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Fractional rotational Brownian motion in a uniform dc external field

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The longitudinal and transverse components of the complex dielectric susceptibility tensor of an assembly of dipolar particles subjected to a dc bias field are evaluated in the context of a fractional noninertial rotational diffusion model. Exact and approximate solutions for the dielectric dispersion and absorption spectra are obtained. It is shown that a knowledge of the effective relaxation times for *normal* rotational diffusion is sufficient to predict accurately the *anomalous* dielectric relaxation behavior of the system for all time scales of interest. Simple equations for the characteristic frequencies of the dielectric loss spectra are obtained in terms of the physical model parameters (dimensionless field and fractional exponent). The model explains the anomalous (Cole-Cole like) relaxation of complex dipolar systems, where the anomalous exponent differs from unity (corresponding to the normal dielectric relaxation), i.e., the relaxation process is characterized by a broad distribution of relaxation times.

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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]. An example is the theory of dielectric relaxation of noninteracting polar molecules due to Debye [3]. That theory is based on the Smoluchowski equation for the noninertial rotational diffusion of the molecules in an external electric field. The Debye theory has a variety of applications in the interpretation of dielectric relaxation measurements of molecular liquids and solutions. However, it cannot explain the experimental data on dielectric relaxation of complex systems such as amorphous polymers, glass-forming liquids, etc. Here the relaxation behavior may deviate considerably from the exponential (Debye) pattern and is characterized by a broad distribution of relaxation times [4]. The relaxation process in such disordered systems is characterized by the temporally nonlocal behavior arising from the energetic disorder which produces obstacles or traps which delay the motion of the particle and introduce memory effects into the motion [5]. The memory effects can be described by a fractional diffusion equation in the derivation of which is incorporated a waiting time probability density function [4]. That function governs the random time intervals between single microscopic jumps (or reorientations in the case of rotational motion) of the particles. The underlying microscopic model is a continuous time random walk (CTRW) [6]. The situation is thus unlike that in a conventional random walk which is characterized by a microscopic time scale which is small compared to the observation time. The microscopic time in the context of the conventional random walk is the time the random walker takes to make a single microscopic jump. In the CTRW, on the other hand, no such microscopic time scale exists because of the power-law dependence of the waiting time probability distribution function leading to the divergence of the characteristic time scale [4]. A common feature of all such systems is that they exhibit anomalous relaxation behavior. Recently, the CTRW has been generalized to include the effect of time-dependent jump probabilities and a fractional kinetic equation for translational and rotational diffusion has been derived when the average waiting time diverges [4,7].

An important task in dielectric relaxation of complex systems is to extend the Debye theory of relaxation of polar molecules to fractional dynamics, so that empirical decay functions, e.g., the stretched exponential of Williams and Watts [8], may be justified. Such a generalization of the Debye theory was given in Refs. [5,7,9]. There, the Debye theory of dielectric relaxation of an assembly of polar molecules is reformulated using a fractional noninertial Fokker-Planck equation for the purpose of extending that theory to explain anomalous dielectric relaxation. It was shown that this model can reproduce nonexponential Cole-Cole-type anomalous dielectric relaxation behavior and that it reduces to the classical Debye model of rotational diffusion when the anomalous exponent is unity.

The application of a strong direct current (dc) electric field $\mathbf{E}_0$ to a polar liquid comprised of dipolar molecules results in a transition from free thermal rotation of the molecules to partial orientation with hindered rotation. This change in the character of the molecular 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 molecule in the field $\mathbf{E}_0$. A similar effect arises in magnetic relaxation of ferrofluids subjected to a strong dc magnetic field $\mathbf{H}_0$. 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 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 $\mathbf{E}_0$. Orientational relaxation of Brownian particles in the context of the normal rotational diffusion in the presence of a dc field has been treated in details in Refs. [2,9–16].

In the present paper, it is demonstrated how the linear response of an assembly of noninteracting polar Brownian particles to a small external field $\mathbf{E}_1$ applied parallel and perpendicular to the bias field $\mathbf{E}_0$ may be calculated in the context of the fractional noninertial rotational diffusion [2] in the same manner as normal rotational diffusion [12]. In order to carry out the calculation, it is assumed that the rotational Brownian motion of a particle may be described by the fractional noninertial Fokker-Planck (Smoluchowski) equation, in which the inertial effects are neglected [7]. Both exact and approximate solutions of this equation are presented. We shall demonstrate that the characteristic times of the normal diffusion process, namely, the integral and effective relaxation times, obtained in Refs. [2,12,17], allow one to evaluate the dielectric response for anomalous diffusion. Moreover, these characteristic times yield a simple analytical equation for the complex dielectric susceptibility tensor describing the anomalous relaxation of the system. The exact solution of the problem reduces to the solution of the infinite hierarchies of differential-recurrence equations for the corresponding relaxation functions. The longitudinal and transverse components of the susceptibility tensor may be calculated exactly from the Laplace transform of these relaxation functions using linear response theory.

II. FRACTIONAL ROTATION DIFFUSION IN AN UNIFORM DC EXTERNAL FIELD

Let us suppose that the uniform dc field $\mathbf{E}_0$ is directed along the Z axis of the laboratory coordinate system and a small probing field $\mathbf{E}_1$ having been applied to the assembly of dipoles in the distant past $(t=-\infty)$ so that equilibrium conditions are fulfilled at time $t=0$, is switched off at $t=0$. 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 molecule, k is the Boltzmann constant, and T is the temperature). Here, the underlying fractional rotational diffusion equation for the evolution of the probability density function $W(\vartheta,\varphi,t)$ of dipole moment orientations in configuration space (ϑ and φ are the polar and azimuthal angles, respectively) is [2,7]

$$\frac{\partial}{\partial t}W = \tau^{1-\sigma}{}_0D_t^{1-\sigma}L_{FP}W, \tag{1}$$

where L_{FP} is the Fokker-Planck operator for normal noninertial rotational diffusion defined by

$$L_{FP}W = \frac{1}{2\tau}\left\{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\partial W}{\partial\vartheta}+\frac{W}{kT}\frac{\partial V}{\partial\vartheta}\right)\right] + \frac{1}{kT\sin^2\vartheta}\frac{\partial}{\partial\varphi}\left(W\frac{\partial V}{\partial\varphi}\right)\right\}, \tag{2}$$

$\tau=\zeta/2kT$ is the characteristic (Debye) relaxation time for the normal diffusion, ζ is the drag coefficient, and V is the orientational potential energy of the particle in the field. For the longitudinal and transverse responses, one has

$$V(\vartheta,t) = -\mu E_0\cos\vartheta - \mu E_1(t)\cos\vartheta \tag{3}$$

and

$$V(\vartheta,\varphi,t) = -\mu E_0\cos\vartheta - \mu E_1(t)\cos\varphi\sin\vartheta, \tag{4}$$

respectively. The operator ${}_0D_t^{1-\sigma}\equiv(\partial/\partial t){}_0D_t^{-\sigma}$ in Eq. (1) is given in terms of the convolution (the Riemann-Liouville fractional integral definition) [4]

$${}_0D_t^{-\sigma}W(\vartheta,\varphi,t) = \frac{1}{\Gamma(\sigma)}\int_0^t \frac{W(\vartheta,\varphi,t')dt'}{(t-t')^{1-\sigma}},$$

where $\Gamma(z)$ is the gamma function. Here, we consider subdiffusion phenomena only $(0<\sigma<1;\sigma=1$ corresponds to the normal diffusion). Thus the fractional derivative is a type of memory function with a slowly decaying power law kernel in the time. Such behavior arises from random torques with an anomalous waiting time distribution, that is, from a fractal time random walk with τ as the intertrapping time [4]. The physical meaning of the parameter σ is the order of the fractional derivative in the fractional differential equation describing the continuum limit of a random walk with a chaotic set of waiting times (often known as a fractal time random walk) [18]. However, a more physically useful definition of σ is as the fractal dimension of the set of waiting times which is the scaling of the waiting time segments in the random walk with magnification. Thus σ measures the statistical self-similarity (or how the whole looks similar to its parts) of the waiting time segments [18,19].

The formal solutions of Eq. (1) are obtained from the Sturm-Liouville representation [3,4,19]

$$W(\vartheta,\varphi,t) = \sum_{p=0}^{\infty}\Phi_p(\vartheta,\varphi)F_p(t). \tag{5}$$

Here, according to Eq. (1), the decay modes $F_p(t)$ obey the equation

$$\frac{d}{dt}F_p(t) = -\lambda_{p,\sigma}^{\gamma}{}_0D_t^{1-\sigma}F_p(t), \tag{6}$$

where the eigenvalues $\lambda_{p,\sigma}$ are expressed in terms of the eigenvalues λ_p^{γ} of the Fokker-Planck operator L_{FP} for the *normal* diffusion, viz.,

$$L_{FP}\Phi_p(\vartheta,\varphi) = -\lambda_p^{\gamma}\Phi_p(\vartheta,\varphi),$$

so that [2–4,19]

$$\lambda_{p,\sigma}^{\gamma} = \lambda_p^{\gamma}\tau^{1-\sigma}. \tag{7}$$

The solution of Eq. (6) is given by [3,4]

$$F_p(t) = E_\sigma(-\lambda_{p,\sigma}^{\gamma}t^{\sigma}),$$

where $E_\sigma(z)$ is the Mittag-Leffler function defined as

$$E_\sigma(z) = \sum_{n=0}^{\infty}\frac{z^n}{\Gamma(1+\sigma n)}.$$

Equation (7) exemplifies how the eigenvalues of the normal distribution process are altered, in this case reduced, by the nonlocal character of the anomalous diffusion process. The eigenvalues of that process are related to their Brownian counterparts by the prefactor $\tau^{1-\sigma}$.

III. DIELECTRIC RESPONSE FUNCTIONS

According to linear response theory [2], the longitudinal and transverse components of the complex dielectric susceptibility $\alpha_\gamma(\omega)=\alpha'_\gamma(\omega)-i\alpha''_\gamma(\omega)(\gamma=\parallel,\perp)$ are defined as

$$\frac{\alpha_\gamma(\omega)}{\alpha'_\gamma(0)}=1-i\omega\int_0^\infty e^{-i\omega t}C_\gamma(t)dt, \tag{8}$$

where

$$C_\parallel(t)=\frac{\langle\cos\vartheta\rangle(t)-\langle\cos\vartheta\rangle_0}{\langle\cos\vartheta\rangle(0)-\langle\cos\vartheta\rangle_0} \tag{9}$$

and

$$C_\perp(t)=\frac{\langle\cos\varphi\sin\vartheta\rangle(t)}{\langle\cos\varphi\sin\vartheta\rangle(0)} \tag{10}$$

are the normalized relaxation functions,

$$\alpha'_\parallel(0)=\frac{\mu^2N_0}{kT}(1+\xi^{-2}-\coth^2\xi)$$

and

$$\alpha'_\perp(0)=\frac{\mu^2N_0}{kT\xi}(\coth\xi-1/\xi)$$

are the components of the static susceptibility tensor, $\xi=\mu E_0/(kT)$ is the dimensionless field parameter, N_0 is the concentration of dipoles, $\langle\cdots\rangle(t)$ denotes the statistical averages over the assembly of particles in the presence of a small probing ac field, and $\langle\cdots\rangle_0$ means the equilibrium statistical averages.

The Sturm-Liouville representation (5) is a formal solution as a knowledge of all eigenfunctions $\Phi_p(\vartheta,\varphi)$ and corresponding eigenvalues λ_p^γ is required. However, this representation is very useful as it allows one readily to obtain a solution for the correlation functions $C_\gamma(t)$. According to Eqs. (5)–(9),

$$C_\gamma(t)=\sum\nolimits_p E_\sigma[-\lambda_p^\gamma\tau(t/\tau)^\sigma] \tag{11}$$

(where $\Sigma_p c_p^\gamma=1$) so that

$$\frac{\alpha_\gamma(\omega)}{\alpha'_\gamma(0)}=\sum\nolimits_p\frac{c_p^\gamma}{1+(i\omega\tau)^\sigma/(\tau\lambda_p^\gamma)} \tag{12}$$

because the Laplace transform of the Mittag-Leffler function is

$$\int_0^\infty e^{-st}E_\sigma[-\lambda_p\tau(t/\tau)^\sigma]dt=\frac{1}{s+\lambda_p(\tau s)^{1-\sigma}}.$$

In the low $(\omega\to0)$ and high $(\omega\to\infty)$ frequency limits, the susceptibility tensor components may readily be evaluated. We have from Eq. (12)

$$\frac{\alpha_\gamma(\omega)}{\alpha'_\gamma(0)}\approx1-\frac{\tau_{int}^\gamma}{\tau}(i\omega\tau)^\sigma+\cdots \tag{13}$$

for $\omega\to0$, and

$$\frac{\alpha_\gamma(\omega)}{\alpha'_\gamma(0)}\sim\frac{\tau}{(i\omega\tau)^\sigma\tau_{ef}^\gamma}+\cdots \tag{14}$$

for $\omega\to\infty$. Here the integral relaxation time τ_{int} (the area under the relaxation function) and the effective relaxation time τ_{ef}^γ (which gives precise information on the initial decay of the relaxation function in the time domain) for *normal* diffusion $(\sigma=1)$ are defined as [2]

$$\tau_{int}^\gamma=\sum\nolimits_p c_p^\gamma/\lambda_p^\gamma \tag{15}$$

and

$$\tau_{ef}^\gamma=1/\sum\nolimits_p c_p^\gamma\lambda_p^\gamma. \tag{16}$$

In general, it is difficult to evaluate τ_{int}^γ and τ_{ef}^γ from Eqs. (15) and (16) [just as $\alpha_\gamma(\omega)$ from Eq. (12)], as a knowledge of all the eigenvalues λ_k^γ and corresponding amplitudes c_k^γ is required. However, τ_{int}^γ and τ_{ef}^γ can be evaluated from their equivalent definitions [7]

$$\tau_{int}^\gamma=\int_0^\infty C_\gamma(t)dt \tag{17}$$

and

$$\tau_{ef}^\gamma=-1/\dot{C}_\gamma(0). \tag{18}$$

We remark that the characteristic times τ_{int}^γ and τ_{ef}^γ, Eqs. (17) and (18), do not exist in anomalous diffusion $(\sigma<1)$. This is obvious from the properties of the Mittag-Leffler function, which has initially $(t\ll\tau)$ a stretched exponential (Kohlrausch) form [3,4] $E_\sigma(-t^\sigma)\sim e^{-t^\sigma/\Gamma(1+\sigma)}$ and long time inverse power law behavior $E_\sigma(-t^\sigma)\sim t^{-\sigma}/\Gamma(1-\sigma)$.

The relaxation times τ_{int}^γ and τ_{ef}^γ were obtained in the context of the normal rotational diffusion model in Refs. [2,12,17] and are given by (in our notation)

$$\tau_{int}^\parallel=\frac{\tau\xi}{(1+\xi^{-2}-\coth^2\xi)\sinh\xi}\int_{-1}^1\frac{e^{\xi z}}{1-z^2}[z-\coth\xi+e^{-\xi(1+z)}\times(1+\coth\xi)]^2dz, \tag{19}$$

$$\frac{\tau_{ef}^\parallel}{\tau}=\frac{\xi}{L(\xi)}-\xi L(\xi)-2, \tag{20}$$

for the longitudinal response and

$$\tau_{int}^\perp=\frac{\tau}{\xi I_{3/2}(\xi)}\sum_{n=1}^\infty(-1)^{n+1}\frac{(2n+1)I_{n+1/2}(\xi)}{n(n+1)}\left.\left(\prod_{k=1}^n\tilde{S}_k^\perp(0)\right)\right|_{\sigma=1}, \tag{21}$$

$$\tau_{ef}^\perp=2\tau\frac{L(\xi)}{\xi-L(\xi)}, \tag{22}$$

for the transverse response, where $L(\xi)=\coth\xi-1/\xi$ is known as the Langevin function and the $\tilde{S}_k^\perp(0)|_{\sigma=1}$ is defined in the Appendix, Eq. (A10). The behavior of the relaxation times τ_{int}^γ and τ_{ef}^γ is very similar: they are very close to each other and decrease with increasing ξ; see Fig. 1.

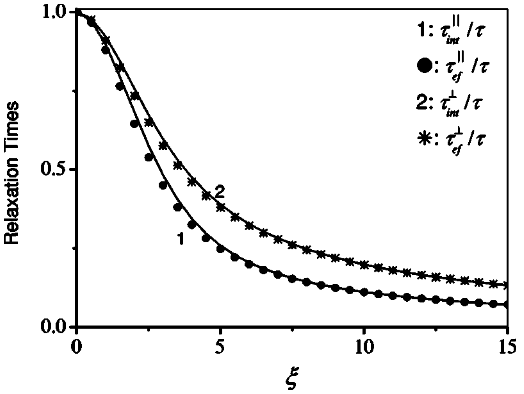

FIG. 1. Integral (τ_{int}^{γ}: solid lines) and effective (τ_{ef}^{γ}: filled circles and asterisks) relaxation times vs ξ for normal rotational diffusion in a dc bias field. Equations (19)–(22) have been used in the calculation.

According to Eq. (12), the infinite number of relaxation modes (corresponding to the eigenvalues λ_k^{γ}) gives a contribution to the spectra $\alpha_{\gamma}(\omega)$. However, as we shall see, these near degenerate individual modes are indistinguishable in the frequency spectrum of $\alpha_{\gamma}(\omega)$ appearing merely as a single band. Thus noting that

$$\tau_{int}^{\gamma} \cong \tau_{ef}^{\gamma}, \tag{23}$$

for all values of ξ (see Fig. 1), the spectrum of $\alpha_{\gamma}(\omega)$ may be approximated by the Cole-Cole equation

$$\frac{\alpha_{\gamma}(\omega)}{\alpha'_{\gamma}(0)} \approx \frac{1}{1+(i\omega/\omega_c^{\gamma})^{\sigma}}, \tag{24}$$

where

$$\omega_c^{\gamma} = \tau^{-1}(\tau/\tau_{ef}^{\gamma})^{1/\sigma} \tag{25}$$

is the characteristic frequency at which the loss spectrum $\alpha''_{\gamma}(\omega)$ attains its maximum. Noting the low temperature behavior of the effective relaxation times, viz., $\tau_{ef}^{\parallel} \sim \tau/\xi$ and $\tau_{ef}^{\perp} \sim 2\tau/\xi$ at $\xi \gg 1$ [2,12], one can readily obtain from Eqs. (20), (22), and (25) at $\xi \gg 1$

$$\omega_c^{\parallel} \sim \tau^{-1}\xi^{1/\sigma} \text{ and } \omega_c^{\perp} \sim \tau^{-1}(2\xi)^{1/\sigma}. \tag{26}$$

The frequencies $\omega_c^{\parallel}$ and $\omega_c^{\perp}$ as functions of ξ and σ are plotted in Figs. 2 and 3. In the time domain, the single-mode approximation Eq. (24) is equivalent to assuming that the relaxation function $C_{\gamma}(t)$ as determined by the exact Eq. (11) (which in general comprises an *infinite number* of Mittag-Leffler functions) may be approximated by *one* Mittag-Leffler function only, viz.

$$C_{\gamma}(t) \approx E_{\sigma}\left[-\frac{\tau}{\tau_{ef}^{\gamma}}\left(\frac{t}{\tau}\right)^{\sigma}\right]. \tag{27}$$

Due to the condition, Eq. (23), the single mode approximation, Eq. (24), correctly predicts $\alpha_{\gamma}(\omega)$ both at low ($\omega \to 0$) and high ($\omega \to \infty$) frequencies; moreover, $\alpha_{\gamma}(\omega)$ may be determined in the entire frequency range as one shall presently see. In order to estimate the accuracy of the approximate Eq. (24), the longitudinal and transverse components of the complex susceptibility are evaluated exactly in the Appendix by converting the problem of solving the fractional diffusion Eq. (1) with V given by Eq. (3) into the calculation of successive convergents of a differential-recurrence relation just as normal diffusion [2,12].

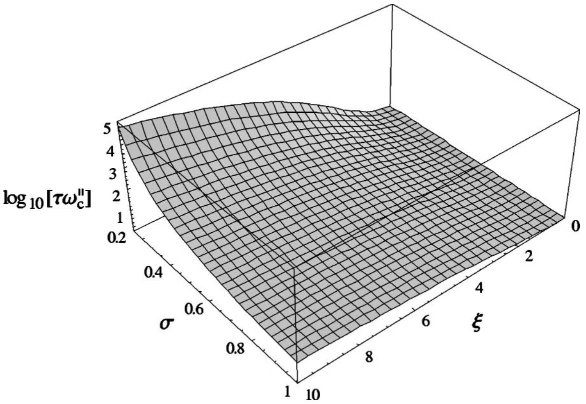

FIG. 2. Frequency $\omega_c^{\parallel}$ as a function of ξ and σ.

IV. RESULTS AND DISCUSSION

The results of the calculation of the normalized $[\mu^2 N_0/(kT)=1]$ loss spectra $\alpha''_{\parallel}(\omega)$ and $\alpha''_{\perp}(\omega)$ from the exact continued fraction solutions and the approximate Eqs. (24) are shown in Figs. 4–7; here, the low- and high-frequency asymptotes, Eqs. (13) and (14), are also presented. Apparently as ξ increases, the spectra shift to higher frequencies in accordance with Eq. (26); simultaneously, the half width of the spectra increases with decreasing σ. Furthermore, the agreement between the exact continued fraction calculations and the approximate Eq. (24) is good [the maximum relative deviation between the corresponding curves does not exceed a few (3–5) percent]. Similar (or even better) agreement exists for *all* values of ξ. The accuracy of the single mode approximation is due to the fact that for $E_1=0$, the potentials (3) and (4) are single-well potentials so that the long-lived mode due to overbarrier relaxation (as in multiwell potentials with two or more metastable states) [19] does not exists.

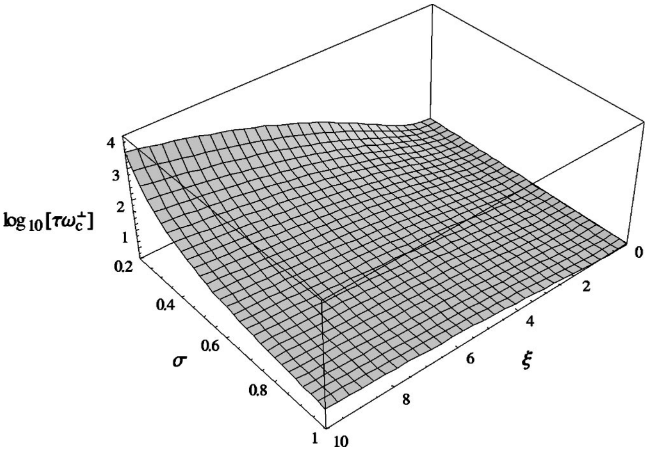

FIG. 3. Frequency $\omega_c^{\perp}$ as a function of ξ and σ.

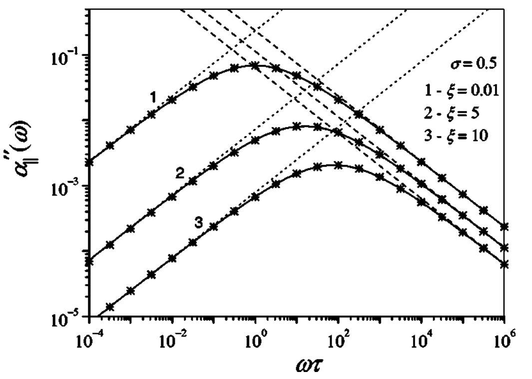

FIG. 4. Dielectric loss spectra $\alpha''_{\parallel}(\omega)$ evaluated from the exact continued fraction solution [Eqs. (8) and (A4): solid lines] for $\sigma = 0.5$ and various values of ξ, and compared with those calculated from the approximate Eq. (24) (stars). The low (dotted lines) and high frequency (dashed lines) asymptotes are calculated from Eqs. (13), (14), (19), and (20), respectively.

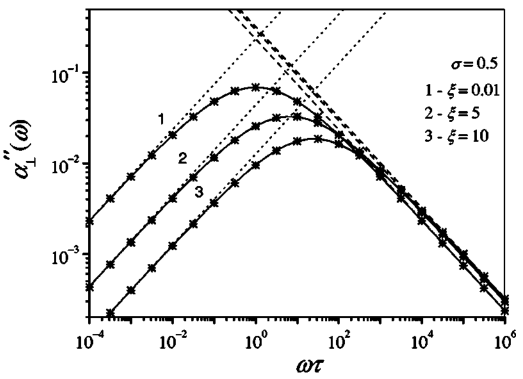

FIG. 6. Dielectric loss spectra $\alpha''_{\perp}(\omega)$ evaluated from the exact continued fraction solution [Eqs. (8) and (A9): solid lines] for $\sigma = 0.5$ and various values of ξ and compared with those calculated from the approximate Eq. (24) (stars). The low (dotted lines) and high frequency (dashed lines) asymptotes are calculated from Eqs. (13), (21), (14), and (22), respectively.

Thus the infinite number of high-frequency "intrawell" modes (these near degenerate modes are indistinguishable appearing merely as a single high-frequency band in the dielectric loss spectrum) may be approximated effectively by a single mode.

Thus one may conclude that Eq. (24) accurately describes the behavior of $\alpha_{\parallel}(\omega)$ and $\alpha_{\perp}(\omega)$ for all frequencies of interest and for all values of the field strength (ξ) and anomalous exponent (σ) parameters, so that the generalized Debye model can explain the anomalous relaxation of complex dipolar systems where the anomalous exponent σ differs from unity (corresponding to the classical Debye theory of dielectric relaxation), i.e., the relaxation process is characterized by a broad distribution of relaxation times. In particular, the theory may be applied to dilute suspensions of fine magnetic particles (ferrofluids) by a simple change of notation. Experiments on the magnetization induced by a weak ac field superimposed on a strong dc magnetic 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 ($10^4 - 10^5$ Bohr magnetons) of single domain particles. As observed by Fannin *et al.* [20,21], with increasing ξ, both the magnetic loss spectra and the relaxation times for ferrofluids in a strong dc magnetic field decrease compared with those in the isotropic case. The anomalous relaxation behavior naturally appears in ferrofluids due to the broad distribution of particle volume ν (for fine particles, the magnetic moment and the Debye relaxation time strongly depend on ν) [21]. The results obtained may be regarded as a generalization of the solution for the normal Brownian motion in a dc bias field [2,12] to fractional dynamics (giving rise to anomalous diffusion). We remark that the single-mode approximation works extremely well both for normal diffusion ($\sigma = 1$) as well. Furthermore, the internal field effects have been neglected. Thus the effects of long-range torques due to the connection between the average moments and the Maxwell fields are not taken into account. Thus the theory developed here is relevant to situations where dipole-dipole interactions have been eliminated by means of suitable extrapolation of data to infinite dilution. It should also be mentioned that just as in the conventional Debye relaxation ($\sigma = 1$), the Cole-Cole-like Eq. (24) may be derived from a number of very different models (see, e.g., Refs. [7,22,23]). However, the advantage of using an approach based on a kinetic equation (such as the fractional Fokker-Plank equation) over all other approaches is that one may explicitly include an external field and exactly calculate its effect on the relaxation process. We also remark

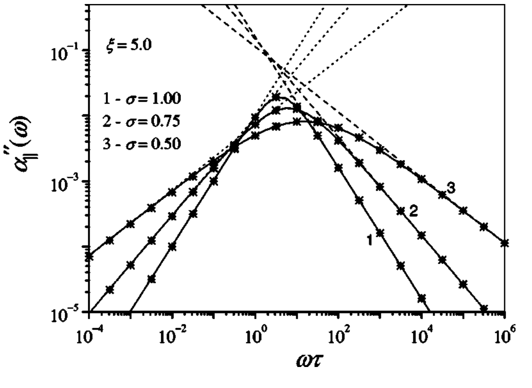

FIG. 5. The same as in Fig. 1 for $\xi = 5$ and various values of σ.

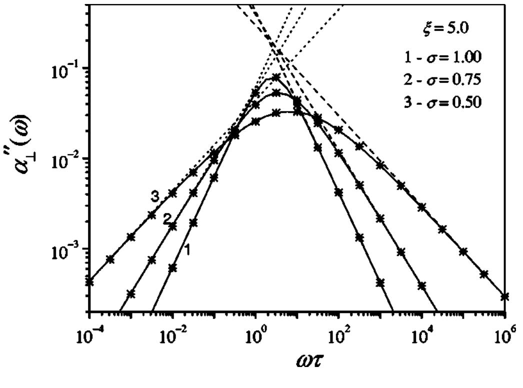

FIG. 7. The same as in Fig. 3 for $\xi = 5$ and various values of σ.

in the context of dielectric relaxation that the area of applicability of these results is restricted to the low frequency range, as defined by the inequality $\omega\tau_\gamma \leqslant 1 (\gamma = \parallel, \perp)$, because the theory does not include the effects of molecular inertia. A consistent treatment of inertial effects must be carried out using the kinetic equation for the probability density function in phase space [2].

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APPENDIX: EXACT CONTINUED FRACTION SOLUTION FOR LONGITUDINAL AND TRANSVERSE RESPONSES

The complex susceptibility components $\alpha_\gamma(\omega)$ can be evaluated from Eq. (12) by calculation eigenvalues λ_k^γ for the normal rotational diffusion [2]. However, $\alpha_\gamma(\omega)$ may be much more effectively calculated by using the continued fraction approach (see Refs. [1,2] for details).

Let us first evaluate the longitudinal response (here W is independent of φ). By expanding the distribution function $W(\vartheta, t)$ in a Fourier series,

$$W(\vartheta,t) = \sum_{n=0}^{\infty} (n + 1/2) P_n(\cos\vartheta) f_n(t),$$

one has from Eq. (1) a differential-recurrence equation just as for normal diffusion [2,12],

$$\dot{f}_n(t) = \tau^{-\sigma}{}_0D_t^{1-\sigma}[q_n^- f_{n-1}(t) + q_n f_n(t) + q_n^+ f_{n+1}(t)](n \geqslant 1), \tag{A1}$$

where the $P_n(z)$ are the Legendre polynomials [24], $f_n(t) = \langle P_n\rangle(t) - \langle P_n\rangle_0$ are the relaxation functions, so that $C_\parallel(t) = f_1(t)/f_1(0)$, and q_n, q_n^-, q_n^+ are defined as

$$q_n = -\frac{n(n+1)}{2}, \quad q_n^- = \frac{\xi n(n+1)}{2(2n+1)}, \quad q_n^+ = -\frac{\xi n(n+1)}{2(2n+1)}.$$

Applying the integration theorem of the one-sided Fourier transformation generalized to fractional calculus [3], we have from Eq. (A1)

$$i\omega\tau\tilde{f}_n(i\omega) - f_n(0) = (i\omega\tau)^{1-\sigma}[q_n^-\tilde{f}_{n-1}(i\omega) + q_n\tilde{f}_n(i\omega) + q_n^+\tilde{f}_{n+1}(i\omega)], \tag{A2}$$

where $\tilde{f}(i\omega)$ denotes one-sided Fourier transform, viz.,

$$\tilde{f}(i\omega) = \int_0^\infty e^{-i\omega t} f(t)\,dt. \tag{A3}$$

The three-term recurrence Eq. (A2) can be solved exactly for the Fourier-Laplace transform $\tilde{f}_1(i\omega)$ in terms of ordinary continued fractions to yield

$$\begin{aligned}\tilde{C}_\parallel(i\omega) &= \frac{\tilde{f}_1(i\omega)}{f_1(0)}\\ &= \frac{2\tau(i\omega\tau)^{\sigma-1}}{\xi f_1(0)} \sum_{n=1}^{\infty} (-1)^{n+1} f_n(0) \frac{2n+1}{n(n+1)} \prod_{k=1}^{n} \tilde{S}_k^\parallel(i\omega),\end{aligned} \tag{A4}$$

where the continued fraction $S_n^\parallel(s)$ is defined by the recurrence equation

$$\begin{aligned}S_n^\parallel(i\omega) &= q_n^-[(i\omega\tau)^\sigma - q_n - q_n^+ S_{n+1}^\parallel(i\omega)]^{-1}\\ &= \frac{\xi}{2n+1}\left[1 + \frac{2(i\omega\tau)^\sigma}{n(n+1)} + \frac{\xi}{2n+1}\tilde{S}_{n+1}^\parallel(i\omega)\right]^{-1}.\end{aligned}$$

The initial values $f_n(0)$ are evaluated just as normal diffusion [2,12],

$$\begin{aligned}f_n(0) &= \xi_1[\langle P_1 P_n\rangle_0 - \langle P_1\rangle_0\langle P_n\rangle_0]\\ &= \xi_1\left[\frac{n+1}{2n+1}\langle P_{n+1}\rangle_0 + \frac{n}{2n+1}\langle P_{n-1}\rangle_0 - \langle P_1\rangle_0\langle P_n\rangle_0\right],\end{aligned} \tag{A5}$$

where

$$\langle P_n\rangle_0 = \frac{I_{n+1/2}(\xi)}{I_{1/2}(\xi)}, \tag{A6}$$

$\xi_1 = \mu E_1/(kT)$ and $I_p(z)$ is the modified Bessel function of the first kind [24]. Here we have used the relation $(2n+1)P_1P_n = (n+1)P_{n+1} + nP_{n-1}$ [24]. In particular, one has

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

The appropriate differential-recurrence equation for the transverse relaxation functions

$$g_n(t) = \langle\cos\varphi P_n^1(\cos\vartheta)\rangle(t) \tag{A7}$$

($P_n^m(z)$ is the associate Legendre function [24]) so that $C_\perp(t) = g_1(t)/g_1(0)$, can be obtained from Eq. (1) with V given by Eq. (4) just as for normal diffusion [2,12],

$$\frac{d}{dt}g_n(t) = \tau^{-\sigma}{}_0D_t^{1-\sigma}[q_n^- g_{n-1}(t) + q_n g_n(t) + q_n^+ g_{n+1}(t)] \quad (n \geqslant 1), \tag{A8}$$

where q_n, q_n^-, q_n^+ are defined as

$$q_n = -\frac{n(n+1)}{2}, \quad q_n^- = \frac{\xi(n+1)^2}{2(2n+1)}, \quad q_n^+ = -\frac{\xi n^2}{2(2n+1)}.$$

Just as the longitudinal response, Eq. (A8) can be solved exactly for the Fourier-Laplace transform $\tilde{g}_1(i\omega)$ in terms of ordinary continued fractions to yield

$$\tilde{C}_\perp(i\omega) = \frac{\tilde{g}_1(i\omega)}{g_1(0)} = \frac{2\tau(i\omega\tau)^{\sigma-1}}{\xi g_1(0)} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2n+1}{n^2(n+1)^2} g_n(0) \prod_{k=1}^{n} S_k^{\perp}(i\omega), \tag{A9}$$

where the continued fraction $S_n^{\parallel}(s)$ is defined by the following recurrence equation:

$$\begin{aligned} S_n^{\perp}(i\omega) &= \frac{q_n^-}{(i\omega\tau)^\sigma - q_n - q_n^+ S_{n+1}^{\perp}(i\omega)} \\ &= \frac{\xi(n+1)}{n(2n+1)} \left[\frac{2(i\omega\tau)^\sigma}{n(n+1)} + 1 \right. \\ &\quad \left. + \frac{\xi n}{(n+1)(2n+1)} \tilde{S}_{n+1}^{\perp}(i\omega) \right]^{-1} \end{aligned} \tag{A10}$$

and the initial values $g_n(0)$ are given by

$$g_n(0) = \xi_1 \frac{n(n+1)}{2(2n+1)} [\langle P_{n-1}\rangle_0 - \langle P_{n+1}\rangle_0] = \xi_1 \frac{n(n+1)}{2\xi} \frac{I_{n+1/2}(\xi)}{I_{1/2}(\xi)}.$$

Equations (A4) and (A9) are the exact solutions of the problem. They allow one to calculate the longitudinal and transverse components of the complex susceptibility from Eqs. (8)–(10).

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