

Anomalous rotational relaxation: A fractional Fokker-Planck equation approach

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(Received 11 November 2004; published 1 April 2005)

In this study we have analytically obtained the relaxation function in terms of rotational correlation functions based on Brownian motion for complex disordered systems in a stochastic framework. We found out that the rotational relaxation function has a fractional form for complex disordered systems, which indicates that relaxation has nonexponential character and obeys the Kohlrausch-William-Watts law, following the Mittag-Leffler decay.

DOI: 10.1103/PhysRevE.71.046103

PACS number(s): 02.50.-r, 05.40.-a, 02.30.-f, 76.20.+q

The relaxation for ordered systems is given by the Maxwell-Debye law [1,2] as

$$\Phi(t) = \Phi_0 \exp(-t/\tau), \quad t \geq 0. \quad (1)$$

On the other hand, relaxation in many complex disordered systems such as metallic glasses, spin glass alloys [3–6], ferroelectric crystals [7], dielectrics [8] deviates from the classical exponential Maxwell-Debye pattern and is often described in terms of the Kohlrausch-William-Watts (KWW) (i.e., stretched exponential) law [8,9],

$$\Phi(t) = \Phi_0 \exp(-t/\tau)^\alpha, \quad (2)$$

for $0 < \alpha < 1$, or by an asymptotic power law

$$\Phi(t) = \Phi_0 (1 + t/\tau)^{-n} \quad (3)$$

with $n > 0$. The relaxation functions in Eqs. (1) and (2) are commonly written in terms of the correlation functions which correspond to decay of the fluctuation of a physical quantity such as magnetization in magnetic materials or polarization in the dielectric materials.

Relaxation function has been derived using the rotational relaxation method for some system. This method has been used by Debye in the context of dielectric relaxation of polar molecules [2]. Debye theory is based on the Smoluchowski equation for the noninertial rotational diffusion of the molecules. In his work on dielectric relaxation of an assembly of noninteracting dipolar molecules Debye considered two models of the process, namely (a) an assembly of fixed axis rotators each having a permanent dipole moment μ and subjected to Brownian motion torques having their origin in the background or heat bath, and (b) the same assembly, however, the restriction to fixed axis rotation is removed. The results in both instances are equivalently the same, if inertial effects are disregarded [10]. The same picture has been applied to the rotational motion of the magnetization vector of a superparamagnetic particle [11], the polarization vector of a polar molecule in a dielectric [10], and heavy molecules [12,13] in liquid and gases. However, Debye theory cannot explain the experimental data on dielectric relaxation of complex systems, since the interactions between dipoles are

ignored. Indeed, the relaxation process in disordered systems is characterized by the temporal nonlocal behavior arising from the energetic disorder which produces obstacles or traps which delay the motion of the particles and introduce memory effects into the motion. Therefore an important task in relaxation of complex systems as well as dielectric relaxation is to extend the Debye theory of relaxation to fractional dynamics, so that empirical decay functions, e.g., the stretched exponential of Kohlrausch [9] and Williams and Watts [8], may be justified. Such a generalization of the Debye theory was given in Refs. [14–16]. We must remark that other generalizations of the Debye model in the context of the fractional dynamics have been discussed in recent striking works [17–21] as well.

Our main aim, in this study, is obtain relaxation function Eq. (2) for some complex disordered systems in terms of rotational correlation functions based on rotational Brownian motion in a stochastic framework.

The most common calculation in which the picture of rotational Brownian motion finds relevance is that of the rotational correlation function $\Phi_l^R(t)$, which can be measured by infrared (ir) and Raman (R) spectroscopies as well as the neutron and ultrasonic scattering techniques [22]. Correlation function $\Phi_l^R(t)$ measures the correlation in time between the direction of the unit vectors (defining the molecular symmetry axis) $\mathbf{u}(0)$ and $\mathbf{u}(t)$. Therefore $\Phi_l^R(t)$ as can be obtained from the ir and Raman spectroscopies may be expressed in the compact form,

$$\Phi_l^R(t) = \langle P_l[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle, \quad (4)$$

where \mathbf{u} is the unit vector along the symmetry axis of the molecule, and P_l is the Legendre polynomial of order l . Argument of P_l is expressed as $\mathbf{u}(0) \cdot \mathbf{u}(t) = \cos \gamma(t)$, where γ is the angle between two different points at the spherical coordinate system. These points are given by (θ_0, ϕ_0) and (θ, ϕ) which denote two different directions separated by an angle γ . These angles satisfy the trigonometric identity,

$$\cos \gamma = \cos \theta_0 \cos \theta + \sin \theta_0 \sin \theta \cos(\phi_0 - \phi). \quad (5)$$

The addition theorem asserts that

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$$P_l(\cos \gamma) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^m(\theta_0, \phi_0) Y_l^{m*}(\theta, \phi). \quad (6)$$

If we inserted Eq. (6) into Eq. (4) the rotational correlation function is expressed in general form using the spherical harmonics addition theorem as

$$\Phi_l(t) = \frac{4\pi}{2l+1} \sum_{m=-l}^l \langle Y_l^m(\theta_0, \phi_0) Y_l^{m*}(\theta, \phi) \rangle. \quad (7)$$

Such a theoretical approach allows us to calculate for arbitrary l . The average in Eq. (7) is calculated using the probability density functions of a Brownian particle which refers to the end of point polarization vector or a real particle. The Brownian motion in disordered space in the presence of an external field $F(x)=-V'(x)$ leads to the fractional Fokker-Planck equation (FFPE) [23–27]:

$$\frac{\partial}{\partial t} W(x_0, 0|x, t) = {}_0D_t^{1-\alpha} L_{FP} W(x_0, 0|x, t), \quad (8)$$

$$L_{FP} = \left[\frac{\partial}{\partial x} \frac{V'(x)}{m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2} \right]. \quad (9)$$

This equation then characterizes the subdiffusion process. The FFPEs are closely related generalized Lévy-type statistics [28] and can be derived from continuous time random walk (CTRW) models [29–34], or from a Langevin equation [35]. In Eq. (8), $W(x_0, 0|x, t)$ implies the conditional probability for Brownian motion, m denotes the mass of the particle, K_α the diffusion constants associated with the transport process, and the friction coefficient η_α is a measure for interaction of the particle with its environment. K_α is a generalization of the Einstein-Stokes-Smoluchowski relation [23–27] which holds for the generalized coefficient η_α which is defined as $K_\alpha = k_B T / m \eta_\alpha$ where k_B is the Boltzmann constant, and T is the temperature. In Eq. (8) the operator ${}_0D_t^{1-\alpha}$ is the known fractional Riemann-Liouville integrodifferential operator [36].

The fractional Riemann-Liouville operator ${}_0D_t^{1-\alpha} = (d/dt) {}_0D_t^{-\alpha}$ is defined through

$${}_0D_t^{1-\alpha} W(\theta_0, \phi_0, 0|\theta, \phi, t) = \frac{1}{\Gamma(\alpha)} \frac{\partial}{\partial t} \int_0^t dt' \frac{W(\theta_0, \phi_0, 0|\theta, \phi, t')}{(t-t')^{1-\alpha}}. \quad (10)$$

The fractional integrodifferentiation operator ${}_0D_t^{1-\alpha}$ contains a convolution integral with a slowly decaying power-law Kernel $M(t) = t^{\alpha-1} / \Gamma(\alpha)$, ensures the non-Markovian nature of the subdiffusion process defined by the fractional diffusion process. Its fundamental property is the fractional integrodifferentiation of a power,

$${}_0D_t^{1-\alpha} t^p = \frac{\Gamma(1+p)}{\Gamma(p+\alpha)} t^{p+\alpha-1}. \quad (11)$$

In fact, it can be shown that the more general relation

$${}_0D_t^p t^q = \frac{\Gamma(1+q)}{\Gamma(1+q-p)} t^{q-p} \quad (12)$$

for any real p, q . Thus the fractional derivative of a constant,

$${}_0D_t^q 1 = \frac{1}{\Gamma(1-q)} t^{-q}, \quad q > 0, \quad (13)$$

reproduces an inverse power law. The special cases of integer order integrodifferentiation of a constant, $d^n 1 / dt^n = 0$, are included through the poles of the Gamma function for $q=1, 2, 3, \dots$.

In the case of $V'(x)=0$, which means that there is no external field, the one-dimensional FFPE can be reduced to a diffusive-type equation:

$$\frac{\partial}{\partial t} W(x_0, 0|x, t) = {}_0D_t^{1-\alpha} K_\alpha \frac{\partial^2}{\partial x^2} W(x_0, 0|x, t). \quad (14)$$

This equation is called the fractional diffusion equation [37–39] which is a particular form of the FFPE, which can represent the spherical coordinates as a function of the angles θ and ϕ as

$$\frac{\partial}{\partial t} W(\theta_0, \phi_0, 0|\theta, \phi, t) = {}_0D_t^{1-\alpha} d_\alpha \nabla^2 W(\theta_0, \phi_0, 0|\theta, \phi, t), \quad (15)$$

where d_α is referred to as the rotational diffusion constant that is related to the translational diffusion constant K_α and the radius a by $d_\alpha = K_\alpha / a^2$ ($a = \text{unit}$),

$$\nabla^2 = \frac{1}{\sin^2 \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{\partial^2}{\partial \phi^2} \right]. \quad (16)$$

The standard method of solution of Eq. (15) is the separation variables [23–27]. If we consider the separation ansatz, as $W = TQ$, where T and Q are temporal and spatial components of the conditional probability function, respectively, we will obtain two eigenequations as

$$\frac{dT(0|t)}{dt} = -\lambda^2 d_{\alpha 0} {}_0D_t^{1-\alpha} T(0|t), \quad (17)$$

$$\nabla^2 Q(\theta_0, \phi_0|\theta, \phi) = -\lambda^2 Q(\theta_0, \phi_0|\theta, \phi). \quad (18)$$

The temporal eigenequation Eq. (17) is but the fractional relaxation equation, the solution of which is given in terms of the Mittag-Leffler function [40],

$$T(0|t) = E_\alpha[-d_\alpha l(l+1)t^\alpha] \equiv \sum_{j=0}^{\infty} \frac{[-d_\alpha l(l+1)t^\alpha]^j}{\Gamma(1+\alpha j)}. \quad (19)$$

As can be seen from the series expansion, the exponential form can be recovered in the Brownian limit $\alpha=1$,

$$E_1[d_1 l(l+1)t^1] = \exp[d_1 l(l+1)t]. \quad (20)$$

This result indicates that for $\alpha=1$ Mittag-Leffler relaxation modes lead to the Maxwell-Debye pattern, on the other hand, for the interval $0 < \alpha < 1$ the Mittag-Leffler function indicates non-Markovian Brownian motion.

On the other hand, a convenient way of expressing the solution of the spatial eigenequation Eq. (18) is by means of spherical harmonics,

$$Q(\theta_0, \phi_0 | \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} Y_l^m(\theta_0, \phi_0) Y_l^{m*}(\theta, \phi). \quad (21)$$

As a result, if solutions Eqs. (19) and (21) are combined, the conditional probability function of a Brownian particle is obtained in terms of the Mittag-Leffler function as

$$W(\theta_0, \phi_0, 0 | \theta, \phi, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} Y_l^m(\theta_0, \phi_0) Y_l^{m*}(\theta, \phi) \times E_{\alpha}[-d_{\alpha} l(l+1)t^{\alpha}]. \quad (22)$$

Equation (22) can be written as a compact in terms of the Euler angles $\Omega_0(\theta_0, \phi_0)$ and $\Omega(\theta, \phi)$, hence

$$W(\Omega_0, 0 | \Omega, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} Y_l^m(\Omega_0) Y_l^{m*}(\Omega) E_{\alpha}[-d_{\alpha} l(l+1)t^{\alpha}]. \quad (23)$$

Also, Eqs. (22) and (23) should be satisfied,

$$W(\Omega_0, 0 | \Omega, 0) = \delta(\Omega_0 - \Omega), \quad (24)$$

for $t=0$.

It is easy to give the correlation function Eq. (7) by what is by now a familiar interpretation as

$$\Phi_l(t) = \frac{4\pi}{2l+1} \sum_{m=-l}^l \int w(\Omega_0) Y_l^m(\Omega_0) W(\Omega_0, 0 | \Omega, t) \times Y_l^{m*}(\Omega) d\Omega_0 d\Omega. \quad (25)$$

In the above equation $w(\Omega_0)$ is an *a priori* probability that the initial orientation is given by Ω_0 , while $W(\Omega_0, 0 | \Omega, t)$ is the conditional probability that the final orientation is determined Ω . Assuming that the reorientations of the spin (or molecular) symmetry axis may be modeled as an isotropic rotational Brownian motion, we may write

$$w(\Omega_0) = 1/4\pi \quad (26)$$

and adopt Eq. (22) as the solution for the conditional probability. Hence Eq. (25) yields

$$\Phi_l(t) = \frac{4\pi}{2l+1} \sum_{m=-l}^l \sum_{l'=m}^l \left(\frac{1}{2l'+1} \right) E_{\alpha}[-d_{\alpha} l'(l'+1)t^{\alpha}] \times \int Y(\Omega_0) Y_{l'}^{m'*}(\Omega_0) d\Omega_0 \int Y_l^m(\Omega) Y_{l'}^{m'*}(\Omega) d\Omega. \quad (27)$$

Using the orthogonal property,

$$\int Y_l^m(\Omega) Y_{l'}^{m'*}(\Omega) d\Omega = \delta_{ll'} \delta_{mm'}. \quad (28)$$

Hence rotational correlation function (27) is written in terms of the Mittag-Leffler function [40],

$$\Phi_l(t) = \Phi_l(0) E_{\alpha}[-d_{\alpha} l(l+1)t^{\alpha}], \quad (29)$$

where the normalized factor of Eq. (29) is given as $\Phi_l(0) = 4\pi/(2l+1)^2$. Equation (29) states simply that the rotational correlation function, starting from the value unity at $t=0$, decays nonexponentially in time with a relaxation time τ_l that is inversely proportional to rotational diffusion constant d_{α} :

$$\tau_{\alpha, l} = [d_{\alpha} l(l+1)]^{-1}. \quad (30)$$

The rotational correlation function (29) is valid for an arbitrary number l , and its interesting property due to the behavior of the Mittag-Leffler functions lies in the observation that it interpolates between an initial stretched exponential (i.e., KWW) behavior,

$$\Phi_l(t) \approx \exp\left[-\frac{t^{\alpha}}{\tau_{\alpha, l} \Gamma(1+\alpha)}\right], \quad (31)$$

and a long-time inverse power-law pattern,

$$\Phi_l(t) \approx \left[\frac{\tau_{\alpha, l} t^{-\alpha}}{\Gamma(1-\alpha)} \right]. \quad (32)$$

In conclusion, it is seen that relaxation functions Eqs. (31) and (32) are compatible with Eqs. (2) and (3) for complex disordered systems, respectively.

While formulating the problem we have disregarded the inertial free motion governed by the rotational kinetic energy among the successive collision. Indeed, the rotational Brownian motion model for complex systems make sense only when friction η_{α} is large, i.e., the collisions are very rapid. There the rotational jumps were imagined to occur by large and arbitrary angles as opposed to the present instance in which only small-angle jumps are considered.

In this study, we have analytically carried out the rotational relaxation function in terms of the rotational correlation function for complex disordered systems based on rotational Brownian motion. To obtain the rotational correlation function we have introduced generalized Fokker-Planck equations of fractional order, which generalizes the Stokes-Einstein-Smoluchowski relation, in consistency with the fluctuation-dissipation theorem. The introduction of the Riemann-Liouville operator includes long-range memory effects which are typically found in complex systems, and consequently a single mode relaxes slowly in time, following the Mittag-Leffler decay.

In conclusion, we have shown that rotational Brownian motion in complex systems such as spin glasses or dielectric materials leads to KWW decays which indicates nonexponential relaxation.

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