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Anomalous Diffusion and Relaxation Close to Thermal Equilibrium: A Fractional Fokker-Planck Equation Approach

Ralf Metzler,[1,*] Eli Barkai,[2,†] and Joseph Klafter[1,‡]

[1]*School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel*

[2]*School of Physics, Tel Aviv University, 69978 Tel Aviv, Israel*

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We introduce a fractional Fokker-Planck equation describing the stochastic evolution of a particle under the combined influence of an external, nonlinear force and a thermal heat bath. For the force-free case, a subdiffusive behavior is recovered. The equation is shown to obey generalized Einstein relations, and its stationary solution is the Boltzmann distribution. The relaxation of single modes is shown to follow a Mittag-Leffler decay. We discuss the example of a particle in a harmonic potential. [S0031-9007(99)09071-7]

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Anomalous diffusion in one dimension is characterized by the occurrence of a mean square displacement of the form

$$\langle(\Delta x)^2\rangle = \frac{2K_\gamma}{\Gamma(1+\gamma)}\, t^\gamma, \tag{1}$$

which deviates from the linear Brownian dependence on time [1]. In Eq. (1), we introduced the generalized diffusion coefficient, which has the dimension $[K_\gamma] = \mathrm{cm}^2\,\mathrm{sec}^{-\gamma}$. In the following, we will deal with the subdiffusive domain $0 < \gamma < 1$. Examples for subdiffusive transport are very diverse, and include charge transport in amorphous semiconductors [2,3], NMR diffusometry in disordered materials [4], and the dynamics of a bead in polymer networks [5].

Normal diffusion problems involving external fields are often modeled in terms of a Fokker-Planck equation (FPE)

$$\dot{W}(x,t) = L_{\mathrm{FP}} W\,, \tag{2}$$

where the linear FP operator is defined through $L_{\mathrm{FP}} = (\frac{\partial}{\partial x}\frac{V'(x)}{m\eta_1} + K_1\frac{\partial^2}{\partial x^2})$, with the external potential $V(x)$ [6]. m denotes the mass of the diffusing particle, and η_1 is the friction coefficient. A rich variety of solution methods exists for Eq. (2) [6]. The basic properties of the FPE are the exponential decay of the modes, the Einstein relations, which are intimately connected with the fluctuation-dissipation theorem and with linear response, and the Gaussian evolution in the force-free case. For an FPE describing systems close to thermal equilibrium, the stationary solution must be given by the Boltzmann distribution.

Our goal in this Letter is to give a stochastic framework which describes anomalous systems, and meets the following requirements: (i) In the absence of an external force field, Eq. (1) is satisfied; (ii) in the presence of an external nonlinear and time independent field the stationary solution should be the Boltzmann distribution; (iii) generalized Einstein relations must be satisfied; and (iv) in the limit $\gamma \to 1$ the standard FPE must be recovered. While other approaches [7–17] fulfill part of these requirements, we know of no simple approach which meets all of these physical demands.

Our approach is based on fractional derivatives. We investigate the one-dimensional fractional Fokker-Planck equation (FFPE) for one variable

$$\dot{W}(x,t) = {}_0D_t^{1-\gamma} L_{\mathrm{FP}} W \tag{3}$$

in respect to its physical properties. Now, the FP operator

$$L_{\mathrm{FP}} = \left(\frac{\partial}{\partial x}\frac{V'(x)}{m\eta_\gamma} + K_\gamma\frac{\partial^2}{\partial x^2}\right) \tag{4}$$

contains the generalized diffusion constant K_γ, and the generalized friction coefficient η_γ with the dimension $[\eta_\gamma] = \mathrm{sec}^{\gamma-2}$. An extension of the FFPE to higher dimensions is made by replacing the spatial derivatives in the one-dimensional FP operator with the corresponding ∇ operators. In Eq. (3), the Riemann-Liouville fractional operator on the right-hand side is defined through [18]

$$ {}_0D_t^{1-\gamma} W = \frac{1}{\Gamma(\gamma)} \frac{\partial}{\partial t} \int_0^t dt' \frac{W(x,t')}{(t-t')^{1-\gamma}} \tag{5}$$

for $0 < \gamma < 1$, so that Eq. (3) is an integro-differential equation. The Riemann-Liouville operator (5) introduces a convolution integral with a slowly decaying power-law kernel, which is typical for memory effects in complex systems. It is easy to see that for $\gamma \to 1$, Eq. (3) reduces to the standard FPE (2). We assume natural boundary conditions; these are $\lim_{x\to\pm\infty} W(x,t) = 0$. The FFPE (3) describes a physical problem, where the system is prepared at $t_0 = 0$ in the state $W(x,0)$.

We show that the generalized FPE (3) fulfills our requirements (i) to (iv). The exponential decay of the modes are modified in such a way that long-tailed memory effects cause a slow power-law decay of the modes, according to a Mittag-Leffler pattern. The equation describes systems close to thermal equilibrium which exhibit subdiffusive behavior.

Schneider and Wyss [9] have proposed a fractional Fick's equation, describing force-free anomalous diffusion of the type found in Eq. (1), which is equivalent to Eq. (3) for $V(x) = \text{const}$. The occurrence of the fractional derivative ${}_0D_t^{1-\gamma}$ is directly related to a long-tailed waiting time distribution in continuous time random walk theory [19]. From a generalization of this random walk concept for motion under the influence of an external force field, the FFPE (3) and the FP operator (4) can be uniquely derived through a generalized master equation [20].

The right-hand side of the FFPE (3) is equivalent to the fractional expression $-{}_0D_t^{1-\gamma}\partial S(x,t)/\partial x$, where $S = (-\frac{V'(x)}{m\eta_\gamma} - K_\gamma \frac{\partial}{\partial x}) W(x,t)$ is the probability current. If a stationary state is reached, S must be constant. Thus, if $S = 0$ for any x, it vanishes for all x [6], and the stationary solution is given by $V'(x)W_{\text{st}}/[m\eta_\gamma] + K_\gamma W'_{\text{st}} = 0$. Comparing this expression with the required Boltzmann distribution $W_{\text{st}} \propto \exp\{-V(x)/[k_BT]\}$, we find a generalization of the Einstein relation, also referred to as Stokes-Einstein-Smoluchowski relation,

$$ K_\gamma = \frac{k_BT}{m\eta_\gamma}, \tag{6}$$

for the generalized coefficients K_γ and η_γ. Thus, processes described by Eq. (3) fulfill the linear relation between generalized friction and diffusion coefficients, reflecting the fluctuation-dissipation theorem.

In the presence of a uniform force field, given by $V(x) = -Fx$, a net drift occurs. We calculate the quantity $\langle \dot{x} \rangle_F = \int dx\, x\dot{W}$ via the FFPE (3), obtaining

$$ \langle x \rangle_F = \frac{F}{m\eta_\gamma} \frac{t^\gamma}{\Gamma(1+\gamma)}. \tag{7}$$

The mean square displacement for the FFPE (3) in absence of a force, can be calculated similarly,

$$ \langle x^2 \rangle_0 = \frac{2K_\gamma t^\gamma}{\Gamma(1+\gamma)}. \tag{8}$$

Note the subscripts F and 0 to indicate presence and absence of the force field. Using Eq. (6), we recover the relation

$$ \langle x \rangle_F = \frac{1}{2} \frac{F\langle x^2 \rangle_0}{k_BT}, \tag{9}$$

connecting the first moment in the presence of a uniform force field with the second moment in absence of the force. Relation (9) is the generalized Einstein relation discussed in Refs. [1,21]. It can be derived from first principles, using a Hamiltonian description of the system, within the linear response regime. Recent experimental results corroborate the validity of Eq. (9) in polymeric systems in the subdiffusive regime; see Refs. [5,22]. The investigation of charge carrier transport in semiconductors in Ref. [3] showed that, up to a prefactor of 2, which could not be determined exactly, Eq. (9) is valid.

We now consider the temporal evolution of $W(x,t)$ in Eq. (3), in the presence of an arbitrary external force field $F(x)$. For the FPE (2), a formal solution is given by the operator expression $W(x,t) = \exp(L_{\text{FP}}t)W(x,0)$. In case of the FFPE (3), we find that

$$ W(x,t) = E_\gamma(L_{\text{FP}}t^\gamma)W(x,0) \tag{10}$$

is the corresponding formal solution, which can be proven easily via Eq. (11) below. Here, E_γ denotes the Mittag-Leffler function [23], which is the natural extension of the exponential function [24]. It is defined through the series

$$ E_\gamma(z) = \sum_0^\infty \frac{z^n}{\Gamma(1+\gamma n)}. \tag{11}$$

The Mittag-Leffler function reduces to the exponential function for $\gamma = 1$. We will later comment on the special role of the Mittag-Leffler function for relaxation phenomena in more detail.

In order to find an analytic solution for the FFPE (3), we introduce the separation ansatz

$$ W_n(x,t) = \varphi_n(x)T_n(t), \tag{12}$$

where the index n refers to a given eigenvalue of L_{FP}. Introducing the ansatz (12) into Eq. (3), yields

$$ \dot{T}_n\varphi_n = \left[{}_0D_t^{1-\gamma}T_n\right]L_{\text{FP}}\varphi_n, \tag{13}$$

so that, after the separation of Eq. (13) through division by $({}_0D_t^{1-\gamma}T_n)\,\varphi_n$, we arrive at the two eigenequations

$$ \dot{T}_n = -\lambda_{n,\gamma}\,{}_0D_t^{1-\gamma}T_n, \tag{14a}$$

$$ L_{\text{FP}}\varphi_n = -\lambda_{n,\gamma}\varphi_n \tag{14b}$$

for the eigenvalue $\lambda_{n,\gamma}$. The $\lambda_{n,\gamma}$ are related to the standard eigenvalues $\lambda_{n,1}$ for the case $\gamma = 1$, discussed extensively in the literature [6], by a dimensional prefactor $\lambda_{n,\gamma} = (\eta_1/\eta_\gamma)\lambda_{n,1}$ [25]. The solution of Eq. (14a) is given in terms of the monotonically decreasing Mittag-Leffler function

$$T_n(t) = E_\gamma(-\lambda_{n,\gamma} t^\gamma), \tag{15}$$

which is always positive. The full solution of Eq. (3) is thus the sum over all eigenvalues

$$W(x, t \,|\, x', 0) = e^{\Phi(x')/2 - \Phi(x)/2} \sum_n \psi_n(x)\psi_n(x') E_\gamma(-\lambda_{n,\gamma} t^\gamma) \tag{16}$$

for an initial distribution concentrated in x'. Here, the functions $\psi_n(x) = e^{\Phi(x)/2}\varphi_n(x)$ are related to the eigenfunctions of the FP operator L_{FP}, $\varphi_n(x)$, via the scaled potential $\Phi(x) = V(x)/[k_B T]$. The ψ_n are eigenfunctions to the Hermitian operator $L = e^{-\Phi} L_{\mathrm{FP}} e^{\Phi}$. L and L_{FP} have the same eigenvalues $\lambda_{n,\gamma}$ [6]. On arranging the eigenvalues in increasing order, i.e., $0 \leq \lambda_{0,\gamma} < \lambda_{1,\gamma} < \lambda_{2,\gamma} < \ldots$, the first eigenvalue is zero if there exists a stationary solution, which is non-negative. This stationary solution is given by

$$W_{\mathrm{st}} = \lim_{t\to\infty} W(x,t) = e^{\Phi(x')/2 - \Phi(x)/2}\psi_0(x)\psi_0(x'), \tag{17}$$

in full accordance with the standard case $\gamma = 1$, and it is nothing else but the Boltzmann distribution. However, the relaxation of a single mode n is not exponential, but decays slowly like $E_\gamma(-\lambda_{n,\gamma} t^\gamma) \sim 1/[\lambda_{n,\gamma} t^\gamma]$ for $[\lambda_{n,\gamma} t^\gamma] \gg 1$.

Before we discuss the FFPE (3) in more detail, let us consider the nonstationary behavior using a simple example, the generalized subdiffusive version of the Ornstein-Uhlenbeck process with the harmonic potential $V(x) = \frac{1}{2} m\omega^2 x^2$, the solution of which is given by

$$W = \sqrt{\frac{m\omega^2}{2\pi k_B T}} \sum_0^\infty \frac{1}{2^n n!} E_\gamma(-n\tilde{t}^\gamma) \times H_n\left(\frac{\tilde{x}'}{\sqrt{2}}\right) H_n\left(\frac{\tilde{x}}{\sqrt{2}}\right) e^{-\tilde{x}^2/2}, \tag{18}$$

using the general solution (16) and reduced coordinates $\tilde{t} = t/\tau$ and $\tilde{x} = x\sqrt{m\omega^2/k_B T}$, as well as $\tau^{-\gamma} \equiv \omega^2/\eta_\gamma$. H_n denote the Hermite polynomials, and the eigenvalues here are $\lambda_{n,\gamma} = n\omega^2/\eta_\gamma$. From Eq. (18) we can see that the behavior of the $n = 0$ term is constant and independent of γ; the remaining terms decay in the course of time. Thus, for all γ, the stationary solution is the same, the Boltzmann distribution.

The first moment of the process can be directly calculated from Eq. (3) to evolve in time like $\langle x\rangle(t) = \langle x\rangle(0) E_\gamma(-[t/\tau]^\gamma)$, reducing to the usual exponential relaxation behavior for $\gamma \to 1$. This time behavior is shown in Fig. 1. The second moment behaves as

$$\langle x^2\rangle(t) = \langle x^2\rangle_{\mathrm{th}} + [\langle x^2\rangle(0) - \langle x^2\rangle_{\mathrm{th}}] E_\gamma(-2[t/\tau]^\gamma) \tag{19}$$

where we introduced the thermal equilibrium value $\langle x^2\rangle_{\mathrm{th}} = k_B T/[m\omega^2]$, reached for $t \to \infty$. The Mittag-Leffler function $E_\gamma(-2[t/\tau]^\gamma)$ behaves as $1 - 2(t/\tau)^\gamma/\Gamma(1+\gamma)$ for short times, and as $(t/\tau)^{-\gamma}/[2\Gamma(1-\gamma)] - (t/\tau)^{-2\gamma}/[4\Gamma(1-2\gamma)]$ for long times. Thus, the short time behavior of Eq. (19) follows Eq. (1) exactly, and is independent of ω. For long times, the thermal equilibrium value $\langle x^2\rangle_{\mathrm{th}}$ is approached slowly, in power-law form, again contrasting the fast equilibration for the standard case.

For the FFPE (3), we find in Laplace space the functional scaling relation $W_\gamma(x,u) = (\eta_\gamma/\eta_1)u^{\gamma-1} W_1(x, (\eta_\gamma/\eta_1)u^\gamma)$, the same initial conditions $W(x,0) = \delta(x - x')$ provided. The subscript refers to the fractional case $\gamma \in (0,1)$ and to the standard situation $\gamma = 1$, respectively. That means that $W_\gamma(x,u)$ in Laplace space is the same distribution on x as $W_1(x, (\eta_\gamma/\eta_1)u^\gamma)$ for the scaled Laplace variable $(\eta_\gamma/\eta_1)u^\gamma$, only rescaled by the factor $(\eta_\gamma/\eta_1)u^{\gamma-1}$.

As in the standard FPE, the FFPE (3) in the force-free case possesses a scaling variable. Using scaling arguments, one can show that $W_{F=0}(x,t) = [K_\gamma t^\gamma]^{-1/2} f(z)$ with the dimensionless similarity variable $z = x/(K_\gamma t^\gamma)^{1/2}$. The asymptotic shape of $W_{F=0}$ is a stretched Gaussian [9]. For arbitrary external potentials $V(x)$, no such simple scaling behavior is found.

One might be tempted to generalize the FPE (2) by the substitution $\dot{W} \to {}_0D_t^\gamma W$, so that an FFPE of the form ${}_0D_t^\gamma W = L_{\mathrm{FP}} W$ would result, instead of our proposition

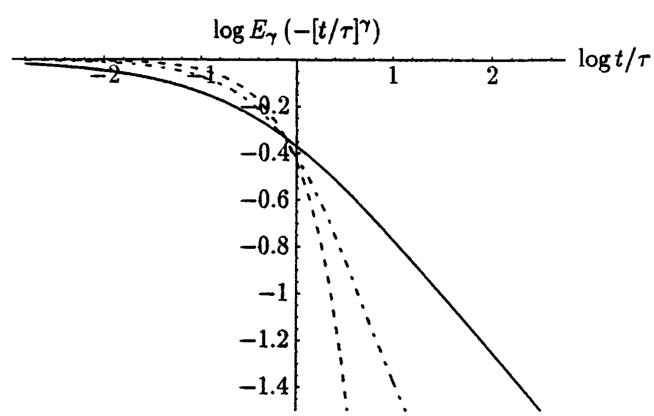

FIG. 1. Mittag-Leffler relaxation compared with the exponential behavior for different values of γ: (– –) $\gamma = 1$ (exponential); (–·–) $\gamma = 0.8$; (—) $\gamma = 1/2$. For $\gamma = 1/2$, the Mittag-Leffler function reduces to $e^{n^2\tilde{t}}\mathrm{erfc}(n\sqrt{\tilde{t}})$. In the decadic log-log plot, the long power-law tails of the Mittag-Leffler decay in comparison to the fast exponential decrease are obvious.

in Eq. (3). However, such an approach is inconsistent, which can be seen, if we integrate both sides of this equation over x. The right-hand side vanishes due to the natural boundary conditions, but for the left-hand side, the result is ${}_0D_t^{\gamma}1 = t^{-\gamma}/\Gamma(1-\gamma)$. Such a shortcoming does not exist in our FFPE (3) [26].

Let us briefly examine the importance of the Mittag-Leffler function, Eq. (15), in relaxation modeling. Besides via the series representation (11), the Mittag-Leffler function is defined through its Laplace transform $\mathcal{L}\{E_\gamma(-(t/\tau)^\gamma)\} = [u + \tau^{-\gamma}u^{1-\gamma}]^{-1}$, or through the fractional differential equation (14a). In Refs. [27,28] it is shown, that the Mittag-Leffler function is the exact relaxation function for an underlying fractal time random walk process, and that this function directly leads to the Cole-Cole behavior [29] for the complex susceptibility, which is broadly used to describe experimental results. Furthermore, the Mittag-Leffler function can be decomposed into single Debye processes, the relaxation time distribution of which is given by a modified, completely asymmetric Lévy distribution [28,30]. This last observation is related to the formulation of Mittag-Leffler relaxation described in Ref. [27]. In Ref. [22], the significance of the Mittag-Leffler function was shown, where its Laplace transform was obtained as a general result for a collision model in the Rayleigh limit.

Concluding, we have introduced a generalized Fokker-Planck equation of fractional order, which generalizes the Stokes-Einstein-Smoluchowski relation, in consistency with the fluctuation-dissipation theorem, and fulfills the generalized Einstein relation. The external force field leads to a stationary solution, which is given by the Boltzmann distribution. The general methods of solution, such as the separation of variables used extensively in literature for $\gamma = 1$, can still be applied, and the example of subdiffusion in a harmonic potential is explicitly solved. 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 now slowly in time, following the Mittag-Leffler decay. It is worth mentioning that fractional kinetic equations have been suggested to model anomalous diffusion in random environments [13–15], and for chaotic Hamiltonian systems [12]. These fractional equations have been used to describe Lévy flights or diverging diffusion. In contrast, we describe subdiffusive systems close to thermal equilibrium.

Recent works have pointed out that nonextensive thermostatistics proposed by Tsallis is the statistical mechanical foundation of anomalous diffusion [31,32]. Here we have shown that anomalous diffusion can be based upon (extensive) Boltzmann statistics.

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*Electronic address: metzler@post.tau.ac.il
†Electronic address: barkai@mit.edu
‡Electronic address: klafter@post.tau.ac.il

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shown that $\lambda_{n,\gamma}$ is indeed independent of η_1, i.e., $\lambda_{n,1} \propto 1/\eta_1$.

[26] The FFPE (3) can also be written like ${}_0D_t^{\gamma} W - t^{-\gamma} W(x,0)/\Gamma(1-\gamma) = L_{\mathrm{FP}} W$, by standard theorems of fractional calculus [18]. Integrating over x, the left-hand side and the right-hand side still both vanish. This alternative formulation of the FFPE (3) incorporates the initial value $W(x,0)$.

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