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Anisotropic rotational diffusion and dielectric relaxation of rigid dipolar particles in a strong external dc field

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Dielectric response functions of polar particles (macromolecules) diluted in a nonpolar solvent subjected to a strong external dc electric field are evaluated using the anisotropic noninertial rotational diffusion model. Simple analytic formulas for the longitudinal and transverse components of the dielectric susceptibility and relaxation times are given using the effective relaxation time method. These formulas are tested against numerical solutions of the underlying infinite hierarchy of differential-recurrence equations for statistical moments (ensemble averages of the Wigner *D* functions) which are obtained by averaging the governing Langevin equation for noninertial rotational Brownian motion over its realizations. The calculations, involving matrix continued fractions, ultimately yield the exact solution of the infinite hierarchy of differential-recurrence relations for the dielectric response functions. In the isotropic rotational diffusion limit, the solution reduces to the known results.

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I. INTRODUCTION

The Brownian motion in a field of force is of fundamental importance in problems involving relaxation and resonance phenomena in stochastic systems [1,2]. Examples are dielectric relaxation of fluids and magnetic relaxation of ferrofluids springing from the rotational Brownian motion of particles in the presence of external fields and thermal agitation (see, e.g., [1,2]). The theory of dielectric relaxation of noninteracting polar molecules was first given by Debye [3]. In the most general formulation, namely, anisotropic rotational diffusion of asymmetric top particles in an electric field (in the *low field strength* limit), a concise theory has been developed by Perrin [4] and others (see, e.g., [5–17]) for the analysis of orientation relaxation of particles in liquids by various spectroscopic methods (such as dielectric and Kerr effect relaxation, fluorescent depolarization, dynamic light scattering, etc.).

The application of a strong direct current (dc) electric field $\mathbf{E}_0$ to an assembly of dipolar particles results in a transition from free thermal rotation of the particles to partial orientation with hindered rotation. This change in the character of the rotational motion under the influence of the 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 particle in the field $\mathbf{E}_0$ [18]. A similar effect arises in magnetic relaxation of dilute suspensions of fine magnetic particles (ferrofluids) subjected to a strong dc magnetic field $\mathbf{H}_0$ (see, e.g., [19,20]). The similarity of the problems of dielectric relaxation of a polar fluid and magnetic relaxation of a ferrofluid is unsurprising because, from a physical point of view, the rotational Brownian motion of magnetic particles (magnetic dipoles) in a constant magnetic field $\mathbf{H}_0$ is similar to that of polar molecules (electric dipoles) in a constant electric field $\mathbf{E}_0$ [2]. Orientational relaxation of dipolar Brownian particles in the presence of a dc field has been treated theoretically in Refs. [21–26]. These predictions allow one to understand qualitatively the relaxation behavior of dipolar particles subjected an external dc bias field, e.g., the dc field dependence of the longitudinal and transverse relaxation times (see, for example, [19,20]). However, these predictions were mostly confined to isotropic rotational diffusion of spherical particles so that the results have a limited range of applicability. For example, for particles of arbitrary shape the components of the rotational diffusion tensor may differ considerably. Further progress in the theoretical treatment of orientational relaxation of Brownian particles in strong external fields has been achieved for the anisotropic noninertial rotational diffusion model in Refs. [27,28] (see also [2], Chap. 7). The method developed in Refs. [27,28] involves transformation of the angular variables in the underlying Langevin equation and subsequent direct averaging over its realizations of the stochastic differential equation so obtained. This approach yields an infinite hierarchy of the differential-recurrence relations for the statistical moments (averaged Wigner's *D* functions [29]) describing the orientational relaxation of particles. The resulting system of moment equations can be solved by a matrix continued fraction method [2]. We remark that the methods of solution for the dielectric response in strong external fields are very similar to those used in the theory of orientational relaxation of molecules in liquid crystals and magnetic relaxation of single domain ferromagnetic particles. The orientational relaxation of molecules in liquid crystals is usually interpreted using the rotational diffusion model of a molecule in a mean field potential *V* (see, for example, Refs. [30–32] and references cited therein). The magnetization relaxation in fine magnetic particles is treated in the context of the rotational diffusion of the magnetization in the magnetocrystalline anisotropy potential *V* [2,33].

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Here the linear response of an assembly of noninteracting polar Brownian particles to a small external (probe) field $\mathbf{E}_1$ superimposed with a strong dc bias field $\mathbf{E}_0$ is calculated in the context of the anisotropic noninertial rotational diffusion using the method developed in Refs. [27,28]. Both exact matrix continued fraction and approximate analytic solutions will be presented. Furthermore, we shall demonstrate that the characteristic times of the rotational diffusion process evaluated using the effective relaxation time method [34] allow one to evaluate the dielectric response for anisotropic diffusion. Moreover, this approach will yield a simple analytical equation for the complex dielectric susceptibility tensor describing the dielectric relaxation of the system.

II. BASIC RELATIONS

We suppose that the magnitude of an externally uniform dc electric field applied to the system of asymmetric top molecules at $t=-\infty$ is suddenly altered at time $t=0$ from $\mathbf{E}_{\mathrm{I}}=\mathbf{E}_0+\mathbf{E}_1$ to $\mathbf{E}_{\mathrm{II}}=\mathbf{E}_0$ (the electric fields $\mathbf{E}_0$ and $\mathbf{E}_1$ are assumed to be applied parallel to the Z axis of the laboratory coordinate system). In addition, it is supposed that the field $\mathbf{E}_1$ is weak (i.e., $\mu E_1 \ll kT$, which is the linear response condition; μ is the permanent dipole moment of a particle, k is Boltzmann's constant, and T is the temperature). We also suppose that the permanent dipole moment of the particle is much greater than the induced dipole moment (the case of polar and polarizable particles can be treated in like manner [28]). We shall also assume that the suspension of Brownian particles is monodisperse, nonconducting, and sufficiently dilute to avoid interparticle correlation effects. Rototranslational effects are also ignored. These effects can also be incorporated in the theory just as in the low field strength limit [16,35].

According to linear response theory (Ref. [2], Chap. 2), the decay of the longitudinal component of the polarization $P_\parallel(t)$, is given by

$$\langle P_\parallel \rangle(t) = \chi_\parallel E_1 C_\parallel(t), \tag{1}$$

where

$$C_\parallel(t) = \frac{\langle u_Z[\Omega(0)]u_Z[\Omega(t)]\rangle_0 - \langle u_Z\rangle_0^2}{\langle u_Z^2\rangle_0 - \langle u_Z\rangle_0^2} \tag{2}$$

is the normalized *equilibrium* autocorrelation function of the longitudinal component of the dipole moment of the particle, $\Omega=\{\alpha,\beta,\gamma\}$ are the Euler angles, which determine the orientation of the molecular (body-fixed) coordinate system xyz with respect to the laboratory coordinate system XYZ [29] (see Fig. 1),

$$u_Z[\Omega(t)] = u_z \cos\beta(t) + u_y \sin\beta(t)\sin\gamma(t) \\ - u_x \sin\beta(t)\cos\gamma(t)$$

is the Z component of the unit vector $\mathbf{u}=\boldsymbol{\mu}/|\boldsymbol{\mu}|$ in the system XYZ, $\boldsymbol{\mu}$ is the permanent dipole moment vector of the particle, u_x,u_y,u_z are the components of $\mathbf{u}$ in the system xyz, and $\chi_\parallel$ is the longitudinal static susceptibility defined as

$$\chi_\parallel = \frac{\mu^2 N_0}{kT}(\langle u_Z^2\rangle_0 - \langle u_Z\rangle_0^2) = \frac{\mu^2 N_0}{kT}\left(1 - 2\frac{L(\xi)}{\xi} - L^2(\xi)\right).$$

Here N_0 is the concentration of particles, $L(\xi)=\coth\xi - 1/\xi$ is the familiar Langevin function and $\xi=\mu E_0/(kT)$. The angular brackets $\langle\,\rangle_0$ denote equilibrium ensemble averaging (in the absence of the probing ac field $\mathbf{E}_1$) defined as $\langle\cdot\rangle_0 = \int \cdot\, W_0(\Omega)d\Omega$, where $W_0(\Omega)=Z^{-1}e^{\xi u_Z(\Omega)}$ is the equilibrium Boltzmann distribution function and $d\Omega = \sin\beta\, d\beta\, d\alpha\, d\gamma$. The equilibrium averages $\langle u_Z\rangle_0$ and $\langle u_Z^2\rangle_0$ are calculated in Appendix A.

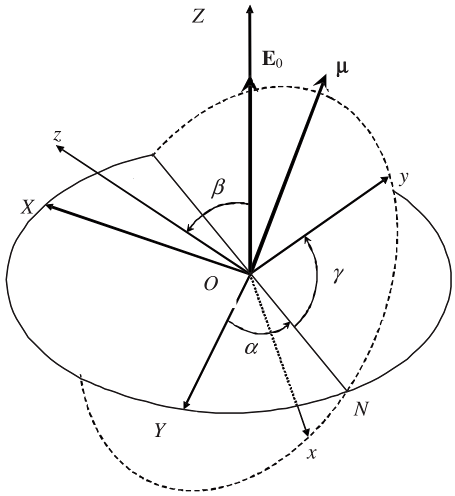

FIG. 1. Geometry of the problem.

The correlation function $C_\parallel(t)$ describes the longitudinal relaxation of $P_\parallel(t)$ in the time domain. Furthermore, a knowledge of $C_\parallel(t)$ allows one to evaluate the ac response of the system to a small ac perturbing field, namely, the longitudinal complex susceptibility $\chi_\parallel(\omega)=\chi'_\parallel(\omega) - i\chi''_\parallel(\omega)$, which is defined as [2]

$$\chi_\parallel(\omega)/\chi_\parallel = 1 - i\omega\int_0^\infty e^{-i\omega t}C_\parallel(t)dt. \tag{3}$$

The behavior of $\chi_\parallel(\omega)$ in the frequency domain is completely determined by the time behavior of $C_\parallel(t)$. The overall behavior of $C_\parallel(t)$ is characterized by the *integral relaxation time* $\tau_{\mathrm{int}}^{\parallel}$ (the area under the relaxation function decay curve) and the *effective relaxation time* $\tau_{\mathrm{eff}}^{\parallel}$ (yielding precise information on the initial decay of the relaxation function in the time domain) [2,34]

$$\tau_{\mathrm{int}}^{\parallel} = \int_0^\infty C_\parallel(t)dt \quad \text{and} \quad \tau_{\mathrm{eff}}^{\parallel} = -1/\dot{C}_\parallel(0). \tag{4}$$

The relaxation times $\tau_{\mathrm{int}}^{\parallel}$ and $\tau_{\mathrm{eff}}^{\parallel}$ may be associated, respectively, with the long and short time behavior of the correlation function $C_\parallel(t)$ and the low- and high-frequency behavior of the complex susceptibility $\chi_\parallel(\omega)$. Indeed, in the low- ($\omega \to 0$) and high- ($\omega\to\infty$) frequency limits, the susceptibility $\chi_\parallel(\omega)$ may easily be evaluated. We have from Eq. (3) [2]

$$\frac{\chi_\parallel(\omega)}{\chi_\parallel} \approx 1 - i\omega\int_0^\infty C_\parallel(t)dt \approx 1 - i\omega\tau_{\mathrm{int}}^{\parallel} + \cdots, \tag{5}$$

$$\frac{\chi_{\parallel}(\omega)}{\chi_{\parallel}} \sim -\frac{\dot{C}_{\parallel}(0)}{i\omega} + \cdots = \frac{1}{i\omega\tau_{\mathrm{eff}}^{\parallel}} + \cdots, \tag{6}$$

for $\omega \to 0$ and $\omega \to \infty$, respectively.

III. CALCULATION OF THE DIELECTRIC RESPONSE

The time-dependent longitudinal component $P_{\parallel}(t)$ of the electric polarization $\mathbf{P}(t)$ of an assembly of polar particles of an arbitrary shape is equivalently given by [14]

$$\begin{aligned} P_{\parallel}(t) &= \mu N_0[\langle u_Z\rangle(t) - \langle u_Z\rangle_0] \\ &= \mu N_0 \sum_{p=-1}^{1} (-1)^p u^{(-p)}[\langle D_{0,p}^1\rangle(t) - \langle D_{0,p}^1\rangle_0], \end{aligned} \tag{7}$$

where $u^{(0)}=u_z$ and $u^{(\pm 1)}=\mp(u_x \pm i u_y)/\sqrt{2}$ are the irreducible spherical tensor components of the first rank [29], $D_{M,M'}^J(\Omega)$ are Wigner's D functions defined as [29]

$$D_{M,M'}^J(\Omega) = e^{-iM\alpha} d_{MM'}^J(\beta) e^{-iM'\gamma},$$

$d_{MM'}^J(\beta)$ is a real function with various explicit forms given, for example, in Ref. [29] and the angular brackets $\langle\ \rangle(t)$ denote statistical averaging.

The calculation of $P_{\parallel}(t)$ requires equations for the first-rank relaxation functions $c_{0,p}^1(t)=\langle D_{0,p}^1\rangle(t)-\langle D_{0,p}^1\rangle_0$ appearing in Eq. (7). These equations can be obtained by averaging the noninertial Langevin equation for the anisotropic rotational diffusion over its realizations in configuration space as described in detail in Refs. [27,28]. Thus one may obtain an infinite hierarchy of linear differential-recurrence relations for the relaxation functions

$$\begin{aligned} c_{0,m}^j(t) &= \langle D_{0,m}^j\rangle(t) - \langle D_{0,m}^j\rangle_0 \\ &\cong \xi_1\{\langle u_Z[\Omega(0)] D_{0,m}^j[\Omega(t)]\rangle_0 - \langle u_Z\rangle_0 \langle D_{0,m}^j\rangle_0\} \end{aligned}$$

(in the approximation of linear response theory), where $\xi_1 = \mu E_1/(kT)$. These are

$$\tau_D \frac{d}{dt} c_{0,m}^j(t) = \sum_{j'=-1}^{1} \sum_{m'=-2}^{2} e_{j,m}^{j',m'} c_{0,m+m'}^{j+j'}(t), \tag{8}$$

where the coefficients $e_{j,m}^{j',m'}$ are given in Appendix B. In the derivation of Eq. (8), we have used the molecular coordinate system xyz in which the diffusion tensor $\hat{D}$ is diagonal: namely,

$$\hat{D} = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix}$$

with distinct (in general) components D_{xx}, D_{yy}, and D_{zz} whose values depend on the shape of the particle. The components D_{xx}, D_{yy}, and D_{zz} can be estimated using either the so-called hydrodynamic approach [4,9,10] or in terms of microscopic parameters [9]. Possible ranges of variations of D_{xx}, D_{yy}, and D_{zz} are discussed, e.g., in Ref. [36].

The recurrence Equation (8) can be solved in terms of matrix continued fractions [1,2]. The solution for the one-sided Fourier transforms $\tilde{c}_{0,m}^1(\omega)=\int_0^{\infty} e^{-i\omega t} c_{0,m}^1(t)dt$ is presented in Appendix B, and allows us to evaluate the longitudinal correlation function $C_{\parallel}(t)$ and dielectric susceptibility $\chi_{\parallel}(\omega)$ as

$$C_{\parallel}(t) = u_x^2 f_x^{\parallel}(t) + u_y^2 f_y^{\parallel}(t) + u_z^2 f_z^{\parallel}(t), \tag{9}$$

$$\frac{\chi_{\parallel}(\omega)}{\chi_{\parallel}} = 1 - i\omega[u_x^2 \tilde{f}_x^{\parallel}(\omega) + u_y^2 \tilde{f}_y^{\parallel}(\omega) + u_z^2 \tilde{f}_z^{\parallel}(\omega)], \tag{10}$$

where $\tilde{f}_i^{\parallel}(\omega)=\int_0^{\infty} e^{-i\omega t} f_i^{\parallel}(t)dt$ and the normalized relaxation functions $f_i^{\parallel}(t)$ are defined as

$$f_x^{\parallel}(t) = \frac{c_{0,-1}^1(t) - c_{0,1}^1(t)}{c_{0,-1}^1(0) - c_{0,1}^1(0)}, \quad f_y^{\parallel}(t) = \frac{c_{0,-1}^1(t) + c_{0,1}^1(t)}{c_{0,-1}^1(0) + c_{0,1}^1(0)},$$

$$f_z^{\parallel}(t) = \frac{c_{0,0}^1(t)}{c_{0,0}^1(0)}. \tag{11}$$

Here we have noted that (see Appendix A)

$$\begin{aligned} \frac{c_{0,-1}^1(0) - c_{0,1}^1(0)}{\sqrt{2}\xi_1 u_x} &= -\frac{c_{0,-1}^1(0) + c_{0,1}^1(0)}{i\sqrt{2}\xi_1 u_y} \\ &= \frac{c_{0,0}^1(0)}{\xi_1 u_z} = 1 - 2\frac{L(\xi)}{\xi} - L^2(\xi). \end{aligned}$$

The complex susceptibility $\chi_{\parallel}(\omega)$ and integral relaxation time $\tau_{\mathrm{int}}^{\parallel}$ can be calculated from Eqs. (3) and (4), respectively.

In the absence of the field $\mathbf{E}_0$, the relaxation functions $f_i^{\parallel}(t)$ defined by Eq. (11) are simple exponentials [2,13]

$$f_x^{\parallel}(t) = e^{-(D_{yy}+D_{zz})t}, \quad f_y^{\parallel}(t) = e^{-(D_{xx}+D_{zz})t}, \quad f_z^{\parallel}(t) = e^{-(D_{xx}+D_{yy})t}.$$

Thus the decay of the longitudinal relaxation function $C_{\parallel}(t)$ in the time domain is given by three exponentials, viz. [2,13],

$$C_{\parallel}(t) = u_x^2 e^{-(D_{yy}+D_{zz})t} + u_y^2 e^{-(D_{xx}+D_{zz})t} + u_z^2 e^{-(D_{xx}+D_{yy})t}.$$

In the frequency domain, the spectrum of $\chi_{\parallel}(\omega)$ comprises three Lorentzians, which is the well-known Perrin equation [4] (in our notation)

$$\begin{aligned} \chi_{\parallel}(\omega) = \frac{\mu^2 N_0}{3kT}\Bigg(& \frac{u_x^2}{1 + i\omega/(D_{yy}+D_{zz})} + \frac{u_y^2}{1 + i\omega/(D_{xx}+D_{zz})} \\ & + \frac{u_z^2}{1 + i\omega/(D_{xx}+D_{yy})}\Bigg). \end{aligned} \tag{12}$$

The solution in terms of matrix continued fractions is very convenient for computations. It allow us to evaluate the time decay of the polarization and the dynamic susceptibility in all ranges of the diffusion constants and applied field parameters as well as the spectra of the relaxation functions, the complex susceptibility, etc. Nevertheless, in practical applications such as the analysis of experimental results, the matrix continued fraction method is of limited use since the dependence of the dielectric response on the model parameters is not obvious from this method. Thus it is desirable to obtain simple approximate formulas describing the dynamical behavior and which helps one to understand the qualitative behavior of dielectric relaxation. Here the matrix continued fraction approach is also very useful as it allows us to determine the accuracy of the approximate solutions. Just as isotropic diffusion [2,22,24], the simplest interpretation of the relaxation behavior, can be given using effective relaxation time approach [2,34].

IV. EFFECTIVE RELAXATION TIME SOLUTION

The relaxation function $f_i^{\parallel}(t)$ appearing in Eq. (9) describes the contribution of rotation of the ith component of the dipole moment $\boldsymbol{\mu}$ about the complementary axes to the dielectric relaxation process. In the presence of the field $\mathbf{E}_0$, the time behavior of the relaxation function $f_i^{\parallel}(t)$ $(i=x, y, z)$ can formally be described as the infinite discrete set of relaxation modes

$$f_i^{\parallel}(t) = \sum_k c_k^i e^{-\lambda_k^i t}, \tag{13}$$

where λ_k^i are the eigenvalues of the Fokker-Planck operator L_{FP} for the anisotropic diffusion model [2] and $\Sigma_k c_k^i = 1$. Thus $f_i^{\parallel}(t)$ contains contributions from *all* the relaxation modes $c_k^i e^{-\lambda_k^i t}$. In the effective relaxation time approximation [2,34], the relaxation functions $f_i^{\parallel}(t)$ can be described for *all* t (due to the near degenerate relaxation modes) by a single exponential

$$f_i^{\parallel}(t) \approx e^{-t/\tau_i^{\parallel}}, \tag{14}$$

where the effective relaxation times τ_i are defined as

$$\tau_i^{\parallel} = -1/\dot{f}_i^{\parallel}(0). \tag{15}$$

Here the time derivative $\dot{f}_i^{\parallel}(0)$ at time $t=0$ of the relaxation functions $f_i^{\parallel}(t)$ can be expressed in terms of equilibrium averages which can be calculated analytically (this is the main advantage of introducing the effective relaxation time [34]; see Appendix A). The calculations yield

$$\tau_x^{\parallel} = (D_{yy} + D_{zz})^{-1} F^{\parallel}(\xi) = \frac{\tau_D F^{\parallel}(\xi)}{1 + \Delta - \Xi/2}, \tag{16}$$

$$\tau_y^{\parallel} = (D_{xx} + D_{zz})^{-1} F^{\parallel}(\xi) = \frac{\tau_D F^{\parallel}(\xi)}{1 + \Delta + \Xi/2}, \tag{17}$$

$$\tau_z^{\parallel} = (D_{xx} + D_{yy})^{-1} F^{\parallel}(\xi) = \tau_D F^{\parallel}(\xi), \tag{18}$$

where the function $F^{\parallel}(\xi)$ (which determines the field dependence of all $\tau_i^{\parallel}$) is given in terms of elementary functions, viz.,

$$F^{\parallel}(\xi) = \frac{\xi}{L(\xi)} - \xi L(\xi) - 2 = \frac{1 + \xi^2 - \xi^2 \coth^2 \xi}{\xi \coth \xi - 1}, \tag{19}$$

$\tau_D = (D_{xx} + D_{yy})^{-1}$ is the characteristic (Debye) relaxation time, and

$$\Delta = \frac{D_{zz}}{D_{xx} + D_{yy}} - \frac{1}{2} \quad \text{and} \quad \Xi = \frac{D_{xx} - D_{yy}}{D_{xx} + D_{yy}} \tag{20}$$

are dimensionless parameters characterizing the anisotropy of the diffusion tensor $\hat{D}$. We remark that the relaxation time τ_D and anisotropy parameters Δ and Ξ may be considered as independent model parameters. The diagonal components D_{xx}, D_{yy}, and D_{zz} are related to τ_D, Δ, and Ξ by the equations

$$D_{xx} = \frac{1 + \Xi}{2\tau_D}, \quad D_{yy} = \frac{1 - \Xi}{2\tau_D}, \quad D_{zz} = \frac{\Delta + 1/2}{\tau_D}.$$

Here possible ranges of variations of the anisotropy parameters Δ and Ξ are $-1/2 < \Delta$ and $-1 < \Xi < 1$.

Thus the longitudinal relaxation function $C_{\parallel}(t)$ from Eq. (9) can be approximated by three exponentials,

$$C_{\parallel}(t) \approx u_x^2 e^{-t/\tau_x^{\parallel}} + u_y^2 e^{-t/\tau_y^{\parallel}} + u_z^2 e^{-t/\tau_z^{\parallel}}. \tag{21}$$

In turn, in the frequency domain, the spectrum of $\chi_{\parallel}(\omega)$ may be approximated by three Lorentzians, viz.,

$$\frac{\chi_{\parallel}(\omega)}{\chi_{\parallel}} \approx \frac{u_x^2}{1 + i\omega\tau_x^{\parallel}} + \frac{u_y^2}{1 + i\omega\tau_y^{\parallel}} + \frac{u_z^2}{1 + i\omega\tau_z^{\parallel}}, \tag{22}$$

where the characteristic frequencies and the half-widths are determined by the three effective relaxation times $\tau_x^{\parallel}$, $\tau_y^{\parallel}$, and $\tau_z^{\parallel}$. The effective relaxation time $\tau_{\mathrm{eff}}^{\parallel} = -1/\dot{C}_{\parallel}(0)$ of the longitudinal correlation function $C_{\parallel}(t)$ is given by

$$\tau_{\mathrm{eff}}^{\parallel} = \frac{\tau_D F^{\parallel}(\xi)}{1 + u_x^2(\Delta - \Xi/2) + u_y^2(\Delta + \Xi/2)}. \tag{23}$$

The behavior of the effective relaxation time $\tau_{\mathrm{eff}}^{\parallel}$ and the integral relaxation time $\tau_{\mathrm{int}}^{\parallel} = u_x^2 \tilde{f}_x^{\parallel}(0) + u_y^2 \tilde{f}_y^{\parallel}(0) + u_z^2 \tilde{f}_z^{\parallel}(0)$ as functions of the external field (ξ) and diffusion tensor anisotropy (Δ and Ξ) parameters is shown in Figs. 2 and 3. Qualitatively, $\tau_{\mathrm{eff}}^{\parallel}$ and $\tau_{\mathrm{int}}^{\parallel}$ display a similar dependence on the external field strength and diffusion tensor component parameters. For isotropic rotational diffusion, $\tau_{\mathrm{int}}^{\parallel}$ is given by [2]

$$\tau_{\mathrm{int}}^{\parallel} = \frac{\tau_D \operatorname{csch} \xi}{\xi(1 + \xi^{-2} - \coth^2 \xi)} \int_{-1}^{1} [z - \coth \xi + e^{-\xi(1+z)}(1 + \coth \xi)]^2 \frac{e^{\xi z} dz}{1 - z^2}. \tag{24}$$

In isotropic diffusion, the relaxation times $\tau_{\mathrm{eff}}^{\parallel}$ and $\tau_{\mathrm{int}}^{\parallel}$ have a very similar behavior [2,24].

A comparison of the results of calculation of the real and imaginary parts of the normalized $(\mu^2 N_0/kT = 1)$ complex susceptibility $\chi_{\parallel}(\omega)$ using the matrix continued fraction and effective relaxation time solutions is given in Figs. 4–6 for various values of the model parameters. Here the predictions of the isotropic diffusion model are shown by dash-dotted lines. The low- (dotted lines) and high- (dashed lines) frequency asymptotes of $\chi_{\parallel}(\omega)$, Eqs. (5) and (6), respectively, are also shown in Figs. 4 and 5 for comparison. Clearly, the simple analytic equations (16) and (22) are in agreement with the matrix continued fraction solution for all frequencies of interest and for a wide range of the bias field strength parameter ξ. Figures 4–6 also show the significant difference between the predictions of isotropic and anisotropic diffusion models.

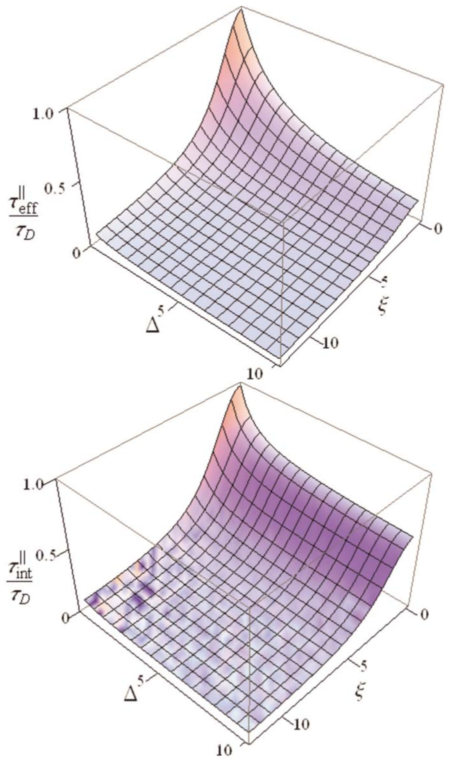

FIG. 2. (Color online) Three-dimensional plots of the effective relaxation times $\tau_{\text{eff}}^{\parallel}$, Eq. (23), in comparison with the integral relaxation time $\tau_{\text{int}}^{\parallel}$, Eq. (4), vs the field parameter ξ and diffusion anisotropy parameter Δ (u_x=0.7, u_y=0, and Ξ=0).

We remark that in some cases, Brownian particles may be treated effectively as uniaxial ones, e.g., rodlike molecules. Here the principal rotational diffusion coefficients D_{xx}, D_{yy}, and D_{zz} are related as $D_{xx} \approx D_{yy} = D_1$ and $D_{zz} = D_2$. Noting Eqs. (16)–(18), the condition of validity of this approximation is given by

$$\left|\frac{\Xi}{2\Delta}\right| = \left|\frac{D_{xx} - D_{yy}}{2(2D_{zz} - D_{xx} - D_{yy})}\right| \ll 1. \tag{25}$$

There are then at most two distinct relaxation times $\tau_z^{\parallel} = \tau_D$ and $\tau_x^{\parallel} = \tau_y^{\parallel} = \tau_D(1+\Delta)^{-1}$, which characterize, respectively, relaxation of the parallel (μ_z) and perpendicular ($\sqrt{\mu_x^2 + \mu_y^2}$) components of the dipole moment (with respect to the particle symmetry axis). The rodlike molecule approximation is often used in the theory of orientation relaxation in liquid crystals [30], where individual molecules are almost never uniaxially symmetric but can be treated to a very good approximation as uniaxial. Furthermore, for some parameter ranges (e.g., for spherical like particles), the characteristic times $\tau_x^{\parallel}$, $\tau_y^{\parallel}$, and $\tau_z^{\parallel}$ are approximately equal so that the spectrum of $\chi''_{\parallel}(\omega)$ appears in these cases as a single Lorentzian band (we recall that in order to observe two distinct peaks in a sum of two Lorentzians, the characteristic frequencies of the Lorentzians must differ by more than a factor of 5.8 [37].) This is the case, e.g., for isotropic rotational diffusion ($D_{xx} = D_{yy} = D_{zz} = D$, i.e., $\Delta = \Xi = 0$) and/or for particles with the dipole moment vector directed along the z axis of the molecular coordinate system xyz, i.e., $u_x = u_y = 0$. Equation (22) predicts, in agreement with the known results [2,22,24], that the longitudinal susceptibility is described by a single Lorentzian, viz.,

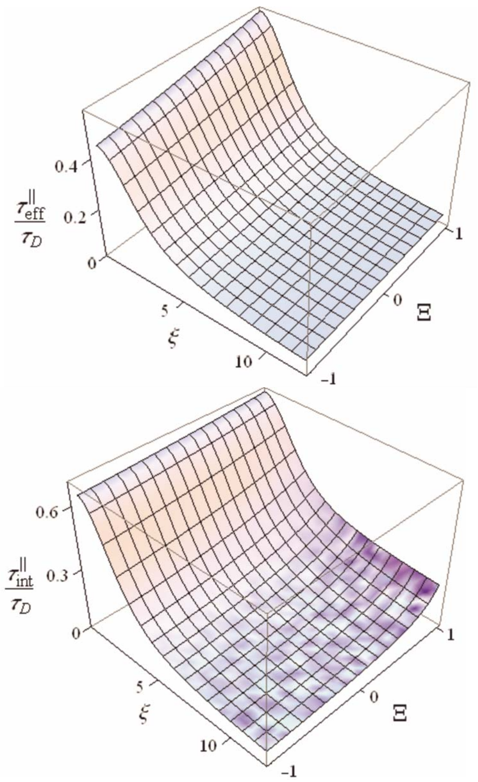

FIG. 3. (Color online) Three-dimensional plots of $\tau_{\text{eff}}^{\parallel}$ and $\tau_{\text{int}}^{\parallel}$ vs the field parameter ξ and diffusion anisotropy parameter Ξ (u_x =0.7, u_y=0, and Δ=2).

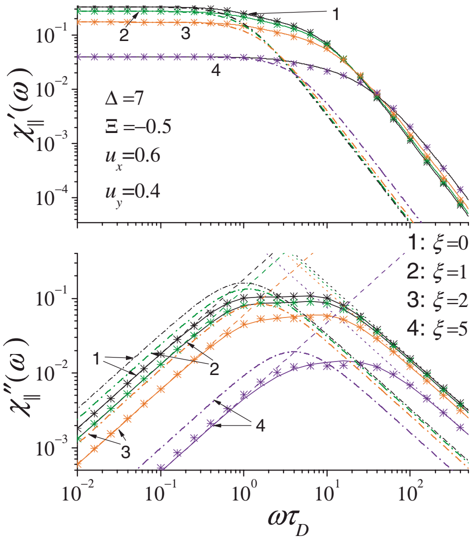

FIG. 4. (Color online) Real and imaginary parts of the normalized complex susceptibility vs the normalized frequency $\omega\tau_D$ for various values of the field parameter ξ=0 (free diffusion), 1, 2, and 5 (u_x=0.4, u_y=0.6, Δ=7, and Ξ=−1/2). Solid lines: matrix continued fraction solution. Stars: the effective relaxation time solution, Eq. (22). Dashed and dotted straight lines: the low- [Eq. (5)] and high- [Eq. (6)] frequency asymptotes, respectively. Dash-dotted lines: isotropic diffusion (Δ=Ξ=0).

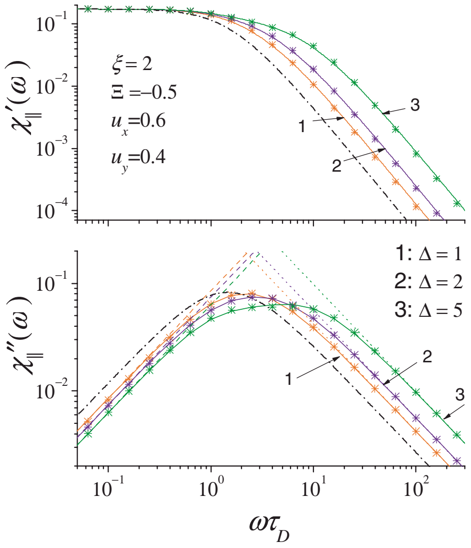

FIG. 5. (Color online) Real and imaginary parts of the normalized complex susceptibility vs $\omega\tau_D$ for various values of the anisotropy parameter $\Delta=1$, 2, and 5 ($\xi=2$, $u_x=0.4$, $u_y=0.6$, and $\Xi=-1/2$). Solid lines: matrix continued fraction solution. Stars: the effective relaxation time solution, Eq. (22). Dashed and dotted straight lines: the low- [Eq. (5)] and high- [Eq. (6)] frequency asymptotes, respectively. Dash-dotted lines: isotropic diffusion ($\Delta=\Xi=0$).

$$\frac{\chi_{\parallel}(\omega)}{\chi_{\parallel}} \approx \frac{1}{1+i\omega\tau_{\text{eff}}^{\parallel}}, \tag{26}$$

where $\tau_{\text{eff}}^{\parallel}=\tau_D F^{\parallel}(\xi)$.

V. TRANSVERSE DIELECTRIC RESPONSE

Calculations of the transverse components of the polarization $P_{\perp}(t)$ defined as

$$P_{\perp}(t) = \mu N_0 \langle u_X\rangle(t) = \frac{\mu N_0}{\sqrt{2}} \sum_{p=-1}^{1} (-1)^p \mu^{(-p)} [\langle D^1_{-1,p}\rangle(t) - \langle D^1_{1,p}\rangle(t)],$$

where

$$u_X = u_z \cos\alpha \sin\beta + \cos\alpha\cos\beta(u_x\cos\gamma - u_y\sin\gamma) - \sin\alpha(u_x\sin\gamma + u_y\cos\gamma)$$

is the X component of the unit vector $\mathbf{u}$ in the laboratory coordinate system XYZ, can be accomplished in like manner. Here it is assumed that a probe field $\mathbf{E}_1$ is applied parallel to the X axis of the laboratory coordinate systems and noted that $\langle u_X\rangle_0=0$ due to cylindrical symmetry about the Z axis. Applying the effective relaxation time approach as before, the transverse complex susceptibility $\chi_{\perp}(\omega)$ can also be approximated by three Lorentzians, viz.,

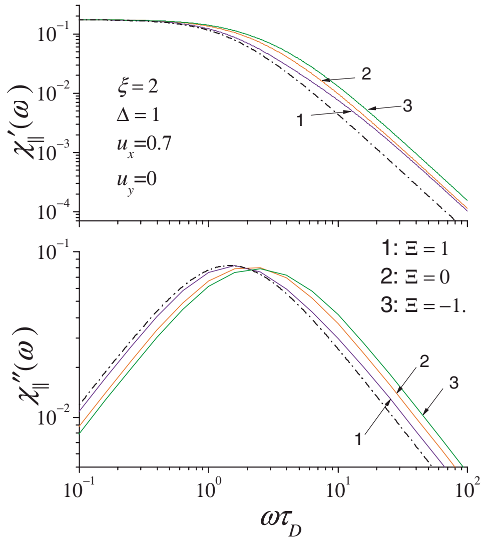

FIG. 6. (Color online) Real and imaginary parts of the normalized complex susceptibility vs $\omega\tau_D$ for various values of the anisotropy parameter $\Xi=1$, 0, and -1 ($\xi=2$, $u_x=0.7$, $u_y=0.0$, and $\Delta=1$). Solid lines: matrix continued fraction solution. Dash-dotted lines: isotropic diffusion ($\Delta=\Xi=0$).

$$\frac{\chi_{\perp}(\omega)}{\chi_{\perp}} \approx \frac{u_x^2}{1+i\omega\tau_x^{\perp}} + \frac{u_y^2}{1+i\omega\tau_y^{\perp}} + \frac{u_z^2}{1+i\omega\tau_z^{\perp}}. \tag{27}$$

Here $\chi_{\perp}=(\mu^2 N_0/kT)\langle u_X^2\rangle_0=(\mu^2 N_0/kT\xi)L(\xi)$ is the transverse static susceptibility, and the effective transverse relaxation times $\tau_i^{\perp}$ are given by

$$\tau_x^{\perp} = \frac{\tau_D F^{\perp}(\xi)}{1+\Delta-\Xi/2}, \quad \tau_y^{\perp} = \frac{\tau_D F^{\perp}(\xi)}{1+\Delta+\Xi/2}, \quad \tau_z^{\perp} = \tau_D F^{\perp}(\xi),$$

where $F^{\perp}(\xi)=2L(\xi)/[\xi-L(\xi)]$. The effective relaxation time $\tau_{\text{eff}}^{\perp}$ of the transverse correlation function $C_{\perp}(t)=\langle u_X[\Omega(0)]u_X[\Omega(t)]\rangle_0/\langle u_X^2\rangle_0$ is expressed as

$$\tau_{\text{eff}}^{\perp} = \frac{\tau_D F^{\perp}(\xi)}{1+u_x^2(\Delta-\Xi/2)+u_y^2(\Delta+\Xi/2)}. \tag{28}$$

For isotropic rotational diffusion, $\chi_{\perp}(\omega)$ can be described by a single Lorentzian, viz.,

$$\frac{\chi_{\perp}(\omega)}{\chi_{\perp}} \approx \frac{1}{1+i\omega\tau_{\text{eff}}^{\perp}} \tag{29}$$

with the effective relaxation time $\tau_{\text{eff}}^{\perp}=\tau_D F^{\perp}(\xi)$, in agreement with the known results [2,24].

VI. CONCLUDING REMARKS

Here we have given both the exact solution (in terms of matrix continued fractions) and an approximate analytic (using the effective relaxation time approach) solution for the dielectric response of an assembly of polar particles undergoing *anisotropic* rotational diffusion in a dc external field. For arbitrary values of the diffusion tensor components, the dipole relaxation functions can be approximated in the time domain by three exponentials with distinct relaxation times in a wide range of the bias field strength parameter ξ, Eqs. (22) and (27). In turn, in the frequency domain, the spectrum of the dynamic susceptibility may be described by three Lorentzians. In the limit of isotropic rotational diffusion, our results are in complete agreement with those obtained using this approximation [2,22,24]; here the individual relaxation modes are indistinguishable in the frequency spectrum (due to their near degenerate behavior) so that the dynamic susceptibility effectively comprises a single Lorentzian with half width given by the simple analytic equations (26) and (29). The model may be applied to the interpretation of experimental data on dielectric responses of dilute solutions of polar macromolecules of arbitrary shape (when components of the rotational diffusion tensor may differ considerably) subjected to a strong dc field. The simple analytic formulas obtained will allow one to carry out a quantitative comparison of theoretical predictions with experiments on dielectric response, where the perturbation approach can no longer be applied. Furthermore, as we have already mentioned in the Introduction, our results can be applied (with small modifications) to the calculation of the *magnetic* response of dilute suspensions of fine magnetic particles (ferrofluids) [19,20] and aqueous solutions of magnetotactic bacteria which contain a magnet inside the body [25]. We remark that experiments on the polarization induced by a weak ac field superimposed on a strong dc field may be realized in practice in a ferrofluid 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 $[(10^4-10^5)\mu_B]$ of single-domain ferromagnetic particles. Moreover, it will be possible to compare the theory with available Brownian dynamics computer simulation data for orientational relaxation in strong fields (see, e.g., [38–41]; in computer simulation it is much easier than in real experiments to achieve large values of the electric field). Our results for the longitudinal susceptibility and relaxation time are in qualitative agreement with experimental data of Block and Hayes [18] for solutions of macromolecules and Fannin *et al.* [19] for ferrofluids [18,19] obtained for the longitudinal component of the susceptibility with the strong dc field applied parallel to a weak ac probe field. According to these data, with increasing the dc field strength ξ, both the loss $\chi''_{\parallel}(\omega)$ and the longitudinal relaxation time decrease compared with those in the absence of the dc field. Clearly these observations are in qualitative agreement with theoretical results shown in Figs. 2 and 3. The experimental data presented in Refs. [18,19] are not sufficient, however, for the estimation of the anisotropy parameters of the rotational diffusion tensor.

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APPENDIX A: CALCULATION OF EQUILIBRIUM AVERAGES

The equilibrium averages appearing in the calculation of dielectric parameters are given below:

$$Z=\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} e^{\xi u_Z}\sin\beta\, d\beta\, d\alpha\, d\gamma = 8\pi^2\frac{\sinh\xi}{\xi},$$

$$\langle u_Z\rangle_0 = Z^{-1}\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} u_Z e^{\xi u_Z}\sin\beta\, d\beta\, d\alpha\, d\gamma = L(\xi),$$

$$\langle u_Z^2\rangle_0 = Z^{-1}\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} u_Z^2 e^{\xi u_Z}\sin\beta\, d\beta\, d\alpha\, d\gamma = 1-2L(\xi)/\xi,$$

$$\langle u_X^2\rangle_0 = Z^{-1}\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} u_X^2 e^{\xi u_Z}\sin\beta\, d\beta\, d\alpha\, d\gamma = L(\xi)/\xi,$$

$$\langle(-\sin\beta\cos\gamma,\sin\beta\sin\gamma,\cos\beta)\rangle_0 = (u_x,u_y,u_z)L(\xi),$$

$$\begin{aligned}&\langle(-\sin\beta\cos\gamma,\sin\beta\sin\gamma,\cos\beta)u_Z\rangle_0\\ &\quad=(u_x,u_y,u_z)[1-2L(\xi)/\xi],\end{aligned}$$

$$\begin{aligned}&\left\langle\left(\frac{c^1_{0,-1}(0)-c^1_{0,1}(0)}{\sqrt{2}}, i\frac{c^1_{0,-1}(0)+c^1_{0,1}(0)}{\sqrt{2}}, c^1_{0,0}(0)\right)u_Z\right\rangle_0\\ &\quad=\xi_1(u_x,u_y,u_z)\left(1-L^2(\xi)-\frac{2}{\xi}L(\xi)\right),\end{aligned}$$

$$\begin{aligned}&-\left\langle\left(\frac{\dot{c}^1_{0,-1}(0)-\dot{c}^1_{0,1}(0)}{\sqrt{2}}, i\frac{\dot{c}^1_{0,-1}(0)+\dot{c}^1_{0,1}(0)}{\sqrt{2}}, \dot{c}^1_{0,0}(0)\right)u_Z\right\rangle_0\\ &\quad=(u_x(1+\Delta-\Xi/2),u_y(1+\Delta+\Xi/2),u_z)\frac{\xi_1 L(\xi)}{\xi\tau_D},\end{aligned}$$

APPENDIX B: MATRIX CONTINUED FRACTION SOLUTION

The coefficients $e^{j',m'}_{j,m}$ in Eq. (8) are given by

$$e^{0,0}_{j,m}=-\Delta m^2-j(j+1)/2,\quad e^{0,\pm1}_{j,m}=0,$$

$$e^{0,\pm2}_{j,m}=-\frac{\Xi}{4}\sqrt{[j^2-(m\pm1)^2][(j+1)^2-(m\pm1)^2]},$$

$$e^{-1,0}_{j,m}=\frac{\xi u_z(j+1)}{2(2j+1)}\sqrt{j^2-m^2},\quad e^{1,0}_{j,m}=-\frac{\xi u_z j}{2(2j+1)}\sqrt{(j+1)^2-m^2},$$

$$\begin{aligned}e^{-1,\pm1}_{j,m}&=\xi\frac{\sqrt{(j\mp m)(j\mp m-1)}}{4(2j+1)}[(\pm u_x-iu_y)(j+1\mp2\Delta m)\\ &\quad+(\mp u_x-iu_y)\Xi(j+1\pm m)],\end{aligned}$$

$$\begin{aligned}e^{1,\pm1}_{j,m}&=\xi\frac{\sqrt{(j\pm m+1)(j\pm m+2)}}{4(2j+1)}[(\pm u_x-iu_y)(j\pm2\Delta m)\\ &\quad+(\mp u_x-iu_y)\Xi(j\mp m)],\end{aligned}$$

$$e^{-1,\pm2}_{j,m}=\frac{\xi u_z\Xi}{4(2j+1)}\sqrt{[j^2-(m\pm1)^2](j\mp m-2)(j\mp m)},$$

$$e^{1,\pm 2}_{j,m} = -\frac{\xi u_z \Xi}{4(2j+1)} \times \sqrt{[(j+1)^2-(m\pm 1)^2](j\pm m+3)(j\pm m+1)}$$

(a method of calculation of $e^{j',m'}_{j,m}$ is described in Ref. [2]; see also [27,28]).

The 13-term recurrence Eq. (8) can be transformed into the matrix three-term recurrence equation

$$\tau_D \frac{d}{dt}\mathbf{C}_j(t) = \mathbf{Q}^-_j \mathbf{C}_{j-1}(t) + \mathbf{Q}_j \mathbf{C}_j(t) + \mathbf{Q}^+_j \mathbf{C}_{j+1}(t), \qquad \text{(B1)}$$

where the matrix elements of the matrices $\mathbf{Q}^-_n$, $\mathbf{Q}^+_n$, and $\mathbf{Q}_n$ are defined by

$$(\mathbf{Q}_j)_{n,m} = \delta_{n,m+2} e^{0,-2}_{j,-j-1+m} + \delta_{n,m} e^{0,0}_{j,-j-1+m} + \delta_{n,m-2} e^{0,2}_{j,-j-3+m},$$

$$(\mathbf{Q}^-_j)_{n,m} = \delta_{n,m+3} e^{-1,-2}_{j,-j+2+m} + \delta_{n,m+2} e^{-1,-1}_{j,-j+1+m} + \delta_{n,m+1} e^{-1,0}_{j,-j+m} + \delta_{n,m} e^{-1,1}_{j,-j-1+m} + \delta_{n,m-1} e^{-1,2}_{j,-j-2+m},$$

$$(\mathbf{Q}^+_j)_{n,m} = \delta_{n,m+1} e^{1,-2}_{j,-j+m} + \delta_{n,m} e^{1,-1}_{j,-j-1+m} + \delta_{n,m-1} e^{1,0}_{j,-j-2+m} + \delta_{n,m-2} e^{1,1}_{j,-j-3+m} + \delta_{n,m-3} e^{1,2}_{j,-j-4+m},$$

and the column vectors $\mathbf{C}_j(t)$ are defined as

$$\mathbf{C}_0(t) = \mathbf{0} \quad \text{and} \quad \mathbf{C}_j(t) = \begin{pmatrix} c^j_{0,-j}(t) \\ \vdots \\ c^j_{0,-1}(t) \\ c^j_{0,0}(t) \\ c^j_{0,1}(t) \\ \vdots \\ c^j_{0,j}(t) \end{pmatrix} \quad (j \geqslant 1).$$

Invoking the general method for solving the matrix recurrence Eq. (B1) [2], we obtain $\tilde{\mathbf{C}}_1(\omega)$,

$$\tilde{\mathbf{C}}_1(\omega) = \tau_D \mathbf{\Delta}^{\xi}_1(\omega) \left[\mathbf{C}_1(0) + \sum_{j=2}^{\infty} \left(\prod_{k=2}^{j} \mathbf{Q}^+_{k-1} \mathbf{\Delta}^{\xi}_k(\omega) \right) \mathbf{C}_j(0) \right], \qquad \text{(B2)}$$

where the matrix continued fractions $\mathbf{\Delta}^{\xi}_k(\omega)$ are defined by the following recurrence equation:

$$\mathbf{\Delta}^{\xi}_k(\omega) = [i\omega\tau_D \mathbf{I}_k - \mathbf{Q}_k - \mathbf{Q}^+_k \mathbf{\Delta}^{\xi}_{k+1}(\omega) \mathbf{Q}^-_{k+1}]^{-1},$$

$\mathbf{I}_k$ is the unity matrix, and the tilde denotes the one-sided Fourier transform, viz., $\tilde{\mathbf{C}}_1(\omega) = \int_0^\infty \tilde{\mathbf{C}}_1(t) e^{-i\omega t} dt$. The initial condition vectors $\mathbf{C}_j(0)$ in Eq. (B2) can also be determined using the matrix continued fractions $\mathbf{\Delta}^{\xi+\xi_1}_k(0)$ and $\mathbf{\Delta}^{\xi}_k(0)$ as (see for details Ref. [28])

$$\mathbf{C}_j(0) = \prod_{k=1}^{j} \mathbf{\Delta}^{\xi+\xi_1}_k(0) \mathbf{Q}^-_k - \prod_{k=1}^{j} \mathbf{\Delta}^{\xi}_k(0) \mathbf{Q}^-_k .$$

Having determined $\tilde{\mathbf{C}}_1(\omega)$, and hence $\tilde{c}^1_{0,0}(\omega)$ and $\tilde{c}^1_{0,\pm 1}(\omega)$, one can estimate from Eqs. (9)–(11) the overall behavior of the dielectric response of dipolar Brownian particles subjected to a dc field.

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