Rotational Brownian motion and dielectric relaxation of polar molecules subjected to a constant bias field: Exact solution

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The longitudinal and transverse components of the complex dielectric susceptibility tensor and dielectric correlation times are calculated exactly for a system of noninteracting polar molecules placed in a constant external electric field. The calculations are carried out in the context of the rotational diffusion model. The theoretical results are compared with experimental data on both the magnetic relaxation of colloidal suspensions of single domain ferromagnetic particles (ferrofluids) and the dielectric relaxation of dilute solutions of polar macromolecules in a bias field. There is good agreement with the experimental data on both of these systems. It is shown that previous analytic results for the correlation time based on the effective eigenvalue method are in general an acceptable approximation to the exact solutions.

I. INTRODUCTION

The application of a strong direct current (dc) biasing electric field E to a polar fluid comprised of permanent dipoles results in a transition from the state of free thermal rotation of the molecules to a state of partial orientation with hindered rotation. This change in the character of the molecular motion under the influence of the bias field has a marked effect on the dielectric properties of the fluid insofar as dispersion and absorption of electromagnetic waves will be observed at the characteristic frequencies of rotation of the molecule in the field E.

In order to include the effect of such a bias field in the frequency dependence of the dielectric properties of the fluid, several attempts have been made (e.g., [1], [2], and references cited therein) to generalize the Debye theory of rotational diffusion. These theoretical analyses made use of linear response theory using either of two approximate methods. The first of these is based on perturbation theory, carried to terms of the order of the bias field squared only, and has been described by Coffey and Paranjape [1]. The second is based on the effective eigenvalue method [2]–[5] and linear response theory. It has the advantage that it allows one to include terms of all orders in the bias field. This method has been applied to the solution of the present problem in [4] and to the similar problem of magnetic relaxation of a ferrofluid (a col-

loidal suspension of single domain ferromagnetic particles) by Martsenyuk, Raĭkher, and Shliomis [5]. The similarity of the problems of dielectric relaxation of a polar fluid and magnetic relaxation of a ferrofluid is not surprising because, from a physical point of view, the rotational Brownian motion of single domain ferromagnetic particles (magnetic dipoles) in a constant magnetic field H, where the Néel relaxation mechanism (that is, reorientation of the magnetization within the particle) is blocked, is similar to that of polar molecules (electric dipoles) in a constant electric field E. Neither of the methods described above may be deemed completely satisfactory as none comprises an exact solution of the set of differential-difference equations generated by the Langevin or Smoluchowski equations underlying the problem, so that the accuracy of the results obtained remains unknown.

It is the purpose of this paper to demonstrate how the linear response of an assembly of noninteracting polar molecules for ac fields applied parallel and perpendicular to the bias field may be calculated exactly. In order to carry out the calculation, it is assumed that the rotational Brownian motion of a polar molecule may be described by the Smoluchowski equation in which the inertia effects are neglected. The problem reduces to the solution of the infinite hierarchy of differential-difference equations for the aftereffect functions [6]. The lowest order aftereffect function in the longitudinal case describes the decay of the polarization following a small change in the bias field. In the transverse case the aftereffect function describes the decay of the polarization following the removal of a small field applied in a direction normal to the bias field.

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The Laplace transform in both cases is presented in terms of infinite continued fractions in the frequency ω and the bias field parameter ξ, which is defined as

$$\xi = \frac{\mu E}{kT} , \tag{1}$$

where μ is the permanent dipole moment of a polar molecule, k is the Boltzmann constant, and T is the temperature. The longitudinal and transverse susceptibilities $\alpha_{\parallel}(\omega)$ and $\alpha_{\perp}(\omega)$ may be written down from the Laplace transform of the corresponding aftereffect functions using linear response theory [6].

On proceeding to the limit of zero frequency in the Laplace transforms of the appropriate aftereffect functions, we derive expressions for the dielectric correlation times for rotation in both two and three dimensions in terms of continued fractions in ξ only. These correlation times are a global characterization of orientational relaxation of dipolar particles and can be compared with those extracted from experimental spectra of the dielectric or magnetic susceptibilities. For rotation in two dimensions these may in turn be represented in terms of a series of modified Bessel functions [7] of integer order. The appropriate functions for rotation in three dimensions are the modified spherical Bessel functions [7] which, in turn, may be expressed in terms of the elementary functions [7]. These expressions may be compared with a numerical solution of the set of linear differential-difference equations when they are arranged in matrix form [3] as

$$\dot{\mathbf{X}} = \mathbf{A}\mathbf{X} . \tag{2}$$

Using this representation, the calculation of correlation times amounts merely to the calculation of $\mathbf{A}^{-1}$ [3].

We shall first present the exact solution for rotation of a dipole in two dimensions, which can be obtained using some results we have given [8] for the problem of Brownian motion of a particle in a tilted periodic potential with a particular application to ring laser gyroscopes. This arrangement also facilitates comparison with our earlier exact results [9] for the dielectric relaxation of a single axis rotator with two equivalent sites. Next we present the solution for rotation of a symmetric top molecule in three dimensions. This requires the construction of a new solution of the set of differential-difference equations rather than an adaptation of an existing one, as is so for rotation in two dimensions. An outline of this solution is given in the Appendix. A comparison of the correlation times from the exact solutions is given with the results of numerical solution of the differential-difference equations and with the results yielded by the effective eigenvalue method [4]. The theoretical prediction for the field dependence of the longitudinal relaxation time is compared with data obtained from dielectric measurements on dilute solutions of polar macromolecules in a nonpolar solvent by Block and Hayes [10] and magnetic measurements on ferrofluids by Fannin, Scaife, and Charles [11].

II. ROTATION IN TWO DIMENSIONS: LONGITUDINAL RESPONSE

We suppose that the dielectric consisting of an assembly of dipolar molecules has been influenced for a long

time by the dc field **E**. We first consider an assembly of the molecules with each molecule compelled to rotate about an axis normal to itself. We also suppose that the electrical interaction between each member of the assembly may be ignored so that on the average all molecules of the assembly behave in the same way. Thus it suffices to consider the behavior of one molecule only. Hence the problem is reduced to considering the rotational Brownian movement in two dimensions of a dipole or rigid rotator subjected to the external field.

The Smoluchowski equation for a rigid dipole free to rotate about an axis normal to itself under the influence of a potential

$$V(\phi) = -\mu E \cos\phi - \mu E_1(t) \cos\phi \tag{3}$$

arising from the steady dc bias field **E** and a small probe field $\mathbf{E}_1(t)$ applied along the x axis is [12]

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial \phi} \left[\frac{W}{\zeta} \frac{\partial V}{\partial \phi} \right] + \frac{1}{\tau} \frac{\partial^2 W}{\partial \phi^2} , \tag{4}$$

where $W(\phi, t)$ is the probability density of orientations of the dipole on the unit circle, ϕ is the angle between the dipole and the x axis, ζ is the friction coefficient arising from the Brownian motion of the surroundings, and τ is the Debye relaxation time for rotation in two dimensions given by

$$\tau = \frac{\zeta}{kT} . \tag{5}$$

Equation (4) corresponds to the Langevin equation [12]

$$\zeta\dot{\phi} + \frac{\partial V(\phi, t)}{\partial \phi} = \lambda(t) , \tag{6}$$

where $\lambda(t)$ is the white noise torque, again due to Brownian movement, so that $\lambda(t)$ has the following properties:

$$\overline{\lambda(t)} = 0 , \tag{7}$$

$$\overline{\lambda(t)\lambda(t')} = 2\zeta kT\delta(t - t') . \tag{8}$$

In order to study the relaxation behavior in the linear response approximation, we suppose that the small constant field $\mathbf{E}_1$ is suddenly switched off at time $t = 0$. In terms of the parameter ξ, this corresponds to decreasing ξ by an amount

$$\xi_1 = \frac{\mu E_1}{kT} \ll 1 . \tag{9}$$

For $t \le 0$ the system was at equilibrium and the probability density W was given by the Boltzmann distribution

$$W(\phi, 0) = W_{\xi + \xi_1}^0(\phi) = \frac{e^{(\xi + \xi_1)\cos\phi}}{\int_0^{2\pi} e^{(\xi + \xi_1)\cos\phi} d\phi} \tag{10}$$

$$\simeq W_\xi^0(\phi)[1 + \xi_1(\cos\phi - \langle \cos\phi \rangle_0)] . \tag{11}$$

The statistical average

$$\langle \ \rangle_0 = \frac{\int_0^{2\pi} (\ ) W_\xi^0(\phi) d\phi}{\int_0^{2\pi} W_\xi^0(\phi) d\phi} \tag{12}$$

is to be evaluated in the absence of ξ_1. This condition is

denoted by the subscript 0 on the angular brackets. As $t \to \infty$, $W(\phi,t)$ tends to the equilibrium distribution $W_\xi^0(\phi)$.

In order to proceed, we assume a solution of Eq. (4) of the form

$$W(\phi,t) = \sum_{n=-\infty}^{\infty} a_p(t) e^{ip\phi} ,$$ (13)

which yields the set of differential-difference equations

$$\dot{f}_p(t) + \frac{p^2}{\tau} f_p(t) = \frac{\xi p}{2\tau} [f_{p-1}(t) - f_{p+1}(t)] ,$$ (14)

where

$$f_p(t) = \langle \cos p\phi \rangle - \langle \cos p\phi \rangle_0$$

$$= \frac{a_{-p}(t) + a_p(t) - a_{-p}(\infty) - a_p(\infty)}{2a_0} ,$$ (15)

$$f_p(0) = \xi_1 \left[\frac{\int_0^{2\pi} \cos\phi \cos(p\phi) e^{\xi \cos\phi} d\phi}{\int_0^{2\pi} e^{\xi \cos\phi} d\phi} - \frac{\int_0^{2\pi} \cos(\phi) e^{\xi \cos\phi} d\phi \int_0^{2\pi} \cos(p\phi) e^{\xi \cos\phi} d\phi}{(\int_0^{2\pi} e^{\xi \cos\phi} d\phi)^2} \right] ,$$ (19)

which, on noting that [13]

$$e^{\xi \cos\phi} = \sum_{m=-\infty}^{\infty} I_m(\xi) e^{im\phi} ,$$ (20)

where the $I_m(\xi)$ are the modified Bessel functions of the first kind, reduces, by the orthogonality property of the circular functions, to

$$f_p(0) = \frac{\xi_1}{2I_0^2(\xi)} \{ I_0(\xi)[I_{p-1}(\xi) + I_{p+1}(\xi)] - 2I_1(\xi)I_p(\xi) \}$$

$$= \xi_1 \left\{ \frac{1}{I_0(\xi)} \frac{dI_p(\xi)}{d\xi} - \frac{I_1(\xi)I_p(\xi)}{I_0^2(\xi)} \right\} .$$ (21)

Here we have made use of the recurrence relation [13]

$$2\frac{dI_\nu(z)}{dz} = I_{\nu-1}(z) + I_{\nu+1}(z) .$$ (22)

The Laplace transform of Eq. (14) is

$$\left[s + \frac{p^2}{\tau} \right] \tilde{f}_p(s) = \frac{\xi p}{2\tau} [\tilde{f}_{p-1}(s) - \tilde{f}_{p+1}(s)] + f_p(0) ,$$ (23)

where

$$\tilde{f}(s) = \int_0^\infty e^{-st} f(t) dt .$$ (24)

Equation (23) has the same form as Eq. (22) of [8] which occurs in the calculation of the beat signal spectrum of the laser gyroscope and so has a similar solution in terms of continued fractions, namely,

$$\tilde{f}_1(s) = \frac{2\tau}{\xi} \sum_{p=1}^{\infty} \frac{(-1)^{p+1}}{p} f_p(0) \prod_{k=1}^{n} \tilde{S}_k(s) ,$$ (25)

where the continued fraction $\tilde{S}_k(s)$ is defined as

$$f_0(t) = 0 .$$ (16)

The quantity of interest is the decay of the polarization of the system $P(t)$ defined as

$$P(t) = \mu N \int_0^{2\pi} (\cos\phi - \langle \cos\phi \rangle_0) W(\phi,t) d\phi, \quad t > 0$$

$$= \mu N f_1(t) ,$$ (17)

where N is the concentration of the dipoles. Here it has been assumed that the polarization arises entirely from molecular orientation so that induced dipole moments are ignored. On taking into account the initial conditions for $W(\phi,t)$ from Eq. (11), we have the initial conditions for $f_p(0)$, namely,

$$f_p(0) = \xi_1[\langle \cos\phi \cos p\phi \rangle_0 - \langle \cos\phi \rangle_0 \langle \cos p\phi \rangle_0] .$$ (18)

Thus we have

$$\tilde{S}_k(s) = \frac{\xi k/2}{\tau s + k^2 + \xi k \tilde{S}_{k+1}(s)/2} .$$ (26)

On taking into account Eq. (25), we obtain

$$\frac{\tilde{f}_1(s)}{f_1(0)} = \frac{2\tau}{\xi} \sum_{p=1}^{\infty} \frac{(-1)^{p+1}}{p} \left[\frac{I_p'(\xi)I_0(\xi) - I_1(\xi)I_p(\xi)}{I_1'(\xi)I_0(\xi) - I_1^2(\xi)} \right]$$

$$\times \prod_{k=1}^{p} \tilde{S}_k(s) .$$ (27)

Having determined the Laplace transform of the decay function $f_1(t)$, we may calculate the longitudinal complex susceptibility $\alpha_\parallel(\omega)$ and the correlation time $T_\parallel$. We have, according to linear response theory [12],

$$\frac{\alpha_\parallel(\omega)}{\alpha_\parallel'(0)} = 1 - i\omega \int_0^\infty \frac{f_1(t)}{f_1(0)} e^{-i\omega t} dt = 1 - i\omega \tilde{C}_\parallel(i\omega) ,$$ (28)

where

$$\tilde{C}_\parallel(i\omega) = \frac{\tilde{f}_1(i\omega)}{f_1(0)}$$ (29)

is the one-sided Fourier transform of the normalized longitudinal autocorrelation function $C_\parallel(t)$ defined as

$$C_\parallel(t) = \frac{\langle \cos\phi(0) \cos\phi(t) \rangle_0 - \langle \cos\phi(0) \rangle_0^2}{\langle \cos^2\phi(0) \rangle_0 - \langle \cos\phi(0) \rangle_0^2}$$ (30)

and

$$\alpha_\parallel'(0) = \frac{\mu N f_1(0)}{E_1} = \frac{\mu^2 N}{kT} \frac{[I_1'(\xi)I_0(\xi) - I_1^2(\xi)]}{I_0^2(\xi)} .$$ (31)

Thus,

$$\frac{\alpha_\parallel(\omega)}{\alpha_\parallel'(0)}=1-\frac{2i\omega\tau}{\xi}\sum_{p=1}^{\infty}\frac{(-1)^{p+1}}{p}$$

$$\times\left[\frac{I_p'(\xi)I_0(\xi)-I_1(\xi)I_p(\xi)}{I_0(\xi)I_1'(\xi)-I_1^2(\xi)}\right]$$

$$\times\prod_{k=1}^{p}\tilde{S}_k(i\omega)\ . \tag{32}$$

The longitudinal correlation time $T_\parallel$ is the area under the curve of the normalized longitudinal autocorrelation function. We have

$$T_\parallel=\lim_{s\to0}\int_0^\infty C_\parallel(t)e^{-st}dt=\lim_{s\to0}\tilde{C}_\parallel(s)=\tilde{C}_\parallel(0)\ , \tag{33}$$

so that

$$T_\parallel=\frac{2\tau}{\xi}\sum_{p=1}^{\infty}\frac{(-1)^{p+1}}{p}\frac{f_p(0)}{f_1(0)}\prod_{k=1}^{p}\tilde{S}_k(0)\ . \tag{34}$$

Now, from Eq. (26),

$$\tilde{S}_k(0)=\frac{\xi/(2k)}{1+\xi\tilde{S}_{k+1}(0)/(2k)}=\frac{I_k(\xi)}{I_{k-1}(\xi)}\ , \tag{35}$$

because the modified Bessel function of the first kind of order ν, $I_\nu(z)$, satisfies [[7], Eq. (9.6.26)]

$$I_{\nu-1}(z)-I_{\nu+1}(z)=2\frac{\nu}{z}I_\nu(z)\ , \tag{36}$$

which is equivalent to

$$\frac{I_\nu(z)}{I_{\nu-1}(z)}=\frac{z/(2\nu)}{1+[zI_{\nu+1}(z)]/[2\nu I_\nu(z)]}\ . \tag{37}$$

Equation (34), when combined with Eq. (35), now yields the exact expression for the correlation time in terms of the modified Bessel functions $I_\nu(z)$, viz.,

$$\frac{T_\parallel}{\tau}=\frac{2}{\xi}\sum_{p=1}^{\infty}\frac{(-1)^{p+1}}{p}\left[\frac{I_p'(\xi)I_0(\xi)-I_1(\xi)I_p(\xi)}{I_0(\xi)I_1'(\xi)-I_1^2(\xi)}\right]$$

$$\times\frac{I_p(\xi)}{I_0(\xi)}\ . \tag{38}$$

On applying the effective eigenvalue method [3] to the problem, we can easily derive an equation for the effective eigenvalue λ_{eff} from Eq. (14) for $p=1$, namely,

$$\lambda_{\text{eff}}=-\frac{\dot{f}_1(0)}{f_1(0)}=\frac{1}{\tau}\left[1+\frac{\xi}{2}\frac{f_2(0)}{f_1(0)}\right]\ , \tag{39}$$

from which the effective relaxation time

$$T_\parallel^{\text{eff}}=\lambda_{\text{eff}}^{-1} \tag{40}$$

is given by

$$T_\parallel^{\text{eff}}=\tau\frac{I_0^2(\xi)+I_0(\xi)I_2(\xi)-2I_1^2(\xi)}{I_0^2(\xi)-I_0(\xi)I_2(\xi)}\ . \tag{41}$$

In general, as is obvious from the definition, the effective relaxation time $T_\parallel^{\text{eff}}$ accurately represents the initial slope of the polarization decay. However, in the case under

consideration the effective eigenvalue approach provides a good approximation at all times, as we shall see below.

In the limit of large ξ, on utilizing the asymptotic expansion of the modified Bessel functions [[7], Eq. (9.7.1)]

$$I_\nu(z)\simeq\frac{e^z}{\sqrt{2\pi z}}\left\{1-\frac{4\nu^2-1}{8z}\right.$$

$$\left.+\frac{(4\nu^2-1)(4\nu^2-3^2)}{2!(8z)^2}-\cdots\right\}\ , \tag{42}$$

we have

$$\frac{T_\parallel}{\tau}\sim\frac{1}{2\xi}\ . \tag{43}$$

Equation (43) should be compared with the corresponding equation [Eq. (74)] of [9] which governs relaxation of a two-dimensional rotator in the bistable potential

$$U(\phi)=-U_0\cos^2\phi\ . \tag{44}$$

Equation (43) for the relaxation time, unlike $T_\parallel$ for the potential of Eq. (44) (cf. [9]), contains no exponential factor showing explicitly that the longitudinal relaxation in the present problem is not governed by an activation process. This is the most pronounced difference between relaxation in a twofold and in a single fold cosine potential.

In the limit of small ξ, on using the Taylor expansion of the modified Bessel functions [[7], Eq. (9.6.10)]

$$I_\nu(z)=(z/2)^\nu\sum_{k=0}^{\infty}\frac{(z/2)^{2k}}{k!\Gamma(\nu+k+1)}\ , \tag{45}$$

we have from Eq. (38)

$$T_\parallel\simeq\tau(1-\tfrac{3}{16}\xi^2+\tfrac{35}{1152}\xi^4-\cdots)\ . \tag{46}$$

In Table I and in Fig. 1 we show the longitudinal relaxation time $T_\parallel$ as a function of ξ. In order to ensure convergence of the set of equations (14) for values of ξ up to 10, a matrix size of 18×18 was used in the numerical evaluation of the reciprocal of the lowest eigenvalue λ_1^{-1}
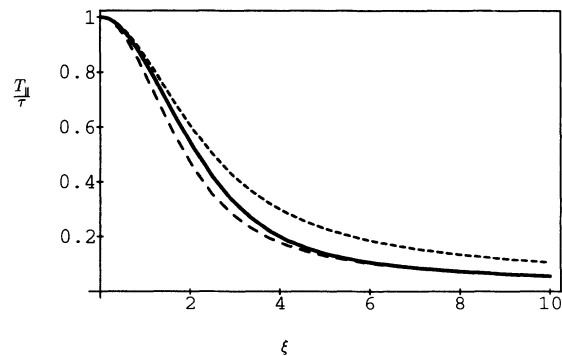

FIG. 1. The longitudinal correlation time $T_\parallel$ as a function of ξ, the bias field parameter for rotation in two dimensions. The numerical solution (the reciprocal of the lowest eigenvalue λ_1^{-1}) of the set of equations (14) (small-dashed line) compared with $T_\parallel$ as calculated from the exact solution (38) (bold line), and $T_\parallel^{\text{eff}}$ as calculated from Eq. (41) (large-dashed line).

TABLE I. Numerical values for $T_\parallel/\tau$ for rotation in two dimensions.

ξ	$T_\parallel/\tau$		
	Eq. (38)	Eq. (14)	Eq. (41)
1	0.838 6	0.858	0.793 8
2	0.545 2	0.607	0.470 7
3	0.323	0.417	0.273 8
4	0.199 6	0.2999	0.178 1
5	0.137 9	0.2296	0.129 8
6	0.105 4	0.1855	0.102 2
7	0.085 99	0.1559	0.084 49
8	0.072 93	0.1345	0.072 11
9	0.063 44	0.1184	0.062 94
10	0.056 19	0.1058	0.055 85

from Eq. (14) and the first 11 terms were taken in the infinite summation of Eq. (38). Details of the method of numerical solution of three term recurrence relations are given elsewhere [9].

III. ROTATION IN TWO DIMENSIONS: TRANSVERSE RESPONSE

Here we consider the response following the removal of a weak constant transverse field E_1 at $t=0$, so that prior to the switching off of E_1 at $t<0$,

$$V(\phi)=-\mu E \cos\phi - \mu E_1(t)\sin\phi , \qquad (47)$$

with $\mu E_1 \ll kT$. The quantities corresponding to f_p are

$$g_p(t)=\langle \sin p\phi \rangle . \qquad (48)$$

We easily find from Eq. (4) that the $g_p(t)$ satisfy

$$\dot{g}_p(t)+\frac{p^2}{\tau}g_p(t)=\frac{\xi p}{2\tau}[g_{p-1}(t)-g_{p+1}(t)] , \qquad (49)$$

with

$$g_{-p}=-g_p \qquad (50)$$

and

$$g_p(0)=\xi_1\langle \sin\phi \sin p\phi \rangle_0 . \qquad (51)$$

Equation (49) also has the same mathematical form as Eq. (14); thus, the solution of Eq. (49) for $\tilde{g}_p(s)$ is

$$\tilde{g}_1(s)=\frac{2\tau}{\xi}\sum_{p=1}^{\infty}\frac{(-1)^{p+1}}{p}g_p(0)\prod_{k=1}^{p}\tilde{S}_k(s) . \qquad (52)$$

Now, according to Eq. (51),

$$g_p(0)=\xi_1\frac{\int_0^{2\pi}\sin\phi \sin(p\phi)e^{\xi\cos\phi}d\phi}{\int_0^{2\pi}e^{\xi\cos\phi}d\phi}$$

$$=\frac{\xi_1}{2}\frac{[I_{p-1}(\xi)-I_{p+1}(\xi)]}{I_0(\xi)}=\frac{\xi_1 p I_p(\xi)}{\xi I_0(\xi)} . \qquad (53)$$

Thus,

$$\frac{\tilde{g}_1(s)}{g_1(0)}=\frac{2\tau}{\xi}\sum_{p=1}^{\infty}(-1)^{p+1}\frac{I_p(\xi)}{I_1(\xi)}\prod_{k=1}^{p}\tilde{S}_k(s) . \qquad (54)$$

The transverse complex susceptibility $\alpha_\perp(\omega)$ is given by

$$\frac{\alpha_\perp(\omega)}{\alpha'_\perp(0)}=1-i\omega\frac{\tilde{g}_1(i\omega)}{g_1(0)}$$

$$=1-\frac{i\omega\tau}{\xi}\sum_{p=1}^{\infty}(-1)^{p+1}\frac{I_p(\xi)}{I_1(\xi)}\prod_{k=1}^{p}\tilde{S}_k(i\omega) , \qquad (55)$$

where

$$\alpha'_\perp(0)=\frac{\mu^2 N}{kT}\frac{I_1(\xi)}{\xi I_0(\xi)} . \qquad (56)$$

The transverse correlation time $T_\perp$ is

$$T_\perp=\frac{\tilde{g}_1(0)}{g_1(0)}=\frac{2\tau}{\xi I_1(\xi)I_0(\xi)}\sum_{p=1}^{\infty}(-1)^{p+1}I_p^2(\xi) . \qquad (57)$$

This differs from $T_\parallel$ solely by virtue of the initial conditions. Equation (57) may be further simplified by using the formula

$$J_0^2(z)+2\sum_{n=1}^{\infty}J_n^2(z)=1 \qquad (58)$$

given on page 361 of [16], where $J_n(z)$ is the Bessel function of the first kind. Since [7], Eq. (9.6.3),

$$I_n(z)=i^n J_n(iz) , \qquad (59)$$

we have

$$\sum_{n=1}^{\infty}(-1)^{n+1}I_n^2(z)=\frac{I_0^2(z)-1}{2} , \qquad (60)$$

from which the summation of Eq. (57) disappears and we obtain an exact equation in closed form for the transverse relaxation time $T_\perp$:

$$\frac{T_\perp}{\tau}=\frac{I_0^2(\xi)-1}{\xi I_1(\xi)I_0(\xi)} . \qquad (61)$$

In the large ξ limit, Eq. (61) predicts that

$$\frac{T_\perp}{\tau}\sim\frac{1}{\xi} . \qquad (62)$$

In the limit of small ξ, we have, as before,

TABLE II. Numerical values for $T_\perp/\tau$ for rotation in two dimensions.

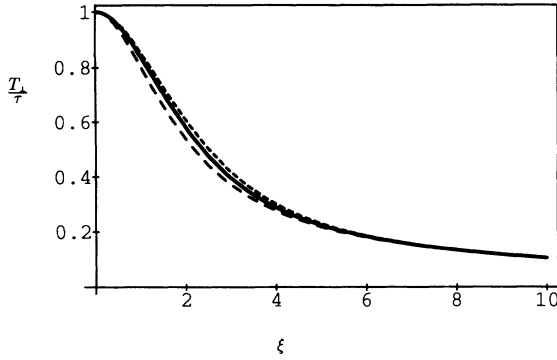| ξ	$T_\perp/\tau$		
	Eq. (61)	Eq. (49)	Eq. (65)
1	0.8426	0.858	0.8063
2	0.5787	0.607	0.5358
3	0.3943	0.417	0.3699
4	0.2872	0.2999	0.2753
5	0.2236	0.2296	0.2175
6	0.1826	0.1855	0.1793
7	0.1543	0.1559	0.1524
8	0.1337	0.1345	0.1324
9	0.1179	0.1184	0.117
10	0.1054	0.1058	0.1048

FIG. 2. The transverse correlation time $T_\perp$ as a function of ξ for rotation in two dimensions. The exact analytic solution (61) is the bold line and the numerical solution of Eq. (49) is the small-dashed line. The large-dashed line is $T_\perp^{\text{eff}}$ [Eq. (65)].

$$T_\perp \simeq \tau(1 - \tfrac{3}{16}\xi^2 + \tfrac{415}{1152}\xi^4 - \cdots) \ . \tag{63}$$

The effective eigenvalue in this instance is from Eq. (49) for $p = 1$:

$$\lambda_{\text{eff}} = -\frac{\dot{g}_1(0)}{g_1(0)} = \frac{1}{\tau}\left[1 + \frac{\xi}{2}\frac{g_2(0)}{2g_1(0)}\right]$$

$$= \frac{1}{\tau}\left[1 + \frac{\xi}{2}\frac{I_1(\xi) - I_3(\xi)}{I_0(\xi) - I_2(\xi)}\right]$$

$$= \frac{1}{\tau}\frac{I_0(\xi) + I_2(\xi)}{I_0(\xi) - I_2(\xi)} \ , \tag{64}$$

so that the effective transverse correlation time $T_\perp^{\text{eff}} = \lambda_{\text{eff}}^{-1}$ is given by

$$\frac{T_\perp^{\text{eff}}}{\tau} = \frac{I_0(\xi) - I_2(\xi)}{I_0(\xi) + I_2(\xi)} \ , \tag{65}$$

where we have made use of Eqs. (22) and (36). In Table II and in Fig. 2 we show the transverse correlation time $T_\perp/\tau$ as a function of ξ. In order to ensure convergence for values of ξ up to 10, a matrix size of 18×18 was used in the evaluation of Eq. (49). It is apparent that the numerical solution and effective eigenvalue solution [Eq. (65)] provide a close approximation to the exact results for all values of ξ. We shall now describe how our exact method may be extended to rotation in three dimensions.

IV. ROTATION IN THREE DIMENSIONS: LONGITUDINAL RESPONSE

The analysis given in Secs. I–III pertains to rotation in two dimensions. This constraint restricts the range of application of the theory since in reality the molecules rotate in space. The theory is generalized below to rotation in three dimensions. More specifically, each dipolar (linear, spherical, or symmetric top) molecule dissolved in a nonpolar solvent is supposed to be free to rotate in space, the molecule being subjected to random torque, having no preferential direction, and to the action of the

ac and dc fields. Again, it is implicitly assumed that the inertia of the molecules may be neglected and further that the electrical dipole-dipole coupling between them may also be ignored so that on the average each molecule behaves in the same way.

Let us suppose that both fields $\mathbf{E}$ and $\mathbf{E}_1(t)$ are along the z axis. The appropriate Smoluchowski equation for rotation of a symmetric top molecule in three dimensions is [14]

$$2\tau_D \sin\vartheta \frac{\partial W}{\partial t} = \frac{\partial}{\partial \vartheta}\left\{\sin\vartheta\left[\frac{1}{kT}\frac{\partial V}{\partial \vartheta}W + \frac{\partial W}{\partial \vartheta}\right]\right\}$$
$$+ \frac{1}{\sin\vartheta}\frac{\partial}{\partial \varphi}\left\{\frac{1}{kT}\frac{\partial V}{\partial \varphi}W + \frac{\partial W}{\partial \varphi}\right\} \ , \tag{66}$$

where

$$V(\vartheta) = -\mu E \cos\vartheta - \mu E_1(t)\cos\vartheta \ , \tag{67}$$

$W(\vartheta, \varphi, t)$ is the probability density of orientations of the dipole μ on the unit sphere where the orientation of μ is specified by the polar and azimuthal angles ϑ and φ, and

$$\tau_D = \frac{\zeta}{2kT} \tag{68}$$

is the Debye relaxation time when $\mathbf{E} = 0$.

Equation (66) is equivalent to the vector Langevin equations [4]

$$\frac{d}{dt}\mu(t) = [\omega(t) \times \mu(t)] \ , \tag{69}$$

$$\zeta\omega(t) = \{\mu(t) \times [\mathbf{E} + \mathbf{E}_1(t)]\} + \lambda(t) \ , \tag{70}$$

or

$$\frac{d}{dt}\mu(t) = (\{\mu(t) \times [\mathbf{E} + \mathbf{E}_1(t)]\} \times \mu(t)) + [\lambda(t) \times \mu(t)] \ , \tag{71}$$

where $\zeta\omega$ is the damping torque due to Brownian movement and $\lambda(t)$ is the white noise driving torque with the following properties:

$$\overline{\lambda_i(t)} = 0 \ , \tag{72}$$

$$\overline{\lambda_i(t)\lambda_j(t')} = 2\zeta kT\delta(t - t')\delta_{ij} \ , \tag{73}$$

where δ_{ij} is Kronecker's δ. For the calculation of the longitudinal response we can disregard the dependence of W on the angle φ and we may assume that the solution of Eq. (66) is of the form

$$W(\vartheta, t) = \sum_{n=0}^{\infty} a_n(t)P_n(\cos\vartheta) \ , \tag{74}$$

where P_n is the Legendre polynomial of order n [7]. The equilibrium Boltzmann distribution $W_\xi^0(\vartheta)$ is given by

$$W_\xi^0(\vartheta) = \frac{e^{\xi\cos\vartheta}}{\int_0^\pi e^{\xi\cos\vartheta}\sin\vartheta\, d\vartheta} \ . \tag{75}$$

The orthogonality properties of the P_n and their recurrence relations, lead to (having switched off the field $\mathbf{E}_1$ at time $t = 0$) the set of differential-difference equa-

tions for

$$f_n(t) = \langle P_n(\cos\vartheta) \rangle - \langle P_n(\cos\vartheta) \rangle_0$$

$$= \frac{a_n(t) - a_n(\infty)}{(2n+1)a_0} ,$$ (76)

where

$$\langle \ \rangle_0 = \frac{\int_0^\pi e^{\xi\cos\vartheta}(\ )\sin\vartheta \, d\vartheta}{\int_0^\pi e^{\xi\cos\vartheta}\sin\vartheta \, d\vartheta} .$$ (77)

The equations are

$$\dot{f}_n(t) + \frac{n(n+1)}{2\tau_D} f_n(t)$$

$$= \frac{\xi}{2\tau_D} \frac{n(n+1)}{2n+1} [f_{n-1}(t) - f_{n+1}(t)] .$$ (78)

We are interested in the decay of the polarization

$$P(t) = \mu N \int_0^\pi (\cos\vartheta - \langle \cos\vartheta \rangle_0) W(\vartheta, t)\sin\vartheta \, d\vartheta$$

$$= \mu N f_1(t) ,$$ (79)

so we require an expression for $f_1(t)$ only. We now, following the method of Sec. II, take the Laplace transform of Eq. (49) which may be arranged as

$$\tilde{R}_n(s) \left[\frac{2\tau_D s}{n(n+1)} + 1 + \frac{\xi \tilde{R}_{n+1}(s)}{(2n+1)} \right]$$

$$= 2\tau_D \frac{f_n(0)}{\tilde{f}_{n-1}(s)} + \frac{\xi}{(2n+1)} ,$$ (80)

where

$$\tilde{R}_n(s) = \frac{\tilde{f}_n(s)}{\tilde{f}_{n-1}(s)} .$$ (81)

Equation (80) is the three-dimensional analog of Eq. (23). Its solution has a similar form to Eq. (25). The details of the solution are given in the Appendix. We have

$$\tilde{f}_1(s) = \frac{\tau_D}{\xi} \sum_{n=1}^\infty (-1)^{n+1} f_n(0) \frac{2(2n+1)}{n(n+1)} \prod_{k=1}^n \tilde{S}_k^\parallel(s) ,$$ (82)

where

$$\tilde{S}_n^\parallel(s) = \frac{\xi/(2n+1)}{2\tau_D s/[n(n+1)] + 1 + \xi \tilde{S}_{n+1}^\parallel(s)/(2n+1)} ,$$ (83)

which is the exact solution of our problem. The initial values $f_n(0)$ are evaluated as follows. We note that

$$f_n(0) = \xi_1(\langle P_1 P_n \rangle_0 - \langle P_1 \rangle_0 \langle P_n \rangle_0)$$

$$= \xi_1 \left[\frac{n+1}{2n+1} \langle P_{n+1} \rangle_0 + \frac{n}{2n+1} \langle P_{n-1} \rangle_0 \right.$$

$$\left. - \langle P_1 \rangle_0 \langle P_n \rangle_0 \right] ,$$ (84)

where we have recalled that ([16], p. 218)

$$(2n+1)\cos\vartheta P_n(\cos\vartheta)$$

$$= (n+1)P_{n+1}(\cos\vartheta) + nP_{n-1}(\cos\vartheta) .$$ (85)

Now, on using Eq. (10.2.36) of [7],

$$e^{z\cos\vartheta} = \left[\frac{\pi}{2z} \right]^{1/2} \sum_{n=0}^\infty (2n+1)I_{n+1/2}(z)P_n(\cos\vartheta) ,$$ (86)

where the $I_{n+1/2}(z)$ are the modified spherical Bessel functions [7], we have, from Eqs. (86) and (77),

$$\langle P_n \rangle_0 = \frac{I_{n+1/2}(\xi)}{I_{1/2}(\xi)} .$$ (87)

Hence, the $f_n(0)$ from Eq. (84) may be expressed in terms of the spherical Bessel functions as

$$f_n(0) = \xi_1 \left[\frac{n+1}{2n+1} \frac{I_{n+3/2}(\xi)}{I_{1/2}(\xi)} + \frac{n}{2n+1} \frac{I_{n-1/2}(\xi)}{I_{1/2}(\xi)} \right.$$

$$\left. - \frac{I_{3/2}(\xi)}{I_{1/2}(\xi)} \frac{I_{n+1/2}(\xi)}{I_{1/2}(\xi)} \right] .$$ (88)

In particular,

$$f_1(0) = \xi_1 \left[\frac{2}{3} \frac{I_{5/2}(\xi)}{I_{1/2}(\xi)} + \frac{1}{3} - \frac{I_{3/2}^2(\xi)}{I_{1/2}^2(\xi)} \right]$$

$$= \xi_1 \left[1 + \frac{1}{\xi^2} - \coth^2\xi \right] .$$ (89)

Here we have used the fact that [[7], Eq. (10.2.13)]

$$\frac{I_{3/2}(\xi)}{I_{1/2}(\xi)} = \coth\xi - \frac{1}{\xi} = L(\xi) ,$$ (90)

$$\frac{I_{5/2}(\xi)}{I_{1/2}(\xi)} = \frac{3}{\xi^2} + 1 - \frac{3\coth\xi}{\xi} = 1 - \frac{3}{\xi}L(\xi) ,$$ (91)

where $L(\xi)$ is known as the Langevin function. Hence, Eq. (82) becomes

$$\tilde{f}_1(s) = \frac{2\tau_D \xi_1}{\xi} \sum_{n=1}^\infty (-1)^{n+1}$$

$$\times \left[\frac{1}{n} \frac{I_{n+3/2}(\xi)}{I_{1/2}(\xi)} + \frac{1}{n+1} \frac{I_{n-1/2}(\xi)}{I_{1/2}(\xi)} \right.$$

$$\left. - \frac{2n+1}{n(n+1)} \frac{I_{3/2}(\xi)I_{n+1/2}(\xi)}{I_{1/2}^2(\xi)} \right]$$

$$\times \prod_{k=1}^n \tilde{S}_k^\parallel(s) .$$ (92)

The longitudinal complex susceptibility is given by

$$\frac{\alpha_\parallel(\omega)}{\alpha'_\parallel(0)} = 1 - i\omega \frac{\tilde{f}_1(i\omega)}{f_1(0)}$$

$$= 1 - \frac{i2\omega\tau_D}{\xi} \sum_{n=1}^\infty (-1)^{n+1} \frac{f_n(0)}{f_1(0)} \frac{(2n+1)}{n(n+1)}$$

$$\times \prod_{k=1}^n \tilde{S}_k^\parallel(i\omega) ,$$ (93)

where

$$\alpha_{\parallel}'(0) = \frac{\mu N f_1(0)}{E_1}$$

$$= \frac{\mu^2 N}{kT} \left[1 + \frac{1}{\xi^2} - \coth^2 \xi \right] . \tag{94}$$

According to linear response theory [12], the quantity $\tilde{f}_1(i\omega)/f_1(0)$ appearing in Eq. (93) is the one-sided Fourier transform of the equilibrium longitudinal dipole autocorrelation function $C_{\parallel}(t)$ defined as

$$C_{\parallel}(t) = \frac{f_1(t)}{f_1(0)} = \frac{\langle \cos\vartheta(0)\cos\vartheta(t)\rangle_0 - \langle \cos\vartheta(0)\rangle_0^2}{\langle \cos^2\vartheta(0)\rangle_0 - \langle \cos\vartheta(0)\rangle_0^2} . \tag{95}$$

The longitudinal correlation time $T_{\parallel}$ is, as before, determined from the $s = 0$ limit of Eq. (92). We have, from the definition of $\tilde{S}_k^{\parallel}(s)$ [Eq. (83)]

$$\tilde{S}_n^{\parallel}(0) = \frac{\xi/(2n+1)}{1 + \xi \tilde{S}_{n+1}^{\parallel}(0)/(2n+1)} . \tag{96}$$

Thus, on comparing Eq. (96) with Eq. (36), we obtain

$$\tilde{S}_k^{\parallel}(0) = \frac{I_{k+1/2}(\xi)}{I_{k-1/2}(\xi)} ; \tag{97}$$

we also have

$$\prod_{k=1}^{n} \tilde{S}_k^{\parallel}(0) = \frac{I_{n+1/2}(\xi)}{I_{1/2}(\xi)} . \tag{98}$$

Thus,

$$T_{\parallel} = \int_0^{\infty} C_{\parallel}(t)dt = \frac{\tilde{f}_1(0)}{f_1(0)}$$

$$= \frac{2\tau_D}{\xi(1 + \xi^{-2} - \coth^2\xi)}$$

$$\times \sum_{n=1}^{\infty} (-1)^{n+1} \frac{I_{n+1/2}(\xi)}{I_{1/2}(\xi)} \left[\frac{1}{n} \frac{I_{n+3/2}(\xi)}{I_{1/2}(\xi)} + \frac{1}{n+1} \frac{I_{n-1/2}(\xi)}{I_{1/2}(\xi)} - \frac{2n+1}{n(n+1)} \frac{I_{3/2}(\xi)I_{n+1/2}(\xi)}{I_{1/2}^2(\xi)} \right] . \tag{99}$$

Equation (99) may also be expressed as a series of elementary functions, taking into account that, according to Eqs. (10.2.12) and (10.2.13) of [7],

$$\frac{I_{n+1/2}(\xi)}{I_{1/2}(\xi)} = \xi[g_n(\xi) + g_{-(n+1)}(\xi)\coth\xi] , \tag{100}$$

where the functions $g_n(\xi)$ satisfy the recurrence relation

$$g_{n-1} - g_{n+1} = \frac{(2n+1)}{\xi} g_n , \tag{101}$$

with

$$g_0(\xi) = 1/\xi, \quad g_1(\xi) = -1/\xi^2 . \tag{102}$$

We can express the correlation time $T_{\parallel}$ in terms of the $g_n(\xi)$ and $\coth\xi$, after some algebra, as follows:

$$T_{\parallel} = \frac{2\xi\tau_D}{(1 + \xi^{-2} - \coth^2\xi)} \sum_{n=1}^{\infty} (-1)^{n+1}[g_n(\xi) + g_{-(n+1)}(\xi)\coth\xi]$$

$$\times \left\{ \frac{g_{n-1}(\xi)}{n} + \frac{g_{n+1}(\xi)}{n+1} + \frac{2n+1}{n(n+1)} \left[\left[g_{-n}(\xi) - g_n(\xi) - \frac{n}{\xi}g_{-(n+1)}(\xi) \right]\coth\xi \right. \right.$$

$$\left. \left. - g_{-(n+1)}(\xi)\coth^2\xi \right] \right\} , \tag{103}$$

which, with the aid of Eqs. (101) and (102), yields $T_{\parallel}$ in terms of elementary functions. The leading terms of Eq. (103) are given by

$$T_{\parallel} = \frac{3\tau_D}{\xi} \left\{ \left[\coth\xi - \frac{1}{\xi} \right] + \frac{5}{3\xi} \left[1 - \frac{3}{\xi^2} \left[\coth\xi - \frac{1}{\xi} \right] \right] \frac{[1 + 2/\xi^2 - \coth\xi(1/\xi + \coth\xi)]}{1 + \xi^{-2} - \coth^2\xi} + \cdots \right\} . \tag{104}$$

TABLE III. Numerical values for $T_\parallel/\tau_D$ for rotation in three dimensions.

| | | $T_\parallel/\tau_D$ | |
ξ	Eq. (99)	Eq. (78)	Eq. (105)
1	0.899	0.9092	0.8815
2	0.6842	0.7155	0.6476
3	0.4844	0.5297	0.4518
4	0.3457	0.3907	0.3259
5	0.2593	0.2946	0.2488
6	0.2053	0.2291	0.1998
7	0.1697	0.1841	0.1666
8	0.1447	0.1528	0.1429
9	0.1262	0.1305	0.125
10	0.1119	0.1142	0.1111

The effective eigenvalue method when applied to this problem yields [4]

$$\frac{T_\parallel^{\text{eff}}}{\tau_D} = -\frac{f_1(0)}{\dot{f}_1(0)} = \left[\frac{\xi I_{1/2}(\xi)}{I_{3/2}(\xi)} - \frac{\xi I_{3/2}(\xi)}{I_{1/2}(\xi)} - 2\right]$$

$$= \frac{\xi}{L(\xi)}\left[1 - \frac{2}{\xi}L(\xi) - L^2(\xi)\right] . \quad (105)$$

On using Eq. (42), it becomes apparent that in the limit of large ξ, Eq. (99) has the following asymptotic behavior:

$$\frac{T_\parallel}{\tau_D} \sim \frac{1}{\xi} . \quad (106)$$

In the opposite limit of small ξ, we have, as before,

$$T_\parallel \simeq \tau_D(1 - \tfrac{1}{9}\xi^2 + \tfrac{1}{90}\xi^4 - \cdots) . \quad (107)$$

In Table III and in Fig. 3 we show the longitudinal relaxation time $T_\parallel$ vs ξ. In order to ensure convergence for values of ξ up to 10, a matrix size of 18×18 was used in the evaluation of Eq. (78) and the first 11 terms were taken in the infinite summation of Eq. (99).
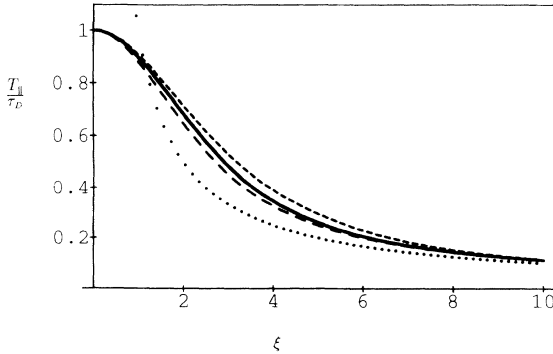

FIG. 3. The longitudinal correlation time $T_\parallel$ as a function of ξ for rotation in three dimensions. The numerical solution of the set of equations (78) (small-dashed line) compared with $T_\parallel$ as calculated from exact equation (99) (bold line) and $T_\parallel^{\text{eff}}$ from Eq. (105) (large-dashed line). The asymptotic equation (106) is the dotted line.

V. ROTATION IN THREE DIMENSIONS: THE TRANSVERSE RESPONSE

Here the probe field $E_1(t)$ is assumed to be along the x axis. The Smoluchowski equation for the probability density $W(\vartheta,\varphi,t)$ is Eq. (66), where

$$V(\vartheta,\varphi) = -\mu E \cos\vartheta - \mu E_1(t)\sin\vartheta \cos\varphi . \quad (108)$$

For the transverse response we should now take into account the dependence of W on the azimuthal angle φ. Thus we seek a solution of Eq. (66) in the form

$$W(\vartheta,\varphi,t) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} a_{m,n}(t)P_n^{|m|}(\cos\vartheta)e^{im\varphi} , \quad (109)$$

where

$$P_n^m(x) = (-1)^m(1-x^2)^{m/2}\frac{d^m}{dx^m}P_n(x) \quad (110)$$

are the associated Legendre functions [7]. On assuming that the field E_1 is switched off at $t=0$ and using the orthogonality properties of the P_n^m and their recurrence relations, we obtain the set of differential-difference equations for

$$g_{n,m}(t) = \langle P_n^{|m|}(\cos\vartheta)\cos m\varphi \rangle$$

$$= \frac{1}{2n+1}\frac{(n+|m|)!}{(n-|m|)!}\frac{a_{n,m}(t)+a_{n,-m}(t)}{2a_{0,0}} . \quad (111)$$

These equations are [4]

$$\frac{d}{dt}g_{n,m}(t) + \frac{n(n+1)}{2\tau_D}g_{n,m}(t)$$

$$= \frac{\xi}{2\tau_D(2n+1)}[(n+1)(n+m)g_{n-1,m}(t)$$

$$- n(n+1-m)g_{n+1,m}(t)] . \quad (112)$$

The polarization decay $P(t)$ is given by

$$P(t) = \mu N \int_0^{2\pi}\int_0^\pi \cos\varphi \sin\vartheta W(\vartheta,\varphi,t)\sin\vartheta \, d\vartheta \, d\varphi$$

$$= \mu N g_{1,1}(t) . \quad (113)$$

Thus we require the terms with $m=1$ only in Eq. (112). On taking the Laplace transform of Eq. (112), we obtain, as before,

$$\tilde{R}_{n,1}(s)\left[\frac{2\tau_D s}{n(n+1)} + 1 + \frac{n\xi}{(n+1)(2n+1)}\tilde{R}_{n+1,1}(s)\right]$$

$$= \frac{2\tau_D}{n(n+1)}\frac{g_{n,1}(0)}{\tilde{g}_{n-1,1}(s)} + \frac{\xi(n+1)}{n(2n+1)} , \quad (114)$$

where

$$\tilde{R}_{n,1}(s) = \frac{\tilde{g}_{n,1}(s)}{\tilde{g}_{n-1,1}(s)} . \quad (115)$$

Equation (114) can also be solved by the above method. Details are given in the Appendix. The result is

$$\tilde{g}_{1,1}(s) = \frac{2\tau_D}{\xi}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{(2n+1)}{n^2(n+1)^2}g_{n,1}(0)$$

$$\times \prod_{k=1}^{n}\tilde{S}_k^\perp(s) , \quad (116)$$

where

$$\widetilde{S}_n^{\perp}(s) = \frac{\xi(n+1)/[n(2n+1)]}{2\tau_D s/[n(n+1)] + 1 + \xi n \widetilde{S}_{n+1}^{\perp}(s)/[(n+1)(2n+1)]} \ . \tag{117}$$

The initial values $g_{n,1}(0)$ are evaluated as follows: On noting that

$$g_{n,1}(0) = \xi_1 \langle P_1^1(\cos\vartheta) P_n^1(\cos\vartheta) \cos^2\varphi \rangle_0$$

$$= \frac{\xi_1}{2} \langle P_1^1(\cos\vartheta) P_n^1(\cos\vartheta) \rangle_0 \tag{118}$$

and on using the recurrence relation ([16], p. 239)

$$(2\nu+1)\sin\vartheta P_\nu^m(\cos\vartheta)$$

$$= (\nu - m + 2)(\nu - m + 1) P_{\nu+1}^{m-1}(\cos\vartheta)$$

$$- (\nu + m)(\nu + m - 1) P_{\nu-1}^{m-1}(\cos\vartheta) \ , \tag{119}$$

with $m = 1$, we obtain

$$g_{n,1}(0) = \xi_1 \frac{n(n+1)}{2(2n+1)} [\langle P_{n-1} \rangle_0 - \langle P_{n+1} \rangle_0]$$

$$= \xi_1 \frac{n(n+1)}{2(2n+1)} \frac{I_{n-1/2}(\xi) - I_{n+3/2}(\xi)}{I_{1/2}(\xi)}$$

$$= \xi_1 \frac{n(n+1)}{2\xi} \frac{I_{n+1/2}(\xi)}{I_{1/2}(\xi)} \ . \tag{120}$$

Here we have also used Eq. (36). Now,

$$g_{1,1}(0) = \frac{\xi_1}{\xi} \frac{I_{3/2}(\xi)}{I_{1/2}(\xi)} \ ; \tag{121}$$

thus,

$$\frac{\widetilde{g}_{1,1}(s)}{g_{1,1}(0)} = \frac{\tau_D}{\xi I_{3/2}(\xi)} \sum_{n=1}^{\infty} (-1)^{n+2} \frac{(2n+1) I_{n+1/2}(\xi)}{n(n+1)}$$

$$\times \prod_{k=1}^{n} \widetilde{S}_k^{\perp}(s) \ . \tag{122}$$

Hence, the transverse complex susceptibility $\alpha_{\perp}(\omega)$ and the correlation time $T_{\perp}$ are given by

$$\frac{\alpha_{\perp}(\omega)}{\alpha_{\perp}(0)} = 1 - i\omega \frac{\widetilde{g}_{1,1}(i\omega)}{g_{1,1}(0)}$$

$$= 1 - \frac{i\omega\tau_D}{\xi I_{3/2}(\xi)} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{(2n+1) I_{n+1/2}(\xi)}{n(n+1)}$$

$$\times \prod_{k=1}^{n} \widetilde{S}_k^{\perp}(i\omega) \tag{123}$$

and

$$T_{\perp} = \frac{\widetilde{g}_{1,1}(0)}{g_{1,1}(0)} = \frac{\tau_D}{\xi I_{3/2}(\xi)} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{(2n+1) I_{n+1/2}(\xi)}{n(n+1)}$$

$$\times \prod_{k=1}^{n} \widetilde{S}_k^{\perp}(0) \ , \tag{124}$$

where

$$\alpha_{\perp}(0) = \frac{\mu^2 N}{\xi kT} \frac{I_{3/2}(\xi)}{I_{1/2}(\xi)} = \frac{\mu^2 N}{kT\xi} L(\xi) \ . \tag{125}$$

By definition, $\widetilde{g}_{1,1}(i\omega)/g_{1,1}(0)$ is the one-sided Fourier transform of the transverse dipole autocorrelation function $C_{\perp}(t)$ defined as

$$C_{\perp}(t) = \frac{g_{1,1}(t)}{g_{1,1}(0)}$$

$$= \frac{\langle \sin\vartheta(0) \cos\varphi(0) \sin\vartheta(t) \cos\varphi(t) \rangle_0}{\langle \sin^2\vartheta(0) \cos^2\varphi(0) \rangle_0} \ . \tag{126}$$

The corresponding effective relaxation time T_1^{eff} is given by [4,5]

$$T_1^{\text{eff}} = -\frac{g_{1,1}(0)}{\dot{g}_{1,1}(0)}$$

$$= 2\tau_D \frac{L(\xi)}{\xi - L(\xi)} = 2\tau_D \frac{I_{3/2}(\xi)}{\xi I_{1/2}(\xi) - I_{3/2}(\xi)} \ . \tag{127}$$

On using the asymptotic expansion (42), we may also deduce that in the limit of large ξ the relaxation time $T_{\perp}$ from Eq. (124) has the following asymptotic behavior:

$$\frac{T_{\perp}}{\tau_D} \sim \frac{2}{\xi} \ , \tag{128}$$

while in the limit of small ξ, we have as before

$$T_{\perp} \simeq \tau_D (1 - \tfrac{1}{12}\xi^2 + \tfrac{17}{2160}\xi^4 - \cdots) \ . \tag{129}$$

In Table IV and in Fig. 4 we show the transverse relaxation time $T_{\perp}$ vs ξ. In order to ensure convergence for values of ξ up to 10, a matrix size of 18×18 was used in the evaluation of Eq. (112) and the first eight terms were
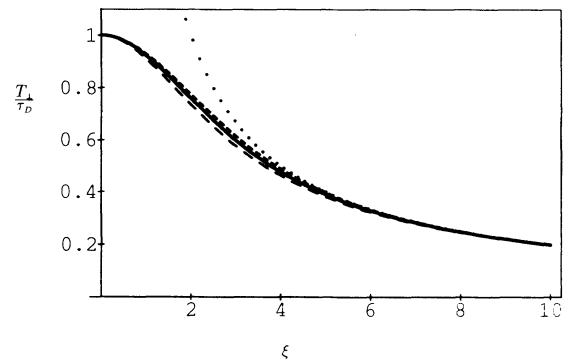

FIG. 4. The transverse correlation time $T_{\perp}$ as a function of ξ for rotation in three dimensions. The numerical solution of the set of equations (112) (small-dashed line) compared with $T_{\perp}$ as calculated from exact equation (124) (bold line), and $T_{\parallel}^{\text{eff}}$ from Eq. (127) (large-dashed line). The asymptotic equation (128) is the dotted line.

TABLE IV. Numerical values for $T_\perp/\tau_D$ for rotation in three dimensions.

ξ	Eq. (124)	$T_\perp/\tau_D$ Eq. (112)	Eq. (127)
1	0.9239	0.9308	0.9114
2	0.7589	0.7751	0.7347
3	0.5982	0.6154	0.5769
4	0.4764	0.489	0.462
5	0.39	0.3978	0.381
6	0.3283	0.3329	0.3226
7	0.2828	0.2856	0.2791
8	0.2482	0.25	0.2456
9	0.221	0.2222	0.2192
10	0.1991	0.2	0.1978

taken in the infinite summation of Eq. (124). In order to ensure convergence of the $\tilde{S}_k^\perp(0)$, it was sufficient to assume that this quantity was zero for $k > 16$.

VI. RESULTS, COMPARISON WITH EXPERIMENTAL DATA, AND DISCUSSION

We have shown how exact analytic expressions may be obtained for the relaxation behavior of an assembly of noninteracting dipoles subject to a strong dc field superimposed on which is an ac field which is so weak as to cause only linear behavior in the response to the field. This allows us to treat in a simple manner the relaxation effects caused by the coupling between the strong dc field and the weak field. The method has the advantage over all previous treatments that exact analytic expressions, valid for all values of ξ, the bias field parameter, are now available for the longitudinal and transverse susceptibilities and correlation times.

Moreover, the comparison of the exact results with the effective eigenvalue solutions [4,5] and numerical calculations of the reciprocal of the lowest eigenvalue (Figs. 1–4 and Tables I–IV) allows us to estimate the accuracy of these approximate approaches. For rotation in three dimensions the differences between the exact, effective, and lowest eigenvalue calculations are of the order of 20% for all values of ξ (see Figs. 3 and 4). This is another pronounced difference (see Sec. II) between the relaxation behavior in a single fold and in a twofold cosine potential. It is well known [9,15] that for the twofold potential, Eq. (44), the effective eigenvalue approach is applicable only for low potential barriers ($U_0 \lesssim kT$) and that there is exponentially large divergence from the exact solution in the limit of high barriers. It appears that the effective eigenvalue technique [3–5] provides a close approximation to the exact solution for any ξ in the case under consideration. Thus, for qualitative evaluation of the correlation times, one can safely use the effective eigenvalue equations (105) and (127) instead of the exact equations (99) or (103) and (124).

The rotational diffusion theory of Debye has been generalized in the paper in order to account for the effect of a constant electric field on the dielectric properties of polar media. The area of applicability of these results is restricted to the low frequency range, as defined by the in-

equality $\omega T_\gamma \lesssim 1$ [T_γ ($\gamma = \|, \perp$) is the relaxation time], because the Debye theory does not include the effects of molecular inertia [12]. A consistent treatment of inertial effects must be carried out using the kinetic equation for the probability density function in configuration-angular velocity space [12], or using an equivalent approach, e.g., the Mori-Zwanzig memory function formalism [12]. The Fokker-Planck and extended rotational diffusion kinetic equations for the probability density function in configuration-angular velocity space were used in [17–20] for the evaluation of the complex dielectric susceptibility tensor of a polar fluid under the influence of a constant external field. These models allow one to estimate dielectric parameters in the whole frequency range of orientational polarization in fluids (up to ~ 5 THz). However, the approaches based on them have the disadvantage that the solutions hitherto obtained for the dielectric spectra require complicated numerical evaluations [18–20] and only approximate analytic equations for the relaxation times, based on the effective eigenvalue technique, have been deduced [19–20].

In Figs. 5 and 6 we plot the real and imaginary parts of the longitudinal and transverse components of the normalized complex susceptibility

$$\chi_\gamma(\omega) = \chi_\gamma'(\omega) - i\chi_\gamma''(\omega)$$

defined as

$$\chi_\gamma(\omega) = \chi_\gamma'(\omega) - i\chi_\gamma''(\omega) = \alpha_\gamma(\omega)/G \quad (\gamma = \|, \perp), \quad (130)$$

where

$$G = \frac{\mu^2 N}{3kT}. \quad (131)$$

The Debye spectra

$$\chi_\gamma^D(\omega) = \frac{\alpha_\gamma(0)/G}{1 + i\omega T_\gamma} \quad (\gamma = \|, \perp), \quad (132)$$

where the relaxation times $T_\|$ and $T_\perp$ are given by exact equations (99) and (124), respectively, are shown in both figures for comparison. Equation (132) is obtained from
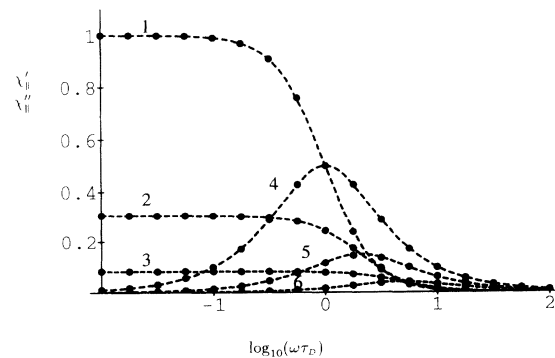

FIG. 5. The real $\chi_\|'$ and imaginary $\chi_\|''$ parts of the normalized longitudinal complex susceptibility as a function of $\log_{10}(\omega\tau_D)$. The circles are the exact solution (93) and the dashed lines are the single relaxation time approximation (132). Curves 1, 2, and 3 are $\chi_\|'$ for $\xi = 0$, 3, and 6, respectively. Curves 4, 5, and 6 are $\chi_\|''$ for $\xi = 0$, 3, and 6, respectively.
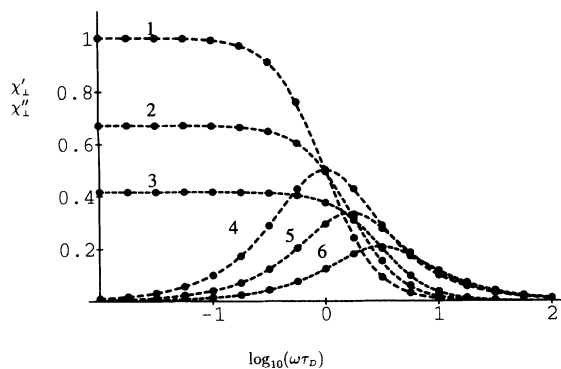
FIG. 6. The real χ_1' and imaginary χ_1'' parts of the normalized transverse complex susceptibility as a function of $\log_{10}(\omega\tau_D)$. The circles are the exact solution (123) and the dashed lines are the single relaxation time approximation (132). Curves 1, 2, and 3 are $\chi_\parallel'$ for $\xi=0$, 3, and 6, respectively. Curves 4, 5, and 6 are $\chi_\parallel''$ for $\xi=0$, 3, and 6 respectively.

FIG. 7. Comparison of the theoretical bias field dependence (dashed lines) of the critical relaxation frequency f_c with experimental data (circles) of Block and Hayes [10] for dilute solutions of polar macromolecules PBLG with molecular weights (1) 4.6×10^5, (2) 2.6×10^5, and (3) 1.1×10^5.

Eq. (28) by assuming that the decay of $f_1(t)$ is a single exponential, namely,

$$f_1(t)=f_1(0)\exp(-t/T_\parallel) \ . \tag{133}$$

One can see that there is no practical difference between the exact equations (93) and (123) for $\chi_\gamma(\omega)$ and the Debye equation (132) for $\chi_\gamma^D(\omega)$. This means that both longitudinal and transverse dielectric relaxation can be effectively described as a single exponential for all values of ξ.

The results of calculations of the complex susceptibilities $\chi_\parallel^*(\omega)$ and $\chi_1^*(\omega)$ for rotation in space are in qualitative agreement with those for rotation in two dimensions. However, there is an essential quantitative difference (order of factor 2) between the susceptibilities calculated for the two- and three-dimensional models. This difference is of importance for comparison with experimental data.

Our results for the longitudinal susceptibility (Fig. 5) and relaxation time [Eqs. (93) and (99)] are in qualitative agreement with available experimental data [10,11]. (These data were obtained for the longitudinal component of the susceptibility with the strong dc field applied parallel to the weak ac probe field.) As observed by Block and Hayes [10] and Fannin, Scaife, and Charles [11], with increasing ξ, both loss [($\propto\chi_\parallel''(\omega)$)] and relaxation time $T_\parallel$ decrease compared with those in the isotropic case. Figure 5 shows clearly that these observations are in qualitative agreement with our results.

In Figure 7 we compare the theoretical and experimental critical relaxation frequency f_c defined as

$$f_c=(2\pi T_\parallel)^{-1} \ , \tag{134}$$

where $T_\parallel$ is given by Eq. (99), for dilute solutions of polar macromolecules of poly-γ-benzyl-L-glutamate (PBLG) in a nonpolar solvent at 298 K [10]. The system was very suitable since dipole moments of the PBLG molecules are large. Thus values of the energy of a dipole in a dc field which are comparable with thermal energy ($\xi\sim1$) can be
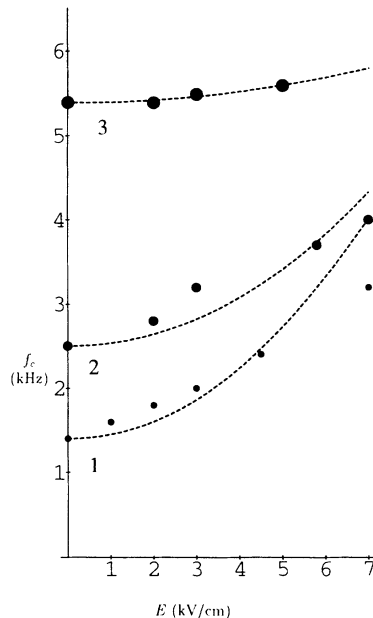
obtained. Comparison with the experimental data of Block and Hayes [10] allowed us to evaluate the average dipole moments μ of the molecules. They are 23.3×10^{-27}, 14.7×10^{-27}, and 4.8×10^{-27} C m for the PBLG molecules with molecular weights 4.6×10^5, 2.6×10^5, and 1.1×10^5, respectively. The data were fitted using a standard least-squares method. The values of μ so obtained are greater than the originally reported data but are in agreement with results of Ullman [21] who suggested that this difference results from a poor estimate of the internal field in the context of a simple model for the evaluation of dipole moments from static dielectric measurements used in [10]. Also, our exact calculation for PBLG with molecular weight 4.6×10^5 is in accordance with results of Ullman [21] based on the numerical solution of Eq. (78).

It should be noted that experiments on the polarization induced by a weak ac field superimposed on a strong dc field will be much easier to carry out on a ferrofluid rather than on a polar fluid as a large value of ξ can be achieved with a moderate constant magnetic field due to the large value of the magnetic dipole moment m (10^4–10^5 Bohr magnetons) of fine ($<$ 100 Å) ferromagnetic particles. In Fig. 8 we compare the theoretical and experimental longitudinal relaxation time $T_\parallel$ for a ferrofluid (a colloidal suspension of cobalt ferrite in hexadecene). On using Eq. (134), the experimental values of $T_\parallel$ were obtained from the experimental data of Fannin, Scaife, and Charles [11] for the spectra of the imaginary part $\chi_\parallel''(\omega)$ of the magnetic susceptibility. The value of the average magnetic dipole moment m of particles is found from the least-squares fit to be 4.29×10^5 Bohr magnetons.
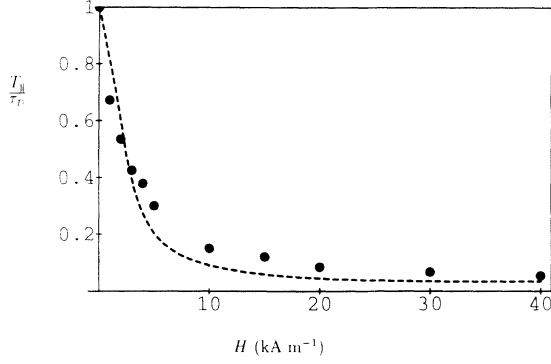
FIG. 8. Comparison of the theoretical (dashed line) and experimental (circles) normalized longitudinal relaxation time $T_\parallel/\tau_D$ against the bias magnetic field H for a ferrofluid. The experimental data are from Fannin, Scaife, and Charles [11].

In conclusion, is should be noted that we have treated the relaxation behavior by solving the infinite hierarchies of the difference-differential equations derived from the diffusion (Smoluchowski) equations. However, as we have already shown in [4], the same results (namely, hierarchies of the difference-differential equations) can be obtained by direct averaging of the underlying Langevin equations without recourse to the Smoluchowski equations.

ACKNOWLEDGMENTS

APPENDIX

First we present the method of solution of Eq. (80) which governs the longitudinal relaxation. We seek a complete solution of the inhomogeneous equation (80) in the form

$$\tilde{R}_n^\parallel(s)=\tilde{S}_s^\parallel(s)+\tilde{Q}_n^\parallel(s) . \tag{A1}$$

We can regard Eq. (A1) as having a particular solution $\tilde{S}_n^\parallel(s)$ and a complementary solution $\tilde{Q}_n^\parallel(s)$. The particular solution satisfies Eq. (80) with $f_n(0)=0$:

$$\tilde{S}_n^\parallel(s)\left[\frac{2\tau_D s}{n(n+1)}+1+\frac{\xi\tilde{S}_{n+1}^\parallel(s)}{(2n+1)}\right]=\frac{\xi}{(2n+1)} . \tag{A2}$$

Equation (80) then becomes

$$\tilde{Q}_n^\parallel(s)\left[\frac{2\tau_D s}{n(n+1)}+1\right]+\frac{\xi}{2n+1}[\tilde{S}_{n+1}^\parallel(s)\tilde{Q}_n^\parallel(s)$$

$$+\tilde{S}_n^\parallel(s)\tilde{Q}_{n+1}^\parallel(s)$$

$$+\tilde{Q}_{n+1}^\parallel(s)\tilde{Q}_n^\parallel(s)]$$

$$=\frac{2\tau_D f_n(0)}{n(n+1)\tilde{f}_{n-1}(s)} . \tag{A3}$$

Let us write

$$q_n^\parallel=\tilde{f}_{n-1}(s)\tilde{Q}_n^\parallel(s) . \tag{A4}$$

Then, on using

$$\tilde{f}_{n-1}(s)[\tilde{S}_n^\parallel(s)+\tilde{Q}_n^\parallel(s)]=\tilde{f}_n(s) , \tag{A5}$$

we obtain

$$q_n^\parallel\left[\frac{2\tau_D s}{n(n+1)}+1\right]+\frac{\xi}{2n+1}[q_{n+1}^\parallel+q_n^\parallel\tilde{S}_{n+1}^\parallel(s)]$$

$$=\frac{2\tau_D f_n(0)}{n(n+1)} . \tag{A6}$$

Solving Eq. (A6) for $q_n^\parallel$, we have

$$q_n^\parallel=\left[\frac{2\tau_D(2n+1)f_n(0)}{\xi n(n+1)}-q_{n+1}^\parallel\right]\tilde{S}_n^\parallel(s) . \tag{A7}$$

Thus, according to Eqs. (A1) and (A3) and Eq. (A4),

$$\tilde{f}_n(s)=\left[\tilde{f}_{n-1}(s)+\frac{2\tau_D(2n+1)f_n(0)}{\xi n(n+1)}-q_{n+1}^\parallel\right]\tilde{S}_n^\parallel(s) . \tag{A8}$$

Since $\tilde{f}_0(s)=0$, we can write down Eq. (A8) for $n=1$ as follows:

$$\tilde{f}_1(s)=\left[\frac{3\tau_D f_1(0)}{\xi}-q_2^\parallel\right]\tilde{S}_1^\parallel(s) . \tag{A9}$$

Now we can obtain an expression for $q_2^\parallel$ from Eq. (A7) for $n=2$ and so on. Thus we derive from Eqs. (A7) and (A9),

$$\tilde{f}_1(s)=\frac{\tau_D}{\xi}\{3f_1(0)\tilde{S}_1^\parallel(s)-\tfrac{5}{3}f_2(0)\tilde{S}_1^\parallel(s)\tilde{S}_2^\parallel(s)$$

$$+\tfrac{7}{6}f_3(0)\tilde{S}_1^\parallel(s)\tilde{S}_2^\parallel(s)\tilde{S}_3^\parallel(s)-\cdots\}$$

$$=\frac{2\tau_D}{\xi}\sum_{n=1}^\infty(-1)^{n+1}f_n(0)\frac{(2n+1)}{n(n+1)}\prod_{k=1}^n\tilde{S}_k^\parallel(s) , \tag{A10}$$

which is Eq. (82).

The same method applied to Eq. (114) leads to the following recurrence relation for the transverse relaxation:

$$\tilde{g}_{n,1}(s)=\left[\tilde{g}_{n-1,1}(s)+\frac{2\tau_D(2n+1)}{\xi(n+1)^2}g_{n,1}(0)\right.$$

$$\left.-\frac{n^2}{(n+1)^2}q_{n+1}^\perp\right]\tilde{S}_n^\perp(s) , \tag{A11}$$

where

$$q_n^\perp=\left[\frac{2\tau_D(2n+1)}{\xi(n+1)^2}g_{n,1}(0)-\frac{n^2}{(n+1)^2}q_{n+1}^\perp\right]\tilde{S}_n^\perp(s) . \tag{A12}$$

Thus, on using Eqs. (A11) and (A12) and noting that $g_{0,1}=0$, we derive

$$\tilde{g}_{1,1}(s) = \frac{\tau_D}{\xi}\left[\tfrac{3}{2}g_{1,1}(0)\tilde{S}_1^{\perp}(s) - \tfrac{5}{18}g_{2,1}(0)\tilde{S}_1^{\perp}(s)\tilde{S}_2^{\perp}(s) + \tfrac{7}{72}g_{3,1}(0)\tilde{S}_1^{\perp}(s)\tilde{S}_2^{\perp}(s)\tilde{S}_3^{\perp}(s) - \cdots\right]$$

$$= \frac{2\tau_D}{\xi}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{(2n+1)}{n^2(n+1)^2}g_{n,1}(0)\prod_{k=1}^{n}\tilde{S}_k^{\perp}(s) \ , \tag{A13}$$

which is Eq. (116).

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