Rotational Brownian Motion of a Pair of Dipoles Coupled via a Classical Heisenberg Interaction[1]

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The rotational Smoluchowski equation for the orientational distribution function of two dipoles with classical Heisenberg interaction is solved exactly. The equilibrium self- and pair time-correlation functions of the two dipole moments are evaluated. They are shown to be approximated well over a wide range of interaction strength by a superposition of two exponentials.

1. INTRODUCTION

The theory of dipolar relaxation was initiated by Debye.[1] He calculated the average moment of a dipole immersed in a liquid on the basis of the rotational diffusion equation for its orientational distribution function. In the absence of an applied field the relaxation is exponential and characterized by a single relaxation time. Debye calculated the relaxation time from the Stokes–Einstein theory of Brownian motion. Later theories of dielectric or magnetic relaxation were extensions of Debye's single dipole picture.

Clearly, in a dense liquid or suspension interactions between dipoles cannot be neglected. Usually these are taken into account in a continuum model of the local field.[2–4] A proper statistical mechanical treatment can be based on a cluster expansion.[5] In particular this requires solution of the

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pair problem. In the following we study the relaxation of two interacting dipoles immersed in a fluid. The electrostatic dipole interaction is difficult to handle due to its dependence on the relative position vector.[6] As a model system we consider two dipoles interacting with a classical isotropic Heisenberg interaction.

The problem was studied earlier by Felderhof and Jones[7] and solved exactly. However, their numerical work was limited to relatively low interaction strength. We show in the following that the solution can be improved by transformation to a convenient matrix representation of the Smoluchowski equation describing the rotational diffusion of two interacting dipoles. This leads to a rapidly convergent numerical scheme which can be used even for high interaction strength. Thus both the preceding work[7] and the present one lead to an algorithm allowing to calculate desired correlation functions with arbitrary precision. The present algorithm is to be preferred, since it leads to faster convergence.

We study in particular the time-correlation functions of the two dipole moments. We find that even for strong interactions both the self-correlation function and the pair correlation function have remarkably simple behavior, and can be characterized to a good approximation by two exponential relaxation modes. These correspond to a single exponential for the total dipole moment, and another one for the staggered order parameter.

2. ORIENTATIONAL TIME-CORRELATION FUNCTIONS

We consider two dipoles with orientations characterized by unit vectors $\mathbf{u}_1, \mathbf{u}_2$. The orientations fluctuate stochastically due to interactions with a heat bath at temperature T. The probability distribution of orientations $P(\mathbf{u}_1, \mathbf{u}_2, t)$ is assumed to satisfy the Smoluchowski equation

$$\frac{\partial P}{\partial t} = \mathscr{D}P \tag{2.1}$$

with Smoluchowski operator $\mathscr{D}$ defined by

$$\mathscr{D}P = D_R \mathsf{L} \cdot [\mathsf{L}P + \beta(\mathsf{L}v)\,P], \tag{2.2}$$

where D_R is the rotational diffusion coefficient for a single dipole, and $\mathsf{L} = (\mathsf{L}_1, \mathsf{L}_2)$ is a rotation operator with components for dipole j

$$\mathsf{L}_j = \mathbf{u}_j \times \frac{\partial}{\partial \mathbf{u}_j}. \tag{2.3}$$

Furthermore, $\beta = 1/k_B T$ and $v(\mathbf{u}_1, \mathbf{u}_2)$ is the pair potential, assumed to be of Heisenberg form

$$v(\mathbf{u}_1, \mathbf{u}_2) = J\mathbf{u}_1 \cdot \mathbf{u}_2 \qquad (2.4)$$

with interaction strength J. We abbreviate $K = \beta J$. The Smoluchowski equation imposes no limitation on the strength of the interaction, as long as there is timescale separation from the inertial regime.

In the course of time the solution of the Smoluchowski equation (2.1) tends to the equilibrium distribution

$$P_{eq}(\mathbf{u}_1, \mathbf{u}_2) = \frac{1}{16\pi^2} \exp[-K\mathbf{u}_1 \cdot \mathbf{u}_2]/Y_0(K) \qquad (2.5)$$

with normalization integral

$$Y_0(K) = \frac{1}{16\pi^2} \int \exp[-K\mathbf{u}_1 \cdot \mathbf{u}_2] \, d\mathbf{u}_1 \, d\mathbf{u}_2. \qquad (2.6)$$

The latter is easily evaluated as

$$Y_0(K) = \frac{\sinh K}{K}. \qquad (2.7)$$

It follows from the H-theorem[8] that the stationary solution is unique. The H-theorem shows that for any initial distribution $P(\mathbf{u}_1, \mathbf{u}_2, 0)$ the solution of Eq. (2.1) tends to the equilibrium solution Eq. (2.5). In the following we choose the unit of time such that $D_R = 1$.

We define the adjoint Smoluchowski operator $\mathscr{L}$ by the relation

$$\mathscr{D}f P_{eq} = P_{eq}\mathscr{L}f. \qquad (2.8)$$

It is given by

$$\mathscr{L} = \mathsf{L}^2 - \beta(\mathsf{L}v) \cdot \mathsf{L}. \qquad (2.9)$$

The corresponding operator L^2 for free diffusion is denoted as $\mathscr{L}_0$. The interaction operator $\mathscr{V}$ is defined as the difference

$$\mathscr{V} = \mathscr{L} - \mathscr{L}_0 = -\beta(\mathsf{L}v) \cdot \mathsf{L}. \qquad (2.10)$$

Several time-correlation functions are of interest. We consider the vector functions[7]

$$\mathbf{P}_\ell^\alpha = (\mathbf{u}_1 \cdot \mathbf{u}_2)^\ell \mathbf{u}_\alpha, \qquad \alpha = 1, 2 \qquad (2.11)$$

We have raised the exponent by unity in comparison with ref. 7 for convenience in the following. By isotropy the equilibrium average of these vectors vanishes. We shall consider the time-correlation function

$$\mathbf{G}_{k\ell}^{\alpha\beta}(t) = \langle \mathbf{P}_k^\alpha(t)\, \mathbf{P}_\ell^\beta(0) \rangle, \tag{2.12}$$

where the angled brackets indicate the average over the equilibrium distribution Eq. (2.5), and the time-dependence is governed by the adjoint Smoluchowski operator $\mathscr{L}$ such that

$$\mathbf{P}_k^\alpha(t) = \exp(\mathscr{L}t)\, \mathbf{P}_k^\alpha(0), \qquad \mathbf{P}_k^\alpha(0) = \mathbf{P}_k^\alpha. \tag{2.13}$$

By isotropy the tensor function $\mathbf{G}_{kl}^{\alpha\beta}(t)$ is proportional to the unit tensor

$$\mathbf{G}_{kl}^{\alpha\beta}(t) = \tfrac{1}{3}\, G_{kl}^{\alpha\beta}(t)\, \mathbf{1}, \tag{2.14}$$

so that it suffices to consider the scalar function $G_{kl}^{\alpha\beta}(t)$. The initial value of the function is[7]

$$G_{kl}^{\alpha\beta}(0) = \frac{Y_{k+l}(K)}{Y_0(K)}\, \delta_{\alpha\beta} + \frac{Y_{k+l+1}(K)}{Y_0(K)}\, (1-\delta_{\alpha\beta}), \tag{2.15}$$

where $Y_l(K)$ is defined by the integral

$$Y_l(K) = \frac{1}{16\pi^2} \int (\mathbf{u}_1 \cdot \mathbf{u}_2)^l \exp(-K\mathbf{u}_1 \cdot \mathbf{u}_2)\, d\mathbf{u}_1\, d\mathbf{u}_2. \tag{2.16}$$

The integral is given by

$$Y_l(K) = \left(-\frac{d}{dK} \right)^l Y_0(K). \tag{2.17}$$

It can be evaluated from recursion relations.[7]

The lowest order function $G_{00}^{\alpha\beta}(t)$ is of particular interest. We shall consider in particular the self- and pair correlation functions $G_s(t)$ and $G_d(t)$ defined by

$$G_s(t) = G_{00}^{11}(t), \qquad G_d(t) = G_{00}^{12}(t). \tag{2.18}$$

We define also

$$G_\pm(t) = 2G_s(t) \pm 2G_d(t). \tag{2.19}$$

In the theory of the effective rotational diffusion coefficient of a suspension[7] the self- and pair correlation functions for the vectors

$$\mathbf{X}_1 = \mathbf{u}_1 - (\mathbf{u}_1 \cdot \mathbf{u}_2)\,\mathbf{u}_2, \qquad \mathbf{X}_2 = u_2 - (\mathbf{u}_1 \cdot \mathbf{u}_2)\,\mathbf{u}_1 \tag{2.20}$$

are of interest. One has

$$\langle \mathbf{X}_\alpha(t)\,\mathbf{X}_\beta(0)\rangle = \tfrac{1}{3}\left[G_{00}^s(t) - 2G_{01}^d(t) + G_{11}^s(t)\right]\delta_{\alpha\beta}\,\mathbf{1}$$
$$+ \tfrac{1}{3}\left[G_{00}^d(t) - 2G_{01}^s(t) + G_{11}^d(t)\right](1-\delta_{\alpha\beta})\,\mathbf{1}. \tag{2.21}$$

The initial value is

$$\langle \mathbf{X}_\alpha\mathbf{X}_\beta\rangle = \frac{W_1(K)}{3\sinh K}\,\delta_{\alpha\beta}\mathbf{1} - \frac{W_2(K)}{3\sinh K}\,(1-\delta_{\alpha\beta})\,\mathbf{1}, \tag{2.22}$$

where $W_l(K)$ is defined by

$$W_l(K) = -K[Y_{l+1}(K) - Y_{l-1}(K)]. \tag{2.23}$$

Hence the relation with the functions $A(K, t)$ and $B(K, t)$ defined in ref. 7 is

$$\langle \mathbf{X}_1(t)\cdot\mathbf{X}_1(0)\rangle = \frac{A(K, t)}{Y_0(K)}, \qquad \langle \mathbf{X}_1(t)\cdot\mathbf{X}_2(0)\rangle = \frac{B(K, t)}{Y_0(K)}. \tag{2.24}$$

In order to study the time-dependence of the correlation functions we must solve the Smoluchowski equation.

3. MOMENT EQUATIONS

We solve the Smoluchowski equation by deriving a set of moment equations. It is important that we minimize the number of equations by exploiting the symmetries of the problem. It turns out that the set of vector functions defined in Eq. (2.11) for integer $l = 0, 1, 2, \ldots$ is sufficient for our purpose. We consider time-correlation functions of the form

$$G_{UU}(t) = \langle \mathbf{U}(t)\cdot\mathbf{U}(0)\rangle, \tag{3.1}$$

where $\mathbf{U}(0) = \mathbf{U}(\mathbf{u}_1, \mathbf{u}_2)$ has an expansion in terms of vector functions (2.11)

$$\mathbf{U} = \sum_{\ell=0}^{\infty} \left[U_l^{(1)}\mathbf{P}_l^1(\mathbf{u}_1, \mathbf{u}_2) + U_\ell^{(2)}\mathbf{P}_l^2(\mathbf{u}_1, \mathbf{u}_2)\right]. \tag{3.2}$$

Since the adjoint Smoluchowski operator $\mathscr{L}$, defined in Eq. (2.9), is symmetric under interchange of particle labels, it is appropriate to consider instead

$$\mathbf{U} = \sum_{\ell=0}^{\infty} [U_\ell^+ \mathbf{P}_l^+(\mathbf{u}_1, \mathbf{u}_2) + U_\ell^- \mathbf{P}_\ell^-(\mathbf{u}_1, \mathbf{u}_2)] \tag{3.3}$$

with

$$\mathbf{P}_\ell^\pm = (\mathbf{u}_1 \cdot \mathbf{u}_2)^\ell (\mathbf{u}_1 \pm \mathbf{u}_2), \tag{3.4}$$

so that

$$U_\ell^\pm = \tfrac{1}{2} (U_\ell^{(1)} \pm U_\ell^{(2)}). \tag{3.5}$$

We define the one-sided Fourier transform of the time-correlation function as

$$\hat{G}_{UU}(\omega) = \int_0^\infty e^{i\omega t} G_{UU}(t) \, dt. \tag{3.6}$$

In calculating this one needs to solve the equation

$$(i\omega + \mathscr{L}) \, \psi = \mathbf{U}. \tag{3.7}$$

By linearity we can put

$$\psi = \psi^+ + \psi^-, \qquad \mathbf{U} = \mathbf{U}^+ + \mathbf{U}^- \tag{3.8}$$

with $\psi^\pm$ satisfying the equation

$$(i\omega + \mathscr{L}) \, \psi^\pm = \mathbf{U}^\pm. \tag{3.9}$$

The function $\psi^\pm$ is symmetric (antisymmetric) under interchange of particle labels. By symmetry the vector function $\psi^\pm$ can be expanded as

$$\psi^\pm(\mathbf{u}_1, \mathbf{u}_2) = \sum_{\ell=0}^\infty A_\ell^\pm \mathbf{P}_\ell^\pm(\mathbf{u}_1, \mathbf{u}_2). \tag{3.10}$$

This implies that Eq. (3.9) has the matrix representation[7]

$$s A_\ell^\pm + \sum_{\ell'=0}^\infty M_{\ell\ell'}^\pm A_{\ell'}^\pm = -U_\ell^\pm \tag{3.11}$$

with variable $s = -i\omega$. The matrix $\mathsf{M}^{\pm}$ is found from the action of the evolution operator $\mathscr{L}$ on the functions $\mathbf{P}_\ell^{\pm}$.

The action of the free diffusion operator is given by

$$\mathscr{L}_0 \mathbf{P}_\ell^{\pm} = 2\ell(\ell-1)\,\mathbf{P}_{\ell-2}^{\pm} \pm 2\ell \mathbf{P}_{\ell-1}^{\pm} - 2(\ell+1)^2\,\mathbf{P}_\ell^{\pm}. \qquad (3.12)$$

The interaction operator $\mathscr{V}$ in Eq. (2.10) can be expressed as

$$\mathscr{V} = -K(\mathbf{u}_1 \times \mathbf{u}_2) \cdot (\mathsf{L}_1 - \mathsf{L}_2). \qquad (3.13)$$

Its action on the vector function $\mathbf{P}_\ell^{\pm}$ is given by

$$(\mathbf{u}_1 \times \mathbf{u}_2) \cdot (\mathsf{L}_1 - \mathsf{L}_2)\,P_\ell^{\pm} = 2\ell \mathbf{P}_{\ell-1}^{\pm} \pm \mathbf{P}_\ell^{\pm} - (2\ell+1)\,\mathbf{P}_{\ell+1}^{\pm}. \qquad (3.14)$$

The matrix $\mathsf{M}^{\pm}$ in Eq. (3.11) therefore reads explicitly

$$M_{\ell\ell'}^{\pm} = [2(\ell+1)^2 \pm K]\,\delta_{\ell\ell'} - 2(\ell+1)(\ell+2)\,\delta_{\ell,\ell'-2}$$
$$- 2(\ell+1)(\pm 1 - K)\,\delta_{\ell,\ell'-1} - (2\ell-1)\,K\delta_{\ell,\ell'+1}. \qquad (3.15)$$

From Eq. (2.15) we find for the desired correlation function

$$\hat{G}_{UU}(\omega) = \frac{-2}{Y_0} \sum_{kl} [A_k^+ U_l^+ (Y_{k+l} + Y_{k+l+1}) + A_k^- U_l^- (Y_{k+l} - Y_{k+l+1})]. \qquad (3.16)$$

In earlier work[7] the equations (3.11) were solved numerically by truncation at sufficiently high multipole order ℓ. We show in the following that it is advantageous to transform first to a different representation in which the matrices are tridiagonal.

4. CHANGE OF REPRESENTATION

The change of representation is based on the observation that the action of the linear operators in the space of vector functions can be mapped onto the action of differential operators on scalar functions of a single variable. The differential equation corresponding to the free diffusion operator $\mathscr{L}_0$ can be solved explicitly in terms of Jacobi polynomials. In the corresponding matrix representation the free diffusion operator is diagonal. Surprisingly, the matrix corresponding to the interaction operator remains tridiagonal.

It is convenient to denote the linear operators in the scalar description by symbols similar to those of the vector problem. Thus we map Eq. (3.12) onto the equation

$$L_0^{\pm} x^\ell = 2\ell(\ell-1)\,x^{\ell-2} \pm 2\ell x^{\ell-1} - 2(\ell+1)^2\,x^\ell, \qquad (4.1)$$

where x is a complex number. Similarly we map Eqs. (3.13) and (3.14) onto the equation

$$V^{\pm} x^{\ell} = -K \left[2\ell x^{\ell-1} \pm x^{\ell} - (2\ell+1) x^{\ell+1} \right]. \tag{4.2}$$

The eigenvalue problem in the space of vector functions

$$\mathscr{L}\psi_{\lambda} = \lambda\psi_{\lambda} \tag{4.3}$$

is therefore mapped onto the pair of eigenvalue problems

$$(L_0^{\pm} + V^{\pm}) f_{\lambda}^{\pm} = \lambda f_{\lambda}^{\pm} \tag{4.4}$$

for scalar functions $f_{\lambda}^{\pm}(x)$. Explicitly we have in the scalar problem by use of Eqs. (4.1) and (4.2)

$$L_0^{\pm} f^{\pm} = 2 \left[\frac{d}{dx}(1-x^2)\frac{df^{\pm}}{dx} - (x \mp 1)\frac{df^{\pm}}{dx} - f^{\pm} \right] \tag{4.5}$$

for the free diffusion operator, and

$$V^{\pm} f^{\pm} = -K \left[2(1-x^2)\frac{df^{\pm}}{dx} - (x \mp 1) f^{\pm} \right] \tag{4.6}$$

for the interaction operator. A function $f^{\pm}(x)$ can be Taylor-expanded as

$$f^{\pm}(x) = \sum_{\ell=0}^{\infty} f_{\ell}^{\pm} x^{\ell} \tag{4.7}$$

and is mapped onto the corresponding vector function

$$\psi^{\pm}(\mathbf{u}_1, \mathbf{u}_2) = \sum_{\ell=0}^{\infty} f_{\ell}^{\pm} \mathbf{P}_{\ell}^{\pm}(\mathbf{u}_1, \mathbf{u}_2). \tag{4.8}$$

In particular, a solution $f_n^{\pm}(x)$ of the eigenvalue problem

$$\frac{d}{dx}(1-x^2)\frac{df_n^{\pm}}{dx} - [x \mp 1 + K(1-x^2)]\frac{df_n^{\pm}}{dx} - f_n^{\pm}$$

$$+ \frac{1}{2} K(x \mp 1) f_n^{\pm} = \frac{1}{2} \lambda_n^{\pm} f_n^{\pm} \tag{4.9}$$

with eigenvalue $\lambda_n^{\pm}$ corresponds to an eigenfunction $F_n^{\pm}(\mathbf{u}_1, \mathbf{u}_2)$ of the Smoluchowski operator with the same eigenvalue. The eigenfunction $\mathbf{F}_n^{\pm}(\mathbf{u}_1, \mathbf{u}_2)$ is symmetric (antisymmetric) in the particle labels.

Substituting Eq. (3.4) we see that we obtain the eigenfunction $\mathbf{F}_n^\pm(\mathbf{u}_1, \mathbf{u}_2)$ from the eigenfunction $f_n^\pm(x)$ simply by interpreting x as the scalar product $\mathbf{u}_1 \cdot \mathbf{u}_2$ and multiplying by $\mathbf{u}_1 \pm \mathbf{u}_2$. With this interpretation the variable x is restricted to the interval $-1 \leqslant x \leqslant 1$, and the eigenfunctions are specified as solutions of the differential equation (4.9) which are regular at $x = \pm 1$.

We denote the eigenfunctions of the unperturbed problem Eq. (4.9) with $K = 0$ by $\{f_{0n}^\pm(x)\}$, and the corresponding eigenvalues by $\lambda_{0n}^\pm$. These eigenfunctions are Jacobi-polynomials.[9] The highest term of the polynomial of order n is proportional to x^n. We find it convenient to normalize the eigenfunctions $f_{0n}^\pm(x)$ such that the coefficient of the highest term equals unity. Then

$$f_{0n}^+(x) = \frac{1}{k_n} P^{(0,\,1)}(x), \qquad f_{0n}^-(x) = \frac{1}{k_n} P^{(1,\,0)}(x) \tag{4.10}$$

with normalization coefficient[9]

$$k_n = \frac{1}{2^n} \binom{2n+1}{n}. \tag{4.11}$$

The eigenvalues are

$$\lambda_{0n}^\pm = -2(n+1)^2. \tag{4.12}$$

We denote the corresponding eigenfunctions of the unperturbed problem Eq. (4.3) with $K = 0$ by $\mathbf{Q}_n^\pm(\mathbf{u}_1, \mathbf{u}_2)$. Explicitly the first few eigenfunctions are

$$\begin{aligned}
\mathbf{Q}_0^\pm(\mathbf{u}_1, \mathbf{u}_2) &= \mathbf{u}_1 \pm \mathbf{u}_2, \\
\mathbf{Q}_1^\pm(\mathbf{u}_1, \mathbf{u}_2) &= \left[\mathbf{u}_1 \cdot \mathbf{u}_2 \mp \tfrac{1}{3}\right](\mathbf{u}_1 \pm \mathbf{u}_2), \\
\mathbf{Q}_2^\pm(\mathbf{u}_1, \mathbf{u}_2) &= \left[(\mathbf{u}_1 \cdot \mathbf{u}_2)^2 \mp \tfrac{2}{5}\mathbf{u}_1 \cdot \mathbf{u}_2 - \tfrac{1}{5}\right](\mathbf{u}_1 \pm \mathbf{u}_2),
\end{aligned} \tag{4.13}$$

with eigenvalues $-2, -8, -18$ respectively.

The explicit expression for the polynomials[9]

$$f_{0n}^\pm(x) = \sum_{\ell=0}^{n} S_{\ell n}^\pm x^\ell \tag{4.14}$$

yields the corresponding expansion

$$\mathbf{Q}_n^\pm(\mathbf{u}_1, \mathbf{u}_2) = \sum_{\ell=0}^n S_{\ell n}^\pm \mathbf{P}_\ell^\pm(\mathbf{u}_1, \mathbf{u}_2) \tag{4.15}$$

of the eigenfunction $\mathbf{Q}_n^\pm(\mathbf{u}_1, \mathbf{u}_2)$ in terms of vector functions $\mathbf{P}_\ell^\pm$. The coefficients $S_{\ell n}^\pm$ can be regarded as elements of matrices $\mathsf{S}^\pm$. With our choice of normalization the diagonal elements of these matrices are equal to unity. From Eq. (4.13) we see that the upper left hand part of the matrices is

$$\mathsf{S}^\pm = \begin{pmatrix} 1 & \mp\frac{1}{3} & \frac{-1}{5} & \cdots \\ 0 & 1 & \mp\frac{2}{5} & \cdots \\ 0 & 0 & 1 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{4.16}$$

Due to the polynomial nature of the eigenfunctions the matrices are triangular. We denote the inverse matrices by

$$\mathsf{T}^\pm = (\mathsf{S}^\pm)^{-1}. \tag{4.17}$$

These matrices are also upper triangular with unity along the diagonal. From $\mathsf{S}^\pm$ truncated at dimension d one can find the truncated $\mathsf{T}^\pm$ by inversion. From Eq. (4.16) one finds for the upper left hand part

$$\mathsf{T}^\pm = \begin{pmatrix} 1 & \pm\frac{1}{3} & \frac{1}{3} & \cdots \\ 0 & 1 & \pm\frac{2}{5} & \cdots \\ 0 & 0 & 1 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{4.18}$$

The matrices yield the inverse expansion

$$x^n = \sum_{\ell=0}^n T_{\ell n}^\pm f_{0\ell}^\pm(x) \tag{4.19}$$

and correspondingly

$$\mathbf{P}_n^\pm(\mathbf{u}_1, \mathbf{u}_2) = \sum_{\ell=0}^n T_{\ell n}^\pm \mathbf{Q}_\ell^\pm(\mathbf{u}_1, \mathbf{u}_2). \tag{4.20}$$

We can use the matrices for a change of representation. By substitution of Eq. (4.20) into Eq. (3.10) we find

$$\psi^\pm(\mathbf{u}_1, \mathbf{u}_2) = \sum_{\ell=0}^\infty C_\ell^\pm \mathbf{Q}_\ell^\pm(\mathbf{u}_1, \mathbf{u}_2) \tag{4.21}$$

with coefficients

$$C_\ell^\pm = \sum_{n=0}^{\ell} T_{\ell n}^\pm A_n^\pm. \tag{4.22}$$

Substituting the inverse transformation into Eq. (3.11) we find the equations

$$sC_\ell^\pm + \sum_{\ell'=0}^{\infty} \hat{M}_{\ell\ell'}^\pm C_{\ell'}^\pm = -\hat{U}_\ell^\pm \tag{4.23}$$

with $\hat{\mathbf{U}}^\pm = \mathsf{T}^\pm \cdot \mathbf{U}^\pm$ and transformed matrix

$$\hat{\mathsf{M}}^\pm = \mathsf{T}^\pm \cdot \mathsf{M}^\pm \cdot \mathsf{S}^\pm. \tag{4.24}$$

We can write in obvious notation

$$\mathsf{M}^\pm = -\mathsf{L}_0^\pm - \mathsf{V}^\pm, \qquad \hat{\mathsf{M}}^\pm = -\hat{\mathsf{L}}_0^\pm - \hat{\mathsf{V}}^\pm. \tag{4.25}$$

The matrices $\mathsf{S}^\pm$ can be constructed from the explicit expression for the Jacobi polynomials.[9] If we consider polynomials up to degree $d-1$ we obtain a $d \times d$-matrix $\mathsf{S}_d^\pm$, from which we find the corresponding $d \times d$-matrix $\mathsf{T}_d^\pm$ by inversion. The matrices $S_d^\pm$ and $\mathsf{T}_d^\pm$ may be used to construct corresponding matrices $\hat{\mathsf{L}}_{0d}^\pm$ and $\hat{\mathsf{V}}_d^\pm$ by transformation of the truncated $\mathsf{L}_0^\pm$ and $\mathsf{V}_0^\pm$. The transformed matrix $\hat{\mathsf{L}}_{0d}^\pm$ is diagonal with the first d eigenvalues $\lambda_n^\pm$ along the diagonal. The transformed matrix $\hat{\mathsf{V}}_d^\pm$ is tridiagonal apart from nonvanishing elements in the last column. Clearly this tends to a tridiagonal matrix $\hat{\mathsf{V}}^\pm$ in the limit $d \to \infty$.

The nearly tridiagonal nature of the matrix $\hat{\mathsf{V}}_d^\pm$ is surprising and requires explanation. The property is related to recursion relations between the Jacobi polynomials, and hence to their hypergeometric nature.

With our choice of normalization the Jacobi polynomials satisfy the three-term recursion relation[9, 10]

$$xf_{0n}^\pm = f_{0,n+1}^\pm \pm \frac{1}{(2n+1)(2n+3)} f_{0n}^\pm + \frac{n(n+1)}{(2n+1)^2} f_{0,n-1}^\pm. \tag{4.26}$$

The relation allows one to construct the higher order polynomials from the initial values $f_{00}^\pm = 1$ and $f_{01}^\pm = x \mp \frac{1}{3}$. The polynomials also satisfy the differential recursion relation[9, 10]

$$(1-x^2)\frac{df_{0n}^\pm}{dx} = -n\left(x \pm \frac{1}{2n+1}\right) f_{0n}^\pm + \frac{2n(n+1)^2}{(2n+1)^2} f_{0,n-1}^\pm. \tag{4.27}$$

We have of course

$$\hat{L}_{0kl}^{\pm} = -2(k+1)^2 \, \delta_{kl}. \tag{4.28}$$

Comparing the recursion relations with Eq. (4.6) we see that the action of the operator $V^{\pm}$ is represented by the matrix $\hat{V}^{\pm}$ with elements

$$\hat{V}_{kl}^{\pm} = K\left((2k-1)\,\delta_{k,\,l-1} \mp \frac{2}{(2k+1)(2k+3)}\,\delta_{kl} - \frac{k(k-1)(2k+1)}{(2k-1)^2}\,\delta_{k,\,l+1} \right). \tag{4.29}$$

We denote the tridiagonal matrix obtained from $\hat{V}^{\pm}$ by truncation at dimension d by $\hat{V}_{td}^{\pm}$. This differs in the last column from the matrix $\hat{V}_d^{\pm}$ considered earlier. The diagonal form of $\hat{L}_{0d}^{\pm}$ and the tridiagonal form of the matrix $\hat{V}_{td}^{\pm}$ allows rapid numerical solution of the truncated set of equations (4.23). The calculation of the quantities $\hat{A}(K, \omega)$ and $\hat{B}(K, \omega)$ defined in Eqs. (2.23) also converges more rapidly with increasing dimension d in the tridiagonal scheme than with truncation in the original Eq. (3.11), as employed earlier.[7]

5. TIME-CORRELATION FUNCTIONS

In this section we present numerical results for the time-correlation functions $G_s(K, t)$ and $G_d(K, t)$ defined in Eq. (2.18). Owing to the rapid convergence of our scheme we can consider a wide range of K-values. Due to the symmetry[7]

$$G_s(-K, t) = G_s(K, t), \qquad G_d(-K, t) = -G_d(K, t) \tag{5.1}$$

it suffices to study positive values of K. We study the behavior in the range $0 < K \leqslant 10$. For $K = 10$ the interaction term in the Smoluchowski operator is an order of magnitude larger than the free diffusion term.

From Eq. (2.15) we find the initial values

$$G_s(K, 0) = 1, \qquad G_d(K, 0) = \frac{Y_1(K)}{Y_0(K)}. \tag{5.2}$$

For large positive values of K the function $G_d(K, 0)$ tends to -1, implying that the second dipole has direction opposite to the first one. The pair correlation function will be calculated from the self-correlation function

and the mutual correlation function according to Eqs. (2.18) and (2.19). From Eqs. (2.11) and (3.3) we find with $\mathbf{U}_s = \mathbf{u}_1$ and $\mathbf{U}_+ = \mathbf{u}_1 + \mathbf{u}_2$

$$U_{sl}^{\pm} = \tfrac{1}{2}\,\delta_{l0}, \qquad U_{+l}^{+} = \delta_{l0}, \qquad U_{+l}^{-} = 0. \tag{5.3}$$

From Eq. (3.11) we see that $A_l^{\pm} \approx -U_l^{\pm}/s$ for large s. It follows from Eq. (3.16) that the self-correlation function can be written as a sum of two terms

$$G_s(K, t) = G_s^{+}(K, t) + G_s^{-}(K, t) \tag{5.4}$$

with the time-evolution of $G_s^{\pm}(K, t)$ governed by the matrix $M^{\pm}(K)$, and with initial values

$$G_s^{\pm}(K, 0) = \frac{Y_0 \pm Y_1}{2Y_0}. \tag{5.5}$$

The mutual correlation function is governed by $\mathsf{M}^{+}(K)$ only, since $\mathbf{u}_1 + \mathbf{u}_2$ is even under particle interchange. It is identical with $4\,G_s^{+}(K, t)$. We have

$$G_{\pm}(K, t) = 4\,G_s^{\pm}(K, t). \tag{5.6}$$

Hence the pair correlation function can be written as a sum of two terms, as in Eq. (5.4), with

$$G_d^{\pm}(K, t) = \pm G_s^{\pm}(K, t). \tag{5.7}$$

We define relaxation functions

$$\Gamma_{\pm}(K, t) = G_s^{\pm}(K, t)/G_s^{\pm}(K, 0) \tag{5.8}$$

with initial value unity. Correspondingly the self-correlation function is given by

$$G_s(K, t) = \frac{Y_0 + Y_1}{2Y_0}\,\Gamma_{+}(K, t) + \frac{Y_0 - Y_1}{2Y_0}\,\Gamma_{-}(K, t), \tag{5.9}$$

and the pair correlation function is given by

$$G_d(K, t) = \frac{Y_0 + Y_1}{2Y_0}\,\Gamma_{+}(K, t) - \frac{Y_0 - Y_1}{2Y_0}\,\Gamma_{-}(K, t). \tag{5.10}$$

We analyze the time-dependence by a method developed elsewhere.[11] The method employs numerical contour integration in the complex s plane to find the relaxation functions as a sum of exponentially decaying contributions. The expression Eq. (3.16) for the Laplace-transform of a correlation function $G_{UU}(t)$ can be transformed to

$$\hat{G}_{UU}(\omega) = (\mathsf{W}^+ \cdot \mathsf{U}^+) \cdot \mathsf{S}^+ \cdot \mathsf{C}^+ + (\mathsf{W}^- \cdot \mathsf{U}^-) \cdot \mathsf{S}^- \cdot \mathsf{C}^-, \tag{5.11}$$

where the matrix $\mathsf{W}^\pm$ has elements

$$W_{kl}^\pm = -2 \frac{Y_{k+l} \pm Y_{k+l+1}}{Y_0}. \tag{5.12}$$

The vector $\mathsf{C}^\pm$ is found from the solution of Eq. (4.23), truncated at sufficiently high order to achieve convergence. The relaxation functions take the form

$$\Gamma_\pm(K, t) = \sum_{j=1}^\infty a_j^\pm(K) \exp[-s_j^\pm(K) t] \tag{5.13}$$

with relaxation rates related to the eigenvalues by

$$s_j^\pm(K) = -\lambda_{j+1}^\pm(K). \tag{5.14}$$

The coefficients $a_j^\pm(K)$ are necessarily positive by general properties of the Smoluchowski equation. By definition we have

$$\sum_{j=1}^\infty a_j^\pm(K) = 1. \tag{5.15}$$

Surprisingly, it turns out that in the range of K considered only the term $j = 1$ contributes appreciably to the sum in Eq. (5.13). Hence the time-correlation functions $G_s(K, t)$ and $G_d(K, t)$ are each to a good approximation given by a sum of two exponentials. One can choose the level of truncation to satisfy the sum rule Eq. (5.15) to any desired accuracy.

In Fig. 1 we plot the lower relaxation rates $s_j^\pm(K)$ as functions of K. In Fig. 2 we plot the values of the remainder $1 - a_1^\pm(K)$. This shows that to a very good approximation the higher order relaxation modes can be neglected. The eigenvectors of the matrix $\hat{\mathsf{M}}^\pm(K)$ can be determined numerically. One finds by inspection that for very large K the lower order eigenvectors are significantly different from the corresponding eigenvectors of $\hat{\mathsf{L}}_0^\pm$. The simple relaxation of the functions $\Gamma_\pm(K, t)$ is therefore surprising.
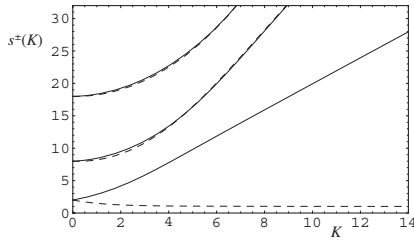
Fig. 1. Plot of the lower relaxation rates $s_j^+(K)$ (solid curves) and $s_j^-(K)$ (dashed curves) as functions of K for $j = 1, 2, 3$ (bottom to top). The rates for $K < 0$ are given by $s_j^+(K) = s_j^-(-K)$.

For $K > 0$ the function $\Gamma_-(K, t)$ relaxes slower than $\Gamma_+(K, t)$, asymptotically with rate $s_1^-(K)$. For large K the rate $s_1^-(K)$ tends to unity. In this limit the pair of dipoles is strongly bound antiferromagnetically. The slow decay with $s_1^-(K) \approx 1$ corresponds to rotational diffusion of the tightly bound pair, with diffusion coefficient equal to half that of a single free dipole. In this picture the higher modes correspond to internal relaxation of the pair to its tightly bound equilibrium configuration. In the limit of large positive K the functions $G_s(K, t)$ and $G_d(K, t)$ become equal and opposite with a slow relaxation given by rotational diffusion of the tightly bound pair.

For large $|K|$ the relaxation rates $s_j^\pm(K)$ vary linearly with K. Corresponding approximate eigenfunctions can be found from an asymptotic analysis.[6]

In Fig. 3 we plot the time-correlation functions $G_s(K, t)$ and $G_d(K, t)/G_d(K, 0)$ as functions of time for $K = 1$. Both functions start at unity, but the second soon is larger than the first. The reason is that soon the second term in Eqs. (5.9) and (5.10) dominates, and in the second function the normalizing factor $|Y_0/Y_1|$ is larger than unity. At interaction
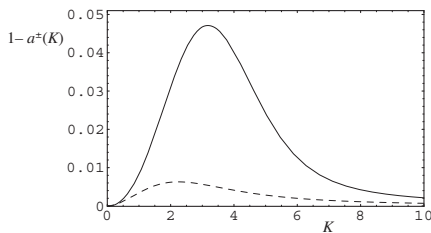

Fig. 2. Plot of the remainder $1 - a_1^+(K)$ (upper curve) and $1 - a_1^-(K)$ (lower curve) as functions of interaction strength K.
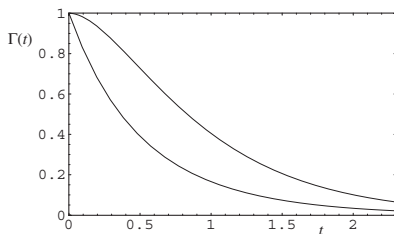
Fig. 3. Plot of the time-correlation function $G_s(k, t)$ (lower curve) and $G_d(K, t)/G_d(K, 0)$ (upper curve) as functions of t for interaction strength $K = 1$.

strength $K = 10$ the difference between the curves is smaller, as shown in Fig. 4. This agrees with the picture discussed above.

As noted above, the decay of the relaxation functions $\Gamma_{\pm}(K, t)$ is remarkably simple. In each case it is given essentially by a single exponential over the whole range of interaction strength, as shown in Fig. 2. Of course, the total dipole moment $\mathbf{u}_1 + \mathbf{u}_2$ and the staggered moment $\mathbf{u}_1 - \mathbf{u}_2$ are rather simple variables, but this cannot be the complete explanation. For the more complicated variables $\mathbf{X}_1 \pm \mathbf{X}_2$ defined in Eq. (2.20) the decay involves essentially two exponentials.[7]

To conclude this section we mention that the eigenvalues and eigenvectors of the matrices $\hat{\mathsf{M}}^{\pm}(K)$ can be studied analytically in perturbation theory. For small interaction strength K Bloch's perturbation theory[12] can be employed. Calculations have been carried out to order thirty.[6] For large interaction strength an asymptotic analysis based on the differential equation (4.9) can be performed.[6] We do not enter into the details here.

6. DISCUSSION

We have presented an exact solution of the rotational Smoluchowski equation for two dipoles with Heisenberg interaction. The time-correlation
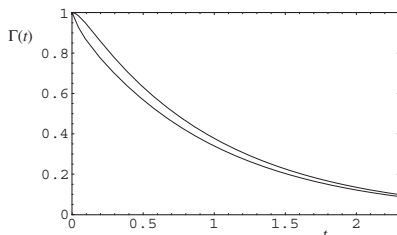

Fig. 4. Same as in Fig. 3 for interaction strength $K = 10$.

functions of the two dipole moments have been evaluated over a wide range of interaction strength. The correlation function of the total dipole moment and that of the staggered moment to a good approximation decay with a single exponential. This must be a peculiarity of the field-free case, since with an applied field already the relaxation of a single dipole is far more complicated.[11, 13]

The problem we have studied has an interest of its own. Its solution is a necessary preliminary for an analysis of the dynamics of Heisenberg liquids[14, 15] and suspensions.[7] In addition, the method used is of relevance for the related problem of dipolar liquids and ferrofluids with true electrostatic or magnetic dipole interaction. In that case the problem of two interacting dipoles is far more complicated than for the Heisenberg interaction considered here, since the dependence on the relative position vector makes the dipole interaction anisotropic. The same is true for the effective interaction between two asymmetric molecules in a liquid.[16, 17] A solution of the pair problem for the dipole case has been presented elsewhere.[6]

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