From a Generalized Chapman−Kolmogorov Equation to the Fractional Klein−Kramers Equation†

Ralf Metzler* and Joseph Klafter‡

School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

Received: September 24, 1999

A non-Markovian generalization of the Chapman−Kolmogorov transition equation for continuous time random processes governed by a waiting time distribution is investigated. It is shown under which conditions a long-tailed waiting time distribution with a diverging characteristic waiting time leads to a fractional generalization of the Klein−Kramers equation. From the latter equation a fractional Rayleigh equation and a fractional Fokker−Planck equation are deduced. These equations are characterized by a slow, nonexponential relaxation of the modes toward the Gibbs−Boltzmann and the Maxwell thermal equilibrium distributions. The derivation sheds some light on the physical origin of the generalized diffusion and friction constants appearing in the fractional Fokker−Planck equation.

I. Introduction

The Klein−Kramers equation[1−6]

$$\frac{\partial W}{\partial t} = \left[-\frac{\partial}{\partial x}v + \frac{\partial}{\partial v}\left(\eta v - \frac{F(x)}{m}\right) + \frac{\eta k_B T}{m}\frac{\partial^2}{\partial v^2}\right]W(x,v,t) \qquad (1)$$

is a bivariate Fokker−Planck equation describing the motion of a passive Brownian test particle of mass m under the influence of an external force field $F(x) = -V'(x)$ in phase (position−velocity) space. η denotes the friction constant and k_BT the Boltzmann temperature. The Klein−Kramers equation (1) determines the temporal change of the probability density function (pdf) $W(x, v, t)$. On the right-hand side of eq 1, the first term describes the spatial drift due to the velocity of the test particle, the second term accounts for the friction and external force feedback to the velocity as expressed through the corresponding Langevin equation, and the third term represents the entropy-based velocity diffusion, i.e., the spreading of the pdf $W(x, v, t)$ on the (x, v) field in the course of time.

The stochastic differential equation corresponding to eq 1 is

$$\frac{dx}{dt} = v, \quad \frac{dv}{dt} = -\eta v + \frac{F(x)}{m} + \Gamma(t) \qquad (2)$$

or, equivalently, the Langevin equation $m\, d^2x/dt^2 = -\eta m\, dx/dt + F(x)\, m\Gamma(t)$, $\Gamma(t)$ being a Gaussian, δ-correlated noise.[5,7] The stationary solution of the Klein−Kramers equation (1), $W_{st}(x, v) \equiv \lim_{t\to\infty} W(x, v, t)$, is the Gibbs−Boltzmann equilibrium distribution

$$W_{st} = N \exp(-\beta E) \qquad (3)$$

where $\beta \equiv (k_BT)^{-1}$ is the Boltzmann factor, $E = (mv^2/2) + V(x)$, and N is a normalization constant depending on $V(x)$.

The distribution in velocity space, related to eq 1 and without the external potential, is governed by the Rayleigh equation[6]

$$\frac{\partial W}{\partial t} = \eta\left[\frac{\partial}{\partial v}v + \frac{k_BT}{m}\frac{\partial^2}{\partial v^2}\right]W(v,t) \qquad (4)$$

with the corresponding Langevin equation $dv/dt = -\eta v + \Gamma(t)$. The Rayleigh equation controls the diffusion of the test particle in velocity space which is confined by the Ornstein−Uhlenbeck term $\eta(\partial/\partial v)vW(v,t)$ corresponding to the velocity damping term $-\eta v$ in the Langevin equation. Equation 4 thus describes the relaxation of the pdf $W(v,t)$ toward the stationary Maxwell distribution $W_{st}(v)$, eq 3, with $E = mv^2/2$ and $N = (\beta m/2\pi)^{1/2}$.

In the high friction limit, one may neglect the inertial term in the corresponding stochastic differential equation (2), to obtain $dx/dt = (F(x)/m\eta) + (1/\eta)\Gamma(t)$, or the monovariate Fokker−Planck equation, often referred to as the Smoluchowski equation

$$\frac{\partial W}{\partial t} = \frac{1}{m\eta}\left[-\frac{\partial}{\partial x}F(x) + k_BT\frac{\partial^2}{\partial x^2}\right]W(x,t) \qquad (5)$$

Equation 5 determines the diffusion of the test particle in position space under the influence of the external force field $F(x)$.[5,6,8,9] Formally, the stationary solution $W_{st}(x)$ of the Fokker−Planck equation (5) given by eq 3 can be obtained from the equilibrium solution $W_{st}(x, v)$ of the Klein−Kramers equation (1) by integration over the velocity variable. However, in passing from the Klein−Kramers equation (1) itself to the Fokker−Planck equation (5), the additional term $(1/\eta)(\partial^2W/\partial t^2)$ occurs which can only be neglected in the long-time, high friction limit, $t \gg \eta^{-1}$;[10] see also below.

The Klein−Kramers equation (1) and the Fokker−Planck equation (5) describe a Brownian test particle the mean squared displacement of which follows, in the force-free limit, the linear time dependence $\langle x^2\rangle_0 = 2Kt$. Hereby, the diffusion coefficient is defined through $K \equiv k_BT/[m\eta]$, by virtue of the Einstein−Stokes relation.[5,6,11] This property of Brownian motion is often

† Part of the special issue "Harvey Scher Festschrift". Dedicated to Prof. Harvey Scher on the occasion of his 60th birthday.

* Corresponding author. E-mail: wetzler@post.tau.ac.il.
‡ E-mail: klafter@post.tau.ac.il.

10.1021/jp9934329 CCC: $19.00
Published on Web 03/11/2000

violated by observing a mean squared displacement of the form[11−15]

$$\langle x^2 \rangle_0 \sim K_\alpha t^\alpha \tag{6}$$

which is the hallmark of anomalous diffusion, with subdiffusion corresponding to $0 < \alpha < 1$ and superdiffusion occurring for $\alpha > 1$. The dimension of the generalized diffusion coefficient is $[K_\alpha] = \mathrm{cm}^2\,\mathrm{s}^{-\alpha}$. Anomalous transport processes characterized through eq 6 are related to Lévy-type distributions and the validity of the generalized central limit theorem.[11,16−18]

Previous extensions of the Klein−Kramers equation (1) have been proposed on the basis of the stochastic differential equation (2) with a Lévy noise $\Gamma(t)$.[19−23] An alternative derivation for quantum Lévy processes has been presented recently.[24] The Lévy flight models lead to nonequilibrium solutions, and the mean squared displacement diverges in the force-free limit.[25] Therefore, this approach is not considered further in the present account.

In the following, the discussion concentrates on the subdiffusive case $0 < \alpha < 1$. Throughout this paper, the derivation is restricted to one-dimensional systems.

II. Toward a Fractional Klein−Kramers Equation

In analogy to the description of a Brownian test particle in an external force field through the Fokker−Planck equation (5), it has been suggested to model a test particle which displays subdiffusion through the fractional Fokker−Planck equation[26−28]

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha}\left[-\frac{\partial}{\partial x}\frac{F(x)}{m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2}\right]W(x,t) \tag{7}$$

The generalized friction constant η_α has the dimension $[\eta_\alpha] = \mathrm{s}^{\alpha-2}$. In the fractional Fokker−Planck equation (7), the fractional Riemann−Liouville operator ${}_0D_t^{1-\alpha} = (\partial/\partial t)\,{}_0D_t^{-\alpha}$ is defined by the convolution[29]

$${}_0D_t^{1-\alpha}W(x,t) \equiv \frac{1}{\Gamma(\alpha)}\frac{\partial}{\partial t}\int_0^t \mathrm{d}t' \frac{W(x,t')}{(t-t')^{1-\alpha}} \tag{8}$$

Consequently, eq 7 includes a slowly decaying memory with a power-law kernel.[27,28] Fractional Fokker−Planck equations of the type (7) are thus prototype model equations for many complex systems which are dominated by non-Markovian memories.[11−15,30,31] In deriving the fractional Fokker−Planck equation (7), a waiting time pdf $w(t)$ is introduced from which the waiting time spans between single jumps are drawn. In this continuous time formulation,[32,33] a waiting time pdf possessing a finite first moment, the characteristic waiting time

$$T \equiv \int_0^\infty \mathrm{d}t\, w(t), \tag{9}$$

leads back to the classical Brownian formulation whereas in the case of a diverging characteristic waiting time, the fractional Fokker−Planck equation (7) emerges from a generalized master equation.[27,28,33]

In order to incorporate such subdiffusive mechanisms into the Klein−Kramers formalism, note that the standard derivation of the Klein−Kramers equation is based on the Chapman−Kolmogorov equation for a Markovian process

$$W(x,v,t+\Delta t) = \int_{-\infty}^{\infty}\mathrm{d}(\Delta x)\int_{-\infty}^{\infty}\mathrm{d}(\Delta v)\, W(x-\Delta x, v-\Delta v,t)\,\Psi(x-\Delta x, v-\Delta v; \Delta x, \Delta v) \tag{10}$$

which describes the temporal evolution of the pdf $W(x,v,t)$ through the incremental transition from the pdf $W(x-\Delta x,v-\Delta v,t)$ to $W(x,v,t+\Delta t)$ during the average time step Δt.[2] The transfer kernel in eq 10 is thereby given through

$$\Psi(x-\Delta x,v-\Delta v;\Delta x,\Delta v) = \psi(x-\Delta x,v-\Delta v;\Delta v)\,\delta(\Delta x - v\Delta t) \tag{11}$$

in Chandrasekhar's notation.[2] The kernel Ψ and its factorized counterpart ψ describe the distribution of transitions with the velocity increment Δv for the field variables v and x where the position increment is connected with the mean time step Δt through $\Delta x = v\Delta t$. Note that in the latter relation expressed by the δ-function in eq 11, Δt is assumed to be a small parameter and v is not allowed to be very large, in order for the friction assumption in eq 2 to hold. Thus, Δx is on average small. Similarly, Δv must remain small in the Langevin approximation. This implies that Ψ is sharply peaked around x and v.

The integration over the increment Δx of eq 10 employs the delta function defined in eq 11. Taylor expansions in Δv and Δt, taking along terms of order Δt, lead to the Klein−Kramers equation (1). The coefficients

$$\langle \Delta v\rangle = -\left(\eta v - \frac{F(x)}{m}\right)\Delta t,\qquad \langle(\Delta v)^2\rangle = \frac{\eta k_B T}{m}\Delta t + O([\Delta t]^2) \tag{12}$$

are determined by the stochastic differential equation (2).[2]

Suppose now that successive jumps do not occur after equidistant time steps Δt but that the waiting time elapsing from one motion event until the next is drawn from a pdf $w(t)$, the waiting time pdf.[32] In this continuous time case, the transition from $W(x-\Delta x,v-\Delta v,t')$ to $W(x,v,t)$ is ruled by the generalized Chapman−Kolmogorov equation[33]

$$W(x,v,t) = \int_0^t \mathrm{d}t' \int_{-\infty}^{\infty}\mathrm{d}(\Delta x)\int_{-\infty}^{\infty}\mathrm{d}(\Delta v)\, W(x-\Delta x,v-\Delta v,t')\,\Psi(x-\Delta x,v-\Delta v;\Delta x,\Delta v)\,w(t-t') + \phi(t)\,W_0(x,v) \tag{13}$$

where the transfer kernel $\Psi(x-\Delta x,v-\Delta v;\Delta x,\Delta v)$ has yet to be specified. Note that the transition from the discrete jump time Δt to the continuous time description based on the waiting time pdf $w(t)$ causes the explicit occurrence of the initial value term $W_0(x,v) \equiv \lim_{t\to 0} W(x,v,t)$. This is due to the possibility that the particle does not execute any jump up to time t, with the cumulative probability $\phi(t) = \int_t^\infty \mathrm{d}t'\, w(t')$.[32] Accordingly, the transfer kernel Ψ is modified, generalizing the relation $\Delta x = v\Delta t$ for the position increment. For short times, it is assumed that the growth of the covered distance, Δx, is proportional to time: $\Delta x = vt$. For longer times, a cutoff time τ^* is introduced. For times $t > \tau^*$ the covered distance is kept constant, according to the relation $\Delta x = v\tau^*$. The physical meaning of this cutoff time τ^* and its connection to a trapping mechanism will be discussed below, and it will be shown that it has an intuitive interpretation. With these preliminaries, the transfer kernel splits up into the two parts:

$$\Psi_{t<\tau^*}(x-\Delta x,v-\Delta v;\Delta x,\Delta v) = \psi(x-\Delta x,v-\Delta v;\Delta v)\,\delta(\Delta x - vt) \tag{14}$$

and

$$\Psi_{t>\tau^*}(x-\Delta x,v-\Delta v;\Delta x,\Delta v) = \psi(x-\Delta x,v-\Delta v;\Delta v)\,\delta(\Delta x - v\tau^*) \quad (15)$$

In the Markov limit $w(t) = \delta(t - \Delta t)$, $\Delta t \le \tau^*$, the characteristic waiting time is $T = \Delta t$, and one finds $\phi(t) = 0$, $t > \Delta t$; $\phi(t) = 1$, $t \le \Delta t$ for the probability $\phi(t)$ that no jump has occurred up to time t. This means that, for $t \le \Delta t$, $W(x,v,t) = W_0(x,v)$ the system is still in the prepared state $W_0(x,v)$, and for $t > \Delta t$ the influence of the initial condition has already relaxed, as is typical for a Markovian renewal process. This Markov limit leads consequently back to the original Chapman–Kolmogorov equation (10) and to the Klein–Kramers equation (1). Moreover, in the long-time limit, it is enough that a characteristic waiting time $T < \infty$ exists, in order to recover the Brownian picture. Conversely, if the first moment of the waiting time pdf, the characteristic waiting time, does not exist, $T \to \infty$, the related random process drops out of the basin of attraction of the central limit theorem. In such a case one recovers a subdiffusive, anomalous time evolution, manifest as fractional dynamics.[11,14,15,27,28,32] This is illustrated in the following.

For times $t > \tau^*$, eq 13 in the cutoff time approximation can be rewritten according to

$$W(x,v,t) = \int_0^{\tau^*}\mathrm{d}t' \int_{-\infty}^{\infty}\mathrm{d}(\Delta v)\, W(x - vt',v - \Delta v,t') \times \psi(x - vt',v - \Delta v;\Delta v)w(t - t') + \int_{\tau^*}^{t}\mathrm{d}t' \int_{-\infty}^{\infty}\mathrm{d}(\Delta v)\, W(x - v\tau^*,v - \Delta v,t') \times \psi(x - v\tau^*,v - \Delta v;\Delta v)\, w(t - t') + \phi(t)\, W_0(x,v) \quad (16)$$

Suppose that the waiting time pdf has the long tail inverse power-law asymptotics

$$w(t) \sim \tau^{\alpha}/t^{1+\alpha} \quad (17)$$

with $0 < \alpha < 1$ and the internal time scale τ. For this choice, the characteristic waiting time T diverges. A typical feature of such a broad distribution is the occurrence of large waiting times with a comparatively high probability. This leads to the dominance of the second integral in eq 16 in the long-time limit $t \gg \max(\tau,\tau^*)$. In this case, the process is governed by the generalized Chapman–Kolmogorov equation:

$$W(x,v,t) = \int_0^{t}\mathrm{d}t' \int_{-\infty}^{\infty}\mathrm{d}(\Delta v)\, W(x - v\tau^*,v - \Delta v,t') \times \psi(x - v\tau^*,v - \Delta v;\Delta v)\, w(t - t') + \phi(t)\, W_0(x,v) \quad (18)$$

By the Laplace transformation of eq 18 and insertion of the long-time analogue $w(u) \sim 1 - (u\tau)^{\alpha}$ of the waiting time pdf in Laplace space, one obtains an equation which contains noninteger powers of the Laplace variable u. In the inverse Laplace transformation, the latter lead to the fractional Riemann–Liouville operator due to the relation $L\{{}_0D_t^{-\alpha}W(x,v,t)\} = u^{-\alpha}W(x,v,u)$. Neglecting terms of order $\tau^{2\alpha}$, $(\tau^*)^2$, $\tau^{\alpha}\tau^*$, and higher, one finds the fractional Klein–Kramers equation

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha}\left[-v\frac{\tau^*}{\tau^{\alpha}}\frac{\partial}{\partial x} - \frac{\langle \Delta v\rangle}{\tau^{\alpha}}\frac{\partial}{\partial v} + \frac{1}{2}\frac{\langle(\Delta v)^2\rangle}{\tau^{\alpha}}\frac{\partial^2}{\partial v^2}\right]W(x,v,t) \quad (19)$$

In this long-time approximation, the first integral in eq 16 plus the error in shifting the lower integral limit in the second integral can be estimated to be of the order $\tau^{\alpha}\tau^*/t^{1+\alpha}$.[34]

Equation 18 demonstrates that τ^* takes on the rôle of the mean time step Δt in the standard derivation of the Klein–Kramers equation (1). Thus it is legitimate to assume that the motion events are characterized by the moments (12). Consequently, one arrives at the fractional Klein–Kramers equation:[35]

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha}\left[-v^*\frac{\partial}{\partial x} + \frac{\partial}{\partial v}\left(\eta^* v - \frac{F^*(x)}{m}\right) + \frac{\eta^* k_B T}{m}\frac{\partial^2}{\partial v^2}\right] \times W(x,v,t) \quad (20)$$

where $v^* \equiv v\tau^*/\tau^{\alpha}$ with $[v^*] = \mathrm{cm\ s}^{-\alpha}$, $\eta^* \equiv \eta\tau^*/\tau^{\alpha}$ with $[\eta^*] = \mathrm{s}^{-\alpha}$, and $F^*(x) \equiv F(x)\tau^*/\tau^{\alpha}$ with $[F^*] = \mathrm{cm\ g\ s}^{-1-\alpha}$. In passing to eq 20, Δt was set equal to τ^*. This step is not necessary but facilitates the notation and corresponds to the interpretation given in the next section. Note that the Stokes operator $((\partial/\partial t) + v\ \partial/\partial x)$ from the standard Klein–Kramers equation (1)[2] is replaced by the operator $((\partial/\partial t) + {}_0D_t^{1-\alpha}\ v^*\ \partial/\partial x)$ which shows the nonlocal drift response.

III. Some Remarks on the Derivation

In the above derivation it has been assumed that for short times $t < \tau^*$ the test particle moves with velocity v in a given direction, and thus covers the distance $\Delta x = vt$. For longer times $t > \tau^*$, another mechanism comes into play which was described by the cutoff time assumption. Consequently, the continuous time version of the Chapman–Kolmogorov equation, eq 13, splits into the two contributions in eq 16. Two different physical realizations of the mechanism in the case of finite and infinite characteristic waiting times are now discussed.

A. The Case of a Finite Characteristic Waiting Time $T < \infty$. The first integral in eq 16 refers to the initial regime featuring the linear growth in time of the traveled distance, $\Delta x = vt$. This contribution is relevant to processes with a finite characteristic time scale. For such Markovian processes, it has been argued that the standard description in terms of the Klein–Kramers equation (1) is recovered in the long-time limit $t \gg \max\{T,\tau^*\}$, up to a scaling factor in time which accounts for the fact that the generalized model considers a multitude of individual steps in respect to Δt, combined to one superstep. Accordingly, the mean time step Δt occurring in the stochastic differential equation (2) corresponds either to the characteristic waiting time T if $T < \tau^*$ or to the cutoff time τ^*.

A physical picture corresponding to this process is a particle which moves in the velocity mode v for a certain time drawn from the pdf $w(t)$. Then, the particle changes direction and initiates a new motion event with a different velocity. If such a walking time however exceeds the threshold time τ^* during one of these motion events, the particle pauses at the current position until the time span drawn from $w(t)$ is over and a new motion is initiated. The average direction of motion is thereby determined through the external field $F(x)$.

Such a scenario might be of relevance for the biophysical problem of a bacterium or an amoeba that roams along in the external field $V(x)$ which might represent a food tracer field, or an electrical or chemical guiding field in studies of taxis which has received some interest; see for instance ref 37. After such microorganisms wander around for a certain time, either they change their direction, following a new signal input, or they take a pause for reorientation, respiration, or simply recreation. Thus, if the pdf $w(t)$ features a $T < \tau^*$, it corresponds to a highly active creature which barely pauses; conversely, it spends a considerable portion of its time at rest if $T > \tau^*$.

B. The Case of a Diverging Characteristic Waiting Time $T \to \infty$. In such cases where the characteristic waiting time diverges, $T \to \infty$, it was argued that the first regime with time-proportional growth of the covered distance can be neglected, and the transport process is dictated by the long tail of the corresponding waiting time pdf (17). The generalized Chapman–Kolmogorov equation that is valid for this kind of process is eq 18, which leads to an interesting physical interpretation of the underlying process leading to subdiffusion and its description in terms of fractional Klein–Kramers and Fokker–Planck equations.[38]

According to eq 18 and its derivation, the mean distance traveled per average motion event is given by $\Delta x = v\tau^*$. Thus, after exploring its environment for the average time τ^*, the test particle encounters a position where it gets immobilized. The particle is only released after some waiting time which is drawn from the waiting time pdf $w(t)$. In this multiple trapping scenario,[36] the test particle moves according to the Markovian stochastic differential equation (2), interrupted through trapping events. The relation $\Delta x = v\tau^*$ consequently characterizes an average transition between two successive trapping events and as such is a measure for the average distance between two adjacent traps. Note that such trapping is known from the motion of charge carriers in amorphous semiconductors.[36] Thus, the fractional Klein–Kramers equation (20) describes systems in which some kind of disorder occasionally interrupts the Markov-style motion of the test particle. The overall dominance of the long tail of the waiting time pdf is manifest in the fractional time evolution.

C. The Rôle of the Langevin Equation (2). The two cases discussed are tailored such that the Langevin equation (2) which provides the expansion coefficients in the Taylor expansion with respect to the velocity increment Δv in the Chapman–Kolmogorov equation remains valid. In the Markovian case discussed in section IIIA, the average step time corresponds to either T or τ^*, and in the subdiffusive case referred to in section IIIB it is given by τ^*. Note that in either case, the kinetic energy of the particle during a trapping-detrapping event is assumed to be conserved.

The Langevin equation provides the dynamics foundation for the transport process under consideration in that it is the physical equation from which the information on the averaged velocity increments $\langle \Delta v \rangle$ and $\langle (\Delta v)^2 \rangle$ is obtained. Especially, the friction constant η, its connection to the diffusion coefficient, and the external force $F(x)$ enter through this stochastic differential equation whose noise average $m\, d^2\langle x \rangle_\Gamma / dt^2 = -\eta \langle v \rangle_\Gamma + F(x)$ corresponds to Newton's equation of motion. It is exactly this dynamics foundation of the fractional Klein–Kramers and Fokker–Planck equations and the coefficients occurring therein which adds to earlier derivations from a kinematics–stochastic approach in terms of waiting time and asymmetric jump length distributions presented in refs 27 and 28. It thus offers some physical insight into the origin of fractional dynamics for systems which exhibit multiple trapping such as the aforementioned charge carrier transport in amorphous semiconductors,[36] the motion of excess electrons in liquids,[39,40] or the phase space dynamics of chaotic Hamiltonian systems,[41] or it may be viewed as the source for the nonstandard dynamics encountered in protein folding.[42]

IV. Discussion of the Fractional Klein–Kramers Equation

In the following discussion of the fractional Klein–Kramers equation (20), the generalizations of the two limiting equations of the Rayleigh and Fokker–Planck types are derived. Thus, integration of the fractional Klein–Kramers equation (20) over $\int dv$ and over $\int v\, dv$ leads to two independent equations whose combination produces the equation

$$\frac{\partial W}{\partial t} + {}_0D_t^{1+\alpha}\frac{1}{\eta^*}W = {}_0D_t^{1-\alpha}\left[-\frac{\partial}{\partial x}\frac{F(x)}{m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2}\right]W(x,t) \quad (21)$$

from which, in the high friction limit, one is led to the fractional Fokker–Planck equation (7), which was discussed in detail in ref 26 and was derived from a generalized master equation and a nonhomogeneous random walk in refs 27 and 28. The constants η_α and K_α introduced in this derivation are now defined as

$$\eta_\alpha \equiv \frac{\eta\tau^\alpha}{\tau^*}, \quad [\eta_\alpha] = s^{\alpha-2}; \qquad K_\alpha \equiv \frac{k_B T}{m\eta_\alpha}, \quad [K_\alpha] = cm^2\, s^{-\alpha} \quad (22)$$

These relations show that the generalized coefficients are based on the proper dynamical quantities, η, m, and τ^*, and that the fractional dimensions emanate from the rescaling with τ^α or, in other words, through the introduction of a fractal waiting time distribution, eq 17. Moreover, the generalized Einstein–Stokes relation connecting K_α with η_α now follows directly from the derivation. The Brownian limit of eqs 19–22 is easily obtained, and it coincides with the known standard equations. Note that $\tau^* = \tau$ does not necessarily have to be fulfilled as a rescaling of variables can account for an additional factor in time. Equation 21, for $\alpha = 1$, is of the telegrapher's or Cattaneo equation[10,43] type. The force-free analogue of eq 21 is called the generalized or fractional Cattaneo equation and, for arbitrary $0 < \alpha < 1$, was discussed and derived from a continuous time flux model in ref 43.

The fractional counterpart of the Rayleigh equation (4) corresponding to the fractional Klein–Kramers equation (20) can be obtained by the integration $\int dx$ in the force-free limit, the result being

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha}\eta^*\left[\frac{\partial}{\partial v}v + \frac{k_B T}{m}\frac{\partial^2}{\partial v^2}\right]W(v,t) \quad (23)$$

The fractional Rayleigh equation (23) is equivalent to the fractional Fokker–Planck equation (7) with a linear force and therefore corresponds to the subdiffusive Ornstein–Uhlenbeck process.[15] This process has been discussed elsewhere;[15,26] the first two moments of eq 23 are calculated below.

V. Discussion of the Fractional Klein–Kramers Equation Continued

Regarding eqs 7, 20, and 23, all of these evolution equations derived from the generalized Chapman–Kolmogorov equation (13) are of the form

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha} L W \quad (24)$$

where the linear operator L denotes the appropriate Klein–Kramers, Fokker–Planck, or Rayleigh operators. Equation 24 relates the momentary change $\partial W/\partial t$ of the pdf W to the previous history of the dynamical evolution of the system, through the fractional Riemann−Liouville operator ${}_0D_t^{1-\alpha}$. Employing standard theorems of fractional calculus,[29] eq 24 can be rewritten in the equivalent form

$$ {}_0D_t^{\alpha}W - \frac{W_0}{\Gamma(1-\alpha)}t^{-\alpha} = LW \tag{25}$$

which explicitly includes the initial value W_0 and thereby underlines its slowly decaying contribution following the inverse power law $t^{-\alpha}$.[28] Note that in the Brownian limit $\alpha = 1$, the Γ-function in eq 25 diverges: $\lim_{\alpha\to 1}\Gamma(1-\alpha) = \infty$, and thus the usual expression $\partial W/\partial t = LW$ is recovered.

Besides Fourier−Laplace techniques, equations of the type (24) can be solved by the separation of variables. With a separation ansatz of the type $W(x,v,t) = T(t)\,\varphi(x,v)$, one obtains the eigenequations[26,27,46]

$$\frac{\mathrm{d}T_n(t)}{\mathrm{d}t} = -{}_0D_t^{1-\alpha}\lambda_{n,\alpha}T_n;\quad L\varphi_n(x,v) = -\lambda_{n,\alpha}\varphi_n \tag{26}$$

for a given eigenvalue $\lambda_{n,\alpha}$. The full solution is then the sum over all eigensolutions. Whereas the spatial part depends on the special form of the operator L, the explicit temporal eigensolution is expressed in terms of the Mittag−Leffler function[47] by

$$T_n(t) = E_\alpha(-\lambda_{n,\alpha}t^\alpha) \tag{27}$$

The series expansion for the Mittag−Leffler function

$$E_\alpha(-\lambda_{n,\alpha}t^\alpha) = \sum_{\nu=0}^{\infty}\frac{(-\lambda_{n,\alpha}t^\alpha)^\nu}{\Gamma(1+\alpha\nu)} \tag{28}$$

shows the close relation to the exponential function: $E_1(-\lambda_{n,1}t) = \exp(-\lambda_{n,1}t)$. Note that with $\lambda^*_{n,\alpha} \equiv \lambda_{n,\alpha}/\Gamma(1+\alpha)$, $E_\alpha(-\lambda_{n,\alpha}t^\alpha) \sim \exp(-\lambda^*_{n,\alpha}t^\alpha)$ for $t \ll 1/(\lambda^*_{n,\alpha})^{1/\alpha}$; namely, for short times, the Mittag−Leffler function evolves in a stretched exponential manner. Conversely, for long times, the Mittag−Leffler function (28) follows the inverse power-law tail $E_\alpha(-\lambda_{n,\alpha}t^\alpha) \sim [\lambda_{n,\alpha}\Gamma(1-\alpha)t^\alpha]^{-1}$, $t \gg 1/(\lambda_{n,\alpha})^{1/\alpha}$. Therefore, the effect of the fractional operator ${}_0D_t^{1-\alpha}$ in the fractional Klein−Kramers equation (20), as well as in the fractional Fokker−Planck equation (7) and the fractional Rayleigh equation (23) deduced from it, is the nonexponential relaxation of single modes n, reflecting the relatively slower decay of the initial condition, as has been seen from eq 25. Due to the considerably longer waiting times experienced by the test particle, the equilibration of the system is decelerated in comparison to the analogous Brownian system. This is now exemplified by the moments derived from these evolution equations.

The moments of a kinetic equation of the type (24) can be derived through integration which leads to simple fractional differential equations for the desired moment. For instance, to obtain $\langle v\rangle$ from the fractional Rayleigh equation (23), the integration $\int v\,\mathrm{d}v$ leads to the equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle v\rangle = \int \mathrm{d}v\; {}_0D_t^{1-\alpha}\eta^*\left[\frac{\partial}{\partial v}v + \frac{k_BT}{m}\frac{\partial^2}{\partial v^2}\right]W(v,t) \tag{29}$$

from which, through integration by parts, one recovers the fractional relaxation equation[45]

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle v\rangle = -{}_0D_t^{1-\alpha}\eta^*\langle v\rangle \tag{30}$$

As in eq 27, the solution of eq 30 is given in terms of the Mittag−Leffler function

$$\langle v\rangle = \langle v\rangle_0 E_\alpha(-\eta^* t^\alpha) \tag{31}$$

By help of the fundamental relation

$${}_0D_t^p t^q = \frac{\Gamma(1+q)}{\Gamma(1+q-p)}t^{q-p} \tag{32}$$

for any real q, p, moments of any order can be obtained from the evolution equations. For the fractional Rayleigh equation (23), the following result for the second-order moment is obtained:

$$\langle v^2\rangle = \langle v^2\rangle_{eq} + (\langle v^2\rangle_0 - \langle v^2\rangle_{eq})E_\alpha(-2\eta^* t^\alpha) \tag{33}$$

with $\langle v^2\rangle_{eq} = \lim_{t\to\infty}\langle v^2\rangle_{eq} = k_BT/m$. In this fractional Rayleigh process, the first moment, eq 31, decays slowly towards the symmetric value $\lim_{t\to 0}\langle v\rangle \equiv 0$. The second moment, eq 33, relaxes in the Mittag−Leffler pattern toward the thermal equilibrium value $\langle v^2\rangle_{eq}$. In eqs 31 and 33, the subscript 0 denotes the initial value determined by $W_0(v)$. In the force-free limit, the mean squared displacement of the fractional Fokker−Planck equation (5) reads $\langle x^2\rangle = 2K_\alpha t^\alpha/(\Gamma(1+\alpha))$, in agreement with eq 6. Further properties of the fractional Fokker−Planck equation (7) were discussed in ref 26.

Due to its phase space nature, the calculation of moments for the fractional Klein−Kramers equation (20) leads to several cases, including joint moments. For example, for $F = 0$, $\int \mathrm{d}x \int v\,\mathrm{d}v$ and $\int \mathrm{d}x \int v^2\,\mathrm{d}v$ lead to the fractional Rayleigh equation results (31) and (33), respectively. $\int x\,\mathrm{d}x \int \mathrm{d}v$ reveals the relation

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle x\rangle\rangle = {}_0D_t^{1-\alpha}\frac{\tau^*}{\tau^\alpha}\langle\langle v\rangle\rangle \tag{34}$$

from which

$$\langle\langle x\rangle\rangle = \langle\langle x\rangle\rangle_0 + \frac{\langle\langle v\rangle\rangle_0}{\eta}[1 - E_\alpha(-\eta^* t^\alpha)] \tag{35}$$

follows. The double means $\langle\langle\cdot\rangle\rangle$ in eqs 34 and 35 denote the averaging over both x and v. Note that eq 34 seems to contradict the Newton-type relation $\mathrm{d}/\mathrm{d}t\langle\langle x\rangle\rangle = \langle\langle v\rangle\rangle$ known in the regular case. This "violation" results from the camouflaging effect of the introduction of the long-tailed waiting time pdf $w(t)$.

For the subdiffusive case $0 < \alpha < 1$, all results are dominated by the Mittag−Leffler functions and noninteger power laws. In the Brownian limit, the usual exponential behaviors and integer power laws are recovered. Finally, the equilibria $W_{st}(x,v)$, $W_{st}(v)$, and $W_{st}(x)$ of the fractional Klein−Kramers equation, the fractional Rayleigh equation, and the fractional Fokker−Planck equation are defined through eq 3, with the corresponding expressions for the Boltzmann energies. They are thus equivalent to the Boltzmann−Gibbs or Maxwell equilibria found in the normal Brownian−Markovian cases.[5,6]

VI. Conclusion

A formal extension of the Chapman−Kolmogorov equation has been discussed. For a broad waiting time pdf with diverging characteristic waiting time, the fractional Klein−Kramers equation has been derived. Thereby, the cutoff time assumption was introduced which follows from the assumption that individual sojourns of the test particle are of finite distance and are ruled by the Langevin equation with Gaussian, δ-correlated noise. The presented model should therefore apply for particles which eventually get stuck in position space. Consequently, the dynamics specified by the moments of the velocity changes, eq 12, remain unchanged. From the resulting fractional Klein–Kramers equation a fractional Rayleigh equation and the subdiffusive fractional Fokker–Planck equation have been deduced. The latter was independently derived from a generalized master equation.[27] The present approach is close to thermal equilibrium and leads to an understanding of the physical nature of the generalized friction and diffusion coefficients occurring in this fractional Fokker–Planck equation.

An interpretation which might be of relevance for biophysical problems has been discussed for such cases where the waiting time pdf $w(t)$ possesses a finite first moment T. Accordingly, a microorganism explores the space in the presence of an external field $V(x)$ which corresponds to a distribution of food, or an externally applied chemical or electrical field.

The alternative case when the particles lock onto a given velocity direction, i.e., move ballistically for time spans with a diverging characteristic time, has been considered by Barkai and Silbey.[44] These authors find an intermediate, superdiffusive long-time behavior of the mean squared displacement according to $\langle x^2\rangle \sim A_\beta t^{2-\beta}$ with $0 < \beta < 1$. Therefore, their model is equivalent to continuous time collision models, and the resulting fractional Fokker–Planck equation is different from the subdiffusive fractional Fokker–Planck equation obtained here. However, the velocity distribution of this model is governed by the same fractional Rayleigh equation found in the present approach. The microscopic distinction between both models lies in the times spent in individual velocity modes, leading to considerably different distances covered by the test particle.

It should finally be stressed that the fractional approach which is of an overall non-Markovian nature differs from the generalized Langevin approach in which a temporal convolution is assumed in the underlying stochastic differential equations.[31] In this case the resulting deterministic Klein–Kramers and Fokker–Planck equations are *local* in time: the generalization of the Langevin equation is transferred to time-dependent coefficients.[48]

Acknowledgment. We thank Eli Barkai and Robert Silbey for sharing their work on generalized Kramers equations with us prior to publication, and for helpful discussions. We gratefully acknowledge financial support from the German–Israeli Foundation (GIF). R.M. was supported in part through an Amos de Shalit fellowship from the MINERVA Foundation and by a Feodor Lynen fellowship from the Alexander von Humboldt Stiftung. R.M. thanks Israela Becker for stimulating discussions about waiting time distributions.

References and Notes

(1) Klein, O. *Ark. Mat. Astr. Fys.* **1922**, *16* (5). Kramers, H. A. *Physica* **1940**, *7*, 284.
(2) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.
(3) Wang, M. Ch.; Uhlenbeck, G. E. *Rev. Mod. Phys.* **1945**, *17*, 323.
(4) References 2 and 3 are reprinted in: *Selected papers on noise and stochastic processes*; Wax, N., Ed.; Dover: New York, 1954.
(5) Risken, H. *The Fokker–Planck equation*; Springer-Verlag: Berlin, 1989.
(6) van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*; North-Holland: Amsterdam, 1981.
(7) Langevin, P. *Comptes Rendus* **1908**, *146*, 530.
(8) Fokker, A. D. *Ann. Phys. (Leipzig)* **1914**, *43*, 810. Planck, M. *Sitzber. Preuss. Akad. Wiss.* **1917**, 324.
(9) Smoluchowski, M. v. *Ann. Phys.* **1915**, *48*, 1103.
(10) Davies, R. W. *Phys. Rev.* **1954**, *93*, 1169.
(11) Bouchaud, J.-P.; Georges, A. *Phys. Rep.* **1990**, *195*, 12.
(12) Blumen, A.; Klafter, J.; Zumofen, G. In *Optical Spectroscopy of Glasses*; Zschokke, I., Ed.; Reidel: Dordrecht, 1986.
(13) Havlin, S.; Ben-Avraham, D. *Adv. Phys.* **1987**, *36*, 695.
(14) Hughes, B. D. *Random Walks and Random Environments*; Oxford University Press: Oxford, 1995; Volume 1: Random Walks.
(15) Metzler, R.; Klafter, J. Submitted for publication.
(16) Lévy, P. *Théorie de l'addition des variables aléatoires*; Gauthier-Villars: Paris, 1954. Gnedenko, B. V.; Kolmogorov, A. N. *Limit Distributions for Sums of Random Variables*; Addison-Wesley: Reading, MA, 1954.
(17) Klafter, J.; Shlesinger, M. F.; Zumofen, G. *Phys. Today* **1996**, *49* (2), 33.
(18) Shlesinger, M. F.; Zaslavsky, G. M.; Klafter, J. *Nature* **1993**, *363*, 31.
(19) West, B. J.; Seshadri, V. *Physica* **1982**, *113A*, 203.
(20) Peseckis, F. *Phys. Rev. A* **1987**, *36*, 892.
(21) The fractional Klein–Kramers equation derived in ref 20 can be written in the form[20]

$$\frac{\partial W}{\partial t} = \left[-v\frac{\partial W}{\partial x} + \left(\eta\frac{\partial}{\partial v}v - \frac{\partial}{\partial v}\frac{F(x)}{m}\right) + b\nabla^\mu\right]W(x,v,t)$$

where ∇^μ denotes the Weyl–Riesz operator defined through $F\{\nabla^\mu f(x)\} = -|k|^\mu f(k)$. From the above equation, it is easy to derive the fractional telegrapher's-type equation

$$\frac{\partial W}{\partial t} + \frac{1}{\eta}\frac{\partial^2 W}{\partial t^2} = \left[-\frac{\partial}{\partial x}\frac{F(x)}{m\eta} + \nabla^\mu\frac{k_B T}{m\eta}\right]W$$

via integration. Neglecting the second-order time derivative in the high friction limit, one recovers the fractional Fokker–Planck equation which was inferred in ref 22 for Lévy flights in a random environment, discussed in some detail in ref 23. This type of fractional Klein–Kramers equation and its related fractional Fokker–Planck equation, i.e., the Lévy noise approach, lead to the divergence of the mean square displacement $\langle x^2\rangle = \infty$, as is typically found for Lévy flights,[25,32] and it will not be pursued here further.
(22) Fogedby, H. C. *Phys. Rev. Lett.* **1994**, *73*, 2517; *Phys. Rev. E* **1994**, *50*, 1657: *Phys. Rev. E* **1998**, *58*, 1690. Honkonen, J. *Phys. Rev. E* **1996**, *53*, 327.
(23) Jespersen, S.; Metzler, R.; Fogedby, H. C. *Phys. Rev. E* **1999**, *59*, 2736.
(24) Kusnezov, D.; Bulgac, A.; Dang, G. D. *Phys. Rev. Lett.* **1999**, *82*, 1136.
(25) Klafter, J.; Blumen, A.; Shlesinger, M. F.; Zumofen, G. *Phys. Rev. A* **1990**, *41*, 1158. Bouchaud, J.-P.; Georges, A. *Phys. Rev. A* **1990**, *41*, 1156.
(26) Metzler, R.; Barkai, E.; Klafter, J. *Phys. Rev. Lett.* **1999**, *82*, 3563.
(27) Metzler, R.; Barkai, E.; Klafter, J. *Europhys. Lett.* **1999**, *46*, 431.
(28) Barkai, E.; Metzler, R.; Klafter, J. *Phys. Rev. E* **2000**, *61*, 132.
(29) Oldham, K. B.; Spanier, J. *The fractional calculus*; Academic Press: New York, 1974.
(30) Zwanzig, R. In *Molecular Fluids*; Balian, R., Weils, G., Eds.; Gordon and Breach: New York, 1976.
(31) Kubo, R.; Toda, M.; Hashitsume, N. *Statistical Physics II*; Solid State Sciences 31; Springer-Verlag: Berlin, 1985.
(32) Klafter, J.; Blumen, A.; Shlesinger, M. F. *Phys. Rev. A* **1987**, *35*, 3081.
(33) An equivalent equation was discussed by: Kenkre, V. M.; Montroll, E. W.; Shlesinger, M. F. *J. Stat. Phys.* **1973**, *9*, 45.
(34) By making use of the majorant criterion. Note that the right-hand side of eq 10 is always less or equal than 1. Moreover, for all $t > t'$, $w(t-t') \le w(t)$, according to eq 17.
(35) The fractional operator comes about by taking a Laplace transformation. In the long-time limit, the Laplace transform of the waiting time follows $w(u) \sim 1 - (u\tau)^\alpha$,[32] and the relation $L\{{}_0D_t^{-\alpha}W(x,v,t)\} = u^{-\alpha}W(x,v,u)$ [29] leads to the result, eq 20.
(36) Pfister, G.; Scher, H. *Adv. Phys.* **1978**, *27*, 747. Scher, H.; Shlesinger, M. F.; Bendler, J. T. *Phys. Today* **1991**, *26*.
(37) Schienbein, M.; Gruler, H. *Phys. Rev. E* **1995**, *52*, 4183.
(38) Metzler, R.; Klafter, J. *Phys. Rev. E*, in press.
(39) Gu, Q.; Schiff, E. A.; Grebner, S.; Schwartz, R. *Phys. Rev. Lett.* **1996**, *76*, 3196.
(40) Shlesinger, M. F.; Klafter, J. *J. Phys. Chem.* **1989**, *93*, 7023.

(41) Zumofen, G.; Klafter, J. *Phys. Rev. E* **1995**, *49*, 4873. Kuznetsov, L.; Zaslavsky, G. M. *Phys. Rev. E* **1998**, *58*, 7330. Benkadda, S.; Kassibrakis, S.; White, R. B.; Zaslavsky, G. M. *Phys. Rev. E* **1997**, *55*, 4909.

(42) Plotkin, S. S.; Wolynes, P. G. *Phys. Rev. Lett*. **1998**, *80*, 5015.

(43) Compte, A.; Metzler, R. *J. Phys. A* **1997**, *30*, 7277. Metzler, R.; Compte, A. *Physica* **1999**, *268A*, 454.

(44) Barkai, E.; Silbey, R. *J. Phys. Chem. B* **2000**, *104*, 3866.

(45) Glöckle, W. G.; Nonnenmacher, T. F. *J. Stat. Phys*. **1993**, *71*, 755.

(46) Metzler, R.; Klafter, J. Submitted for publication.

(47) *Tables of Integral Transforms*; Erdélyi, A. Bateman Manuscript Project Vol. I; McGraw-Hill: New York, 1954.

(48) Wang, K. G.; Dong, L. K.; Wu, X. F.; Zhu, F. W.; Ko, T. *Physica* **1994**, *203A*, 53. Wang, K. G.; Tokuyama, M. *Physica* **1999**, *265A*, 341.