

Microscopic models for dielectric relaxation in disordered systems

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It is shown how the Debye rotational diffusion model of dielectric relaxation of polar molecules (which may be described in microscopic fashion as the diffusion limit of a discrete time random walk on the surface of the unit sphere) may be extended to yield the empirical Havriliak-Negami (HN) equation of anomalous dielectric relaxation from a microscopic model based on a kinetic equation just as in the Debye model. This kinetic equation is obtained by means of a generalization of the noninertial Fokker-Planck equation of conventional Brownian motion (generally known as the Smoluchowski equation) to fractional kinetics governed by the HN relaxation mechanism. For the simple case of noninteracting dipoles it may be solved by Fourier transform techniques to yield the Green function and the complex dielectric susceptibility corresponding to the HN anomalous relaxation mechanism.

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I. INTRODUCTION

One of the most striking features of the dielectric relaxation of disordered materials such as glass-forming liquids and amorphous polymers is the failure of the Debye [1,2] theory of dielectric relaxation to adequately describe the low-frequency spectrum, where the relaxation behavior may deviate considerably from the exponential (Debye) pattern and is characterized by a broad distribution of relaxation times. Such behavior has been given the title *anomalous dielectric relaxation* and was first systematically described in the pioneering paper [3] of Cole and Cole in 1941 on dielectric relaxation in polar liquids. These and subsequent investigators have proposed [4,5] (see also [6]) various empirical formulas describing the departure from the Debye behavior. In specific terms, the normal Debye relaxation process is characterized by a complex susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ of the form

$$\chi(\omega) = \frac{\chi_0}{1 + i\omega\tau}, \quad (1)$$

where χ_0 is the static susceptibility and τ is a characteristic relaxation time known in the present context as the Debye relaxation time. Equation (1) adequately describes the low-frequency behavior of the observed complex susceptibility of many simple polar liquids.

Equation (1) may be derived using a variety of microscopic models of the relaxation process. For example Debye [1,2] derived Eq. (1) by considering the rotational Brownian motion (excluding the inertial effects) of an assembly of

electrically noninteracting dipoles. We shall term this model the first Debye model. This model applies when one has (1) a dilute solution of dipolar molecules in a nonpolar liquid; (2) axially symmetric molecules; and (3) isotropy of the liquid, even on an atomic scale in the time average over a time interval small compared with the Debye relaxation time τ .

Debye proceeded by extending Einstein's treatment of the translational Brownian motion to rotational Brownian motion of noninteracting permanent dipoles in the presence of an external time-varying field and solving the appropriate Fokker-Planck equation. Here that equation is the Smoluchowski equation, which is an approximate Fokker-Planck equation [7] in the space of angular coordinates for the distribution function of the orientations of the dipoles on the surface of the unit sphere when the influence of the inertia of the molecules on the relaxation process is ignored. The Debye method then yields the mean dipole moment in the direction of the applied field and the complex susceptibility $\chi(\omega)$, Eq. (1). The Smoluchowski equation applies [8] to strong dissipative coupling to the bath so that the first Debye model always contains the assumption that the dipolar molecule is bound so strongly to the surrounding molecules that large jumps of the dipole direction are extremely unlikely. This behavior according to Fröhlich [8] may be true in a number of cases but others may exist in which the opposite (large jumps) is much more likely. A dipolar molecule will then [8] make many jumps over the potential barrier separating it from another dipole direction during the time required for an appreciable change in direction by viscous flow. Clearly, such behavior holds for solids where flow may be considered as entirely absent; however, it may also be ex-

pected where the viscosity is so high that flow is practically negligible. In liquids it might also happen that the motion which prevails is different for different kinds of dissolved molecules. Moreover, both large and small jump transitions may exist simultaneously.

The above observations lead us to the second microscopic model considered by Debye [2] (and much extended by Fröhlich [8]), which is a Poisson-like process, where relaxation occurs due to the crossing by large jumps of rare members of an assembly of dipoles over an internal potential barrier in a solid due to the shuttling action of thermal agitation. This microscopic model also produces a relaxation spectrum of the form of Eq. (1); however, the overbarrier relaxation time has Arrhenius-like behavior as it depends exponentially on the height of the potential barrier. The Debye-Fröhlich model also constitutes a rotational Brownian motion model based on the Fokker-Planck or Langevin equations, as is apparent by considering a continuous distribution of orientations [7] and a double- (multiwell) potential rather than the discrete orientation approximation treated by Debye and Fröhlich. It should be noted that if a continuous distribution of orientations is used then the prefactor of the exponential in the overbarrier relaxation time depends strongly on the dissipative coupling to the heat bath and the shape of the potential, as emphasized by Kramers [9] in his famous study of the escape of particles over potential barriers due to the shuttling action of thermal agitation. Moreover, the use of the Fokker-Planck equation allows one to account for the contribution of the fast decays in the wells of the potential to the relaxation process.

The Debye-Fröhlich model is also very useful as a picture of the solid-state-like process of reversal (i.e., longitudinal or Néel relaxation) of the magnetization in fine single domain ferromagnetic nanoparticles possessing an internal potential barrier due to their inherent magnetocrystalline anisotropy [7]. In this context, taking into account the intrinsic differences between dielectric and magnetic relaxation, the model is known as the Néel-Brown model [10–13] of magnetic relaxation. If, on the other hand, the model is applied to the longitudinal dielectric relaxation of nematic liquid crystals, it is known as the Maier-Saupe model [7].

Thus the Debye equation (1) may be satisfactorily explained in terms of the thermal fluctuations of an assembly of dipoles embedded in a heat bath giving rise to rotational Brownian motion described by the Fokker-Planck or Langevin equations. The advantage of a formulation in terms of the Brownian motion is that the kinetic equations of that theory may be used to extend the Debye calculation to more complicated situations [7] involving the inertial effects of the molecules and interactions between the molecules. Moreover, the microscopic mechanisms underlying the Debye behavior may be clearly understood in terms of the diffusion limit of a discrete time random walk on the surface of the unit sphere.

Returning to anomalous dielectric relaxation, it appears that a significant amount of experimental data on disordered systems supports the following empirical expressions for dielectric loss spectra, namely, the Cole-Cole equation [6]

$$\chi(\omega) = \frac{\chi_0}{1 + (i\omega\tau)^\sigma}, \quad 0 < \sigma \leq 1, \quad (2)$$

the Cole-Davidson equation

$$\chi(\omega) = \frac{\chi_0}{(1 + i\omega\tau)^\nu}, \quad 0 < \nu \leq 1, \quad (3)$$

and the Havriliak-Negami equation

$$\chi(\omega) = \frac{\chi_0}{[1 + (i\omega\tau)^\sigma]^\nu}, \quad 0 < \sigma \leq 1, \quad 0 < \nu \leq 1, \quad (4)$$

which is a combination of the Cole-Cole and Cole-Davidson equations. Each of the above equations by use of the superposition principle exhibits a broad distribution of relaxation times [6,8]. In the notation of Fröhlich [8], we have

$$\chi(\omega) = \int_0^\infty \frac{f(T)dT}{1 + i\omega T}. \quad (5)$$

The equation is the mathematical expression [6] of the idea that the dielectric behaves as a collection of individual components, each being described by a Debye equation with relaxation time T ; $f(T)$ is the relaxation time distribution function. In both Cole-Cole and Cole-Davidson relaxation mechanisms, unlike the Debye equation, where the distribution function is a δ function, the relaxation time distribution (first evaluated for the Cole-Cole relaxation by Cole and Cole [3]) exhibits long time tails [e.g., Eqs. (3.104) and (3.105) of Ref. [6]] typical of Lévy probability distributions. This observation has been formalized for Cole-Cole relaxation by Glöckle and Nonnenmacher in Ref. [14].

Returning to Eqs. (2) and (4), the Cole-Cole parameter σ is a *broadening* parameter as the curve of $\chi''(\omega)$ versus ω broadens as σ is reduced. On the other hand, the Cole-Davidson parameter ν in Eqs. (3) and (4) is a *skewing* parameter, as in the Cole-Cole plot of $\chi''(\omega)$ versus $\chi'(\omega)$ the circular arc characteristic of the Debye equation is shifted toward the low-frequency end of the spectrum [6]. An explanation of this behavior is the ν -fold degeneracy induced in the Debye equation (1) by the Cole-Davidson parameter ν , causing the simple pole $-1/\tau$ of the Debye equation to become a branch point of order ν , i.e., a ν -fold degenerate eigenvalue.

As far as the physical mechanism underlying the Cole-Cole equation is concerned, we first remark that Eq. (2) arises from the diffusion limit of a *continuous* time random walk [15]. In this context one should recall that the Einstein theory of the Brownian motion relies on the diffusion limit of a *discrete* time random walk. Here the random walker makes a jump of a fixed mean square length in a fixed time, so that the only random variable is the direction of the walker, leading automatically by means of the central limit theorem (in the limit of a large sequence of jumps) to the Wiener process describing the Brownian motion [7]. The continuous time random walk (CTRW), on the other hand, was introduced by Montroll and Weiss [16] as a way of rendering time continuous in a random walk without necessarily appealing to the diffusion limit. In the most general case of the CTRW, the random walker may jump an arbitrary length in arbitrary

time. However, the jump length and jump time random variables are not statistically independent [17–20]. In other words, a given jump length is penalized by a time cost, and vice versa. A simple case of the CTRW arises when one assumes that the jump length and jump time random variables are decoupled and that the jump length variances are always finite (so that the central limit theorem applies in the limit of a large sequence of jump lengths [7]); however, the jump times may be arbitrarily long so that they obey a Lévy distribution with its characteristic long tail [17–21]. Thus the jump length distribution ultimately becomes Gaussian with finite jump length variance, while the mean waiting time between jumps diverges on account of the underlying Lévy waiting time distribution. Such walks, which possess a discrete hierarchy of time scales [22], not all of which have the same probability of occurrence, are known [18] as *fractal time random walks*. In the limit of a large sequence of jump times, they give rise [15,17] to a fractional Fokker-Planck equation in configuration space. If this equation is now adapted to rotational Brownian motion as used by Debye [1,2] for the normal Fokker-Planck equation in his first model, then the Cole-Cole equation (2) automatically follows [7,21]. Inertial effects have also been included in the model [23].

The second model of Debye or the Debye-Fröhlich model may also be generalized to fractional diffusion [7,24] (including inertial effects [25]). Moreover, it has been shown [24] that the Cole-Cole equation arises naturally from the solution of a fractional Fokker-Planck equation in the configuration space of orientations derived from the diffusion limit of a CTRW. The broadening of the dielectric loss curve characteristic of the Cole-Cole spectrum may then be easily explained on a microscopic level by means of the relation [7,24]

$$\lambda_{p,\sigma} = \lambda_p \tau^{1-\sigma} \quad (6)$$

between the eigenvalues $\lambda_{p,\sigma}$ and λ_p of the fractional and normal configuration space Fokker-Planck equations, respectively. Here the relaxation behavior appears [7] as a superposition of Cole-Cole equations if the inertial effects are ignored. The fractal time random walk picture, whereby a particle is trapped in a given configuration for an arbitrarily long period before executing a jump [7,15], immediately suggests that the Cole-Cole parameter σ (here the fractal dimension of the set of waiting times between jumps) arises from the anisotropy of the material on a microscopic scale. Thus assumption 3 underpinning the Debye theory breaks down for Cole-Cole relaxation. The microscopic anisotropy gives rise to a distribution of microscopic potential barrier heights [22] which in turn, because the individual jump probabilities are a hierarchy of Poisson processes [18], give rise to a hierarchy of relaxation times not all of which have the same probability of occurrence. Such models are usually known as random activation energy models (see Ref. [19], p. 280). They appear to be consistent with the concept of a distribution of microscopic Debye-like mechanisms embodied in Eq. (5) and the Lévy-like behavior [Ref. [6], Eqs. (3.104) and (3.105)] of the various relaxation time distributions and with the breakdown in anomalous relaxation of

Einstein's ansatz [7,15,20] that in Brownian motion the random walker executes a discrete jump of finite mean square length in an average time τ .

Here we demonstrate how both the Cole-Davidson and Havriliak-Negami (HN) anomalous behaviors may be embodied, just like the Cole-Cole behavior, in a fractional generalization of the Fokker-Planck equation in configuration space for the first Debye model of nonelectrically interacting dipoles. In what follows, we shall use a cumulant expansion originally given by Nigmatullin and Ryabov [26] who proposed a phenomenological fractional ordinary differential equation describing the Cole-Davidson behavior. In addition, we shall demonstrate how the aftereffect function [7] following the removal of a small constant field may be given for the HN model in terms of a Fox H function [27] extrapolating between the stretched exponential (Kohlrausch-Williams-Watts) law [cf. Eq. (34) below] at short times and the inverse long time tail power law [cf. Eq. (35) below] at long times [17]. The Debye relaxation time in this case [19] plays the role of a time scale demarking the transition from a stretched exponential law to a power law. In Cole-Cole relaxation, the Fox H function reduces to the well-known Mittag-Leffler function [17].

II. FRACTIONAL FOKKER-PLANCK EQUATIONS

In order to generalize the normal Fokker-Planck equation excluding inertial effects to fractional diffusion, we first recall the general form of that equation in operator representation [28],

$$\frac{\partial W(\mathbf{x},t)}{\partial t} + L_{FP}W(\mathbf{x},t) = 0, \quad t > 0, \quad W(\mathbf{x},0) = W_0(\mathbf{x}), \quad (7)$$

where $W(\mathbf{x},t)$ is the probability density (distribution) function of a variable \mathbf{x} and L_{FP} is the Fokker-Planck operator. Equation (7) can equivalently be rewritten as an equation for an impulse response so that the initial condition appears as the amplitude of a forcing function $\delta(t)$, viz. [29],

$$\frac{\partial \bar{W}(\mathbf{x},t)}{\partial t} + L_{FP}\bar{W}(\mathbf{x},t) = \delta(t)W_0(\mathbf{x}), \quad (8)$$

where $\bar{W}(\mathbf{x},t) = \theta(t)W(\mathbf{x},t)$, $\theta(t)$ is the Heaviside unit step function, and $\delta(t)$ is the Dirac delta function.

For anomalous diffusion corresponding to the Cole-Cole equation (2), the fractional Fokker-Planck equation was derived for translational motion by Metzler and Klafter [17,30] and extended to rotational motion by Coffey *et al.* [7,15,21]. Equation (8) can now be rewritten as

$$\frac{\partial}{\partial t} \bar{W}(\mathbf{x},t) + \tau^{1-\sigma} {}_0D_t^{1-\sigma} L_{FP}\bar{W}(\mathbf{x},t) = \delta(t)W_0(\mathbf{x}), \quad (9)$$

where the fractional derivative is given by the Riemann-Liouville definition

$${}_0D_t^{-\sigma}[f(t)] = \frac{1}{\Gamma(\sigma)} \int_0^t \frac{f(\tau)d\tau}{(t-\tau)^{1-\sigma}}, \quad (10)$$

and $\Gamma(z)$ is the gamma function [31] [a derivation of Eq. (9) by taking the diffusion limit of a CTRW has been given in Refs. [15,17]]. Here, just as in the translational diffusion equation treated in Ref. [17], we consider subdiffusion $0 < \sigma < 1$ phenomena only ($\sigma=1$ corresponds to normal diffusion). Thus, the fractional derivative is a type of memory function with a slowly decaying power law kernel in time. Equation (9) leads to anomalous (Cole-Cole-like) behavior of the complex susceptibility [7]. 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 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, i.e., a fractal time random walk. 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 a random walk with magnification. Thus, σ measures the statistical self-similarity (or how the whole looks similar to its parts [18]) 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 [19,22] is needed. For example, a fractal time Poisson process [18] 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. [18] where a formula for σ is given and is also discussed in Ref. [19]. 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. This microscopic picture 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. Equation (9) may be written in an equivalent form as [17,19]

$$\tau^\sigma {}_0D_t^\sigma \bar{W}(\mathbf{x}, t) + \tau L_{FP} \bar{W}(\mathbf{x}, t) = \frac{(t/\tau)^{-\sigma}}{\Gamma(1-\sigma)} W_0(\mathbf{x}). \quad (11)$$

Equations (9) and (11) and are fractional analogs of the conventional Fokker-Planck equation (8) giving rise to the Cole-Cole anomalous behavior [7,17].

Another approach to fractionalizing the Fokker-Planck equation so as to incorporate Cole-Davidson behavior can now be written by extending a hypothesis of Nigmatullin and Ryabov [26]. They noted that the ordinary first-order differential equation describing an exponential decay

$$\frac{d}{dt}f(t) + \Omega_0 f(t) = 0$$

with initial condition $f(t)|_{t=0}=f(0)$ may be written as an equation for an impulse response, viz.,

$$e^{-\Omega_0 t} \frac{d}{dt} e^{\Omega_0 t} \theta(t) f(t) = f(0) \delta(t), \quad (12)$$

which in turn may be written as [recalling that the derivative of the step function is the Dirac delta function $\partial_t \theta(-t) = -\delta(t)$ [29]]

$$e^{-\Omega_0 t} \frac{d}{dt} \{e^{\Omega_0 t} [\theta(t) f(t) + \theta(-t) f(0)]\} = \theta(-t) \Omega_0 f(0). \quad (13)$$

In order to obtain in heuristic fashion a fractional analog of Eq. (13), one may simply replace the ordinary derivative by a fractional derivative [26], so that Eq. (13) becomes

$$e^{-\Omega_0 t} {}_0D_t^\nu \{e^{\Omega_0 t} [\theta(t) f(t) + \theta(-t) f(0)]\} = \theta(-t) \Omega_0 f(0). \quad (14)$$

In the particular application to dielectric relaxation, $f(t)$ is the aftereffect function following the removal of a constant field [7]. The solution of Eq. (14) rendered in the frequency domain yields the Cole-Davidson equation (3) [26].

The approach of Nigmatullin and Ryabov [26] is, however, entirely phenomenological as no underlying kinetic equation is involved. Nevertheless, their method may also be applied to the Fokker-Planck equation (8) so that a kinetic equation, and thus a microscopic model, is involved. Indeed, we can rewrite the normal Fokker-Planck equation (8) as an equation for an impulse response in the form of the right hand side of Eq. (12), viz.,

$$e^{-L_{FP} t} \frac{\partial}{\partial t} [e^{L_{FP} t} \bar{W}(\mathbf{x}, t)] = \delta(t) W_0(\mathbf{x}). \quad (15)$$

Equation (15) assumes the form of Eq. (13), viz.,

$$e^{-L_{FP} t} \frac{\partial}{\partial t} e^{L_{FP} t} [\bar{W}(\mathbf{x}, t) + \theta(-t) W_0(\mathbf{x})] = \theta(-t) L_{FP} W_0(\mathbf{x}). \quad (16)$$

For the purpose of using a kinetic equation incorporating the Cole-Davidson mechanism according to the heuristic procedure of Nigmatullin and Ryabov [26], we may replace the partial time derivative in Eq. (16) by a fractional time derivative ${}_0D_t^\nu$. Thus Eq. (16) becomes [cf. Eq. (14)]

$$\tau^{\nu-1} e^{-L_{FP} t} {}_0D_t^\nu e^{L_{FP} t} [\bar{W}(\mathbf{x}, t) + \theta(-t) W_0(\mathbf{x})] = \theta(-t) L_{FP} W_0(\mathbf{x}). \quad (17)$$

Next we recall the cumulant operator expansion for the operator $e^{-B} A e^B$, namely [26],

$$e^{-B} A e^B = A + \frac{[A, B]}{1!} + \frac{[[A, B], B]}{2!} + \dots$$

This expansion allows one to represent Eq. (17) as the series of operators

$$\tau^{\nu-1} \left({}_0D_t^\nu + \frac{[{}_0D_t^\nu, L_{FP}t]}{1!} + \frac{[[{}_0D_t^\nu, L_{FP}t], L_{FP}t]}{2!} + \dots \right) \times [\bar{W} + \theta(-t)W_0] = \theta(-t)L_{FP}W_0. \quad (18)$$

This series can be simplified by using the relationship between fractional derivatives [31]

$${}_0D_t^\nu[tf(t)] - t {}_0D_t^\nu[f(t)] = \nu {}_0D_t^{\nu-1}[f(t)].$$

Thus Eq. (18) reduces to

$$\tau^{\nu-1} \left({}_0D_t^\nu + \frac{\nu L_{FP} {}_0D_t^{\nu-1}}{1!} + \frac{\nu(\nu-1)L_{FP}^2 {}_0D_t^{\nu-2}}{2!} + \dots \right) \times [\bar{W} + \theta(-t)W_0] = \theta(-t)L_{FP}W_0,$$

which in turn assumes the shifted fractional differential operator form, viz.,

$$(\tau {}_0D_t^\nu + \tau L_{FP})^\nu [\bar{W}(\mathbf{x}, t) + \theta(-t)W_0(\mathbf{x})] = \tau \theta(-t)L_{FP}W_0(\mathbf{x}). \quad (19)$$

Here we have recalled the binomial expansion

$$(a+b)^\nu = \sum_{n=0}^{\infty} \frac{(-1)^n (-\nu)_n}{n!} a^{\nu-n} b^n, \quad (20)$$

where $(a)_n = \Gamma(n+a)/\Gamma(a)$ is a Pochhammer symbol [32]. Equation (19) represents the generalization (by *heuristic reasoning*) of the normal Fokker-Planck equation to anomalous diffusion governed by a Cole-Davidson relaxation mechanism.

In like manner, combining the ideas embodied in the fractional diffusion Eq. (11) describing Cole-Cole relaxation and Eq. (17) describing Cole-Davidson relaxation, we may introduce the fractional kinetic equation

$$[\tau^\sigma {}_0D_t^\sigma + \tau L_{FP}]^\nu [\bar{W}(\mathbf{x}, t) + \theta(-t)W_0(\mathbf{x})] = \tau \theta(-t)L_{FP}W_0(\mathbf{x}). \quad (21)$$

For two particular cases $\nu=1$, $0 < \sigma < 1$ and $\sigma=1$, $0 < \nu < 1$, Eq. (21) reduces to Eqs. (11) and (19), respectively. Equation (21) represents a fractional generalization of the normal Fokker-Planck equation incorporating the HN relaxation mechanism. Thus in any model described by a Fokker-Planck equation the effect of the HN mechanism on the normal diffusion response may be included by solving Eq. (21). It allows one to generalize both the original Debye model and the Debye-Fröhlich model to include this relaxation mechanism. In the particular case of the first Debye model, namely, an assembly of noninteracting dipoles, Eq. (21) will yield the simple HN Eq. (4) as demonstrated in Sec. IV.

III. GREEN FUNCTIONS FOR ROTATIONAL MOTION IN PLANE

In order to demonstrate how the anomalous relaxation behavior described by the hitherto empirical Eqs. (2)–(4) may be obtained from our fractional generalizations of the Fokker-Planck equation in configuration space (in effect,

fractional Smoluchowski equations), Eq. (21), we first consider the fractional rotational motion of a fixed axis rotator [1], which for the normal diffusion is the first Debye model. Here a typical member of the assembly is a rigid dipole of moment μ rotating about a fixed axis through its center. The orientation of the dipole is specified by the angular coordinate ϕ (the azimuth) constituting a system of one rotational degree of freedom. Electrical interactions between the dipoles are ignored. The normal Fokker-Planck equation for the time evolution of the probability density function $W(\phi, t)$ on the unit circle in configuration space is then

$$\frac{\partial}{\partial t} W(\phi, t) + L_{FP}W(\phi, t) = 0, \quad W(\phi, 0) = W_0(\phi), \quad (22)$$

where the Fokker-Planck operator is defined as

$$L_{FP}W = -\tau^{-1} \left[\frac{1}{kT} \frac{\partial}{\partial \phi} \left(W \frac{\partial}{\partial \phi} V \right) + \frac{\partial^2}{\partial \phi^2} W \right]. \quad (23)$$

Here τ is the intertrapping time scale, which is identified with the Debye or free diffusion relaxation time $\tau = \zeta/(kT)$, where ζ is the viscous drag coefficient of a dipole (at ambient temperatures, τ is of the order 10^{-11} s for molecular liquids and solutions), and V is the potential arising from an external applied electric field. In the absence of external fields the Fokker-Planck operator becomes

$$L_{FP} = -\tau^{-1} \frac{\partial^2}{\partial \phi^2}. \quad (24)$$

Equation (21) thus becomes

$$[\tau^\sigma {}_0D_t^\sigma + \tau L_{FP}]^\nu [\bar{W}(\phi, t) + \theta(-t)W_0(\phi)] = \tau \theta(-t)L_{FP}W_0(\phi). \quad (25)$$

Here we wish to obtain the aftereffect solution for an assembly of fixed axis rotators. Recalling that for rotation the probability density function must be periodic in ϕ , we expand $\bar{W}(\phi, t)$ in the Fourier series

$$\bar{W}(\phi, t) = \theta(t) \sum_{p=-\infty}^{\infty} f_p(t) e^{ip\phi}. \quad (26)$$

Moreover, W must be real so that the Fourier coefficient $f_p(t)$, which is the characteristic function of W must satisfy $f_{-p}(t) = f_p^*(t)$, where the asterisk denotes the complex conjugate. Substitution of Eq. (26) into Eq. (19) now yields

$$\sum_{n=0}^{\infty} \frac{(-1)^n (-\nu)_n}{n!} p^{2n} \tau^{\sigma\nu-n} {}_0D_t^{\sigma\nu-n} [\theta(t)f_p(t) + f_p(0)\theta(-t)] = p^2 \theta(-t)f_p(0). \quad (27)$$

Here we have noted Eq. (20) and

$$L_{FP}e^{ip\phi} = -\tau^{-1} \frac{\partial^2}{\partial \phi^2} e^{ip\phi} = \tau^{-1} p^2 e^{ip\phi},$$

$$L_{FP}^\nu \bar{W}(\phi, t) = \theta(t) \tau^{-\nu} \sum_{p=-\infty}^{\infty} f_p(t) p^{2\nu} e^{ip\phi}, \quad (28)$$

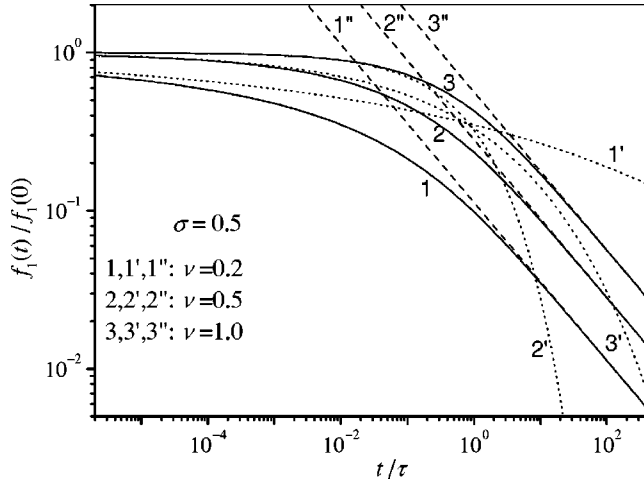


FIG. 1. $f_1(t)/f_1(0)$ as a function of t/τ for $\sigma=0.5$ and different values of ν [Eq. (A4), solid line] with the short [Eq. (34), dotted lines] and long [Eq. (35), dashed lines] time asymptotes.

$$W_0(\phi) = \sum_{p=-\infty}^{\infty} f_p(0) e^{ip\phi}. \quad (29)$$

By using the integration theorem [31] of two-sided Fourier transformations generalized to fractional calculus [31], viz.,

$$F\{ {}_0D_t^\alpha \theta(t) f(t) \} = (i\omega)^\alpha \tilde{f}(\omega), \quad (30)$$

where

$$\tilde{f}(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} \theta(t) f(t) dt = \int_0^{\infty} e^{-i\omega t} f(t) dt,$$

with inverse

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} \tilde{f}(\omega) d\omega,$$

we have from Eq. (27)

$$\left[\tilde{f}_p(\omega) - \frac{f_p(0)}{i\omega} \right] \sum_{n=0}^{\infty} \frac{(-1)^n (-\nu)_n}{n!} p^{2n} (i\omega\tau)^{\sigma\nu-n} = -\frac{p^2}{i\omega} f_p(0). \quad (31)$$

Using Eq. (20), Eq. (31) can be further rearranged as

$$[f_p(0) - i\omega \tilde{f}_p(\omega)] [p^2 + (i\omega\tau)^\sigma]^\nu = p^2 f_p(0). \quad (32)$$

Here we have also recalled that $D_t^{\nu-n} \theta(-t) = -D_t^{\nu-n-1} \delta(t)$. We remark that posing the problem of the step-off solution in terms of an impulse response in the time domain with the initial conditions regarded as the amplitude of the impulse has enabled us to obtain the solution in a very simple way using the generalized Fourier integration theorem Eq. (30), which unlike the corresponding generalized Laplace transform integration theorem [31] does not involve the initial conditions. The same result may, however, be obtained with the help of the Laplace transform if we rearrange Eq. (21) as an equation for the time dependent part of the distribution function only, so that initial conditions are not involved.

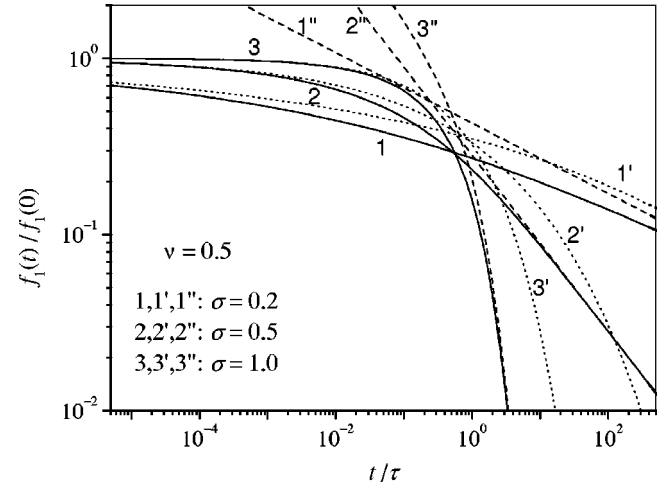


FIG. 2. $f_1(t)/f_1(0)$ as a function of t/τ for $\nu=0.5$ and different values of σ [Eq. (A4), solid line] with the short [Eq. (34), dotted lines] and long [Eqs. (35) (for $\sigma=0.2$ and 0.5) and (36) (for $\sigma=1$), dashed lines] time asymptotes.

Inverting Eq. (32), we have for the inverse Fourier transform over ω (see the Appendix)

$$\frac{f_p(t)}{f_p(0)} = 1 - \frac{p^{2(1-\nu)}}{\Gamma(\nu)} H_{1,2}^{1,1} \left(p^2 (t/\tau)^\sigma \left| \begin{matrix} (1,1) \\ (\nu,1), (0,\sigma) \end{matrix} \right. \right), \quad (33)$$

where $H_{1,2}^{1,1}$ is the Fox H function [27]. The function $f_p(t)/f_p(0)$ has initially ($t \ll \tau$) the stretched exponential form

$$\frac{f_p(t)}{f_p(0)} \sim e^{-p^2 (t/\tau)^{\sigma\nu/\Gamma(1+\nu\sigma)}}. \quad (34)$$

In contrast, at long times ($t \gg \tau$), it has the inverse power law behavior

$$\frac{f_p(t)}{f_p(0)} \sim 1 - p^{2(1-\nu)} + \frac{\Gamma(\nu+1)(t/\tau)^{-\sigma}}{p^{2\nu}\Gamma(\nu)\Gamma(1-\sigma)}. \quad (35)$$

The behavior of $f_p(t)/f_p(0)$ for $p=1$ is shown in Figs. 1 and 2 for various values of σ and ν ; the asymptotes Eqs. (34) and (35) are also shown in these figures for comparison. For pure Cole-Davidson relaxation, where $\sigma=1$ (see Fig. 2), the following asymptote must be used instead of Eq. (35):

$$\frac{f_1(t)}{f_1(0)} \sim \frac{e^{-t/\tau} (t/\tau)^{\nu-1}}{\Gamma(\nu)}, \quad (36)$$

as this is the correct asymptote for the incomplete Gamma function (see below). Thus the decay of $f_1(t)/f_1(0)$ is essentially exponential in the limit of long times in Cole-Davidson relaxation. Thus it is apparent from Eqs. (35) and (36) that the origin of the long time tail is the parameter σ , which is ultimately due to the trapping effects inherent in the fractal time random walk, i.e., the microscopic disorder. As far as the short time behavior Eq. (34) is concerned, the role of ν is to enhance the stretched exponential behavior for given σ .

If the initial distribution function is a δ function, viz., $W_0(\phi) = \delta(\phi - \phi_0)$, the solution (Green function) is given by

$$W(\phi, t | \phi_0, 0) = \frac{1}{2\pi} \sum_{p=-\infty}^{\infty} \left[1 - \frac{p^{2(1-\nu)}}{\Gamma(\nu)} H_{1,2}^{1,1} \right. \\ \left. \times \left(p^2(t/\tau)^\sigma \left| \begin{matrix} (1,1) \\ (\nu,1), (0,\sigma) \end{matrix} \right| \right) \right] e^{ip(\phi-\phi_0)}, \quad t \geq 0. \quad (37)$$

Here we have noted that [29]

$$\delta(\phi) = \frac{1}{2\pi} \sum_{p=-\infty}^{\infty} e^{ip\phi}.$$

For two particular cases $\nu=1$, $0 < \sigma < 1$ (Cole-Cole relaxation mechanism) and $\sigma=1$, $0 < \nu < 1$ (Cole-Davidson relaxation mechanism), Eq. (37) can be considerably simplified. Here Eq. (37) becomes, respectively (see the Appendix),

$$W(\phi, t | \phi_0, 0) = \frac{1}{2\pi} \sum_{p=-\infty}^{\infty} E_\sigma[-p^2(t/\tau)^\sigma] e^{ip(\phi-\phi_0)}, \quad t \geq 0, \quad (38)$$

and

$$W(\phi, t | \phi_0, 0) = \frac{1}{2\pi} \sum_{p=-\infty}^{\infty} \left[1 - \frac{p^{2(1-\nu)}}{\Gamma(\nu)} \gamma(\nu, p^2 t/\tau) \right] e^{ip(\phi-\phi_0)}, \quad t \geq 0, \quad (39)$$

where $E_\sigma(z)$ and $\gamma(a, z)$ are the Mittag-Leffler and incomplete Gamma functions, respectively, defined as [17–19,32]

$$E_\sigma(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(1+n\sigma)}, \quad (40)$$

$$\gamma(a, z) = \int_0^z t^{a-1} e^{-t} dt = \frac{1}{a} \sum_{n=0}^{\infty} \frac{(-z)^{n+a}}{(a+n)n!}. \quad (41)$$

For $\sigma=1$, Eq. (38) yields the Green function for normal rotational diffusion of a planar rotator, viz.,

$$W(\phi, t | \phi_0, 0) = \frac{1}{2\pi} \sum_{p=-\infty}^{\infty} e^{ip(\phi-\phi_0)-p^2 t/\tau}, \quad t \geq 0,$$

which, we emphasize, is periodic in ϕ . For comparison, we note the Green function $W(x, t | x_0, 0)$ for translational diffusion of a free particle along the x axis, where the diffusion equation is [7]

$$\frac{\partial W}{\partial t} = D \frac{\partial^2 W}{\partial x^2}, \quad -\infty < x < \infty.$$

In terms of characteristic functions, one has [7]

$$W(x, t | x_0, 0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\xi(x-x_0)-\xi^2 D t/2} d\xi = \frac{1}{\sqrt{4\pi D t}} e^{-(x-x_0)^2/(4Dt)}, \quad t \geq 0$$

(here the continuous ξ replaces the discrete p of the rotational case).

IV. COMPLEX SUSCEPTIBILITY

In order to calculate dielectric response functions, 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 [7,21]). Thus the initial distribution function $W(\phi, 0)$ is given by the Boltzmann distribution, viz.,

$$W(\phi, 0) = C e^{\mu E \cos \phi/(kT)} \approx \frac{1}{2\pi} \left[1 + \frac{\mu E}{kT} \cos \phi \right],$$

where C and 2π are the normalizing constants. Just as in Sec. III, one readily obtains the corresponding aftereffect solution

$$W(\phi, t) = \frac{1}{2\pi} \left\{ 1 + \frac{\mu E}{kT} f_1(t) \cos \phi \right\}, \quad (42)$$

where the aftereffect function $f_1(t)$ is given by Eq. (33) for $p=1$ with $f_1(0)=1$, namely,

$$f_1(t) = 1 - \frac{1}{\Gamma(\nu)} H_{1,2}^{1,1} \left((t/\tau)^\sigma \left| \begin{matrix} (1,1) \\ (\nu,1), (0,\sigma) \end{matrix} \right| \right). \quad (43)$$

Equation (42) allows us to readily evaluate the polarization $P(t)$, viz.,

$$P(t) = N_0 \mu \int_0^{2\pi} \cos \phi W(\phi, t) d\phi = \frac{\mu^2 N_0 E}{2kT} f_1(t) \quad (44)$$

(N_0 is the number of dipoles per unit volume), and the complex dielectric susceptibility, which is defined by linear response theory as [6,7]

$$\frac{\chi(\omega)}{\chi_0} = 1 - i\omega \tilde{f}_1(i\omega). \quad (45)$$

Thus we have the Havriliak-Negami equation

$$\frac{\chi(\omega)}{\chi_0} = \frac{1}{(1 + (i\tau\omega)^\nu)^\nu}, \quad (46)$$

where $\chi_0 = \mu^2 N_0 / (2kT)$. We remark that Eq. (46) can be obtained by extracting $f_1(t)$ from the Green function, Eq. (37), and noting the linear response theory relation [7]

$$\frac{f_1(t)}{f_1(0)} = \frac{\langle \cos \phi(0) \cos \phi(t) \rangle_0}{\langle \cos^2 \phi(0) \rangle_0}, \quad (47)$$

relating the aftereffect function to the equilibrium dipole moment autocorrelation function. Here $\langle \cdots \rangle_0$ means the equilibrium statistical average over the equilibrium distribution function $W_{eq}(\phi)$. The autocorrelation function from Eq. (47) is defined as

$$\begin{aligned} & \langle \cos \phi(0) \cos \phi(t) \rangle_0 \\ &= \int \int \cos \phi_0 \cos \phi W_{eq}(\phi) W(\phi, t | \phi_0, 0) d\phi d\phi_0. \end{aligned} \quad (48)$$

As $W_{eq}(\phi) = 1/(2\pi)$ for rotation in a plane, one can readily verify that Eqs. (45), (47), and (48) yield Eq. (46).

So far we have considered the planar rotator model. However, the above equations can be generalized as in Ref. [21] for rotation in space. Here, the space coordinate is the polar angle ϑ (the colatitude) and the Fokker-Planck operator for normal rotational diffusion assumes the form [7]

$$\begin{aligned} L_{FP}W(\vartheta, t) &= \frac{1}{2\tau \sin \vartheta} \frac{\partial}{\partial \vartheta} \\ &\times \left[\sin \vartheta \left(W(\vartheta, t) \frac{\partial}{\partial \vartheta} V(\vartheta, t) + \frac{\partial}{\partial \vartheta} W(\vartheta, t) \right) \right], \end{aligned} \quad (49)$$

where the time $\tau = \zeta/(2kT)$ is the Debye relaxation time for rotation in space, so that Eq. (21) now becomes

$$[\tau^\sigma D_t^\sigma + \tau L_{FP}]^\nu [\bar{W}(\vartheta, t) + \theta(-t)W_0(\vartheta)] = \tau \theta(-t) L_{FP}W_0(\vartheta). \quad (50)$$

By expanding $\bar{W}(\vartheta, t)$ in the Fourier series

$$\bar{W}(\vartheta, t) = \theta(t) \sum_{p=0}^{\infty} f_p(t) P_p(\cos \vartheta)$$

[$P_n(z)$ are the Legendre polynomials [32] which now constitute the appropriate basis set], Eq. (50) may be solved just as in Sec. III, to yield the corresponding results for rotation in space, viz., the aftereffect function Eq. (43) and the complex susceptibility Eq. (46), where $\chi_0 = \mu^2 N_0 / (3kT)$ and $\tau = \zeta / (2kT)$. Apparently, as in normal diffusion, the results differ from the corresponding two-dimensional analogs by only a factor of 2/3 in χ_0 and the appropriate definition of the Debye relaxation time.

V. RESULTS AND DISCUSSION

Thus we have demonstrated how the empirical Havriliak-Negami equation (4) can be obtained from a microscopic model, namely, the fractional Fokker-Planck equation (21) applied to noninteracting rotators. This model can explain the anomalous relaxation of complex dipolar systems, where the anomalous exponents σ and ν differ 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. Hence, the empirical Havriliak-Negami equation of anomalous dielectric relaxation which has been extensively used to analyze the experimental dielectric loss of disordered glassy systems (see, e.g., Refs. [33,34]) may be formulated in terms of a microscopic model just as the original Debye equation. This is essentially accomplished in the first instance by using the Debye model

and then replacing the Brownian motion collision operator (or the underlying *stosszahlansatz*) by a fractional derivative collision operator, which then allows one to write down a fractional probability density diffusion or kinetic equation in the space of orientations. The solution of this fractional kinetic equation for the first Debye model, namely, nonelectrically interacting dipoles, then leads to the HN equation in the same way as the solution of the underlying normal rotational diffusion equation yields the Debye equation (1). A complete understanding of the HN mechanism requires an understanding of the microscopic origin of the parameters σ and ν . As far as σ is concerned, this fractional exponent arises naturally from the diffusion limit of a fractal time walk [15] and may be construed as arising from a chaotic set [22] of microscopic potential barrier heights, i.e., σ has its origin in random activation energy models [19]. Further evidence for the random activation energy model concept as the generator of the Cole-Cole mechanism is provided by the recent experimental results of Fannin and Giannitis [35]. They successfully applied the Cole-Cole equation to the analysis of complex magnetic susceptibility data on ferrofluids with a distribution of particle sizes giving rise naturally to a distribution of Arrhenius-like (Néel) microscopic relaxation times. Here the volume of the particles appears explicitly in the argument of the experimental relaxation time. The particle size distribution then automatically leads to a hierarchy of Néel relaxation times. The Cole-Cole parameter σ is thus a measure of the particle size distribution. Thus our understanding of the parameter σ may be said to be reasonably complete. The same cannot, however, be said concerning our understanding of the Cole-Davidson parameter ν (although some reasons for its origin have been advanced by Nigmatulin and Ryabov [26] in their phenomenological treatment of the Cole-Davidson relaxation process). Here, unlike the Cole-Cole relaxation mechanism based on a fractal time random walk, it is not clear how the kinetic equation for the Cole-Davidson relaxation mechanism and its extension for the HN relaxation may be derived from anything other than replacing the partial time derivative in the Fokker-Planck equation by a fractional partial time derivative of order ν . This represents a gap in our understanding of the Cole-Davidson process. Despite these reservations, the model kinetic equations (17) and (21) are important as they allow one to incorporate the Cole-Davidson and HN mechanisms into the existing rigorous theory of Debye and Cole-Cole relaxation.

The kinetic equation or fractional Fokker-Planck Eq. (21) which we have proposed may be applied to a system with HN behavior in the presence of an external potential. The advantage of being in possession of a kinetic equation incorporating the HN mechanism then becomes apparent as it now possible to study the effect of the anomalous behavior on fundamental parameters associated with the Brownian motion in a potential such as the Kramers escape rate. Moreover, it is possible to generalize the Debye-Fröhlich model of relaxation over a potential barrier to incorporate the HN mechanism and so to estimate the effect of anomalous relaxation on the stochastic resonance effect [36]. Such a generalization has already been accomplished for the Cole-Cole mechanism [$\nu=1$ in Eq. (21)] in Refs. [7,24]. There it has

been shown just as in the corresponding normal diffusion problem that the overall relaxation behavior is a superposition of Cole-Cole mechanisms with the aftereffect function given by a superposition of Mittag-Leffler functions. These replace the decaying exponentials of the corresponding normal diffusion. Furthermore, the eigenvalues $\lambda_{p,\sigma}$ of the kinetic equation corresponding to the Cole-Cole relaxation process are related to those of the normal Fokker-Planck equation by Eq. (6) allowing one to determine the characteristic frequencies of the anomalous relaxation process in terms of the Kramers escape rate (approximately λ_1 for high barriers). An important result described in Ref. [24] is that the multimodal decay process may be accurately approximated in both the normal and Cole-Cole cases by a two-relaxation-mode formula, one mode arising from the over-barrier relaxation, the other from the fast near-degenerate decay modes in the wells of the potential, which may be treated as a single effective decay. Similar considerations will apply to the general fractional Eq. (21) incorporating the HN mechanism. Since Eq. (21) is linear and since the decay modes are characterized by the Fox functions rather than the Mittag-Leffler functions of the Cole-Cole relaxation, then the relaxation behavior in the HN mechanism will be governed by a superposition of Fox functions. This will lead in the frequency domain to a superposition of HN functions. We remark that in the Cole-Davidson and HN mechanisms which both involve branch points in the fractional diffusion operator the analysis of the aftereffect solution has been greatly facilitated by writing the appropriate kinetic equation as an equation for an impulse response using the properties of the unit step and δ functions. The advantage of such a formulation of the problem is that it avoids the difficulties associated with the inherent dependence of fractional derivatives on initial conditions. These difficulties are completely eliminated by considering the impulse response, which allows us to solve the problem using two-sided Fourier transforms so that the initial conditions are involved only as a forcing function.

Finally, we remark that in the context of stochastic resonance [7,36] Eqs. (2)–(4) for the complex susceptibility and their extensions to diffusion in a potential may be regarded as transfer functions [37] (Fourier transforms of the true impulse response of the system) whence the spectral density may be easily calculated using the Wiener-Khinchin theorem [37] so that the effect of anomalous diffusion on the stochastic resonance may be ascertained.

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APPENDIX: CALCULATION OF INVERSE FOURIER TRANSFORMS

For simplicity, we calculate $f_p(t)$ for $p=1$. Commencing with Eq. (32) for $p=1$, we have

$$\frac{\tilde{f}_1(i\omega)}{f_1(0)} = \frac{1}{i\omega} - \frac{1}{i\omega[1+(i\omega\tau)^\sigma]^\nu} = \frac{1}{f_1(0)} \int_0^\infty e^{-i\omega t} f_1(t) dt. \quad (\text{A1})$$

The inverse Laplace transformation yields

$$\frac{f_1(t)}{f_1(0)} = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{du}{u} e^{ut} \left[1 - \frac{1}{[1+(u\tau)^\sigma]^\nu} \right]. \quad (\text{A2})$$

The part inside the brackets in Eq. (A2) can be rearranged as follows:

$$\frac{1}{[1+(u\tau)^\sigma]^\nu} = \frac{1}{(u\tau)^{\sigma\nu}} [1+(u\tau)^{-\sigma}]^{-\nu}.$$

Using Eq. (20), we have [[30], Eqs. (6.1.22) and (15.1.1)]

$$\begin{aligned} [1+(u\tau)^{-\sigma}]^{-\nu} &= 1 - \nu(u\tau)^{-\sigma} + \frac{\nu(\nu+1)}{2!}(u\tau)^{-2\sigma} \\ &\quad - \frac{\nu(\nu+1)(\nu+2)}{3!}(u\tau)^{-3\sigma} + \dots \\ &= \sum_{n=0}^{\infty} \frac{(\nu)_n}{n!} [-(u\tau)^{-\sigma}]^n = {}_1F_0(\nu; ; -(u\tau)^{-\sigma}), \end{aligned} \quad (\text{A3})$$

where ${}_1F_0(a; ; z)$ is the hypergeometric function [31]. This equation is then substituted back into Eq. (A2) to get

$$\begin{aligned} \frac{f_1(t)}{f_1(0)} &= \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{du}{u} e^{ut} \left[1 - (u\tau)^{-\sigma\nu} \sum_{n=0}^{\infty} \frac{(\nu)_n}{n!} [-(u\tau)^{-\sigma}]^n \right] \\ &= 1 - \tau^{-\sigma\nu} \sum_{n=0}^{\infty} \frac{(\nu)_n (-\tau^{-\sigma})^n}{n!} \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{du}{u} e^{ut} u^{-\sigma n - \sigma\nu} \\ &= 1 - (t/\tau)^{\sigma\nu} \sum_{n=0}^{\infty} \frac{(\nu)_n}{n!} \frac{[-(t/\tau)^\sigma]^n}{\Gamma(1+\sigma\nu+\sigma n)}. \end{aligned} \quad (\text{A4})$$

Finally,

$$\frac{f_1(t)}{f_1(0)} = 1 - (t/\tau)^{\sigma\nu} \tilde{\phi}(\nu; \sigma, 1 + \sigma\nu; -(t/\tau)^\sigma) \quad (\text{A5})$$

where $\tilde{\phi}$ is a generalization of a Wright function [38] containing an extra Pochhammer symbol. Equation (A5) can also be expressed in terms of the Fox H function $H_{1,2}^{1,1}$, viz. [39],

$$\frac{f_1(t)}{f_1(0)} = 1 - \frac{1}{\Gamma(\nu)} H_{1,2}^{1,1} \left((t/\tau)^\sigma \left| \begin{matrix} (1,1) \\ (\nu,1), (0,\sigma) \end{matrix} \right. \right). \quad (\text{A6})$$

For $p \neq 1$, the corresponding equation is

$$\begin{aligned} \frac{f_p(t)}{f_p(0)} &= 1 - \frac{p^2(t/\tau)^{\sigma\nu}}{\Gamma(\nu)} \sum_{n=0}^{\infty} \frac{(-1)^n \Gamma(\nu+n) [p^2(t/\tau)^\sigma]^n}{\Gamma(1+\sigma\nu+\sigma n) n!} \\ &= 1 - \frac{p^{2(1-\nu)}}{\Gamma(\nu)} H_{1,2}^{1,1} \left(p^2(t/\tau)^\sigma \left| \begin{matrix} (1,1) \\ (\nu,1), (0,\sigma) \end{matrix} \right. \right). \end{aligned} \quad (\text{A7})$$

For $\nu=1$ and $\sigma=1$, the function $f_p(t)$ from Eq. (A7) reduces, respectively, to

$$\begin{aligned} \frac{f_p(t)}{f_p(0)} &= \sum_{n=0}^{\infty} \frac{[-p^2(t/\tau)^\sigma]^n}{\Gamma(1+n\sigma)} \\ &= H_{1,2}^{1,1} \left(p^2(t/\tau)^\sigma \middle| \begin{matrix} (0,1) \\ (0,1), (0,\sigma) \end{matrix} \right) = E_\sigma(-p^2(t/\tau)^\sigma) \end{aligned} \quad (\text{A8})$$

and

$$\begin{aligned} \frac{f_p(t)}{f_p(0)} &= 1 - \frac{p^{2(1-\nu)}}{\Gamma(\nu)} H_{1,2}^{1,1} \left(p^2 t/\tau \middle| \begin{matrix} (1,1) \\ (\nu,1), (0,1) \end{matrix} \right) \\ &= 1 - \frac{p^{2(1-\nu)}}{\Gamma(\nu)} \gamma(\nu, p^2 t/\tau). \end{aligned} \quad (\text{A9})$$

The Mittag-Leffler function $E_\sigma(z)$ and the incomplete Gamma function $\gamma(a, z)$ are defined by Eqs. (40) and (41); for $p=1$, the corresponding equations have been obtained in Ref. [39].

Solutions of Eq. (11), which governs the Cole-Cole mechanism, have already been given in Refs. [20,21]. Here we give separately details of the aftereffect solution for an assembly of fixed axis rotators. Thus we expand the probability density function $\bar{W}(\phi, t)$ in the Fourier series, Eq. (26) By substituting Eq. (26) into Eq. (11), applying the Fourier transformation and using Eqs. (30), we have

$$[(i\omega)^\sigma + p^2/\tau^\sigma] \tilde{f}_p(\omega) = (i\omega)^{\sigma-1} f_p(0)$$

or

$$\tilde{f}_p(\omega) = \frac{\tau(i\omega\tau)^{\sigma-1}}{(i\omega\tau)^\sigma + p^2} f_p(0). \quad (\text{A10})$$

Noting that the Laplace transform of the Mittag-Leffler function is

$$\int_0^\infty e^{-i\omega t} E_\sigma[-p^2(t/\sigma)^\sigma] dt = \frac{\tau}{i\omega\tau + p^2(i\omega\tau)^{1-\sigma}},$$

one has Eq. (A8) [7,17]. The Green function is given by Eq. (38).

In like manner for the Cole-Davidson mechanism, substitution of Eq. (26) into Eq. (19) yields

$$\begin{aligned} \sum_{n=0}^{\infty} \frac{(-1)^n \Gamma(n-\nu)}{\Gamma(n+1)\Gamma(-\nu)} p^{2n} \tau^{\nu-n} {}_0D_t^{\nu-n} [\theta(t)f_p(t) + f_p(0)\theta(-t)] \\ = \theta(-t)p^2 f_p(0). \end{aligned} \quad (\text{A11})$$

Recalling that $D_t^{\nu-n}\theta(-t) = -D_t^{\nu-n-1}\delta(t)$ and using Eq. (30), we have

$$\left[\tilde{f}_p(\omega) - \frac{f_p(0)}{i\omega} \right] \sum_{n=0}^{\infty} \frac{(-1)^n \Gamma(n-\nu)}{\Gamma(n+1)\Gamma(-\nu)} p^{2n} (i\omega\tau)^{\nu-n} = -\frac{p^2}{i\omega} f_p(0)$$

or

$$[f_p(0) - i\omega \tilde{f}_p(\omega)] (p^2 + i\omega\tau)^\nu = p^2 f_p(0). \quad (\text{A12})$$

Using the known relation

$$\int_0^\infty \gamma(\nu, ct) e^{-i\omega t} dt = \frac{\Gamma(\nu)}{i\omega(1+i\omega/c)^\nu},$$

one can readily obtain Eq. (A9).

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