Bimodal approximation for anomalous diffusion in a potential

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(Received 21 May 2003; published 20 February 2004)

Exact and approximate solutions of the fractional diffusion equation for an assembly of fixed-axis dipoles are derived for anomalous noninertial rotational diffusion in a double-well potential. It is shown that knowledge of three time constants characterizing the *normal* diffusion, viz., the integral relaxation time, the effective relaxation time, and the inverse of the smallest eigenvalue of the Fokker-Planck operator, is sufficient to accurately predict the *anomalous* relaxation behavior for all time scales of interest.

DOI: 10.1103/PhysRevE.69.021105 PACS number(s): 05.40.Jc, 05.45.Df, 77.22.−d

I. INTRODUCTION

The Brownian motion in a potential is of fundamental importance in problems involving relaxation and resonance phenomena in stochastic systems [1]. A rudimentary example is the theory of dielectric relaxation of noninteracting polar molecules due to Debye [2]. That theory is based on the Smoluchowski equation for the noninertial rotational diffusion of the molecules. Moreover, because interactions between dipoles are ignored, the only potential arises from the spatially uniform weak external ac field. The Debye theory cannot, however, 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 [1]. The relaxation process in such disordered systems is characterized by the temporal 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. The memory effects can be described by a fractional diffusion equation in the derivation of which is incorporated a waiting time probability density function [3,4]. That function governs the random time intervals between single microscopic jumps (or reorientations in the case of rotational motion) of the particles. It follows that 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 [5], may be justified. Such a generalization of the Debye theory was given in Ref. [6].

As far as interacting dipoles in the fractional Brownian dynamics are concerned the problem is much more difficult than in normal diffusion. In normal diffusion, the particular problem treated was the Brownian motion of dipoles in a periodic potential (see, e.g., Refs. [1,7–9]) representing the interactions. The relevance to the present problem is that one may simply model relaxation effects involving escape of dipoles over a potential barrier again as Debye-like relaxation, however, the relaxation time depends exponentially on the barrier height through the Arrhenius law. The overbarrier relaxation due to normal diffusion has been extensively discussed by Fröhlich [10] using transition state theory [11,12] and a rate equation approach originally suggested by Debye [2]. Likewise anomalous diffusion in a potential may be treated by using the fractional equivalent of the diffusion equation [3,4]. This diffusion equation allows one to include explicitly in Fröhlich's model as generalized to fractional dynamics (i) the influence of the dissipative coupling to the heat bath on the Arrhenius (overbarrier) process and (ii) the influence of the fast (high-frequency) intrawell relaxation modes on the relaxation process.

The fractional translational diffusion in a potential is discussed in Refs. [3,4]. Just as with normal diffusion, the fractional diffusion equation can in general be solved by the method of separation of the variables. The separation procedure yields an equation of Sturm-Liouville type. However, no explicit solution for the fractional diffusion in a potential has ever been presented (the only exception is a solution for the harmonic potential given by Metzler *et al.* [13] in terms of an eigenfunction expansion with Mittag-Leffler temporal behavior). Here, we shall present both exact and approximate solutions for the anomalous rotational diffusion and dielectric relaxation of an assembly of fixed axis dipoles rotating in a double-well potential representing the internal field due to neighboring molecules. This model has been treated in detail for normal diffusion in Refs. [1,7,9,14]. Here, we shall demonstrate that the characteristic times of the normal diffusion process, namely, the inverse of the smallest nonvanishing eigenvalue, the integral and effective relaxation times, obtained in Refs. [1,7,9,14], also allow us to evaluate the dielectric response of the system for anomalous diffusion. Moreover, these characteristic times yield a simple analytical

equation for the complex dielectric susceptibility $\chi(\omega)$ describing the anomalous relaxation of the system.

II. FRACTIONAL ROTATION DIFFUSION AND DIELECTRIC RELAXATION IN A POTENTIAL

The fractional diffusion equation may be derived using the integral equation for a continuous time random walk (CTRW) [15]. 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 and the waiting time is randomly distributed so that the characteristic time scale diverges [3,4]. A common feature of all such systems is that they exhibit anomalous relaxation behavior. Such behavior is in contrast to the normal diffusion and relaxation which takes place in a regular space. Recently the CTRW has been generalized to include the effect of time-dependent jump probabilities and a fractional diffusion equation in a single coordinate has been derived when the average waiting time diverges [3,4]. As far as rotational Brownian motion is concerned such an equation may be obtained from its translational counterpart [Eq. (101) of Ref. [4]] by simply replacing the position x by the angular coordinate ϕ. Thus, for fractional rotational diffusion in an external potential $V(\phi,t)$, one has

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

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

$$L_{\mathrm{FP}} W = \tau^{-1}\left[\frac{\partial}{\partial\phi}\left(\frac{W}{kT}\frac{\partial V}{\partial\phi}\right) + \frac{\partial^2 W}{\partial\phi^2}\right],$$

$\tau = \zeta/(kT)$ is the Debye relaxation time for rotation about a fixed axis, ζ is the friction coefficient, and kT is the thermal energy. 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]

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

Here, just as with the translational diffusion equation treated in Refs. [3,4], we consider subdiffusion $0<\sigma<1$ phenomena only ($\sigma=1$ 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. If $V=0$, Eq. (1) leads to anomalous (Cole-Cole-like) behavior of the complex susceptibility [6]. 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. 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). However, a more physical and 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 [16]) of the waiting time segments. In order to construct such an entity in practice a whole discrete hierarchy of time scales such as will arise from energetic disorder is needed. For example, a fractal time Poisson process [16] with a waiting time distribution assumes the typical form of a Lévy stable distribution in the limit of large τ. This is explicitly discussed in Ref. [16], where a formula for σ is given and is also discussed in Ref. [17]. The fractal time process is essentially generated by energetic disorder treated as far as the ensuing temporal behavior is concerned by considering jumps over the wells of a chaotic potential barrier landscape. The microscopic picture presented in Refs. [16,17] appears to completely support the commonly used experimental representation of the Cole-Cole behavior as a distribution of Debye-like relaxation mechanisms with a continuous relaxation time distribution function.

The solutions of Eq. (1) are obtained from the Sturm-Liouville representation [4,13]

$$W(\phi,t) = \sum_{p=0}^{\infty} \Phi_p(\phi) F_p(t). \tag{2}$$

Here, the decay modes $F_p(t)$ obey the equation

$$\frac{d}{dt}F_p(t) = -\lambda_{p,\sigma}\, {}_0D_t^{1-\sigma} F_p(t). \tag{3}$$

The eigenvalues $\lambda_{p,\sigma}$ may be expressed in terms of the eigenvalues λ_p of the Fokker-Planck operator L_{FP} for *normal diffusion* [i.e., $L_{\mathrm{FP}}\Phi_p(\phi) = -\lambda_p \Phi_p(\phi)$] so that

$$\lambda_{p,\sigma} = \lambda_p \tau^{1-\sigma}. \tag{4}$$

The solutions of Eq. (3) are the Mittag-Leffler functions $E_\sigma(z)$ [3,4], viz.,

$$F_p(t) = E_\sigma(-\lambda_{p,\sigma} t^\sigma). \tag{5}$$

Equation (4) 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 the local process are related to their Brownian counterparts by the prefactor $\tau^{1-\sigma}$. This scaling effect is significant in the context of escape of particles over potential barriers. There, the smallest nonvanishing eigenvalue λ_1 of the Fokker-Planck equation, written for the Brownian motion in a potential, yields in the high barrier limit, the Kramers escape rate [11,12]. Since we consider the anomalous diffusion analogue of the overdamped Brownian motion, the scaling Eq. (4) shows that the overdamped Kramers escape rate for normal diffusion $\Gamma \sim \lambda_1 \sim e^{-\Delta V/(kT)}$ (ΔV is the barrier height) is slowed by the factor $\tau^{1-\sigma}$ so that $\lambda_{1,\sigma} \sim \tau^{1-\sigma}\lambda_1 = \tau^{1-\sigma}\Gamma$. Therefore, in the present context, the Kramers es-

cape rate can be best understood as playing the role of a decay parameter in the Mittag-Leffler functions governing the highly *nonexponential* relaxation behavior of the system.

In order to understand how the anomalous relaxation behavior influences the dielectric properties, we first recall that according to linear response theory [18], the longitudinal complex dielectric susceptibility $\chi(\omega)=\chi'(\omega)-i\chi''(\omega)$ is defined as

$$\frac{\chi(\omega)}{\chi'(0)}=1-i\omega\int_0^\infty e^{-i\omega t}C_\sigma(t)dt, \tag{6}$$

where $\chi'(0)$ is the static susceptibility,

$$C_\sigma(t)=\frac{\langle\cos\phi\rangle(t)-\langle\cos\phi\rangle_0}{\langle\cos\phi\rangle(0)-\langle\cos\phi\rangle_0}=\sum_p c_p E_\sigma[-\tau\lambda_p(t/\tau)^\sigma] \tag{7}$$

is the normalized relaxation function $C(t)$,

$$c_p=\frac{\int_0^{2\pi}(\cos\phi-\langle\cos\phi\rangle_0)\Phi_p(\phi)d\phi}{\sum_p\int_0^{2\pi}(\cos\phi-\langle\cos\phi\rangle_0)\Phi_p(\phi)d\phi},$$

$\Sigma_p c_p=1$, $\langle\cdots\rangle(t)$ denotes the statistical averages over the assembly of rotators in the presence of a small probing ac electric field, and $\langle\cdots\rangle_0$ means the equilibrium statistical averages. Noting that the Laplace transform of the Mittag-Leffler function is

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

we have from Eqs. (6) and (7)

$$\frac{\chi(\omega)}{\chi'(0)}=\sum_p\frac{c_p}{1+(i\omega\tau)^\sigma/(\tau\lambda_p)}. \tag{8}$$

The susceptibility may be simply evaluated in the low ($\omega\to0$) and high ($\omega\to\infty$) frequency limits. We obtain from Eq. (8)

$$\frac{\chi(\omega)}{\chi'(0)}\approx1-\frac{\tau_{\rm int}}{\tau}(i\omega\tau)^\sigma+\cdots \tag{9}$$

for $\omega\to0$ and

$$\frac{\chi(\omega)}{\chi'(0)}\sim\frac{\tau}{(i\omega\tau)^\sigma\tau_{\rm ef}}+\cdots, \tag{10}$$

for $\omega\to\infty$, where the parameters $\tau_{\rm int}$ and $\tau_{\rm ef}$ are defined as

$$\tau_{\rm int}=\sum_p c_p/\lambda_p \quad\text{and}\quad \tau_{\rm ef}=1\Big/\sum_p c_p\lambda_p. \tag{11}$$

For *normal diffusion*, these parameters correspond to the integral relaxation time $\tau_{\rm int}$ [the area under the corresponding relaxation function $C_1(t)=\Sigma_p c_p e^{-\lambda_p t}$] and the effective relaxation time $\tau_{\rm ef}$ [which gives precise information on the initial decay of the relaxation function $C_1(t)$]. In general, it is difficult to evaluate $\tau_{\rm int}$ and $\tau_{\rm ef}$ from Eqs. (11) [just as it is to evaluate $\chi(\omega)$ from Eq. (8)], as a knowledge of all the eigenvalues λ_k and their corresponding amplitudes c_k is required. However, $\tau_{\rm int}$ and $\tau_{\rm ef}$ can be evaluated from their equivalent definitions

$$\tau_{\rm ef}=-1/\dot{C}_1(0) \quad\text{and}\quad \tau_{\rm int}=\int_0^\infty C_1(t)dt. \tag{12}$$

For one-dimensional rotational Brownian motion in a potential, $\tau_{\rm int}$ and $\tau_{\rm ef}$ defined by Eq. (12) may be expressed in closed form, viz. [1],

$$\tau_{\rm ef}=\tau\frac{1+\langle\cos2\phi\rangle_0-2\langle\cos\phi\rangle_0^2}{1-\langle\cos2\phi\rangle_0} \tag{13}$$

and [1,14,19]

$$\tau_{\rm int}=\frac{\tau}{Z(\langle\cos^2\phi\rangle_0-\langle\cos\phi\rangle_0^2)}\int_0^{2\pi}e^{V(\phi)/kT}\Bigg[\int_0^\phi(\cos x-\langle\cos\phi\rangle_0)e^{-V(x)/kT}dx\Bigg]^2d\phi, \tag{14}$$

where

$$Z=\int_0^{2\pi}e^{-V(\phi)/kT}d\phi.$$

We note that the characteristic times $\tau_{\rm int}$ and $\tau_{\rm ef}$ do not exist in anomalous diffusion ($\sigma\neq1$). This is obvious from the properties of the Mittag-Leffler function, which has initially ($t\ll\tau$) stretched exponential (Kohlrausch) form [3,4]

$$E_\sigma[-(t/\tau)^\sigma]\sim e^{-(t/\tau)^\sigma/\Gamma(1+\sigma)}$$

and long time inverse power law behavior

$$E_\sigma[-(t/\tau)^\sigma]\sim\frac{1}{(t/\tau)^\sigma\Gamma(1-\sigma)},$$

and so describes nonexponential relaxation.

III. BIMODAL APPROXIMATION

As we shall see, two bands appear in the dielectric loss spectrum of $\chi''(\omega)$. The low-frequency band is due to the slowest (overbarrier) relaxation mode; the characteristic frequency ω_c and the half-width of this band are determined by λ_1. Thus, the anomalous low-frequency behavior is dominated by the barrier crossing mode as in the normal diffusion. The high-frequency band is due to ''intrawell'' modes corresponding to the eigenvalues λ_k ($k\neq1$). These near degenerate ''intrawell'' modes are indistinguishable in the frequency spectrum of $\chi''(\omega)$ appearing merely as a single high-frequency band. Thus, the spectrum of the longitudinal susceptibility $\chi(\omega)$ may essentially be approximated by a sum of two Cole-Cole mechanisms, viz.,

$$\frac{\chi(\omega)}{\chi'(0)}=\frac{\Delta_1}{1+(i\omega/\omega_c)^\sigma}+\frac{1-\Delta_1}{1+(i\omega/\omega_W)^\sigma}, \tag{15}$$

where the characteristic frequencies ω_c and ω_W are given by

$$\omega_c=\tau^{-1}(\tau\lambda_1)^{1/\sigma},\quad \omega_W=\tau^{-1}(\tau/\tau_W)^{1/\sigma}. \tag{16}$$

Here, we implicitly suppose that the contribution of the high-frequency modes may be approximated by a single mode with characteristic frequency ω_W. In the time domain, such a bimodal approximation is equivalent to assuming that the relaxation function $C_\sigma(t)$ as determined by the exact Eq. (7) (which in general comprises an *infinite number* of Mittag-Leffler functions) may be approximated by *two* Mittag-Leffler functions only, viz.,

$$C_\sigma(t)\approx\Delta_1 E_\sigma[-(t/\tau)^\sigma\tau\lambda_1]+(1-\Delta_1)E_\sigma[-(t/\tau)^\sigma\tau/\tau_W].$$

The parameters Δ_1 and τ_W in Eqs. (15) and (16) may be determined from the condition that the approximate Eq. (15) must obey the exact asymptotic Eqs. (9) and (10) yielding

$$\tau_{\rm int}=\Delta_1/\lambda_1+\tau_W(1-\Delta_1)$$

and

$$\tau_{\rm ef}^{-1}=\Delta_1\lambda_1+\tau_W^{-1}(1-\Delta_1).$$

It follows that Δ_1 and τ_W may readily be evaluated from the above equations yielding

$$\Delta_1=\frac{\tau_{\rm int}/\tau_{\rm ef}-1}{\lambda_1\tau_{\rm int}-2+1/(\lambda_1\tau_{\rm ef})}, \tag{17}$$

$$\tau_W=\frac{\lambda_1\tau_{\rm int}-1}{\lambda_1-1/\tau_{\rm ef}}. \tag{18}$$

Equation (15) involving the integral relaxation time $\tau_{\rm int}$, the effective relaxation time $\tau_{\rm ef}$, and the smallest nonvanishing eigenvalue λ_1 correctly predicts $\chi(\omega)$ both at low ($\omega\to0$) and high ($\omega\to\infty$) frequencies. Moreover, $\chi(\omega)$ may be determined in the entire frequency range $0\leqslant\omega<\infty$ as we shall presently see.

IV. DOUBLE-WELL POTENTIAL: APPROXIMATE AND EXACT SOLUTIONS

As an example, we evaluate in the context of the two-mode approximation the longitudinal susceptibility $\chi(\omega)$ of a fixed axis rotator in a double-well potential $V(\phi)=U\sin^2\phi$ (the normal noninertial diffusion in this model has been treated in detail in Refs. [1,7,9,14]). This potential determines two potential minima on the sites at $\phi=0$ and $\phi=\pi$ as well as two energy barriers located at $\phi=\pi/2$ and $\phi=3\pi/2$. Here, we can use known equations for $\tau_{\rm int}$, $\tau_{\rm ef}$, and λ_1 for the normal diffusion [1,9,14]; these equations are (in the notation of this paper)

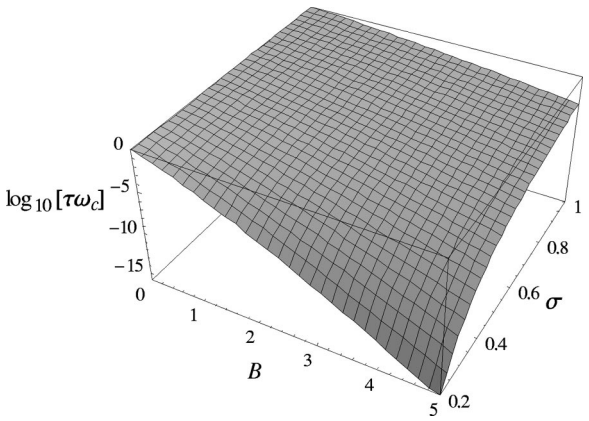

FIG. 1. Characteristic frequency ω_c as a function of σ and B.

$$\tau_{\rm int}=\frac{\tau e^{2B}}{4B[I_1(B)+I_0(B)]}\int_0^\pi e^{-B\cos2\phi}\,{\rm erf}^2(\sqrt{2B}\sin\phi)\,d\phi,$$

$$\tau_{\rm ef}=\tau\frac{I_0(B)+I_1(B)}{I_0(B)-I_1(B)},$$

$$\lambda_1\tau=\left[\frac{\pi}{1-e^{-2B}}\sum_{p=0}^{\infty}\frac{(-1)^p}{2p+1}I^2_{p+1/2}(B)\right]^{-1},$$

where $B=U/(2kT)$ is the barrier height parameter, erf(z) is the error function, and $I_p(z)$ is the modified Bessel function of the first kind. We recall that in the high barrier limit ($B\gg1$), $\lambda_1^{-1}\sim\tau_{\rm int}\sim\tau\pi e^{2B}/8B$ and $\tau_{\rm ef}\sim4B\tau$ [1,7,9] yielding simple asymptotic equations for the characteristic frequencies ω_c and ω_W from Eqs. (16), viz.,

$$\omega_c\sim(8B/\pi)^{1/\sigma}e^{-2B/\sigma}/\tau \tag{19}$$

and

$$\omega_W\sim(8B)^{1/\sigma}/\tau. \tag{20}$$

Thus, ω_c and ω_W depend not only on the barrier height (as in normal diffusion) but also on the anomalous exponent σ which substantially modifies the dielectric loss spectra. For example, for $\tau\sim10^{-10}$ s, ω_c of the normal diffusion ($\sigma=1$) will be reduced by a factor of the order 10^5 for $\sigma=1/2$. The characteristic frequency $\omega_c=\tau^{-1}(\tau\lambda_1)^{1/\sigma}$ is shown in Fig. 1 as a function of σ and B.

In order to estimate the accuracy of the two-mode approximation, we calculate $\chi(\omega)$ by converting the solution of the fractional diffusion Eq. (1) into the calculation of successive convergents of a differential-recurrence relation just as normal diffusion [1,9]. We suppose that a uniform field **E** (having been applied to the assembly of dipoles at a time $t=-\infty$ so that equilibrium conditions prevail by the time $t=0$) is switched off at $t=0$. In addition, we suppose that the field is weak (i.e., $\mu E\ll kT$ which is the linear response condition [18]). By expanding the distribution function $W(\phi,t)$ in Fourier series

$$W(\phi,t)=\sum_{p=-\infty}^{\infty} e^{ip\phi}c_p(t),$$

we have from Eq. (1) the differential-recurrence equation

$$\dot{f}_p(t)=\tau^{-\sigma}\,{}_0D_t^{1-\sigma}\{Bp[f_{p-2}(t)-f_{p+2}(t)]-p^2f_p(t)\},$$

$$(t\geqslant 0), \tag{21}$$

where

$$f_p(t)=\mathrm{Re}[c_p(t)]/(2\pi)=\langle\cos p\phi\rangle(t).$$

Applying the integration theorem of Laplace transformation generalized to fractional calculus [3,4], we have from Eq. (21)

$$s\tau\tilde{f}_p(s)-f_p(0)=(s\tau)^{1-\sigma}\{Bp[\tilde{f}_{p-2}(s)-\tilde{f}_{p+2}(s)]-p^2\tilde{f}_p(s)\}, \tag{22}$$

where $\tilde{f}(s)$ denotes the Laplace transform of $f(t)$. The *exact* solution of the three-term recurrence Eq. (22) can be obtained, just as normal diffusion, in continued fraction form (see Refs. [1,9] for details). On noting that the initial values $f_p(0)$ may be expressed in terms of $I_p(B)$ [9], we have

$$\frac{\tilde{f}_1(s)}{f_1(0)}=\frac{\tau(s\tau)^{\sigma-1}}{(s\tau)^{\sigma}+1-B+BpS_3(s)}\left[1+\sum_{p=1}^{\infty}\frac{(-1)^p}{2p+1}\times\frac{I_{p+1}(B)+I_p(B)}{I_1(B)+I_0(B)}\prod_{k=1}^{p}S_{2k+1}(s)\right] \tag{23}$$

with successive convergents being calculated from the continued fraction

$$S_p(s)=\frac{Bp}{(s\tau)^{\sigma}+p^2+BpS_{p+2}(s)}=\cfrac{Bp}{(s\tau)^{\sigma}+p^2+\cfrac{B^2p(p+2)}{(s\tau)^{\sigma}+(p+2)^2+\cfrac{B^2(p+2)(p+4)}{(s\tau)^{\sigma}+(p+4)^2+\cdots}}}.$$

Thus, by setting $s=i\omega$ and by noting that $\tilde{C}_{\sigma}(i\omega)=\tilde{f}_1(i\omega)/f_1(0)$, we may calculate the complex susceptibility $\chi(\omega)$ from Eq. (6), where the static susceptibility $\chi'(0)$ is [9]

$$\chi'(0)=\frac{\mu^2N_0}{kT}\langle\cos^2\phi\rangle_0=\frac{\mu^2N_0}{kT}\frac{I_1(B)+I_0(B)}{2I_0(B)}$$

(μ is the dipole moment and N_0 is the number of dipoles per unit volume). The ease of calculation of $\chi(\omega)$ from Eq. (23) represents the chief advantage of the continued fraction in comparison to the Sturm-Liouville method as applied to anomalous diffusion.

V. RESULTS AND DISCUSSION

Calculations of the normalized $[\mu^2N_0/(kT)=1]$ susceptibility $\chi(\omega)$ from the exact continued fraction solution Eq. (23) and the approximate Eqs. (15) and (16) are shown in Figs. 2 and 3. Here, the low- and high-frequency asymptotes, Eqs. (9) and (10), are also presented demonstrating that the bimodal approximation obeys the exact asymptotic Eqs. (9) and (10). Two bands, which appear in the dielectric loss spectrum of $\chi''(\omega)$ at $2B\gg 1$ (in the high barrier limit), reach maximum at characteristic frequencies ω_c and ω_W given by Eqs. (19) and (20), respectively. Apparently, the agreement between the exact continued fraction calculations and the approximate Eq. (15) is very good [the maximum relative deviation between the corresponding curves, which appears at $\omega\sim\tau^{-1}$, does not exceed a few (3-5) percent]. Similar (or even better) agreement exists for *all* values of B and σ. Such a good accuracy of the bimodal approximation is due to the fact that the infinite number of high-frequency ''intrawell'' modes (these near degenerate modes are indistinguishable

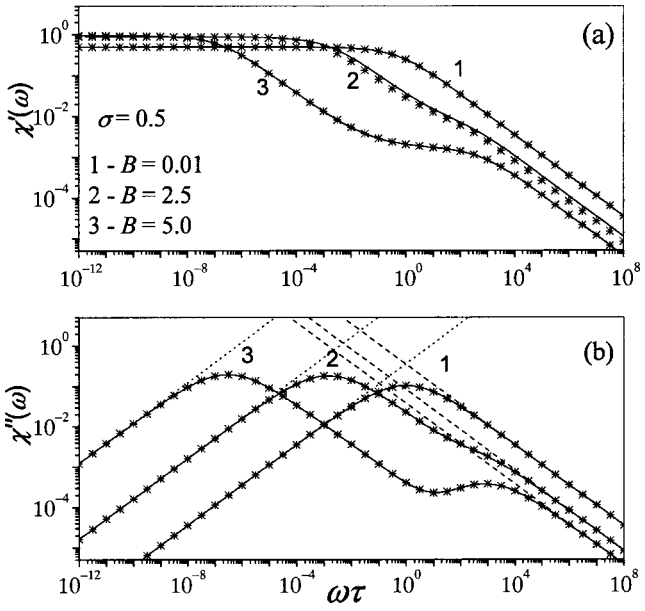

FIG. 2. The real (a) and imaginary (b) parts of the complex susceptibility evaluated from the exact continued fraction solution [Eqs. (23): solid lines] for $\sigma=0.5$ and various values of B and compared with those calculated from the approximate Eq. (15) (stars). The low- (dotted lines) and high-frequency (dashed lines) asymptotes are calculated from Eqs. (9) and (10), respectively.

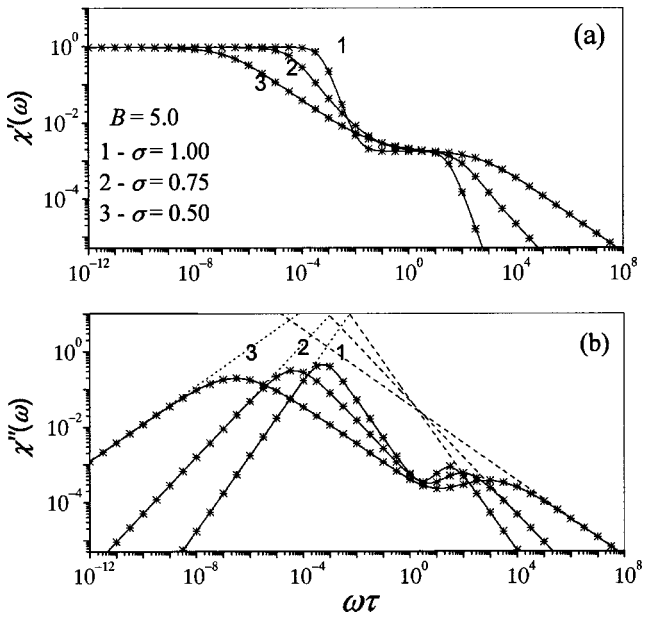

FIG. 3. The same as in Fig. 2 for $B=5$ and various values of σ.

appearing merely as a single Cole-Cole high-frequency band in the dielectric loss spectrum) may be approximated effectively by a single mode. Thus, one may conclude that Eq. (15) accurately describes the behavior of $\chi(\omega)$ for all frequencies of interest and for all values of the barrier height (B) and anomalous exponent (σ) parameters. We remark that bimodal approximation works extremely well both for anomalous ($\sigma \neq 1$) and normal ($\sigma = 1$) cases (various applications for the normal diffusion in a potential are given in Refs. [1] and [19]).

Thus, the *anomalous* relaxation in a double-well potential is effectively determined by the bimodal approximation, Eq. (15); the characteristic times of the *normal* diffusion process, namely, the inverse of the smallest nonvanishing eigenvalue, the integral and effective relaxation times appearing as time parameters. The bimodal approximation constitutes an example of the solution of the noninertial fractional diffusion equation in a periodic potential and is to our knowledge the first example of such a solution. Moreover, the simple asymptotic Eqs. (19) and (20) allow one to easily evaluate the characteristic frequencies of the dielectric loss spectrum in terms of the physical model parameters B and σ. Thus, Fröhlich's model of relaxation over potential barrier based on the concept of *normal* diffusion may be generalized to *anomalous* diffusion in disordered energyscapes giving rise to temporally nonlocal behavior [4]. Furthermore, one may conjecture that the generalized Fröhlich 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. The results obtained may be regarded as a generalization of the solution for the normal Brownian motion in a cosine periodic potential [1,9] to fractional dynamics (giving rise to anomalous diffusion). Moreover, the exact continued fraction solution clearly indicates how many existing results of the classical theory of the Brownian motion in a potential [1,20] may be extended to fractional dynamics.

It should be mentioned that if one is interested only in low-frequency ($\omega \leqslant \omega_c$) part of the dielectric spectrum, one may use a more simple single mode (Cole-Cole) equation for the normalized complex susceptibility, namely,

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{1+(i\omega/\omega_c)^{\sigma}}. \tag{24}$$

The characteristic frequencies ω_c is given by Eq. (16). In passing, we must remark 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. [6,17,21,22]). 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 potential and exactly calculate its effect on the relaxation process. Moreover, with a simple extension to diffusion in phase space, one may include the inertial effects of the dipoles [23].

ACKNOWLEDGMENTS

The support of this work by EOARD (Contract No. FA8655-03-01-3027) is gratefully acknowledged.

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