

Anomalous diffusion and dielectric relaxation in an N -fold cosine potential

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The fractional Klein-Kramers (Fokker-Planck) equation describing the fractal time dynamics of an assembly of fixed axis dipoles rotating in an N -fold cosine potential representing the internal field due to neighboring molecules is solved using matrix continued fractions. The result can be considered as a generalization of the solution for the normal Brownian motion in a cosine periodic potential to fractional dynamics (giving rise to anomalous diffusion) and also represents a generalization of Fröhlich's model of relaxation over a potential barrier. The solution includes both inertial and strong internal field effects, which in combination produce a strong resonance peak (Poley absorption) at high frequencies due to librations of the dipoles in the potential, an anomalous relaxation band at low frequencies mainly arising from overbarrier relaxation, and a weaker relaxation band at midfrequencies due to the fast intrawell modes. The high-frequency behavior is controlled by the inertia of the dipole, so that the Gordon sum rule for dipolar absorption is satisfied, ensuring a return to optical transparency at very high frequencies. Application of the model to the broadband (0–THz) dielectric loss spectrum of a dilute solution of the probe dipolar molecule CH_2Cl_2 in glassy decalin is demonstrated.

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I. INTRODUCTION

The theory of rotational Brownian motion in the presence of a potential arising from internal fields is of fundamental importance in a number of problems involving relaxation and resonance phenomena in stochastic systems [1]. A rudimentary example is the theory of dielectric relaxation of non-interacting polar molecules due to Debye [2], which is based on a kinetic equation, namely, the (approximate) Smoluchowski equation for the rotational diffusion of the molecules. There, because interactions between dipoles are ignored, the only potential arises from the spatially uniform weak external ac field. The complex dielectric susceptibility from this theory agrees substantially with experimental data in the microwave region, predicting the observed broadband absorption. The Debye theory has very recently been generalized to anomalous dielectric relaxation which (excluding inertial effects) is characterized by a nonexponential dielectric decay function [3]. In general, for noninteracting dipoles the usual exponential decay function of the Debye theory is replaced by a Mittag-Leffler function which exhibits stretched exponential behavior at short times and a long time tail [4,5]. The complex dielectric susceptibility yielded by that function (Cole-Cole behavior) [6] is substantially in accord with experimental data on dielectric relaxation of amorphous polymers, glass-forming liquids, etc. [5,6]. Moreover, Nigmatullin and Ryabov [6] have shown how other relaxation behaviors such as the Davidson-Cole function may also be modeled using fractional calculus [6].

In the context of this paper, we emphasize that neither the Debye theory nor its various [3,6] extensions to fractional

Brownian motion include the inertia or internal field effects. Inertial effects in the theory of the normal Brownian motion were studied by Rocard [7], Gross [8], and Sack [9]. Gross and Sack [8,9] studied these effects by solving the Fokker-Planck equation (which for a separable and additive Hamiltonian is known as the Klein-Kramers equation) for the distribution function of dipolar rotators in phase space. They obtained the complex susceptibility in exact continued fraction form, so predicting a return to optical transparency at high frequencies, unlike the infinite integral absorption predicted by the Debye theory. The earlier Rocard result may be recovered from their continued fraction solution for small inertial effects. Their calculations have very recently been extended to fractional Brownian motion by Coffey *et al.* [10,11], ensuring a return to optical transparency at high frequencies in fractional dynamics just as in the conventional Brownian dynamics. The approach developed in [10,11] was based on the fractional Klein-Kramers equation proposed by Barkai and Silbey [12]. The solution for the complex susceptibility given in Refs. [10,11] emerges in continued fraction form in a manner entirely analogous to the conventional Brownian motion result because of a useful generalization of the integration theorem of Laplace transformation to fractional calculus [4].

As far as the inclusion of an internal field potential combined with inertial effects is concerned, the problem is much more difficult than that of including inertia alone, in both the normal and fractional Brownian dynamics. Thus, referring to normal Brownian dynamics, all the initial attempts to solve the problem were made in the noninertial limit [13–16]. In particular, in Ref. [16] it was shown by representing the con-

figuration space distribution function in Fourier series how the complex susceptibility, etc., could be obtained exactly in scalar continued fraction form by Laplace transformation of the differential recurrence relations for the Fourier coefficients. The particular problem treated was the Brownian motion of a rotator about a fixed axis in the presence of a $\cos 2\theta$ potential, where θ is the angular coordinate of the rotator. Moreover, it was demonstrated, using the final value theorem [17] for Laplace transforms, how the correlation time of the dielectric decay function could be obtained in closed form [16]. The relevance to the present problem of this potential is that it is possible to model relaxation effects involving escape of dipoles over a potential barrier [16]. We remark in passing that, in the context of the present work, overbarrier relaxation due to normal diffusion has been extensively discussed by Fröhlich [18]. This model again gives rise to Debye-like relaxation behavior; however, the relaxation time depends exponentially on the barrier height through the Arrhenius law. Fröhlich used transition state theory [19,20] and a rate equation approach originally suggested by Debye [2] so that a discrete set of orientations for the dipoles of the assembly is implicitly assumed. A continuous distribution of orientations may be treated by the use of methods based on the Klein-Kramers equation or its fractional equivalent. These diffusion equations also allow one to include explicitly in Fröhlich's model in both discrete (normal) and fractal time dynamics the influence of (i) the dissipative coupling to the heat bath on the Arrhenius (overbarrier) process and (ii) molecular librations and the fast (high-frequency) intrawell relaxation modes on the relaxation process. Moreover, the diffusion equation method when applied to a system of dipoles with an internal field potential also indicates how the original kinetic equation approach of Debye may be reconciled with his rate equation treatment.

The Fokker-Planck equation approach described in Ref. [16] was subsequently extended to many problems in dielectric relaxation of liquid crystals and magnetic relaxation of single domain ferromagnetic particles involving rotation in space. These are comprehensively summarized in Ref. [1]. Although the noninertial rotational motion in space in the presence of a mean field potential has been fully described, almost all the discussion concerning *inertial effects* and an *internal field* potential has been in the context of the motion of a rotator about a fixed axis in a periodic potential representing the internal field [21–23]. This problem, on expanding the phase space distribution function in the Klein-Kramers equation in a Fourier series, leads to a differential recurrence relation in two characteristic numbers, namely, the order n of the Hermite polynomials $H_n(\eta\dot{\theta})$ in the angular velocity $\dot{\theta}$ and q of the circular functions $e^{-iq\theta}$, where $\eta = \sqrt{I/2kT}$, I is the moment of inertia of a rotator, and kT is the thermal energy. The differential recurrence relation in two variables is a particular example of that given by Brinkman [24] in his attempt to justify the approximate Smoluchowski equation for the distribution function in configuration space from the Klein-Kramers equation for the translational Brownian motion in phase space (for a summary of the applications to dielectric relaxation, see Refs.

[22], [23]). There the problem of calculating the complex susceptibility has been formulated, and numerical solutions for the angular velocity correlation function have been given in Ref. [23]. However, the complex polarizability was not calculated.

The first attempt to calculate the complex polarizability including inertial effects and a potential arising from the internal field was made by Reid [25], who gave numerical results in a limited number of specialized cases. Only very recently, however, has it become possible to treat the calculation of the Fourier coefficients in a systematic way for the conventional Brownian motion. The difficulty arises because when inertial effects are included the two recurring numbers n and q always give rise to a matrix recurrence relation. Matrix continued fractions are therefore an ideal way of solving such recurrence relations. This has been accomplished in Ref. [26], where it was shown that the linear and nonlinear responses of an assembly of fixed axis rotators in the presence of a strong spatially uniform external field (that is, a $\cos \theta$ potential) may be systematically solved using the matrix continued fraction method. This method has also been extended to calculate the linear dielectric response of the cage model of polar liquids originally proposed by Hill [27,28].

It is the purpose of this paper to generalize the results [10,11] by including the effect of an internal field potential (and so dielectric relaxation due to barrier crossing by dipoles) in the fractional Brownian dynamics. As in [10,11], our approach is based on the fractional Klein-Kramers equation for the translational Brownian motion in a potential proposed by Barkai and Silbey [12]. The solution of the rotational analog of this fractional Klein-Kramers equation is accomplished using the matrix continued fraction method and the generalized integration theorem (i.e., the properties of the inverse linear differential operator) of Laplace transformation [17,29]. These methods also allow us to consider the mechanism underlying the high-frequency (far infrared) absorption peak in fractional dynamics. Moreover, they facilitate the extension of the important cage model of polar fluids [27,28] to fractional dynamics. In order to simplify our presentation we confine ourselves to the linear response to a small ac applied field.

II. RECURRENCE RELATIONS FOR STATISTICAL AVERAGES FOR ROTATION ABOUT A FIXED AXIS

We illustrate by considering one of the simplest microscopic models of dielectric relaxation, namely, an assembly of rigid dipoles each of moment μ rotating about a fixed axis through its center [8,9,23]. A dipole has moment of inertia I and is specified by the angular coordinate θ so that it constitutes a system of one (rotational) degree of freedom. The internal field due to molecular interactions is represented by an N -fold cosine potential:

$$V(\theta) = -V_0 \cos N\theta. \quad (1)$$

We suppose that a uniform field \mathbf{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 [30]). For $t \leq 0$ and $t \rightarrow \infty$, the distribution functions are linearized Boltzmann distributions, viz. [31,32],

$$W_{t \leq 0} \approx \frac{e^{-(\eta\dot{\theta})^2 + \xi_V \cos N\theta} [1 + \xi \cos(\theta - \Theta)]}{\int_{\Omega} e^{-(\eta\dot{\theta})^2 + \xi_V \cos N\theta} [1 + \xi \cos(\theta - \Theta)] d\Omega} \\ = W_0(\theta, \dot{\theta}) [1 + \xi \cos(\theta - \Theta) - \xi \langle \cos(\theta - \Theta) \rangle_0] \quad (2)$$

and

$$W_{t \rightarrow \infty} \equiv W_0(\theta, \dot{\theta}) = Z^{-1} e^{-(\eta\dot{\theta})^2 + \xi_V \cos N\theta}, \quad (3)$$

respectively. Here Z is the partition function, Θ is the angle between \mathbf{E} and the z axis in the plane zx ,

$$\xi = \frac{\mu E}{kT}, \quad \xi_V = \frac{V_0}{kT}, \quad (4)$$

and $\langle \rangle_0$ means the equilibrium statistical average over $W_0(\theta, \dot{\theta})$.

Our goal is to evaluate the transient relaxation of the electric polarization defined as [31,32]

$$P_E(t) = \mu N_0 [\langle \cos(\theta - \Theta) \rangle(t) - \langle \cos(\theta - \Theta) \rangle_0] \\ = (\cos \Theta) P_{\parallel}(t) + (\sin \Theta) P_{\perp}(t), \quad (5)$$

where

$$P_{\parallel}(t) = \mu N_0 [\langle \cos \theta \rangle(t) - \langle \cos \theta \rangle_0], \quad (6)$$

and

$$P_{\perp}(t) = \mu N_0 [\langle \sin \theta \rangle(t) - \langle \sin \theta \rangle_0] \quad (7)$$

are the longitudinal and transverse components of the polarization, N_0 is the concentration of dipoles, and the angular brackets $\langle \rangle(t)$ denote the statistical averages over the assembly of rotators. According to linear response theory [31,32], the decay of the longitudinal and transverse components of the polarization of a system of noninteracting planar dipoles, when a small uniform external field \mathbf{E} is switched off at time $t=0$, is

$$P_{\parallel}(t) = (\cos \Theta) E C_{\parallel}(t) \quad (8)$$

and

$$P_{\perp}(t) = (\sin \Theta) E C_{\perp}(t), \quad (9)$$

where [28,29]

$$C_{\parallel}(t) = \frac{\mu^2 N_0}{kT} [\langle \cos \theta(0) \cos \theta(t) \rangle_0 - \langle \cos \theta(0) \rangle_0^2] \quad (10)$$

and

$$C_{\perp}(t) = \frac{\mu^2 N_0}{kT} [\langle \sin \theta(0) \sin \theta(t) \rangle_0 - \langle \sin \theta(0) \rangle_0^2] \quad (11)$$

are the longitudinal and transverse relaxation functions. The longitudinal and transverse components of the complex susceptibility tensor are defined as

$$\chi_{\gamma}(\omega) = \chi'_{\gamma}(\omega) - i \chi''_{\gamma}(\omega) \\ = C_{\gamma}(0) - i \omega \int_0^{\infty} e^{-i\omega t} C_{\gamma}(t) dt \quad (\gamma = \parallel, \perp). \quad (12)$$

By supposing that the local configuration potential is uniformly distributed in a plane, we may define the averaged susceptibility $\chi(\omega)$ as

$$\chi(\omega) = [\chi_{\parallel}(\omega) + \chi_{\perp}(\omega)]/2, \quad (13)$$

which yields after elementary manipulation of Eqs. (10) and (11)

$$\chi(\omega) = \frac{\mu^2 N_0}{2kT} \left[1 - i \omega \int_0^{\infty} \langle \cos \Delta \theta(t) \rangle_0 e^{-i\omega t} dt \right], \quad (14)$$

where $\Delta \theta(t) = \theta(t) - \theta(0)$.

The starting point in our calculation of $\chi(\omega)$ from Eq. (14) is the fractional Klein-Kramers equation for the probability density function $W(\theta, \dot{\theta}, t)$ in the phase space $(\theta, \dot{\theta})$ [10,11], which is identical to that for the one-dimensional translational Brownian motion of a particle [12], except that rotational quantities (angle θ , moment of inertia I , etc.) replace translational ones (position x , mass m , etc.), so that for $t > 0$ the hydrodynamical derivative is

$$\frac{\partial W}{\partial t} + \dot{\theta} \frac{\partial W}{\partial \dot{\theta}} - N V_0 \sin N\theta \frac{\partial W}{I \partial \theta} \\ = {}_0 D_t^{1-\alpha} \tau^{1-\alpha} \beta \left(\frac{\partial}{\partial \dot{\theta}} (\dot{\theta} W) + \frac{kT}{I} \frac{\partial^2 W}{\partial \theta^2} \right). \quad (15)$$

Here $\beta = \zeta/I$, ζ is the damping coefficient of a dipole, τ is the intertrapping time scale, which we identify with the Debye relaxation time ζ/kT (at ambient temperatures, τ is of the order 10^{-11} s for molecular liquids and solutions), and α is the anomalous exponent or order of the fractional derivative characterizing the fractal time process. Thus the fractional dynamics emerges from the competition of Brownian motion events of average duration τ interrupted by trapping events whose duration is broadly distributed [4]. Equation (15) with anomalous exponent α such that $1 \leq 2 - \alpha \leq 2$ describes anomalous enhanced diffusion in configuration space according to Barkai and Silbey [12]. The value $\alpha = 1$ corresponds to normal diffusion. Here the operator ${}_0 D_t^{1-\alpha} \equiv (\partial/\partial t) {}_0 D_t^{-\alpha}$ in Eq. (15) is defined in terms of the convolution (the Riemann-Liouville fractional integral definition) [4]

$${}_0D_t^{-\alpha}W(\theta, \dot{\theta}, t) = \frac{1}{\Gamma(\alpha)} \int_0^t \frac{W(\theta, \dot{\theta}, t') dt'}{(t-t')^{1-\alpha}}. \quad (16)$$

Thus, the fractional derivative is a type of memory function [4]. Moreover, a slowly decaying power-law kernel in the Riemann-Liouville operator (16) is typical of memory effects in complex systems.

We seek a solution of the fractional Klein-Kramers equation, Eq. (3), for the case $E=0$ at $t>0$ by using the method of separation of variables in the form of the Fourier series

$$W(\theta, \dot{\theta}, t) = \frac{1}{2} \eta \pi^{-3/2} e^{-\eta^2 \dot{\theta}^2} \times \sum_{n=0}^{\infty} \sum_{q=-\infty}^{\infty} \frac{1}{2^n n!} f_{n,q}(t) H_n(\eta \dot{\theta}) e^{iq\theta}, \quad (17)$$

where $H_n(x)$ are the Hermite polynomials. Noting that [33]

$$\frac{d}{dx} H_{n+1}(x) = 2n H_{n-1}(x), \quad (18)$$

$$H_{n+1}(x) = 2x H_n(x) - 2n H_{n-1}(x), \quad (19)$$

and

$$\int_{-\infty}^{\infty} H_n(x) H_m(x) e^{-x^2} dx = \sqrt{\pi} 2^n n! \delta_{n,m}, \quad (20)$$

we have the recurrence relation for

$$f_{n,q}(t) = \langle H_n(\eta \dot{\theta}) e^{-iq\theta} \rangle(t), \quad (21)$$

which is given by

$$\begin{aligned} \eta \dot{f}_{n,q}(t) + \frac{iq}{2} [f_{n+1,q}(t) + 2n f_{n-1,q}(t)] \\ + \frac{inN\xi_V}{2} [f_{n-1,q+N}(t) - f_{n-1,q-N}(t)] \\ = -{}_0D_t^{1-\alpha} \tau^{1-\alpha} n \beta' f_{n,q}(t), \end{aligned} \quad (22)$$

where $\beta' = \beta \eta$. On using the integration theorem [17] of Laplace transformation generalized to fractional calculus [4], viz.,

$$L\{{}_0D_t^{1-\alpha} f(t)\} = \begin{cases} s^{1-\alpha} \tilde{f}(s) - D_t^{-\alpha} f(t)|_{t=0} & (0 < \alpha < 1), \\ s^{1-\alpha} \tilde{f}(s) & (1 \leq \alpha < 2), \end{cases} \quad (23)$$

where $\tilde{f}(s) = L\{f(t)\} = \int_0^{\infty} e^{-st} f(t) dt$, we have from Eq. (22)

$$2\eta s \tilde{f}_{0,q}(s) + iq \tilde{f}_{1,q}(s) = 2\eta f_{0,q}(0), \quad (24)$$

$$\begin{aligned} [2\eta s + n\gamma'^{2-\alpha}(\eta s)^{1-\alpha}] \tilde{f}_{n,q}(s) + iq [\tilde{f}_{n+1,q}(s) \\ + 2n \tilde{f}_{n-1,q}(s)] + inN\xi_V [\tilde{f}_{n-1,q+N}(s) - \tilde{f}_{n-1,q-N}(s)] \\ = 0 \quad (n \geq 1). \end{aligned} \quad (25)$$

Here $\gamma' = \tau/\eta = \zeta \sqrt{2/IkT}$ is the inertial effects parameter (so that large γ' characterizes small inertial effects, and vice versa; $\gamma' = \sqrt{2/\gamma_S}$, where $\gamma_S = IkT/\zeta^2$ is the inertial parameter used by Sack [9]) and $f_{n,q}(0) = 0$ for $n \geq 1$ because

$$\langle H_n e^{-iq\theta} \rangle_0 = 0 \quad (26)$$

for the equilibrium Maxwell-Boltzmann distribution [1]. We remark that the calculation of the longitudinal and transverse components of the complex susceptibility tensor differs only in the term $f_{0,q}(0)$ which must be evaluated at $\Theta=0$ and $\pi/2$, respectively. The calculation of the averaged susceptibility from Eqs. (13) and (14) can be carried out formally by solving Eqs. (24) and (25) for the functions

$$c_{n,q}(t) = \langle H_n(\eta \dot{\theta}) e^{-i[q\theta(t) - \theta(0)]} \rangle_0, \quad (27)$$

which obey the same recurrence Eq. (22) as the $f_{n,q}(t)$. The complex susceptibility is then given by

$$\chi(\omega) = \frac{\mu^2 N_0}{2kT} [1 - i\omega \tilde{c}_{0,1}(i\omega)]. \quad (28)$$

III. MATRIX CONTINUED FRACTION SOLUTION OF EQS. (24) AND (25) FOR $N=2$

As we already mentioned in the Introduction, we choose as an example of an internal field potential a double-well potential ($N=2$) which will allow us to treat overbarrier relaxation [16] (for $N=1$ corresponding to a uniform electric field this process does not exist). In order to solve Eqs. (24) and (25), we shall use matrix continued fractions [1,26]. This is accomplished as follows. We introduce the column vectors

$$\tilde{\mathbf{C}}_1(\omega) = \begin{pmatrix} \vdots \\ \tilde{c}_{0,-2}(i\omega) \\ \tilde{c}_{0,-1}(i\omega) \\ \tilde{c}_{0,1}(i\omega) \\ \tilde{c}_{0,2}(i\omega) \\ \vdots \end{pmatrix}, \quad \tilde{\mathbf{C}}_n(i\omega) = \begin{pmatrix} \vdots \\ \tilde{c}_{n-1,-2}(i\omega) \\ \tilde{c}_{n-1,-1}(i\omega) \\ \tilde{c}_{n-1,0}(i\omega) \\ \tilde{c}_{n-1,1}(i\omega) \\ \tilde{c}_{n-1,2}(i\omega) \\ \vdots \end{pmatrix} \quad (n \geq 2). \quad (29)$$

Now, from the recurrence Eqs. (24) and (25) we have the matrix recurrence equations

$$\begin{aligned} [2i\eta\omega - \mathbf{Q}_n(\omega)] \tilde{\mathbf{C}}_n(\omega) - \mathbf{Q}_n^+ \tilde{\mathbf{C}}_{n+1}(\omega) - \mathbf{Q}_n^- \tilde{\mathbf{C}}_{n-1}(\omega) \\ = 2\eta \delta_{n,1} \mathbf{C}_1(0) \quad (n \geq 1), \end{aligned} \quad (30)$$

where

$$\mathbf{C}_1(0) = \frac{1}{I_0(\xi_V)} \begin{pmatrix} \vdots \\ I_3(\xi_V) \\ 0 \\ I_2(\xi_V) \\ 0 \\ I_1(\xi_V) \\ I_0(\xi_V) \\ 0 \\ I_1(\xi_V) \\ 0 \\ I_2(\xi_V) \\ \vdots \end{pmatrix} \quad (31)$$

$$\mathbf{Q}_n(\omega) = -\gamma'^{2-\alpha} (i\eta\omega)^{1-\alpha} (n-1) \mathbf{I}, \quad (32)$$

$$\mathbf{Q}_n^+ = -i \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\ \cdots & -2 & 0 & 0 & 0 & 0 & \cdots & & & \\ \cdots & 0 & -1 & 0 & 0 & 0 & \cdots & & & \\ \cdots & 0 & 0 & 0 & 0 & 0 & \cdots & & & \\ \cdots & 0 & 0 & 0 & 1 & 0 & \cdots & & & \\ \cdots & 0 & 0 & 0 & 0 & 2 & \cdots & & & \\ \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (33)$$

and the matrices $\mathbf{Q}_n(\omega)$, \mathbf{Q}_n^+ , and \mathbf{Q}_n^- are defined by

$$\mathbf{Q}_n^- = -2i(n-1) \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\ \cdots & -\xi_V & 0 & -2 & 0 & \xi_V & \cdots & 0 & 0 & 0 & \cdots \\ \cdots & \cdots & -\xi_V & 0 & -1 & 0 & \xi_V & \cdots & 0 & 0 & \cdots \\ \cdots & 0 & \cdots & -\xi_V & 0 & 0 & 0 & \xi_V & \cdots & 0 & \cdots \\ \cdots & 0 & 0 & \cdots & -\xi_V & 0 & 1 & 0 & \xi_V & \cdots & \cdots \\ \cdots & 0 & 0 & 0 & \cdots & -\xi_V & 0 & 2 & 0 & \xi_V & \cdots \\ \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (34)$$

and \mathbf{I} is the unit matrix of infinite dimension. The exceptions are the matrices \mathbf{Q}_1^+ and \mathbf{Q}_2^- , which are given by

$$\mathbf{Q}_1^+ = -i \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\ \cdots & -2 & 0 & 0 & 0 & 0 & \cdots & & & \\ \cdots & 0 & -1 & 0 & 0 & 0 & \cdots & & & \\ \cdots & 0 & 0 & 0 & 1 & 0 & \cdots & & & \\ \cdots & 0 & 0 & 0 & 0 & 2 & \cdots & & & \\ \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (35)$$

$$\mathbf{Q}_2^- = -2i \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \\ \cdots & -\xi_V & 0 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots \\ \cdots & 0 & -\xi_V & 0 & -1 & \xi_V & 0 & 0 & 0 & 0 & \cdots \\ \cdots & 0 & 0 & -\xi_V & 0 & 0 & \xi_V & 0 & 0 & 0 & \cdots \\ \cdots & 0 & 0 & 0 & -\xi_V & 1 & 0 & \xi_V & 0 & 0 & \cdots \\ \cdots & 0 & 0 & 0 & 0 & 0 & 2 & 0 & \xi_V & \cdots & \\ \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (36)$$

Here we have taken into account the initial conditions for $c_{0,q}(0)$, viz.,

$$c_{0,q}(0) = \langle e^{-i(q-1)\theta} \rangle_0 = \frac{\int_0^{2\pi} e^{-i(q-1)\theta} e^{\xi_V \cos N\theta} d\theta}{\int_0^{2\pi} e^{\xi_V \cos N\theta} d\theta}$$

$$= \delta_{q-1,mN} \frac{I_m(\xi_V)}{I_0(\xi_V)}, \quad (37)$$

where I_n are modified Bessel functions of the first kind of order n [33]. In order to prove Eq. (37), we noted that [33]

$$e^{-i(q-1)\theta} e^{\xi_V \cos N\theta} = \sum_{m=-\infty}^{\infty} I_m(\xi_V) e^{i(mN-q+1)\theta}. \quad (38)$$

By invoking the general method for solving the matrix recurrence Eq. (30) [1,26], we have the exact solution for the spectrum $\tilde{\mathcal{C}}_1(\omega)$ in terms of a matrix continued fraction, viz.,

$$\tilde{\mathcal{C}}_1(\omega) = 2\eta\Delta_1(i\omega)\mathcal{C}_1(0), \quad (39)$$

where the matrix continued fraction $\Delta_n(i\omega)$ is defined by

$$\Delta_n(i\omega) = [2i\eta\omega\mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^+ \Delta_{n+1}(i\omega) \mathbf{Q}_{n+1}^-]^{-1}. \quad (40)$$

IV. RESULTS AND DISCUSSION

The *exact* matrix continued fraction solution [Eq. (39)] we have obtained is very convenient for the purpose of computation (various algorithms for calculating matrix continued fractions are discussed in Ref. [21], Chap. 9). As far as practical calculation of the infinite matrix continued fraction Eq. (40) is concerned, we approximate that by some matrix continued fraction of finite order (by setting $\mathbf{Q}_n^-, \mathbf{Q}_n^+ = \mathbf{0}$ at some $n=N$). Simultaneously, we restrict the dimensions of the matrices $\mathbf{Q}_n^-, \mathbf{Q}_n^+$, and \mathbf{Q}_n to some finite number M . Both of the numbers N and M depend on the barrier height ξ_V and damping γ' parameters and must be chosen by taking into account the desired degree of accuracy of the calculation (with decreasing γ' and increasing ξ_V both N and M must be increased). Having calculated $\tilde{\mathcal{C}}_1(\omega)$ from Eqs. (39) and (40), we may evaluate the complex dielectric susceptibility $\chi(\omega)$ from Eq. (28) for all values of the model parameters η , γ' , ξ_V , and α .

The real $\chi'(\omega)$ and imaginary $\chi''(\omega)$ parts of the complex susceptibility for various values of α (which in the present context pertains to *anomalous diffusion in velocity space*), ξ_V (which is the barrier height parameter), and γ' (which characterizes the effects of molecular inertia: $\gamma' \rightarrow 0$ and $\gamma' \rightarrow \infty$ characterize large and small inertial effects, respectively) are shown in Figs. 1–7 (the calculations were carried out for $\mu^2 N_0 / 2kT = 1$). For $\xi_V = 0$, the calculation shows that the matrix continued fraction algorithm yields the same results as the exact analytic solution for the free rotational diffusion obtained in Ref. [10], viz.,

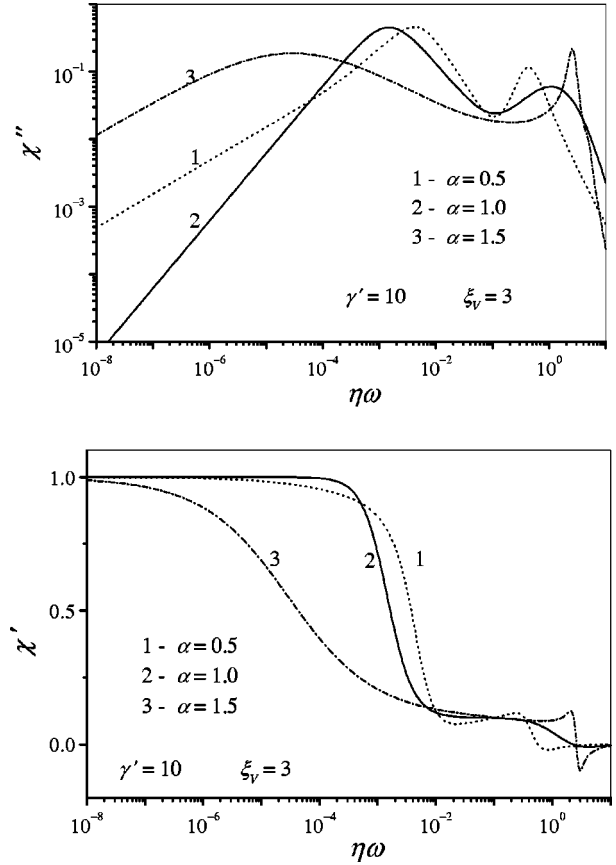


FIG. 1. Real and imaginary parts of the complex susceptibility $\chi(\eta\omega)$ vs normalized frequency $\eta\omega$ for $\gamma' = 10$ and $\xi_V = 3$ and various values of the fractional parameter α .

$$\chi(\omega) = \frac{\mu^2 N_0}{2kT} \left\{ 1 - \frac{(i\tau\omega)^{2-\alpha}}{1 + (i\tau\omega)^{2-\alpha}} \right. \\ \left. \times M(1, 1 + B[1 + (i\tau\omega)^{2-\alpha}], B) \right\}, \quad (41)$$

where $B = 2\gamma'^{-2}(i\omega\tau)^{2(\alpha-1)}$ and $M(a, b, z)$ is the confluent hypergeometric (Kummer) function [33].

The shape of the dielectric spectra strongly depends on the anomalous exponent α (Fig. 1), ξ_V (Figs. 2–4), and γ' (Figs. 5–7). In general, *three* bands may appear in the dielectric loss $\chi''(\omega)$ spectra; the corresponding dispersion regions are visible in the spectra of $\chi'(\omega)$. One anomalous relaxation band dominates the low-frequency part of the spectra and is due to the slow overbarrier relaxation of the dipoles in the double-well cosine potential as identified by Fröhlich [18]. The characteristic frequency ω_R of this low-frequency band strongly depends on the barrier height ξ_V and the friction parameter γ' as well as on the anomalous exponent α . Regarding the barrier height dependence, the frequency ω_R decreases exponentially as the barrier height ξ_V is raised. This behavior occurs because the probability of escape of a dipole from one well to another over the potential barrier exponentially decreases with increasing ξ_V (cf. Figs. 2–4). As far as the dependence of the low-frequency part of the spectrum for small inertial effects ($\gamma' > 10$) is concerned, the

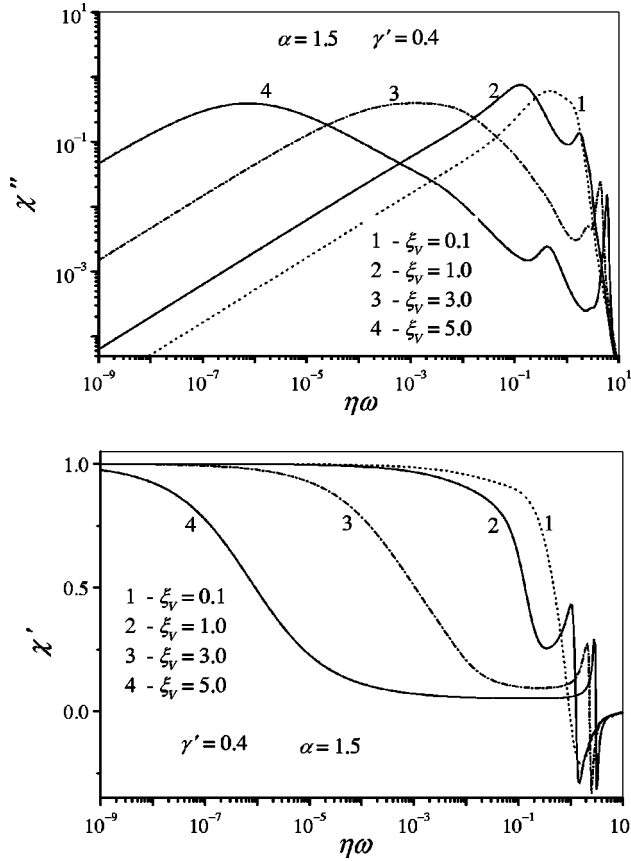


FIG. 2. Real and imaginary parts of the complex susceptibility $\chi(\eta\omega)$ vs normalized frequency $\eta\omega$ for $\alpha=1.5$ and $\gamma'=0.4$ and various values of the barrier height parameter ξ_V .

frequency ω_R decreases as γ' increases as is apparent by inspection of curves 3–6 in Figs. 5–7. For large inertial effects ($\gamma' < 0.1$) the frequency ω_R decreases with decreasing γ' for given values of ξ_V for the enhanced diffusion in configuration space ($\alpha < 1$) and for normal diffusion $\alpha = 1$ (cf. curves 1–3 in Figs. 5 and 6); for the subdiffusion ($\alpha > 1$), however, this frequency does not show such a behavior.

We remark that a very high-frequency band is visible in all the figures. This band is due to the fast inertial librations of the dipoles in the potential wells. This band corresponds to the terahertz (far-infrared) range of frequencies and is usually associated with the Poley absorption [22]. For $\xi_V \gg 1$, the characteristic frequency of librations ω_L increases as $\sim \sqrt{V_0/I}$ (this frequency is weakly dependent on α). As far as the behavior as a function of γ' is concerned, the amplitude of the high-frequency band decreases progressively with increasing γ' for small inertial effects $\gamma' \gg 1$, as one would intuitively expect. On the other hand, for large inertial effects $\gamma' \ll 1$, a fine structure appears in the high-frequency part of the spectra [due to resonances at high harmonic frequencies of the almost free motion in the (anharmonic) cosine potential], again in accordance with intuition. We further remark that the high-frequency ($\omega \gg \omega_L$) behavior of $\chi''(\omega)$ is entirely determined by the inertia of the system. Moreover, just as in the normal Brownian dynamics, the inertial effects produce a rapid falloff of $\chi''(\omega)$ at high frequencies. It is easily

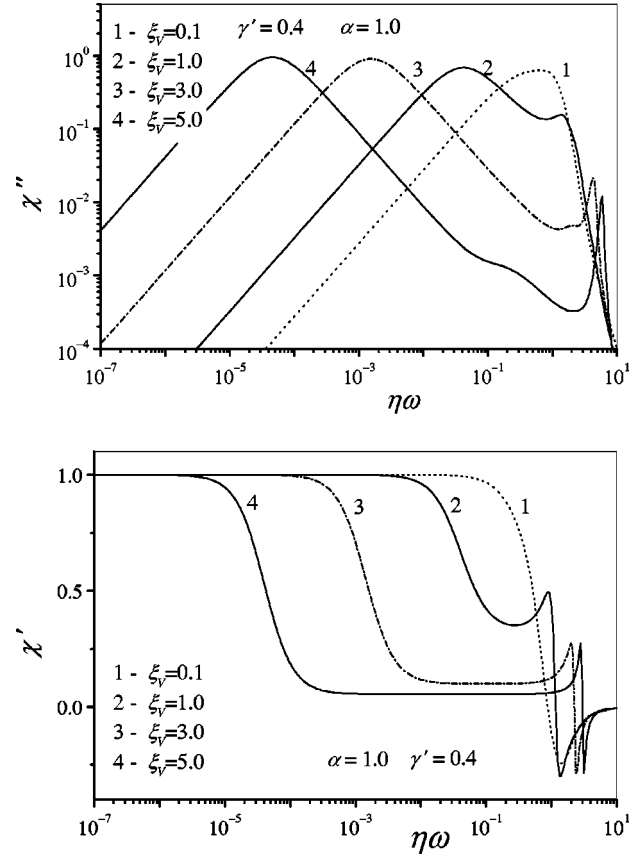


FIG. 3. The same as Fig. 1 for $\alpha=1.0$.

demonstrated [10] that the fractional model under consideration satisfies the Gordon sum rule for the dipole integral absorption of rotators in a plane, viz.,

$$\int_0^{\infty} \omega \chi''(\omega) d\omega = \frac{\pi N_0 \mu^2}{4I}. \quad (42)$$

It is significant that the right hand side of Eq. (42) is determined by molecular parameters only and is independent of the model parameters α , ξ_V , and ζ . For $\alpha=1$, the anomalous rotational diffusion solution coincides with that for normal rotational diffusion.

Finally, it is apparent that between the low-frequency and very high-frequency bands, at some values of model parameters, a *third* band exists in the dielectric loss spectra (see, e.g., Fig. 5). This band is due to the high-frequency relaxation modes of the dipoles in the potential wells (without crossing the potential barrier) which will always exist in the spectra even in the noninertial limit [16]. Such relaxation modes are generally termed the *intrawell modes*. The characteristic frequency of this band depends on the barrier height ξ_V and the anomalous exponent α .

In Fig. 8, a comparison is shown of experimental data for a 10% v/v solution of a probe molecule CH_2Cl_2 in glassy decalin at 110 K [34] with the theoretical dielectric loss spectrum $\varepsilon''(\omega) \sim (\varepsilon_0 - \varepsilon_\infty) \chi''(\omega) / \chi'(0)$ calculated from Eqs. (28) and (39). The reduced moment of inertia I_r used in the calculation is defined by $I_r^{-1} = I_b^{-1} + I_c^{-1}$, where I_b and I_c are

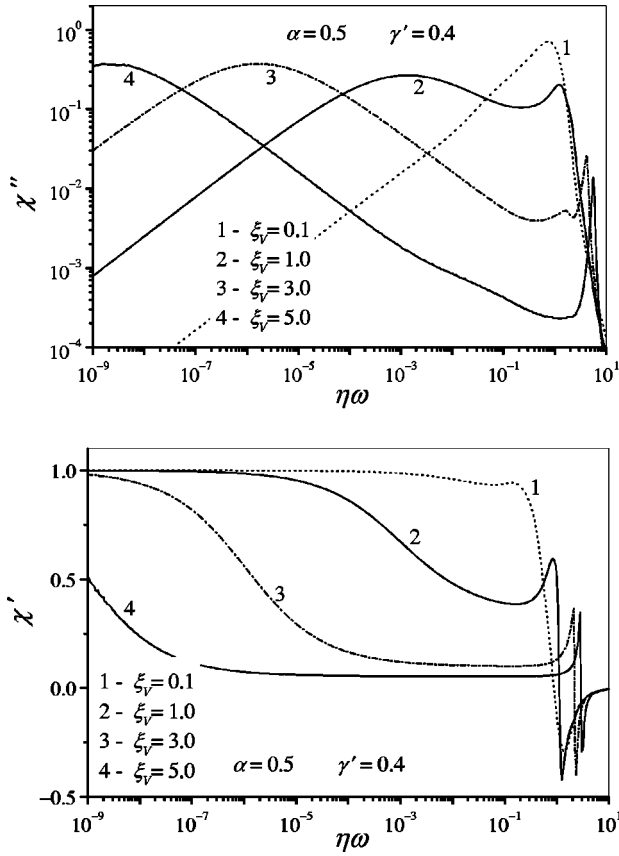


FIG. 4. The same as Fig. 1 for $\alpha=0.5$.

the principal moments of inertia about molecular axes perpendicular to the principal axis a along which the dipole moment vector is directed. For the CH_2Cl_2 molecule $I_r = 0.24 \times 10^{-38} \text{ g cm}^2$ [22]. The use of the reduced moment I_r allows one to obtain the correct value for the dipolar integral absorption for two-dimensional models. The phenomenological model parameters ξ_V , γ' , and α were adjusted by using the best fit of experimental data. It is known that in order to describe the low-frequency dielectric relaxation in such organic glasses, one must consider anomalous diffusion and relaxation [22]. The high-frequency Poley absorption is also observed in molecular glasses in the far-infrared region (e.g., [22,34]). Figure 8 indicates that our generalized Fröhlich model explains qualitatively the main features of the *whole* broadband (0–THz) dielectric loss spectrum of the CH_2Cl_2 /decalin solution, in contrast to the normal diffusion in a periodic potential (curve 2), which cannot explain the anomalous dielectric relaxation behavior at low frequencies. One can also see in Fig. 8 that the low-frequency part of the loss spectrum $\hat{\chi}''(\omega)$, which may be approximated by the modified Debye (Cole-Cole) equation

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{1 + (i\omega/\omega_R)^{2-\alpha}}, \quad (43)$$

is also explained by the generalized Fröhlich model.

We remark that all the above results are obtained by using the Barkai-Silbey [12] fractional form of the Klein-Kramers

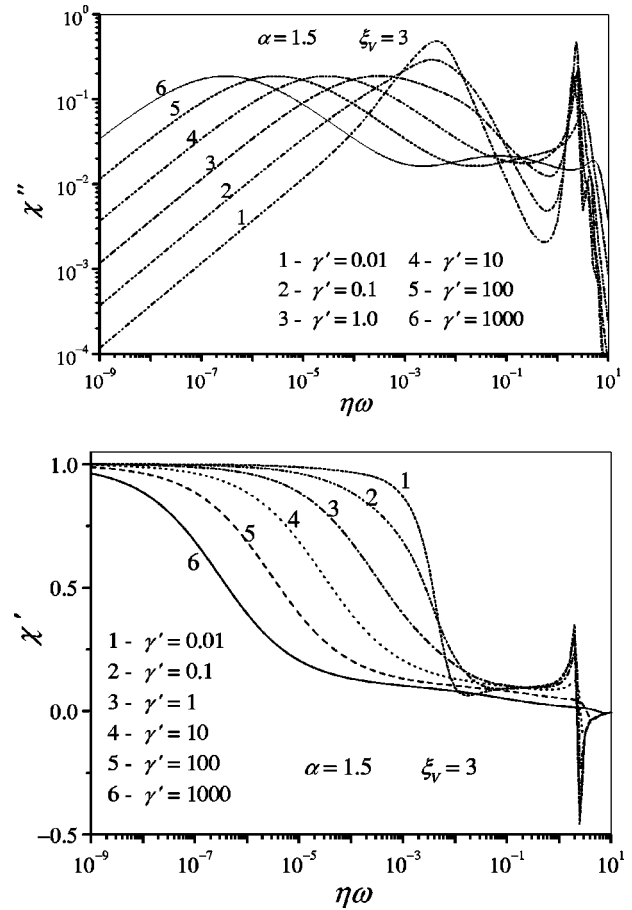


FIG. 5. Real and imaginary parts of the complex susceptibility $\chi(\eta\omega)$ vs normalized frequency $\eta\omega$ for $\alpha=1.5$ and $\xi_V=3$ and various values of the friction parameter γ' .

equation for the evolution of the probability distribution function in phase space. In that equation, the fractional derivative, or memory term, acts only on the right hand side, that is, on the diffusion or dissipative term. Thus, the form of the Liouville operator, or convective derivative is preserved [cf. the right-hand side of Eq. (15)]. Thus, Eq. (15) has the conventional form of a Boltzmann equation for the single particle distribution function. The preservation of the Liouville operator is equivalent to stating that the Newtonian form of the equations of motion underlying the Klein-Kramers equation is preserved. Thus, the high-frequency behavior is entirely controlled by the inertia of the system and does not depend on the anomalous exponent. Consequently, the fundamental sum rule for the dipole integral absorption of single axis rotators is satisfied, ensuring a return to transparency at high frequencies as demanded on physical grounds. These conclusions have been verified by solving the Barkai-Silbey equation for the simple problem of the dielectric relaxation of an assembly of noninteracting dipoles following the removal of a constant field [10]. That equation is simply Eq. (15) in the absence of an external potential.

At this stage, it is appropriate to mention yet another generalization to fractional dynamics of the Klein-Kramers equation, which has been proposed in Refs. [35], [36], and in a modified form in [37]. Here, unlike Eq. (15), the fractional

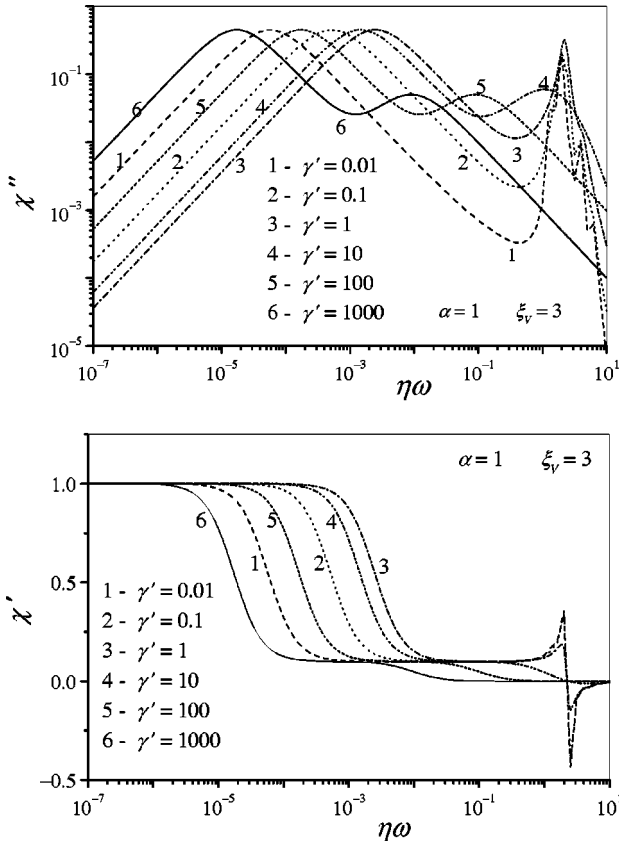


FIG. 6. The same as Fig. 4 for $\alpha=1.0$.

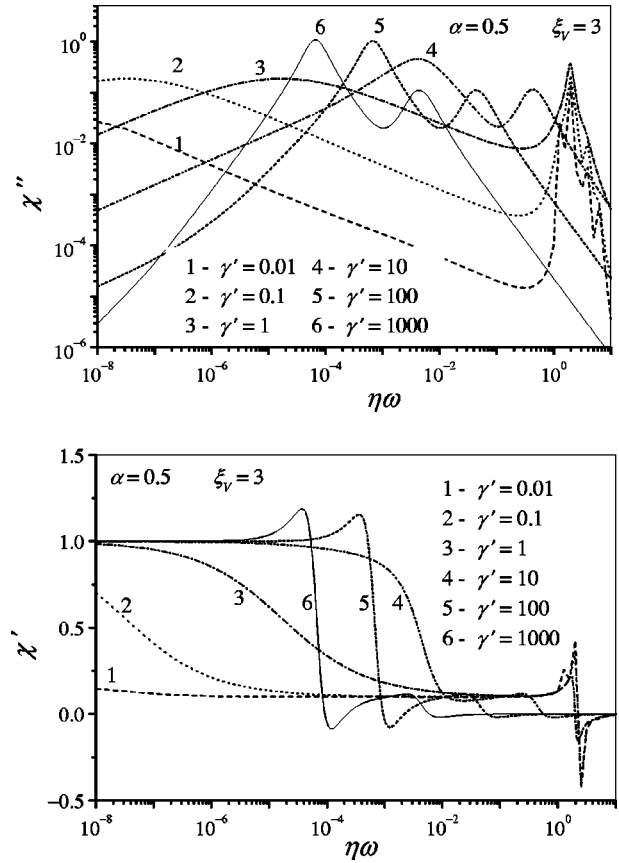


FIG. 7. The same as Fig. 4 for $\alpha=0.5$.

derivative acts on the convective as well as the diffusive terms in the normal Klein-Kramers equation. This equation, in the notation of Eq. (15), reads

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha} \tau^{1-\alpha} \left\{ -\theta \frac{\partial W}{\partial \theta} + NV_0 \sin N\theta \frac{\partial W}{I \partial \theta} + \beta \left[\frac{\partial}{\partial \theta} (\theta W) + \frac{kT}{I} \frac{\partial^2 W}{\partial \theta^2} \right] \right\}. \quad (44)$$

Equation (44) may also be solved exactly [38] in terms of a scalar continued fraction just like Eq. (15) for the complex susceptibility of an assembly of noninteracting dipoles. However, the complex susceptibility so rendered does not satisfy the Gordon sum rule, the absorption coefficient $\omega \chi''(\omega)$ showing a marked divergence at high frequencies as ω increases [38]. Thus, the high-frequency behavior of the dielectric susceptibility predicted by Eq. (44) is physically unacceptable, unlike that predicted by the Barkai-Silbey equation. The root of the problem appears to be the supposition that the fractional derivative, or memory function, acts on the convective terms. If it is allowed to act on these terms, then the high-frequency behavior is no longer entirely inertia

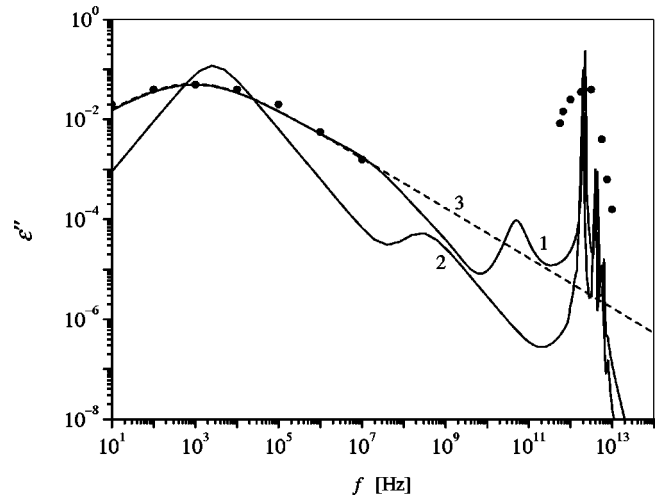


FIG. 8. Broadband dielectric loss spectrum of 10% (vol/vol) solution of probe molecule CH_2Cl_2 in glassy decalin at 110 K. Symbols are the experimental data [34]. Curve 1 is the best fit for the anomalous diffusion in the double-well cosine potential ($\alpha=1.5$, $\xi_V=8$, and $\gamma=0.003$); curve 2 is the best fit for the normal diffusion ($\alpha=1$, $\xi_V=7$, and $\gamma=0.001$) in the double-well cosine potential; filled circles are the noninertial Eq. (43). The dashed line (3) is the Cole-Cole equation (43).

controlled; it depends on the dissipation through the anomalous exponent, with the result that the Gordon sum rules are violated, and infinite absorption ensues. This is the reason for the use of the Barkai-Silbey equation. We also remark that the Barkai-Silbey equation was originally given for subdiffusion in velocity space ($\alpha < 1$), or for enhanced diffusion in configuration space ($\sigma > 1$). However, the most interesting case is subdiffusion in configuration space, corresponding to the Cole-Cole equation in dielectric theory. This suggests extending the Barkai-Silbey equation to *enhanced* diffusion in velocity space, corresponding to *subdiffusion* in configuration space, since $\sigma = 2 - \alpha$. The justification for doing this is simply that this generalization yields physically meaningful results for the broadband spectrum of the complex susceptibility $\hat{\chi}(\omega)$, as well as yielding the Cole-Cole equation in the limit $\gamma \rightarrow 0$. It is also apparent that the Barkai-Silbey equation must have its origin in a Lévy (rather than a purely fractal) time random walk [36], as unlike Eq. (44) it does not separate into temporal and spatial parts. Moreover, the exponential decay of the normal diffusion theory is not replaced by a Mittag-Leffler function, as in a fractal time random walk [36]. Such behavior is indicative of coupling between the jump length probability distribution and the waiting time probability distribution, that is, the jump length and waiting time are not independent random variables.

Concerning the previous paragraph, we remark that a general characteristic of the systems we have treated is that they

are nonlocal in both space and time and so give rise to anomalous diffusion [39]. The generalized Fröhlich model we have outlined incorporates both resonance and relaxation behavior and so may simultaneously explain both the anomalous relaxation (low-frequency) and far-infrared absorption spectra of complex dipolar systems. Moreover, a third mid-frequency relaxation band may appear in the dielectric loss spectra at low temperatures due to intrawell relaxation modes. The present calculation also constitutes an example of the solution of the fractional Klein-Kramers equation for anomalous diffusion in a periodic potential and is to our knowledge the first example of such a solution. The approach, which is grounded in a theorem [29] of operational calculus generalized to fractional exponents [39] and continued fraction methods, clearly indicates how many existing results of the classical theory of Brownian motion in a potential may be extended to fractional dynamics.

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