I} - (\hat{\rho} \cdot \hat{r})\hat{\rho}\hat{r}] \ , \tag{C6}$$

where the tensors $\mathbf{A}$ and $\mathbf{B}$ are defined by

$$\mathbf{A}(\mathbf{x}, \mathbf{y}, \mathbf{z}) = \{ \tfrac{15}{2} (\hat{x} \cdot \hat{y})^2 [25(\hat{z} \cdot \hat{y})^2 - 7]$$

$$+ 15(\hat{x} \cdot \hat{y})[(\hat{x} \cdot \hat{y}) - 5(\hat{x} \cdot \hat{z})(\hat{y} \cdot \hat{z})] - \tfrac{25}{2} [3(\hat{y} \cdot \hat{z})^2 - 1] \} \hat{z} \cdot \hat{x} \ , \tag{C7}$$

$$\mathbf{B}(\mathbf{x}, \mathbf{y}, \mathbf{z}) = \{ (\hat{x} \cdot \hat{y})(\hat{z} \cdot \hat{y})[(\hat{x} \cdot \hat{z})\mathbf{I} - \hat{x}\hat{z}] + [(\hat{x} \cdot \hat{z})^2$$

$$- 10(\mathbf{x} \cdot \mathbf{y})(\mathbf{y} \cdot \mathbf{z})](\hat{z} \times \hat{y})(\hat{x} \times \hat{y}) + (\hat{x} \cdot \hat{y})(\hat{z} \times \hat{y})(\hat{x} \times \hat{z})$$

$$+ (\hat{z} \cdot \hat{y})(\hat{z} \times \hat{x})(\hat{x} \times \hat{y}) \} \ . \tag{C8}$$

In these expressions R_k is the radius of particle k, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\rho = \mathbf{r}_{12}$, $\mathbf{r} = \mathbf{r}_{23}$, and $\mu = \mathbf{r}_{31}$. The translational results (C3) and (C4) have been given in slightly different form by Kynch[22] in a discussion of sedimentation. The rotational terms seem to be new.

Note that in the limit $\rho = -\mathbf{r}$ Eqs. (C4) and (C6) may be identified with the terms $(\mathbf{T}_T^{(2)})_{ii}$ and $(\mathbf{T}_R^{(2)})_{ii}$ of the self-diffusion tensors given in Eqs. (17). This provides a useful check on the results.

While our results for $\mathbf{D}^{(3)}$ are exact (to the order calculated), they are sufficiently complex that further calculations with them are quite difficult. For example, by a suitable averaging procedure correction terms to the rotational (or translational) diffusion coefficient of order ϕ^2 (where ϕ is the volume fraction of Brownian particles) may be obtained. However, even in the dilute hard sphere gas limit these calculations are very difficult due to the geometrical requirement that the three spheres not overlap during the integration over configurations. Therefore, we conclude with some qualitative remarks about the effects of three-body interactions.

Due to the strong dependence of the three body terms on interparticle separation, the most important contributions to an average over positions will come from configurations where μ, ρ, and r are nearly equal and not large compared with $2R$. We therefore evaluate the contribution to $(\mathbf{D}_R^{(3)})_{11}$ from the configuration where the three particles are at the vertices of an equilateral triangle. The torque $\mathbf{N}_1$ applied to particle 1 may be decomposed into components $\mathbf{N}_1^\parallel$ and $\mathbf{N}_1^\perp$, which are, respectively, parallel and perpendicular to the plane of the three particles. Then it may be shown that

$$(\mathbf{D}_R^{(3)})_{11} \cdot \mathbf{N}_1^\perp \propto [2x^2 + 2z^2(10x^2 + x)] \mathbf{N}_1^\perp \ , \tag{C9}$$

$$(\mathbf{D}_R^{(3)})_{11} \cdot \mathbf{N}_1^\parallel \propto 2x^3 \mathbf{N}_1^\parallel - x^2(\hat{\rho}\hat{\mu} + \hat{\mu}\hat{\rho}) \cdot \mathbf{N}_1^\parallel \ , \tag{C10}$$

where $x = \cos(2\pi/3)$ and $z = \sin(2\pi/3)$. From Eqs. (17) we find

$$(\mathbf{T}_R^{(2)})_{11} \cdot \mathbf{N}_1^\perp \propto -2\mathbf{N}_1^\perp \ , \tag{C11}$$

$$(\mathbf{T}_R^{(2)})_{11} \cdot \mathbf{N}_1^\parallel \propto -2\mathbf{N}_1^\parallel + (\hat{\rho}^2 + \hat{\mu}^2) \cdot \mathbf{N}_1^\parallel \ . \tag{C12}$$

It is clear that Eqs. (C9) and (C11) and the second terms of Eqs. (C10) and (C12) tend to cancel, as suggested in the main text.

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[17] The integration may be performed by an expansion in series, giving

$$C_{lm}(t) = e^{-l(l+1)Dt}$$
$$\{M(-\tfrac{1}{2}, \tfrac{1}{2}, \alpha/R_v^6) - (2R/R_v)^3 M(-\tfrac{1}{2}, \tfrac{1}{2}, \alpha/(2R)^6)\},$$
$$\alpha = \tfrac{5}{2}R^6 l(l+1)Dt, \qquad R_v = (3V/4\pi)^{1/3},$$

in terms of the confluent hypergeometric function $M(a, b, z)$. An asymptotic expansion yields the divergent result,

$$C_{lm}(t) \sim e^{-l(l+1)Dt} \left[1 + (2R/R_v)^3 \frac{(2R)^6}{2\alpha} e^{\alpha/(2R)^6} \right],$$

in the limit $\alpha \to \infty$, $R_v \to \infty$, $\alpha/R_v^6 \ll 1$.

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