

# ANOMALOUS STOCHASTIC PROCESSES IN THE FRACTIONAL DYNAMICS FRAMEWORK: FOKKER–PLANCK EQUATION, DISPERSIVE TRANSPORT, AND NON-EXPONENTIAL RELAXATION

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*Advances in Chemical Physics, Volume 116*, edited by I. Prigogine and Stuart A. Rice.  
ISBN 0-471-40541-8 © 2001 John Wiley & Sons, Inc.

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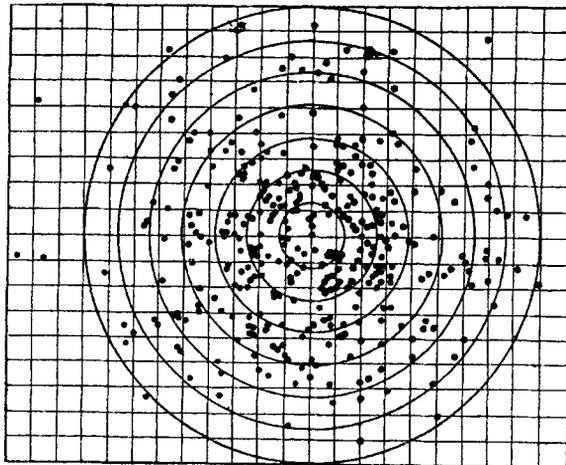
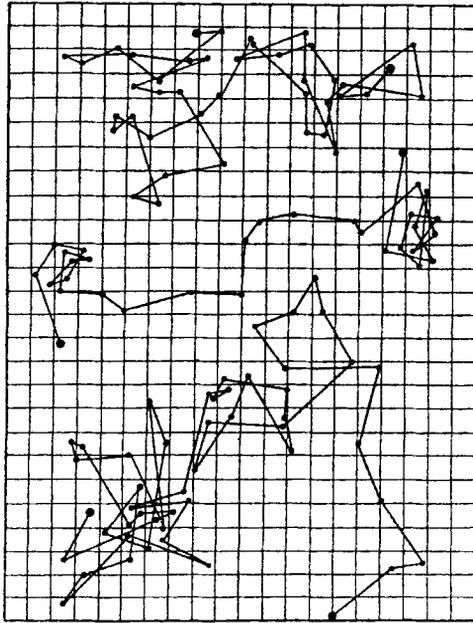
## I. INTRODUCTION

Brownian motion [1] denotes the erroneous motion of a massive particle in a bath of molecules whose ongoing bombardments are the cause for the particle's random walk, which is displayed in Fig. 1. The compelling story of the experimental investigation of Brownian motion [1, 2], with its theoretical description [3–9] being worked out hand in glove with each other, added much to the halcyon development of physics at the end of the nineteenth and in the first half of the twentieth centuries. The importance of the understanding of Brownian motion was honored by the Nobel Prize for Jean Perrin in 1926 for his investigations leading to the determination of Avogadro's number in terms of microscopic quantities, according to Einstein's theory. Today, Brownian motion is well understood, with its continuum description drawing on the central limit theorem according to which the probability density function (pdf) to find the particle at a certain position  $x$  at a given time  $t$  is a universal Gaussian whose second moment, the mean squared displacement  $\langle x^2(t) \rangle = 2dKt$ , grows linearly in time, in any dimension [7–16].

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**Figure 1.** Recorded random walk trajectories by Jean Baptiste Perrin [2]. **Upper panel:** Three designs obtained by tracing a small grain of putty (*mastic*, used for varnish) at intervals of 30 s. One of the patterns contains 50 single points. **Lower panel:** The starting point of each motion event is shifted to the origin. The figure illustrates the pdf of the traveled distance  $r$  to be in the interval  $(r, r + dr)$ , according to  $(2\pi\xi^2)^{-1} \exp(-r^2/[2\xi^2]) 2\pi r dr$ , in two dimensions, with the length variance  $\xi^2$ . These figures constitute part of the measurement of Perrin, Dabrowski, and Chaudesaigues, leading to the determination of the Avogadro number. The result given by Perrin is  $70.5 \cdot 10^{22}$ . The remarkable *œuvre* of Perrin discusses all possibilities of obtaining Avogadro's number known at that time. Concerning the trajectories displayed in the upper part of this figure, Perrin makes an interesting statement: “Si, en effet, on faisait des pointés de seconde en seconde, chacun de ces segments rectilignes se trouverait remplacé par un contour polygonal de 30 côtés relativement aussi compliqué que le dessin ici reproduit, et ainsi de suite.” [If, veritably, one took the position from second to second, each of these rectilinear segments would be replaced by a polygonal contour of 30 edges, each itself being as complicated as the reproduced design, and so forth.] This already anticipates Lévy's cognizance of the self-similar nature [11], as well as of the nondifferentiability recognized by N. Wiener [7].

Brownian transport processes and the related relaxation dynamics in the presence and absence of an external potential are most conveniently described in terms of partial differential equations of the Fokker–Planck (Smoluchowski) [13, 14, 17–19], Rayleigh [13, 20], and Klein–Kramers [13, 14,



21, 22] types. These equations are closely connected to the exponential equilibration of the system and the exponential decay of the survival probability in the Kramers escape problem that is in turn connected to chemical reaction kinetics. Due to its universal character, the Brownian transport theory was believed to prevail in any nonpathological system.

Toward the end of the 1960s, however, surprising data were obtained for the charge carrier transport in amorphous semiconductors, then an important issue in the development of photocopiers and solar cells. Apparently, these data could not be satisfactorily accounted for by the traditional Brownian description of random walks that the charge carriers were a priori supposed to perform. It was Scher, then staff researcher at the Xerox company, who saw himself confronted with this conundrum. Eventually, in collaboration with Montroll, Lax, and Shlesinger, it had been realized that these puzzling data could be understood by the invocation of a random walk description in which each step of the walker occurs at a random time which is chosen from a random distribution  $w(t)$  so broad that it is actually scale-free; that is, it does not possess a characteristic time scale. Coming up with the assumption of a power-law form for this distribution,  $w(t) \sim A_\alpha t^{-\alpha}/t^{1+\alpha}$  [23], the breakthrough was achieved. The resulting continuous-time random walk model with this "fractal time" waiting time distribution has been put on a solid mathematical and physical foundation and has been a successfully applied theory [24].

Amorphous semiconductors have been *the* testing ground for the new theoretical concepts for which the detailed physical mechanisms developed could be impressively corroborated by experiments [24–26]. In the course of time, more and more systems appeared to exhibit "strange kinetics," with a sublinearly growing mean squared displacement and with nonexponential relaxation patterns. Slow diffusion was observed for the tracer dispersion in Rayleigh–Bénard convection systems [27], for polymer dynamics and for a bead immersed in a polymeric fluid [28, 29], and for diffusion in porous media [30, 31]. Strange kinetics is related to the growth of a submonolayer film on a solid surface in the presence of repulsive impurities: The latter are supposed to give rise to anomalous diffusion of the atoms which are deposited on the surface, a process that finally leads to a typical scaling of the island density of the emerging growth pattern [32]. Recently, there has been growing interest in such slow transport in the investigation of tracer dispersion in groundwater systems which might render important new insight into the ecological impact of deposited chemicals or radioactive waste [33], and the cognisance of strange kinetics has been taken in protein dynamics [34, 35]. Another boost for the continuous-time random walk theory came from its applications to chaotic systems where broadly distributed waiting times arise for the sticking of a trajectory in deterministic maps, or close to stable islands [36]. Strange kinetics even stretches far

into the nanoscale reign, being related to the power-law blinking kinetics of quantum dots [37] or to the broad distribution of waiting times in subrecoil laser cooling [38]. It is common to these complex systems that some kind of disorder—that is, the presence of spatial or temporal constraints—reduces the spatiodynamical degrees of freedom of the random motion of the particle under consideration. This presence of constraints leads to the temporally non-local behavior, to the slowly decaying memory expressed in the transport and relaxation dynamics of such systems, and consequently to the observation of strange kinetics.

Here, we present an approach for the description of such anomalous transport processes that is based on the continuous-time random walk theory for a power-law waiting time distribution  $w(t)$  but which can be used to find the probability density function of the random walker *in the presence of an external force field*, or in phase space. This framework is *fractional dynamics*, and we show how the traditional kinetic equations can be generalized and solved within this approach.

The anomalous transport processes on which we focus and which correspond to the above examples are, in the force-free limit, characterized by the power-law form [15, 16, 39–42]

$$\langle x^2(t) \rangle \sim K_\alpha^* t^\alpha, \quad \alpha \neq 1 \quad (1)$$

of the mean squared displacement which leads to a spectrum of diffusion processes, depending on the anomalous exponent  $\alpha$ . In Eq. (1),  $K_\alpha^*$  is a generalized diffusion constant of dimension  $\text{cm}^2/\text{s}^\alpha$  which will be specified below. For the power-law form of the waiting time distribution,  $w(t) \sim A_\alpha \tau^\alpha / t^{1+\alpha}$  with  $\alpha$  ranging in the interval  $\alpha \in (0, 1)$ , one observes *slow diffusion*, or *subdiffusion*. Thus,  $\alpha$  becomes an essential characteristic quantity of the underlying kinetic process. In that sense, anomalous transport processes are nonuniversal. However, these processes are subject to a superordinate limit theorem that is connected with Lévy (stable) distributions [41, 43] and that guarantees the existence of a limit distribution for the anomalous process in the same way as the central limit theorem enforces the Gaussian limit distribution of the Brownian process. In fact, the central limit theorem is a special case located on the verge of the basin of attraction of this more general theorem. The anomalous exponent  $\alpha$  characterizes the special system under consideration, and therefore it has to be determined independently. It may depend on thermodynamic parameters like temperature, pressure, and so on.

Among the most striking changes brought about by fractional dynamics is the substitution of the traditionally obtained exponential system equilibration of time-dependent system quantities by the Mittag-Leffler pattern [44–46]

that interpolates between an initial stretched exponential and a final inverse power-law pattern,

$$\exp\left(-\frac{t}{\tau}\right) \longrightarrow E_{\alpha}(-(t/\tau)^{\alpha}) \sim \begin{cases} \exp\left(-\frac{t^{\alpha}}{\tau^{\alpha}\Gamma(1+\alpha)}\right), & t \ll \tau \\ (\Gamma(1-\alpha)(t/\tau)^{\alpha})^{-1}, & t \gg \tau. \end{cases} \quad (2)$$

In what follows, we present a generalized stochastics framework for the description of slow ( $0 < \alpha < 1$ ) transport in position and phase space, on the basis of fractional dynamics. Accordingly, complex systems close to thermodynamic equilibrium which exhibit a self-similar memory are governed by the fractional Fokker–Planck, Rayleigh, and Klein–Kramers equations. We demonstrate that fractional dynamics may arise for multiple trapping systems with broadly distributed trapping times. More generally, it is equivalent to a generalized master equation with a power-law memory kernel that can be connected to a continuous-time random walk approach.

The advantage of the fractional formulation in comparison to other approaches lies in its proximity to the classical partial differential equations and their methods of solution.

Note that throughout the presentation, we concentrate on the one-dimensional case.

## II. THE RISE OF FRACTIONAL DYNAMICS

### A. The Master Equation

The discrete Markovian master equation [13–16]

$$W_j(t + \Delta t) = \sum_{j' \neq j} A_{j,j'} W_{j'}(t) \quad (3)$$

describes the evolution of the pdf  $W_j(t)$  during the time step  $\Delta t$  as determined by the transfer matrix  $A_{j,j'}$ .  $W_j(t)$  denotes the probability to find the random walker at site  $j$  at the given time  $t$ . The continuum limit with respect to the position coordinate  $j$  relies on a Taylor expansion in the step length  $\Delta x$  of the corresponding transfer function  $A(x)$ . If this expansion converges and  $\Delta x$  can be regarded a small parameter, one recovers the Fokker–Planck (Smoluchowski) equation [13–19, 47]

$$\frac{\partial W}{\partial t} = \left( -\frac{\partial F(x)}{\partial x} \frac{1}{m\eta} + K \frac{\partial^2}{\partial x^2} \right) W(x, t) \quad (4)$$

for the pdf  $W(x, t)$  in the time-independent external force field  $F(x) = -\frac{d}{dx}\Phi(x)$ . Here,  $m$  is the mass of the particle,  $\eta$  the friction constant quantifying the effective interaction with the environment, and  $K$  is the diffusion constant. The latter two are connected via the Einstein–Stokes relation  $K = k_B T / (m\eta)$ , where  $k_B T$  is the Boltzmann temperature [5]. The coefficients in Eq. (4) are given by

$$\frac{F(x)}{m\eta} \equiv \lim_{\Delta x \rightarrow 0, \Delta t \rightarrow 0} \frac{\Delta x}{\Delta t} (A_+(x) - A_-(x)), \quad K \equiv \lim_{\Delta x \rightarrow 0, \Delta t \rightarrow 0} \frac{(\Delta x)^2}{2\Delta t}, \quad (5)$$

where the continuum version  $A_{\pm}(x)$  of the transfer matrix  $A_{j,j'}$  denotes the probability of coming from the left or right of the position  $x$ . For taking these limits, the normalization condition  $A_+(x) + A_-(x) = 1$  was imposed, and we assumed that the system is close to thermal Gibbs–Boltzmann equilibrium; that is,  $A_+(x - \Delta x) \sim (1 - 2\beta\Delta x F(x))A_-(x)$ , where  $\beta \equiv (k_B T)^{-1}$  is the Boltzmann factor.

## B. Long-Tailed Waiting Times Processes and the Generalized Master Equation

The emergence of slow kinetics with its typical slowly decaying memory effects is tightly connected to a scale-free waiting time pdf; that is, the temporal occurrence of the motion events performed by the random walking particle is broadly distributed such that no characteristic waiting time exists. It has been demonstrated that it is the assumption of the power-law form for the waiting time pdf which leads to the explanation of the kinetics of a broad diversity of systems such as the examples quoted above.

Systems that display strange kinetics no longer fall into the basin of attraction of the central limit theorem, as can be anticipated from the anomalous form (1) of the mean squared displacement. Instead, they are connected with the Lévy–Gnedenko generalized central limit theorem, and consequently with Lévy distributions [43]. The latter feature asymptotic power-law behaviors, and thus the asymptotic power-law form of the waiting time pdf,  $w(t) \sim A_x \tau^\alpha / t^{1+\alpha}$ , may belong to the family of completely asymmetric or one-sided Lévy distributions  $\mathbf{L}_x^+$ , that is,

$$w(t) = \mathbf{L}_x^+(t/\tau) \sim A_x \frac{\tau^\alpha}{t^{1+\alpha}}, \quad 0 < \alpha < 1, \quad (6)$$

see the compilation in Appendix A.<sup>1</sup> Due to its long-tailed nature, the waiting time pdf (6) fulfills the criterion that it possesses no characteristic time scale:

<sup>1</sup>We choose the representation in terms of a Lévy distribution for convenience because it includes the Brownian limit. Indeed, any waiting time pdf  $w(t)$  with the asymptotic power-law trend following Eq. (6) leads to the same results as obtained in the following for  $0 < \alpha < 1$ .

$T \equiv \int_0^\infty w(t)t dt \rightarrow \infty$ , manifesting the self-similar nature of this waiting process that has also prompted the coinage of “fractal time” processes [48]. Note that in the limit  $\alpha \rightarrow 1$ , this waiting time pdf reduces to the singular form  $L_1^+(t/\tau) = \delta(t - \tau)$  with finite  $T = \tau$  that leads back to the temporally local Markovian formulation of classical Brownian transport. In fact, for any waiting time pdf with a finite characteristic time  $T$ , one recovers the Brownian picture, such as for the Poissonian form  $w(t) = \tau^{-1}e^{-t/\tau}$ .

In the continuous-time random walk model, a random walker is pictured to execute jumps at time steps chosen from the waiting time pdf  $w(t)$ . In the isotropic and homogeneous (that is, force-free) case, the distance covered in a single jump event can be drawn from the jump length pdf  $\lambda(x)$ . Then, the probability  $\eta(x, t)$  of just having arrived at position  $x$  is given through [49]

$$\eta(x, t) = \int_{-\infty}^{\infty} dx' \int_0^{\infty} dt' \eta(x', t') \lambda(x - x') w(t - t') + \delta(x) \delta(t), \quad (7)$$

where the initial condition is  $\delta(x)$ . Consequently, the pdf  $W(x, t)$  of being in  $x$  at time  $t$  is given by

$$W(x, t) = \int_0^t dt' \eta(x, t') \Psi(t - t'), \quad (8)$$

in terms of the convoluted pdf  $\eta(x, t)$  of just having arrived in  $x$  at time  $t'$ , and not having moved since. The latter is defined by the cumulative probability

$$\Psi(t) = 1 - \int_0^t dt' w(t') \quad (9)$$

assigned to the probability of no jump event during the time interval  $(0, t)$ . Converting Eq. (9) to Fourier–Laplace space which is defined through

$$f(u) \equiv \mathcal{L}\{f(t)\} = \int_0^\infty f(t) e^{-ut} dt \quad (10a)$$

$$g(k) \equiv \mathcal{F}\{g(x)\} = \int_{-\infty}^\infty g(x) e^{ikx} dx, \quad (10b)$$

the transformed pdf  $W(x, t)$  obeys the algebraic relation [49]

$$W(k, u) = \frac{1 - w(u)}{u} \frac{W_0(k)}{1 - \lambda(k)w(u)}, \quad (11)$$

where  $W_0(k)$  denotes the Fourier transform of the initial condition  $W_0(x) \equiv \lim_{t \rightarrow 0^+} W(x, t)$ . If now the jump length pdf is such that it possesses a finite variance, its Fourier transform is accordingly given through  $\lambda(k) \sim 1 - Ck^2$  for small wavenumber  $k$ . Conversely, the small  $u$  expansion of our waiting time pdf  $w(t) = \mathbf{L}_\alpha^+(t/\tau)$  follows:

$$w(u) \sim 1 - (u\tau)^\alpha. \tag{12}$$

If the two pdfs  $\lambda$  and  $w$  are plugged into Eq. (11), the short wavenumber and short Laplace frequency limit  $(k, u) \rightarrow (0, 0)$  reveals

$$W(k, u) - \frac{1}{u} = -u^{-\alpha} \frac{C}{\tau^\alpha} k^2 W(k, u), \tag{13}$$

for  $W_0(x) = \delta(x)$ . The Laplace inversion of Eq. (13) involves the term  $u^{-\alpha} W(k, u)$ . With the definition of the Riemann–Liouville fractional operator [Eq. (21) below], this expression corresponds to the Riemann–Liouville fractional integral  ${}_0D_t^{-\alpha} W(x, t)$  in  $(x, t)$  space. Consequently, one recovers by Fourier–Laplace inversion of Eq. (13) the fractional diffusion equation [50–54]

$$W(x, t) - W_0(x) = {}_0D_t^{-\alpha} K_\alpha \frac{\partial^2}{\partial x^2} W(x, t) \tag{14}$$

in the integral formulation. Equation (14) was first discussed and solved by Schneider and Wyss [50]. Note that we identified  $K_\alpha \equiv C/\tau^\alpha$  [49, 53, 54]. Alternatively, Eq. (14) can be rephrased in the differential form

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha} K_\alpha \frac{\partial^2}{\partial x^2} W(x, t) \tag{15}$$

by operation of the ordinary differential  $\partial/\partial t$ . The fractional diffusion equation (15) for the initial condition  $W_0(x) = \delta(x)$  can be solved in closed form, invoking Fox’s  $H$ -functions  $H_{p,q}^{m,n}$  [55, 56], to obtain

$$W(x, t) = \frac{1}{\sqrt{4K_\alpha t^\alpha}} H_{1,1}^{1,0} \left[ \frac{|x|}{\sqrt{K_\alpha t^\alpha}} \left| \begin{matrix} (1 - \frac{\alpha}{2}, \frac{\alpha}{2}) \\ (0, 1) \end{matrix} \right. \right], \tag{16}$$

which is equivalent to the result found by Schneider and Wyss in terms of  $H_{1,2}^{2,0}$  [50]. Through the Fox function formulation one finds the series representation

$$W(x, t) = \frac{1}{\sqrt{4K_\alpha t^\alpha}} \sum_{n=0}^{\infty} \frac{(-1)^n}{n! \Gamma(1 - \alpha[n + 1]/2)} \left( \frac{x^2}{K_\alpha t^\alpha} \right)^{n/2} \tag{17}$$

and the asymptotic expansion

$$\begin{aligned}
 W(x, t) \sim & \frac{1}{\sqrt{4\pi K_\alpha t^\alpha}} \sqrt{\frac{1}{2-\alpha}} \left(\frac{2}{\alpha}\right)^{(1-\alpha)/(2-\alpha)} \left(\frac{|x|}{\sqrt{K_\alpha t^\alpha}}\right)^{-(1-\alpha)/(2-\alpha)} \\
 & \times \exp\left(-\frac{2-\alpha}{2} \left(\frac{\alpha}{2}\right)^{\alpha/(2-\alpha)} \left[\frac{|x|}{\sqrt{K_\alpha t^\alpha}}\right]^{1/(1-\alpha/2)}\right)
 \end{aligned} \tag{18}$$

valid for  $|x| \gg \sqrt{K_\alpha t^\alpha}$ . The functional form of the result (18) has prompted the coinage of *stretched Gaussian* form, and it is equivalent to the continuous-time random walk findings reported by Zumofen and Klafter [57].

If an external force field acts on the random walker, it has been shown [58, 59] that in the diffusion limit, this broad waiting time process is governed by the fractional Fokker–Planck equation (FFPE) [60]

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha} \left( -\frac{\partial F(x)}{\partial x m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2} \right) W(x, t), \tag{19}$$

which is discussed in detail in the next section. Equations (15) and (19) feature the Riemann–Liouville operator

$${}_0D_t^{1-\alpha} = \frac{\partial}{\partial t} {}_0D_t^{-\alpha} \tag{20}$$

whose definition is given in terms of the convolution [61]

$${}_0D_t^{-\alpha} W(x, t) = \frac{1}{\Gamma(\alpha)} \int_0^t dt' \frac{W(x, t')}{(t-t')^{1-\alpha}}. \tag{21}$$

It is interesting to note that the notion of noninteger order differentials goes back to one of the founders of classical calculus, Leibniz, who mentions the problem as an interesting topic in a letter to de l’Hôpital in 1695. Numerous famous mathematicians have worked on the field which eventually was to become fractional calculus. Of the several different definitions in use, the Riemann–Liouville version defined through Eq. (21) corresponds to physical problems with a defined initial condition at  $t = 0$ . The (Riemann–Liouville) fractional integral (21) generalizes the Cauchy multiple integral to a “real-value folded” integration. Fractional differentiation is defined as a fractional integration, followed by an ordinary differentiation:

$${}_0D_t^q f(t) \equiv \frac{d^n}{dt^n} ({}_0D_t^{-(n-q)} f(t)), \quad n-1 \geq q < n. \tag{22}$$

The fractional differentiation of a power

$${}_0D_t^q t^p = \frac{\Gamma(1+p)}{\Gamma(1+p-q)} t^{p-q} \tag{23}$$

is analogous to the standard case; however, note that the fractional differentiation of a constant does not vanish:

$${}_0D_t^q 1 = \frac{1}{\Gamma(1-q)} t^{-q}. \tag{24}$$

Expression (24) reduces to the standard  $\frac{d^n}{dt^n} 1 = 0$  for  $q \rightarrow n$ , due to the divergence of the gamma function  $\Gamma(z)$  for nonpositive integers. The fractional Riemann–Liouville integral operator  ${}_0D_t^{-q}$  fulfills the generalized integration theorem of the Laplace transformation:

$$\mathcal{L}\{ {}_0D_t^{-q} f(t) \} = u^{-q} f(u), \quad q \in \mathbb{R}_0^+. \tag{25}$$

In the limit  $\alpha \rightarrow 1$ , the Riemann–Liouville fractional integral  ${}_0D_t^{-\alpha}$  reduces to an ordinary integration so that  $\lim_{\alpha \rightarrow 1} {}_0D_t^{1-\alpha} \equiv \frac{\partial}{\partial t} \int_0^t dt'$  becomes the identity operator; that is, Eqs. (15) and (19) simplify to the standard diffusion and Fokker–Planck equations, respectively.

According to Eq. (21), the FFPE (19) involves a slowly decaying, self-similar memory so that the present state  $W(x, t)$  of the system depends strongly on its history  $W(x, t')$ ,  $t' < t$ , in contrast to its Brownian counterpart which is local in time. In the force-free case,  $F(x) = 0$ , the FFPE (19) reduces to the fractional diffusion equation (15).

It has been shown that the FFPE (19) is equivalent to the generalized master equation [58]

$$\frac{\partial W}{\partial t} = \int_{-\infty}^{\infty} dx' \int_0^t dt' K(x, x'; t-t') W(x', t') \tag{26}$$

with the kernel

$$K(x, x'; u) \equiv uw(u) \frac{\Lambda(x, x') - \delta(x)}{1-w(u)} \tag{27}$$

given in Laplace space. Here, the transfer function  $\Lambda(x, x')$  generalizes the homogeneous jump length pdf  $\lambda(x-x')$  of the standard continuous-time random walk model, and thus it quantifies the local anisotropy and gives rise to the drift and diffusion terms [58].  $\Lambda$  may be defined through  $\Lambda(x, x') \equiv$

$\lambda(x - x')(A(x')\Theta(x - x') + B(x')\Theta(x' - x))$  in terms of the probabilities to jump left or right, as introduced through the Heaviside functions  $\Theta(x)$  [58].

For systems that exhibit slow anomalous transport, the incorporation of external fields is in complete analogy to the existing Brownian framework which itself is included in the fractional formulation for the limit  $\alpha \rightarrow 1$ : The FFPE (19) combines the linear competition of drift and diffusion of the classical Fokker–Planck equation with the prevalence of a new relaxation pattern. As we are going to show, also the solution methods for fractional equations are similar to the known methods from standard partial differential equations. However, the temporal behavior of systems ruled by fractional dynamics mirrors the self–similar nature of its nonlocal formulation, manifested in the Mittag-Leffler pattern dominating the system equilibration.

### C. Boundary Value Problems for the Fractional Diffusion Equation

Exemplifying the convenience of the fractional approach, we address the imposition of boundary value problems on the fractional diffusion equation which was demonstrated in Ref. 62. In this force-free case for which the kernel, Eq. (27), takes on the homogeneous form  $K(x, x'; u) = uw(u)$  ( $\lambda(x - x') - \delta(x)$ )/(1 -  $w(u)$ ), one can apply the method of images in order to construct the solution [12].

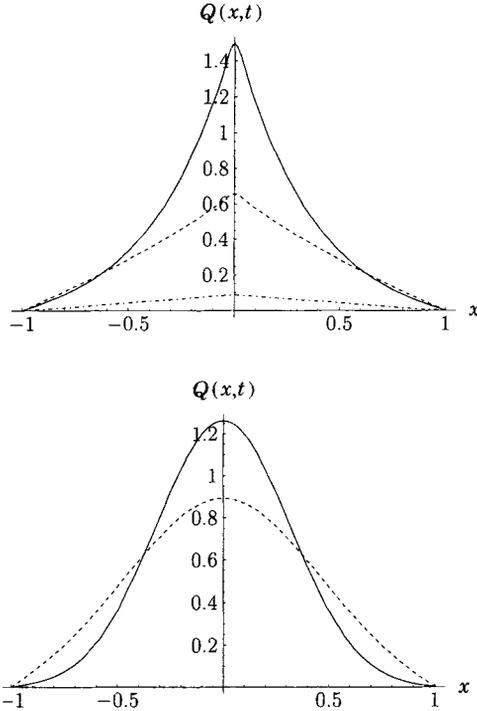
Let us address the example of subdiffusion modelled through Eq. (15) in a box with absorbing boundary conditions, located at  $x = \pm a$ , and the symmetric initial condition  $W_0(x) = \delta(x)$ ; that is, the corresponding pdf  $Q(x, t)$  has to fulfill  $Q(\pm a, t) = 0$  and  $Q_0(x) = \delta(x)$ . The solution to this boundary value problem is obtained in the same way as for the classical case [12], resulting in [62]

$$Q(x, t) = \sum_{m=-\infty}^{\infty} (W(x + 4ma, t) - W(4ma - x + 2a, t)), \quad (28)$$

where the image function  $Q(x, t)$  fulfills the boundary condition. The sum (28) can be transformed to the more convenient representation [62]

$$Q(x, t) = \frac{1}{a} \sum_{m=0}^{\infty} e^{\pi i(2m+1)x/(2a)} E_{\alpha} \left( -K_{\alpha} \frac{(2m+1)^2 \pi^2}{4a^2} t^{\alpha} \right), \quad (29)$$

which can be evaluated numerically. Equation (29) involves the Mittag-Leffler function  $E_{\alpha}(z)$  instead of the classical exponential functions. We will comment on the Mittag-Leffler function in Appendix B. The result for  $\alpha = 1/2$  is displayed in Fig. 2, in comparison to the Brownian result. The subdiffusive solution features distinct humps in the center, close to the



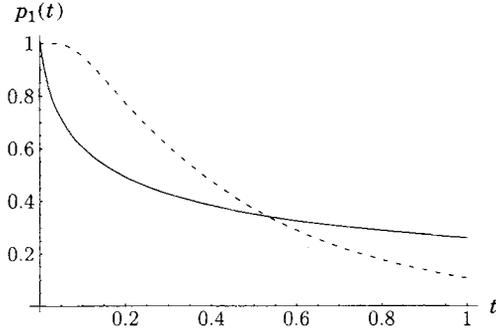
**Figure 2.** Probability density function  $Q(x, t)$  for absorbing boundaries in  $x = \pm 1$ . Top: The subdiffusive case,  $\alpha = 1/2$ . Bottom: The Brownian case,  $\alpha = 1$ . The curves are drawn for the times  $t = 0.005, 0.1, 10$  on the top and for  $t = 0.05, 0.1, 10$  on the bottom. Note the distinct cusp-like shape of the subdiffusive solution in comparison to the smooth Brownian counterpart. For the longest time, the Brownian solution has almost completely decayed.

initial condition that persists on that point, in contrast to the fast smoothing in the Brownian case. The temporal decay of the survival probability (i.e., the overall probability of not having been absorbed), is given through the integral

$$p_a(t) = \int_{-a}^a dx Q(x, t), \tag{30}$$

which for Eq. (29) becomes

$$p_a(t) = \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{(-1)^m}{2m+1} E_{\alpha} \left( -K_x \frac{(2m+1)^2 \pi^2}{4a^2} t^{\alpha} \right). \tag{31}$$



**Figure 3.** Survival probability for absorbing boundary conditions positioned at  $x = \pm 1$ , plotted for the subdiffusive case  $\alpha = 1/2$  and the Brownian case  $\alpha = 1$  (dashed curve). For longer times, the faster (exponential) decay of the Brownian solution, in comparison to the power-law asymptotic of the Mittag-Leffler behavior, is obvious.

This function has the long-time behavior  $p_a(t) \sim C_\alpha t^{-\alpha}$ , where  $C_\alpha$  is a constant. The survival probability for the subdiffusive case is plotted in Fig. 3 and compared with the Brownian survival. Clearly, for long times, the survival probability in the subdiffusive system decays in a much slower fashion.

A recent work has demonstrated that the formulation of reaction–diffusion problems in systems that display slow diffusion within a continuous-time random walk model with a broad waiting time pdf of the form (6) leads to a fractional reaction–diffusion equation that includes a source or sink term in the same additive way as in the Brownian limit [63]. With the fractional formulation for single-species slow reaction–diffusion obtained by the authors still being linear, no pattern formation due to Turing instabilities can arise. This is due to the fact that fractional systems of the type (15) are close to Gibbs–Boltzmann thermodynamic equilibrium as shown in the next section.

### III. THE FRACTIONAL FOKKER–PLANCK EQUATION

#### A. The Classical Fokker–Planck Equation

The formulation of the Fokker–Planck equation is due to Fokker’s and Planck’s independent works on the description of the Brownian motion of particles [17, 18]. Commonly, an  $N$  variables equation of the type

$$\frac{\partial W}{\partial t} = \left( - \sum_{i=1}^N \frac{\partial}{\partial x_i} D_i^{(1)}(\{x\}) + \sum_{i,j=1}^N \frac{\partial^2}{\partial x_i \partial x_j} D_{ij}^{(2)}(\{x\}) \right) W(\{x\}, t), \quad (32)$$

where the drift vector  $D_i^{(1)}$  and the diffusion tensor  $D_{ij}^{(2)}$  may depend on the position  $x \equiv \{x_1, x_2, \dots, x_N\}$ , is called Fokker–Planck equation [14]. In the following, we deal with the monivariate ( $N = 1$ ) and bivariate ( $N = 2$ ) cases, and we assume a constant, purely diagonal diffusion tensor.

The monivariate Fokker–Planck equation with a position dependent diffusion coefficient  $D^{(2)}(x)$ ,

$$\frac{\partial W}{\partial t} = \left( -\frac{\partial}{\partial x} D^{(1)}(x) + \frac{\partial^2}{\partial x^2} D^{(2)}(x) \right) W(x, t), \quad (33)$$

can be transformed in general onto the so-called normalized Fokker–Planck equation (4) with the diffusion *constant*  $K$  [14]. In the latter formulation, we have chosen the coefficients according to the Smoluchowski model in which the drift caused by the external force field  $F(x)$  is moderated through the friction constant  $\eta$ . In Eq. (4), the pdf  $W$  approaches the Gibbs–Boltzmann equilibrium

$$W_{\text{st}}(x) \equiv \lim_{t \rightarrow \infty} W(x, t) = N \exp(-\beta\Phi(x)), \quad (34)$$

where  $\beta \equiv (k_B T)^{-1}$  is the Boltzmann factor, and the normalization constant  $N$  explicitly depends on the potential  $\Phi(x)$  that is defined through  $\Phi(x) = -\int^x dx' F(x')$ . The diffusion and friction constants are related through the Einstein–Stokes relation  $K = k_B T / m\eta$ , fulfilling the fluctuation–dissipation condition.

A one-dimensional Fokker–Planck equation was used by Smoluchowski [19], and the bivariate Fokker–Planck equation in phase space was investigated by Klein [21] and Kramers [22]. Note that, in essence, the Rayleigh equation [23] is a monivariate Fokker–Planck equation in velocity space. Physically, the Fokker–Planck equation describes the temporal change of the pdf of a particle subjected to diffusive motion and an external drift, manifest in the second- and first-order spatial derivatives, respectively. Mathematically, it is a linear second-order parabolic partial differential equation, and it is also referred to as a forward Kolmogorov equation. The most comprehensive reference for Fokker–Planck equations is probably Risken’s monograph [14].

## B. Basic Properties

Before discussing the FFPE (19) in detail, we note that the fractional approach 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 is the Boltzmann distribution; **(iii)**

generalized Einstein relations are satisfied; and (iv) in the limit  $\alpha \rightarrow 1$ , the standard FPE is recovered. While other approaches like fractional Brownian motion [64], the continuous time random walk [23, 25, 65], modified diffusion equations [66], generalized Langevin equations [67], fractional equations for Lévy flights in external fields [68–71], local fractional equations [72], or generalized thermostatics [73] fulfill part of these requirements, we know of no other simple approach that meets all of these physical demands. Together with the straightforward mathematical tractability of fractional equations, these are the major criteria why we regard the fractional approach as especially suited.

The FFPE (19) contains the generalized friction constant  $\eta_\alpha$  and the generalized diffusion constant  $K_\alpha$ , of dimensions  $[\eta_\alpha] = \text{s}^{\alpha-2}$  and  $[K_\alpha] = \text{cm}^2 \text{s}^{-\alpha}$ . The physical origin of these fractional dimensions will be explained in the next section. In what follows, we assume natural boundary conditions, that is,  $\lim_{|x| \rightarrow \infty} W(x, t) = 0$ . The FFPE (19) describes a physical problem, where the system is prepared at  $t_0 = 0$  in the state  $W(x, 0)$ .

The right-hand side of the FFPE (19) is equivalent to the fractional expression

$$- {}_0D_t^{1-\alpha} \frac{\partial S(x, t)}{\partial x}, \quad (35)$$

where

$$S(x, t) = \left( \frac{F(x)}{m\eta_\alpha} - K_\alpha \frac{\partial}{\partial x} \right) W(x, t) \quad (36)$$

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  $x$  [14], and the stationary solution is defined by  $-F(x)W_{\text{st}}/[m\eta_\alpha] + K_\alpha W'_{\text{st}} = 0$ . Comparing the resulting expression  $W_{\text{st}}(x) \propto \exp(-\Phi(x)/[K_\alpha m\eta_\alpha])$  to the required Boltzmann distribution  $W_{\text{st}} \propto \exp(-\Phi(x)/[k_B T])$ , we find a generalization of the Einstein–Stokes relation, also referred to as the Stokes–Einstein–Smoluchowski relation [16],

$$K_\alpha = \frac{k_B T}{m\eta_\alpha}, \quad (37)$$

for the generalized coefficients  $K_\alpha$  and  $\eta_\alpha$  [60]. Thus, processes described by Eq. (19) 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  $\Phi(x) = -Fx$ , a net drift occurs. Calculating

the first moment  $\frac{d}{dt} \langle x(t) \rangle_F = \int dx x \frac{\partial}{\partial t} W$  via the FFPE (19), we obtain

$$\langle x(t) \rangle_F = \frac{F}{m\eta_\alpha} \frac{t^\alpha}{\Gamma(1 + \alpha)}. \quad (38)$$

The mean squared displacement for the FFPE (19) in the absence of a force can be calculated similarly:

$$\langle x^2(t) \rangle_0 = \frac{2K_\alpha t^\alpha}{\Gamma(1 + \alpha)}. \quad (39)$$

Note the subscripts  $F$  and  $0$  to indicate presence and absence of the force field. Using Eq. (37), we recover the relation [60]

$$\langle x(t) \rangle_F = \frac{1}{2} \frac{F \langle x^2(t) \rangle_0}{k_B T}, \quad (40)$$

connecting the first moment in the presence of the uniform force field with the second moment in absence of the force. Relation (40) is the second Einstein relation discussed in Refs. 41 and 74. It can be derived from first principles, using a Hamiltonian description of the system, within the linear response régime. Recent experimental results corroborate the validity of Eq. (37) in polymeric systems in the subdiffusive domain (see Ref. 29). The investigation of charge carrier transport in semiconductors in Ref. 26 showed that, up to a prefactor 2 that could not be determined exactly, Eq. (40) is valid.

The temporal evolution of the pdf  $W(x, t)$  in Eq. (19), in the presence of the arbitrary external force field  $F(x)$ , is formally given in terms of the operator expression [60]

$$W(x, t) = E_\alpha(L(x)t^\alpha)W(x, 0), \quad L(x) \equiv \left( -\frac{\partial F(x)}{\partial x m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2} \right), \quad (41)$$

which is the Mittag-Leffler generalization of the traditional exponential relation  $W(x, t) = \exp(L(x)t)$ . The Mittag-Leffler function  $E_\alpha$  [44–46] that appears in Eq. (41) is defined in Appendix B, and it includes the exponential in the Brownian limit  $\alpha \rightarrow 1$ . We note that the FFPE (19) was derived from a generalized master equation that was based upon a nonhomogeneous continuous-time random walk model in Ref. 58, as well as from a continuous-time master equation in Ref. 59. It was obtained as the diffusion limit of a fractional Klein–Kramers equation from a multiple trapping model in Ref. 75, as reviewed below.

### C. Methods of Solution and the Nonexponential Mode Relaxation

For a specified form of the Fokker–Planck operator  $L(x)$ , one can find an explicit solution  $W(x, t)$  of the FFPE (19) through separation of variables. Indeed, inserting the separation ansatz

$$W_n(x, t) = \varphi_n(x)T_n(t), \quad (42)$$

where  $n$  labels a certain eigenvalue of the Fokker–Planck operator  $L(x)$ , into the FFPE (19) yields the factorized equation

$$\frac{dT_n}{dt} \varphi_n = ({}_0D_t^{1-\alpha} T_n) L(x) \varphi_n. \quad (43)$$

The complete solution  $W(x, t)$  is then expressed through the sum over the particular solutions  $W_n(x, t)$ , over the set of eigenvalues  $\{n\}$ . After the separation of Eq. (43) through division by  $({}_0D_t^{1-\alpha} T_n) \varphi_n$ , one arrives at the two eigen-equations

$$\frac{dT_n}{dt} = -\lambda_{n,x} {}_0D_t^{1-\alpha} T_n, \quad (44a)$$

$$L(x) \varphi_n = -\lambda_{n,x} \varphi_n \quad (44b)$$

for the eigenvalue  $\lambda_{n,x}$ . The latter are related to their Brownian counterparts  $\lambda_{n,1}$  for the same external potential field  $\Phi(x)$  by the dimensional prefactor  $\lambda_{n,x} = (\eta/\eta_x) \lambda_{n,1}$ . The temporal eigensolution to Eq. (44a) is given in terms of the Mittag-Leffler function

$$T_n(t) = E_\alpha(-\lambda_{n,x} t^\alpha). \quad (45)$$

The complete solution of the FFPE (19) is thus composed by the sum

$$W(x, t|x', 0) = \exp(\tilde{\Phi}(x')/2 - \tilde{\Phi}(x)/2) \sum_{\{n\}} \psi_n(x) \psi_n(x') E_\alpha(-\lambda_{n,x} t^\alpha) \quad (46)$$

over the set of eigenvalues,  $\{n\}$ , for an initial distribution concentrated in  $x'$ . In Eq. (46), the functions  $\psi_n(x) \equiv e^{\tilde{\Phi}(x)/2} \varphi_n(x)$  are related to the eigenfunctions of the Fokker–Planck operator  $L(x)$ ,  $\varphi_n(x)$ , via the scaled potential  $\tilde{\Phi}(x) \equiv \Phi(x)/(k_B T)$ . Note that the  $\psi_n$  are eigenfunctions to the Hermitian operator  $\tilde{L} = e^{-\tilde{\Phi}} L(x) e^{\tilde{\Phi}}$ , where  $\tilde{L}(x)$  and  $L(x)$  have the same eigenvalues  $\lambda_{n,x}$  [14]. For a nonpathological case, the set of eigenvalues,  $\{n\}$ , is discrete and the eigenvalues are nonnegative. Thus, on arranging the eigenvalues in

increasing order, (i.e.,  $0 \leq \lambda_{0,\alpha} < \lambda_{1,\alpha} < \lambda_{2,\alpha} < \dots$ ), the first eigenvalue is zero iff there exists a stationary solution fulfilling the condition

$$\frac{\partial W(x, t)}{\partial t} = 0. \tag{47}$$

This stationary solution is then necessarily given through

$$W_{\text{st}}(x) = \lim_{t \rightarrow \infty} W(x, t) = e^{\tilde{\Phi}(x')/2 - \tilde{\Phi}(x)/2} \psi_0(x) \psi_0(x'), \tag{48}$$

in full accordance with the Brownian case  $\alpha = 1$ : It is the Gibbs–Boltzmann distribution. In contrast to this equivalence, it should be emphasized, the relaxation of a single mode  $n$  is subexponential, decaying slowly in the Mittag-Leffler fashion. This new relaxation pattern is distinguished by its interpolation between an initial stretched exponential (Kohlrausch) function and a final inverse power-law behavior (compare Appendix B).

An important property of the FFPE (19) is the functional scaling relation [60, 76]

$$W_\alpha(x, u) = \frac{\eta_\alpha}{\eta} u^{\alpha-1} W_1\left(x, \frac{\eta_\alpha}{\eta} u^\alpha\right) \tag{49}$$

in Laplace space, connecting the fractional solution  $W_\alpha(x, t)$  determined by the FFPE (19), with its Brownian analogue  $W_1(x, t)$ . In order for Eq. (49) to hold, the initial conditions  $W_\alpha(x, 0)$  and  $W_1(x, 0)$  must, of course, be identical. That means that the fractional solution  $W_\alpha(x, t)$  exists iff the Brownian solution  $W_1(x)$  exists. In Laplace space,  $W_\alpha(x, u)$  is the same distribution on  $x$  as  $W_1(x, (\eta_\alpha/\eta)u^\alpha)$  for the scaled Laplace variable  $(\eta_\alpha/\eta)u^\alpha$ , only rescaled by the factor  $(\eta_\alpha/\eta)u^{\alpha-1}$ . As suggested by Barkai and Silbey [77], relation (49) can be reformulated in terms of the transformation

$$W_\alpha(v, t) = \int_0^\infty E(s, t) W_1(v, s) ds. \tag{50}$$

The kernel  $E(s, t)$  is given through [78]

$$E(s, t) = \frac{t}{\alpha s} \mathbf{L}_\alpha^\dagger \left( \frac{t}{(\eta_\alpha s / \eta)^{1/\alpha}} \right) \tag{51}$$

involving the one-sided Lévy distribution  $\mathbf{L}_\alpha^+$ ; that is,  $E(s, t)$  has the characteristic function

$$E(s, u) = \frac{\eta_\alpha}{\eta} u^{\alpha-1} \exp\left(-\frac{\eta_\alpha}{\eta} u^\alpha s\right) \tag{52}$$

whose Laplace inversion leads to the representation [78]

$$E(s, t) = \frac{1}{\alpha s} H_{1,1}^{1,0} \left[ \frac{(\eta_\alpha s / \eta)^{1/\alpha}}{t} \middle| \begin{matrix} (1, 1) \\ (\frac{1}{\alpha}, \frac{1}{\alpha}) \end{matrix} \right] \tag{53}$$

in terms of the Fox function  $H_{1,1}^{1,0}$  [55, 56], with the series expansion

$$E(s, t) = \frac{1}{s} \sum_{n=0}^{\infty} \frac{(-1)^n}{\Gamma(1 - \alpha - \alpha n) \Gamma(1 + n)} \left( \frac{\eta_\alpha s / \eta}{t^\alpha} \right)^{1+n} . \tag{54}$$

The transformation defined through Eq. (50) is a convenient tool for the numerical evaluation of the solution of the FFPE (19), once the Brownian solution is known. The scaling connection (49) and the transformation (50) guarantee the positivity of the fractional solution if only the corresponding Brownian solution is a proper pdf.

#### D. A Word on the Mittag-Leffler Function

Let us briefly examine the importance of the Mittag-Leffler function in relaxation modelling. The mathematical properties of the Mittag-Leffler function are compiled in Appendix B. Besides via the series representation, the Mittag-Leffler function is defined through its Laplace transform

$$\mathcal{L}\{E_\alpha(-(t/\tau)^\alpha)\} = (u + \tau^{-\alpha} u^{1-\alpha})^{-1}, \tag{55}$$

or through the fractional relaxation equation [79]

$$f(t) - 1 = -\tau^{-\alpha} {}_0D_t^{-\alpha} f(t). \tag{56}$$

In Refs. 80 and 81 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 [82] 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 mod-

ified, completely asymmetric Lévy distribution [43, 81]. This last observation is related to the formulation of Mittag-Leffler relaxation described in Ref. 80. In Refs. 83 and 84, 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.

The Mittag-Leffler function, or combinations thereof, has been obtained from fractional rheological models, and it convincingly describes the behavior of a number of rubbery and nonrubbery polymeric substances [79, 85]. The numerical behavior of the Mittag-Leffler function is equivalent to asymptotic power-law patterns that are often used to fit experimental data, see the comparative discussion of data from early events in peptide folding in Ref. 86, where the asymptotic power-law was confronted with the stretched exponential fit function.

### E. The Fractional Ornstein–Uhlenbeck Process

As an application of the method of the separation of variables, we consider the nonstationary behavior in the generalized, fractional version of the Brownian harmonic oscillator with the parabolic potential

$$\Phi(x) = \frac{1}{2} m\omega^2 x^2, \tag{57}$$

which leads to the FFPE

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha} \left( \frac{\partial}{\partial x} \frac{\omega^2}{\eta_x} x + \frac{k_B T}{m\eta_x} \frac{\partial^2}{\partial x^2} \right) W(x, t). \tag{58}$$

Equation (58) is equivalent to the fractional Rayleigh equation [75, 77], and therefore we refer to Eq. (58) as the fractional Ornstein–Uhlenbeck process. For the sharp initial condition  $W_0(x) = \delta(x - x_0)$ , the solution to this process is, according to Eq. (46), given by

$$W = \sqrt{\frac{m\omega^2}{2\pi k_B T}} \sum_0^\infty \frac{1}{2^n n!} E_\alpha(-n\tilde{t}^\alpha) H_n\left(\frac{\tilde{x}_0}{\sqrt{2}}\right) H_n\left(\frac{\tilde{x}}{\sqrt{2}}\right) e^{-\tilde{x}^2/2}, \tag{59}$$

employing the reduced variables  $\tilde{t} = t/\tau$  and  $\tilde{x} = x\sqrt{m\omega^2/(k_B T)}$ , as well as  $\tau^{-\alpha} \equiv \omega^2/\eta_x$ .  $H_n$  denotes the Hermite polynomials, and the eigenvalues are  $\lambda_{n,x} = n\omega^2/\eta_x$ . The stationary solution corresponding to the lowest eigenvalue  $n = 0$ , is constant and independent of  $\alpha$ . The remaining terms decay in the course of time. Thus, for all  $\alpha$ , the stationary solution is the Gibbs–Boltzmann distribution, as anticipated by the stationarity condition. The fractional solu-

tion (59) is displayed in Fig. 4, where we compare between the convergence of the series representation (59), and the numerical evaluation using the transformation (50).

The first moment of the fractional Ornstein–Uhlenbeck process can be calculated from Eq. (58). It evolves in time like

$$\langle x(t) \rangle = x_0 E_\alpha(- (t/\tau)^\alpha), \quad (60)$$

reducing to the usual exponential relaxation behavior for  $\alpha \rightarrow 1$ . The second moment is given through

$$\langle x^2(t) \rangle = \langle x^2 \rangle_{th} + (x_0^2 - \langle x^2 \rangle_{th}) E_\alpha(-2(t/\tau)^\alpha). \quad (61)$$

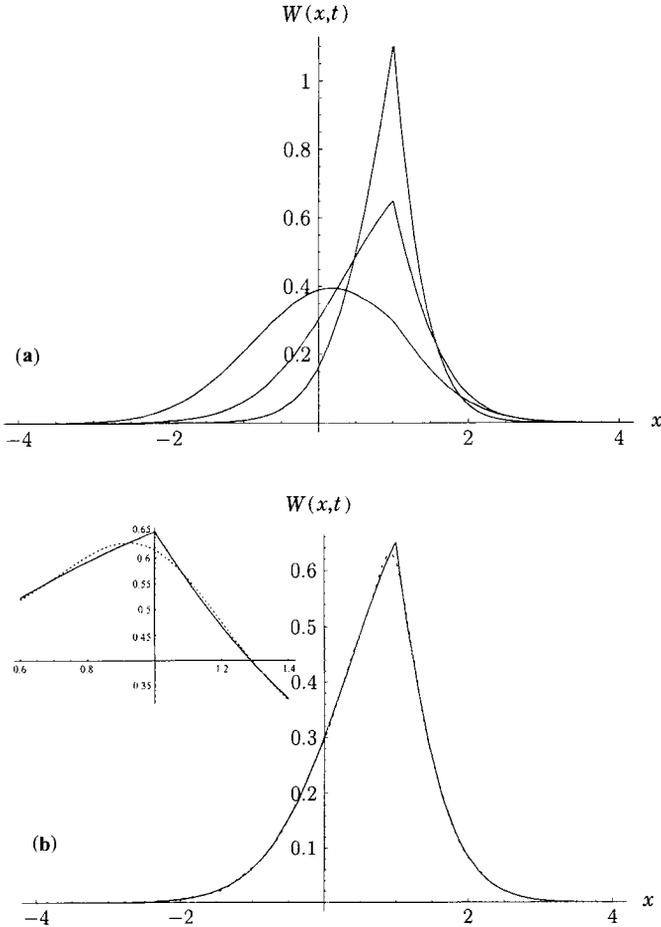
Accordingly, the thermal equilibrium value  $\langle x^2 \rangle_{th} = k_B T / [m\omega^2]$  is reached for  $t \rightarrow \infty$ . The Mittag-Leffler function  $E_\alpha(-2(t/\tau)^\alpha)$  behaves like  $1 - 2(t/\tau)^\alpha / \Gamma(1 + \alpha)$  for short times and like  $(t/\tau)^{-\alpha} / [2\Gamma(1 - \alpha)] - (t/\tau)^{-2\alpha} / [4\Gamma(1 - 2\alpha)]$  for long times. Thus, for  $x_0 = 0$  the short-time behavior of Eq. (61) follows Eq. (1) exactly and is independent of  $\omega$ . For long times, the thermal equilibrium value  $\langle x^2 \rangle_{th}$  is approached slowly, in power-law form. This is illustrated in Fig. 5.

## IV. THE FRACTIONAL KRAMERS ESCAPE PROBLEM

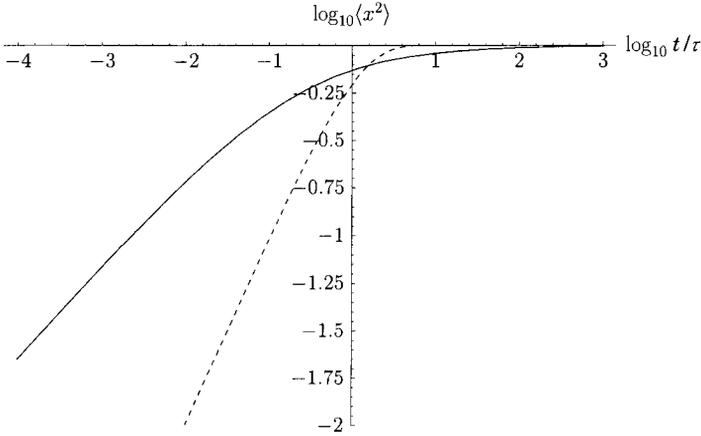
### A. The Classical Kramers Escape Problem

An interesting application of fractional dynamics is the modeling of the Kramers escape rate in complex systems where fractional dynamics prevails. Traditionally, such reaction rate problems [87] are formulated through the Smoluchowski [19, 88] and Onsager [89] models in terms of diffusion in the presence of absorbing bodies, or in terms of the famed Kramers model dating back to his seminal paper of 1940 [22]. Kramers considered a point particle in phase space diffusing in the potential  $V(x)$ . Being initially caught in a potential well, the particle can only escape over a potential barrier. Kramers promoted this model for the study of the dependence of the escape rate on temperature and viscosity. Alternative approaches for calculating rate reactions include the consideration of Markovian first passage time problems by Pontryagin, Andronow, and Witt [90], as well as first passage time problems for the master equation considered by Landau and Teller [91], Montroll and Shuler [92], Weiss [93], and, more recently, Bar-Haim and Klafter [94], Benichou et al. [95], and Abe et al. [96].

Extensions of the Kramers model are considered necessary [92–94, 97–99] although there are refined versions of the original formulation [100, 101]. Such non-Markovian dynamics has been taken into consideration



**Figure 4.** (a) Pdf  $W(x,t)$ , Eq. (59), of the fractional Ornstein–Uhlenbeck process, for the anomalous diffusion exponent  $\alpha = 1/2$ . The initial value is chosen to be  $W_0(x) = \delta(x - 1)$ . The maximum clearly slides toward the origin, acquiring an inversion symmetric shape. The curves are drawn for the times  $t = 0.02, 0.2$ , and  $20$ , employing the integral relation with the Brownian solution. Note the distinct cusps around the initial position. (b) Comparison of the numerical behavior of the summation representation (dashed) with 151 summation terms and the integral representation (A transform). The latter is obtained by *Mathematica* employing the numerical integration command *NIntegrate*. The cusp which is a typical feature for subdiffusive processes is much more pronounced in the curve obtained through the integral transformation. The computation time for the latter is even shorter than for the calculation of the truncated sum so that this representation is preferable for numerical purposes.

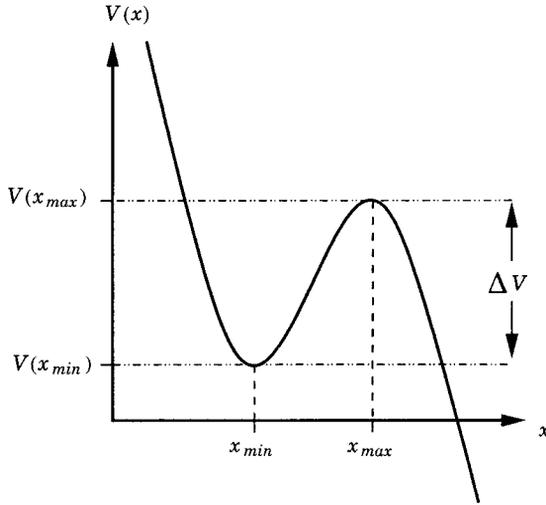


**Figure 5.** Mean squared displacement for the fractional ( $\alpha = 1/2$ , full line) and normal (dashed) Ornstein-Uhlenbeck process. The Brownian process shows the typical proportionality to  $t$  for small times; it approaches the saturation value much faster than its subdiffusive analogue, which starts off with the  $t^{1/2}$  behavior and approaches the thermal equilibrium value by a power law, compare Eq. (61)

through generalized Langevin equations in the well-known models by Grote and Hynes [97] and by Hänggi et al. [98]. On the level of the Kramers equation, these generalized models lead to a formulation that is local in time and contains time-dependent coefficients. Consequently the associated Kramers survival probability still decays exponentially, but with a frequency-dependent rate [67, 97, 98]. This contrasts the dynamic descriptions related to the generalized master equation that are nonlocal in time, and exhibit memory on the macroscopic level of the pdf [102]. In systems where this memory decays in the long-tailed, self-similar power-law fashion, fractional dynamics leads to the Mittag-Leffler survival pattern, as we are going to discuss in this section.

In the standard overdamped version of the Kramers problem, the escape of a particle subject to a Gaussian white noise over a potential barrier is considered in the limit of low diffusivity—that is, where the barrier height  $\Delta V$  is large in comparison to the diffusion constant  $K$  [14] (compare Fig.6). Then, the probability current over the potential barrier top near  $x_{\max}$  is small, and the time change of the pdf is equally small. In this quasi-stationary situation, the probability current is approximately position independent. The temporal decay of the probability to find the particle within the potential well is then given by the exponential function [14, 22]

$$p(t) = e^{-r_K t}, \quad (62a)$$



**Figure 6.** Potential well in the Kramers rate model. Initially the particle is assumed to be caught in the potential hole of depth  $\Delta V \equiv V(x_{max}) - V(x_{min})$ . The  $x$ -axis corresponds to a reaction coordinate.

where the Kramers rate is defined through [14, 22]

$$r_K = \frac{1}{2\pi m \eta} \sqrt{V''(x_{min})|V''(x_{max})|} \exp(-\beta \Delta V) \tag{62b}$$

with  $\Delta V = V(x_{max}) - V(x_{min})$ . In Eq. (62b), the exponential function contains the Boltzmann factor  $\beta \equiv (k_B T)^{-1}$  so that the inverse Kramers rate follows the Arrhenius activation [103]  $r_K^{-1} \propto e^{E^*/T}$  with  $E^* \equiv \Delta V/k_B$ . Similarly, the Kramers rate in the low viscosity limit is given through [22]

$$r_K = \eta \beta \Delta V \exp(-\beta \Delta V). \tag{62c}$$

According to Kramers' treatment, the proportionality of the Kramers rate to  $\eta$  in the low viscosity limit turns over to the inverse proportionality in the high viscosity. The interpolating behavior for arbitrary  $\eta$  was studied by Mel'nikov and Meshkov [104].

**B. The Fractional Generalization of the Kramers Escape Problem: Mittag-Leffler Decay of the Survival Probability**

Let us now derive the fractional counterpart to the exponential decay pattern (62a). To this end, we note that the solution  $W_x$  of the fractional Klein-

Kramers and Fokker–Planck equations can be expressed in terms of its Brownian analogue,  $W_1$ , according to Eq. (49). Application of relation (49) to the Laplace transform  $p(u) = (r_K + u)^{-1}$  of the exponential survival probability, Eq. (62a), produces

$$p_\alpha(u) = \frac{1}{u + r_K^{(\alpha)} u^{1-\alpha}}. \quad (63)$$

By comparison with Eq. (55), the Laplace inversion of Eq. (63) leads to the Mittag-Leffler shape [105]

$$p_\alpha(t) = E_\alpha\left(-r_K^{(\alpha)} t^\alpha\right) \quad (64a)$$

of the survival probability which includes the fractional Kramers rate

$$r_K^{(\alpha)} = \frac{\eta}{\eta_\alpha} r_K. \quad (64b)$$

The fraction  $\eta/\eta_\alpha = \vartheta$  is thus the rescaling of the classical Kramers rate according to the parameters classifying the multiple trapping system with broadly distributed waiting times. Similarly, in the underdamped case, one finds the fractional Kramers rate

$$r_K^{(\alpha)} = \frac{\eta^*}{\eta} r_K, \quad (64c)$$

where  $\eta^* \equiv \vartheta\eta$  replaces the classical friction  $\eta$ . According to Eqs. (64b) and (64c), our fractional Kramers model leads to the turnover in the friction dependence from  $r_K^{(\alpha)} \propto \eta^*$  to  $r_K^{(\alpha)} \propto 1/\eta_\alpha$ . This seemingly more complicated turnover can be reconciled with the standard picture. Indeed, on combining the elementary constant  $\vartheta$  with the other constants in expressions (64b) and (64c), the traditional turnover  $r_K^{(\alpha)} \propto \eta$  to  $r_K^{(\alpha)} \propto 1/\eta$  is recovered for the fractional Kramers rate. This latter observation is due to the linearity of the fractional operator. As a consequence we note that the Arrhenius activation nature of the Kramers rate is preserved in systems controlled by fractional dynamics.

Often, one defines nonexponential relaxations in terms of a time-dependent rate coefficient  $k(t)$  through  $p(t) = \exp(-k(t)t)$ . For the fractional Kramers model one therefore obtains the rate coefficient  $k(t) = |\ln E_\alpha(-r_K^{(\alpha)} t^\alpha)|/t$  which leads to two limiting cases, the short-time self-simi-

lar behavior

$$k(t) \sim \frac{r_K^{(\alpha)}}{t^{1-\alpha}\Gamma(1+\alpha)}, \quad t^\alpha \ll r_K^{(\alpha)}, \quad (65a)$$

and the long-time logarithmic pattern

$$k(t) \sim \frac{\alpha}{t} \ln(t[r_K^{(\alpha)}\Gamma(1-\alpha)]^{1/\alpha}), \quad t^\alpha \gg r_K^{(\alpha)}. \quad (65b)$$

It is interesting to note that the latter, up to some constants, is given by  $k(t) \sim \ln t/t$  which is in this sense universal; that is, the functional form is independent of the waiting time index  $\alpha$ .

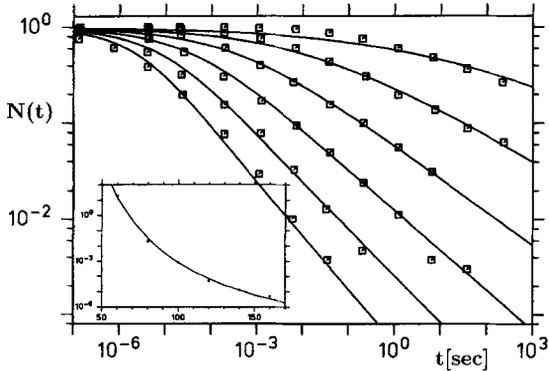
### C. An Example from Protein Dynamics

Let us discuss a possible application of this fractional Kramers model to protein dynamics. It was noted before [106–109] that the dynamic process in proteins, like the rebinding process of carbon monoxide CO to myoglobin Mb,



after photodissociation is highly nonexponential and can be fitted by either a stretched exponential or an asymptotic power law, the latter being numerically equivalent to the Mittag-Leffler behavior. Glöckle and Nonnenmacher [110] have investigated the data within a fractional relaxation model; that is, they applied a Mittag-Leffler fit, as reproduced in Fig. 7. Interestingly, they observed an Arrhenius dependence of the rate of the process. In more detail, these authors assume that the fractional parameter  $\alpha$  features a linear temperature dependence,  $\alpha(T) = 0.41T/120 \text{ K}$  which might take the change of the protein–solvent system into account. From the data analysis they find a remarkable agreement with the Mittag-Leffler behavior, and the Arrhenius activation is given by  $\tau = \tau_m e^{E_\tau/T}$  for the characteristic time which is related to the fractional Kramers rate through  $r_K^{(\alpha)} \equiv \tau^{-\alpha}$ . Conversely, the associated fractional Kramers rate is temperature-independent for this  $\alpha(T) \propto T$  model! The activation energy obtained from the data analysis according to the Mittag-Leffler/Arrhenius model,  $E_\tau$ , complies well with the generally accepted values [110]. Thus, selecting out the temperature dependence of  $\alpha$ , one exactly finds the Arrhenius dependence as predicted by the fractional Fokker–Planck model. The insert in Fig. 7 shows this Arrhenius activation of  $\tau$  as found in Ref. 110.

It has been claimed that reactions in proteins can, as an approximation, be formulated within the Kramers reaction theory of barrier crossing [106]. The highly nonexponential relaxation pattern can now be explained by our model,



**Figure 7.** Mittag-Leffler model for the rebinding of CO to Mb, after a photodissociation. Data from Austin et al. [108]. The temperature dependence of  $\tau_0$  follows the Arrhenius law shown in the insert, with the parameters  $\tau_m = 3.4 \times 10^{-10}$  s and  $E_t = 1470$  K.

bearing in mind that the dynamic topology caused by the protein strand is basically equivalent to the polymer chains leading to the observation of subdiffusion in the experiment of Amblard et al. [29]. Consequently, both the fractional relaxation (Mittag-Leffler) behavior and the Arrhenius dependence found by Glöckle and Nonnenmacher can now be understood from our fractional dynamics model.

In addition to the Kramers escape approach to ligand rebinding, a stochastic model was developed by Zwanzig [111] and by Eizenberg and Klafter [112], who assumed a fluctuating bottleneck through which the ligand passes, the process leading to an exponential survival for a white Gaussian noise. We have generalized this model in Ref. 62 within fractional dynamics, recovering the Mittag-Leffler behavior found above.

## V. THE FRACTIONAL KLEIN-KRAMERS EQUATION: FRACTIONAL DYNAMICS IN PHASE SPACE

### A. The Multiple Trapping Model

We now turn toward the phase space description of a test particle performing fractional dynamics, drawing upon Langevin's treatment of the Brownian motion of a scalar test particle in a bath of smaller atoms or molecules exerting random collisions upon that particle. In that course, Langevin [6] amended Newton's law of motion with a fluctuating force  $m\Gamma(t)$ . From this Langevin equation, it follows that the fluctuation-averaged phase space dynamics is governed by the Klein-Kramers equation [9, 13, 14, 21], the solution of which, the pdf  $W(x, v, t)$  to find the test particle at the position

$x, \dots, x + dx$  with the velocity  $v, \dots, v + dv$ , at time  $t$ , describes the macroscopic dynamics of the system. Thus, we can distinguish the two limiting cases of (a) the Rayleigh equation controlling the velocity distribution  $W(v, t)$  in the force-free limit and (b) the Fokker–Planck–Smoluchowski equation.

Indeed, a similar theory can be developed for systems displaying fractional dynamics. Starting off from the classical Langevin equation with  $\delta$ -correlated Gaussian noise, fractional dynamics emerges from the competition of subsequent Langevin dominated motion events of average duration  $\tau^*$ , interrupted through trapping events whose duration is broadly distributed. This multiple trapping scenario is of a quite general nature, and it offers physical insight into fractional dynamics as described by the fractional Fokker–Planck equation.

During the Langevin sections of the particle motion, the dynamics is controlled by the Langevin equation in the external force field  $F(x) = -\Phi'(x)$ ,

$$m \frac{d^2x}{dt^2} = -m\eta v + F(x) + m\Gamma(t), \quad v = \frac{dx}{dt}, \quad (67)$$

which describes the ongoing erroneous bombardment through small surrounding atoms or molecules via the fluctuating,  $\delta$ -correlated Gaussian noise  $\Gamma(t)$ . The velocity-proportional damping caused by effective interactions with the environment is characterized by the friction constant  $\eta$ . Averaging out the fluctuations, one finds the moments of the mean velocity increments [9],

$$\langle \Delta v \rangle = \left( \eta v - \frac{F(x)}{m} \right) \Delta t, \quad \langle (\Delta v)^2 \rangle = \frac{\eta k_B T}{m} \Delta t + O([\Delta t]^2), \quad (68)$$

from the Langevin equation (67) which are both proportional to the mean jump time  $\Delta t$ . Note that the noise-averaged Eq. (67),  $m \langle \ddot{x} \rangle_F = -m\eta \langle v \rangle_F + F(x)$ , corresponds to Newton's law of motion.

In the usual derivations of the Klein–Kramers equation, the moments of the velocity increments, Eq. (68), are taken as expansion coefficients in the Chapman–Kolmogorov equation [9]. Generalizations of this procedure start off with the assumption of a memory integral in the Langevin equation to finally produce a Fokker–Planck equation with time-dependent coefficients [67]. We are now going to describe an alternative approach based on the Langevin equation (67) which leads to a fractional Klein–Kramers equation— that is, a temporally nonlocal behavior.

Let us define the (multiple) trapping events. As mentioned before, trapping describes the occasional immobilization of the random walking test particle

for a waiting time which rules the time span elapsing between the immobilization and the subsequent release of the test particle. This waiting time is drawn from the waiting time pdf  $w(t)$ . Such trapping has been recognized as the mechanism underlying the dispersive charge carrier transport in amorphous semiconductors [23, 25, 26] and the motion of excess electrons in liquids [113], and it occurs in the phase space dynamics of chaotic Hamiltonian systems [36].

In addition to trapping, it is supposed that the kinetic energy of a particle during a trapping–detrapping event is conserved, and that each trapping period is followed by a motion event during which the particle moves in the bath of surrounding smaller particles in which it undergoes the same collisions as underlie the standard Brownian counterpart. Each of these motion events following release from the trap is supposed to endure for the mean time  $\tau^*$ . This means that while not being trapped, the test particle features a Markov behavior described by the Langevin equation (67). The immobilizing–release–walking scenario therefore combines trapping periods and Langevin dynamics in a sequential manner. The overall process is, in essence, the phase space extension of the multiple trapping model conceived in Ref. 23. In our model, the length  $x^* = v_{th}\tau^*$ , where  $v_{th} \equiv \sqrt{\lim_{t \rightarrow \infty} \langle v^2(t) \rangle}$  is the thermal velocity, is the average distance between adjacent traps visited.

## B. The Fractional Klein–Kramers Equation and the Related Equations

Fractional dynamics emerges as the macroscopic limit of the combination of the Langevin and the trapping processes. After straightforward calculations based on the continuous-time version of the Chapman–Kolmogorov equation [75, 114] which are valid in the long-time limit  $t \gg \max\{\tau, \tau^*\}$ , one obtains the fractional Klein–Kramers equation

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha} \left( -v^* \frac{\partial}{\partial x} + \frac{\partial}{\partial v} \left( \eta^* v - \frac{F^*(x)}{m} \right) + \eta^* \frac{k_B T}{m} \frac{\partial^2}{\partial v^2} \right) W(x, v, t). \quad (69)$$

Here, the Klein–Kramers operator has the same structure as in the Brownian case, except for the occurrence of the asterisked quantities that are defined through  $v^* \equiv v\vartheta$ ,  $\eta^* \equiv \eta\vartheta$ , and  $F^*(x) \equiv F(x)\vartheta$  whereby the factor  $\vartheta$  is the ratio

$$\vartheta \equiv \frac{\tau^*}{\tau^\alpha} \quad (70)$$

of the intertrapping time scale  $\tau^*$  and the internal waiting time scale  $\tau$  from Eq. (6). The stationary solution of the fractional Klein–Kramers equation

[Eq. (69)],  $W_{\text{st}}(x, v) \equiv \lim_{t \rightarrow \infty} W(x, v, t)$  is given by the Gibbs–Boltzmann equilibrium distribution  $W_{\text{st}}(x, v) = N \exp\{-\beta E\}$  where  $E = \frac{1}{2}mv^2 + \Phi(x)$ , and  $N$  is the appropriate normalization constant. In the Brownian limit  $\lim_{\alpha \rightarrow 1}$ , Eq. (69) reduces to the standard Klein–Kramers equation, as expected.

Integration of Eq. (69) over velocity, and of  $v$  times Eq. (69) over velocity, results in two equations whose combination leads to the fractional equation [75, 115]

$$\frac{\partial W}{\partial t} + {}_0D_t^{1+\alpha} \frac{1}{\eta^*} W = {}_0D_t^{1-\alpha} \left( -\frac{\partial F(x)}{\partial x m \eta_x} + K_x \frac{\partial^2}{\partial x^2} \right) W(x, t). \quad (71)$$

Equation (71) reduces to the telegrapher’s-type equation found in the Brownian limit  $\alpha = 1$  [115]. In the usual high-friction or long-time limit, one recovers the fractional Fokker–Planck equation (19). The generalized friction and diffusion coefficients in Eq. (19) are defined by [75]

$$\eta_x \equiv \frac{\eta}{\vartheta} \quad (72a)$$

and

$$K_x \equiv \frac{k_B T}{m \eta_x} = \vartheta K \quad (72b)$$

and are thus to be understood as a rescaled version of the well-defined physical quantities  $\eta$  and  $K$ . Moreover, the generalized Einstein–Stokes relation (37) has now been obtained as a direct consequence of the interplay between the Langevin diffusion with the long-tailed trapping process.

The integration of the fractional Klein–Kramers equation (69) over the position coordinate leads in, the force-free limit, to the fractional Rayleigh equation

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha} \eta^* \left( \frac{\partial}{\partial v} v + \frac{k_B T}{m} \frac{\partial^2}{\partial v^2} \right) W(v, t), \quad (73)$$

which is an example of the fractional Ornstein–Uhlenbeck process discussed in the preceding section. The solution of Eq. (73), the pdf  $W(v, t)$ , describes the equilibration of the velocity distribution toward the Maxwell distribution  $W_{\text{st}}(v) = \sqrt{\frac{\beta m}{2\pi}} \exp(-\beta \frac{m}{2} v^2)$  with the thermal velocity  $v_{\text{th}}^2 = k_B T/m$ .

This model for subdiffusion in the external force field  $F(x) = -\Phi'(x)$  provides a basis for fractional evolution equations, starting from Langevin dynamics that is combined with long-tailed trapping events possessing a

diverging characteristic waiting time  $T$ . The first stage hosts the microscopic Brownian process, characterized by the mean stepping time  $\tau^*$  that is basically equivalent to a multiple of the mean jump time  $\Delta t$  in Eq. (68). If the characteristic waiting time is finite,  $T < \infty$ , the trapping mechanism also possesses its characteristic time scale. Therefore, the second stage brings two Poissonian processes together, and the macroscopic process defined as the long-time limit with respect to  $\max\{\tau^*, T\}$  is Markovian, being determined by the standard Brownian Klein–Kramers equation. Conversely, if  $T \rightarrow \infty$  diverges, the time scales of the microscopic Brownian motion,  $\tau^*$ , separates from the combined trapping–detraping process. The latter occasionally features very long waiting times so that individual trapping events do not have a typical time scale and cannot be distinguished from the sampling of many trapping events on the macroscopic level, a situation that is typical for self-similar processes. The overall dynamics becomes fractional.

The combined process is governed by the long-tailed form of the waiting time pdf, manifested in the fractional nature of the associated Eq. (69). Physically, this causes the rescaling of the fundamental quantity  $\eta$  by the scaling factor  $\vartheta$  to result in the generalized friction constant  $\eta_\alpha = \eta/\vartheta$ . It is interesting to note that the kinematics level, force-free multiple trapping process from Ref. 113 in  $(x, t)$ -coordinates reveals the subdiffusive mean square displacement  $\langle x^2(t) \rangle \propto t^\alpha$ .

The Langevin picture rules the Markov motion parts in between successive trapping states. On this stage the test particle consequently obeys Newton’s law, in the noise-averaged sense defined above. Conversely, averaging the fractional Klein–Kramers equation (69) over velocity and position coordinates, one recovers the memory relation  $\frac{d}{dt} \langle \langle x(t) \rangle \rangle = \vartheta {}_0D_t^{1-\alpha} \langle \langle v(t) \rangle \rangle$  between the mean position  $\langle \langle x(t) \rangle \rangle$  and the mean velocity  $\langle \langle v(t) \rangle \rangle$ . This “violation” is only due to the additional waiting time averaging that camouflages the Langevin-dominated motion events.

## VI. CONCLUSIONS

Anomalous transport features have been reported for an increasing number of (complex) systems. Many of these systems underlie some sort of a generalized limit theorem that is connected with Lévy statistics and thus with self-similar evolution patterns. This fact is mirrored in the long-time prevalence of power-law time behaviors of the related physical quantities.

Fractional dynamics is a made-to-measure approach to the description of temporally nonlocal systems, the kinetics of which is governed by a self-similar memory. Fractional kinetic equations are operator equations that are mathematically close to the well-studied, analogous Brownian evolution equations of the Klein–Kramers, Rayleigh, or Fokker–Planck types. Consequently, methods such as the separation of variables can be applied. More-

over, the fractional solution exists if only the corresponding Brownian solution exists.

The characteristic changes brought about by fractional dynamics in comparison to the Brownian case include the temporal nonlocality of the approach manifest in the convolution character of the fractional Riemann–Liouville operator. Initial conditions relax slowly, and thus they influence the evolution of the system even for long times [62, 116]; furthermore, the Mittag-Leffler behavior replaces the exponential relaxation patterns of Brownian systems. Still, the associated fractional equations are linear and thus extensive, and the limit solution equilibrates toward the classical Gibbs–Boltzmann and Maxwell distributions, and thus the processes are close to equilibrium, in contrast to the Lévy flight or generalised thermostatistics models under discussion.

The physical foundation of fractional dynamics has been developed. Multiple trapping featuring a competition between Langevin-dominated motion events possessing a characteristic time scale and broadly distributed trapping events has been shown to give rise to fractional dynamics in the long-time limit. Consequently, the coming into existence of the generalized diffusion and friction constants can be understood as a rescaling resulting from this competition between Langevin and trapping regimes in which finally the generalized central limit theorem guarantees the dominance of the broad waiting time pdf.

In our presentation, we concentrated on the modeling of subdiffusive phenomena—that is, modeling of processes whose mean squared displacement in the force-free limit follows the power-law dependence  $\langle x^2(t) \rangle \propto t^\kappa$  for  $0 < \kappa < 1$ . The extension of fractional dynamics to systems where the transport is subballistic but superdiffusive,  $1 < \kappa < 2$ , is presently under discussion [77, 78], (compare also Ref. 117).

We finally note that a more mathematically oriented account of fractional equations in the description of anomalous kinetic processes has recently been published [118].

### Acknowledgments

We gratefully acknowledge discussions with Eli Barkai, Brian Berkowitz, Joshua Jortner, Shaul Mukamel, Theo Nonnenmacher, Ilia Rips, Harvey Scher, Michael Shlesinger, Igor Sokolov, and Gert Zumofen. Financial assistance from the German–Israeli Foundation (GIF) and the TMR programme of the European Commission (SISITOMAS) is acknowledged as well. RM was supported in part by a Feodor–Lynen fellowship from the Alexander von Humboldt Stiftung, by an Amos de Shalit fellowship from the Minerva foundation, and by an Emmy Noether fellowship from the DFG.

## APPENDIX A: A PRIMER ON LÉVY DISTRIBUTIONS

Historically, the central limit theorem, which guarantees the existence of the all important Gaussian limit distribution for processes with a finite variance,

had grown out of the inequality of Bienaymé, the theorems of Bernoulli and de Moivre-Laplace, and the law of large numbers. The central limit theorem has received a central role in the exact sciences and beyond, over centuries. Toward the turn of the twentieth century, mathematicians became interested in the possibility of a limit theorem for processes without a finite variance, ideas whose fundamentals actually go back to Cauchy. Such a generalized framework was conceived by Paul Lévy (after which the generalized normal distributions are named), A. Ya. Khintchine, W. Feller, A. M. Kolmogorov, and B. V. Gnedenko, among others.

According to Lévy [43], a distribution  $F$  is stable iff for the two positive constants  $c_1$  and  $c_2$  there exists a positive constant  $c$  such that the random variable  $X$  given by

$$c_1 X_1 + c_2 X_2 = cX \quad (\text{A1})$$

is a random variable following the same distribution  $F$  as the independent, identically distributed (iid) random variables  $X_1$  and  $X_2$ . Alternatively, if

$$\varphi(z) \equiv \langle e^{iXz} \rangle = \int_{-\infty}^{\infty} e^{iXz} dF(X) \quad (\text{A2})$$

denotes the characteristic function of the distribution  $F$ , then  $F$  is stable iff

$$\varphi(c_1 z) \varphi(c_2 z) = \varphi(cz). \quad (\text{A3})$$

A more general definition is given by Feller [12]. We denote a Lévy stable pdf  $dF(x)$  as  $L_\alpha(x)$  and call  $\alpha$  the Lévy (stable) index. It can be shown that a stable law has a characteristic function of the form

$$\psi(z) = \log \varphi(z) = i\gamma z - c|z|^\alpha \left\{ 1 + i\beta \frac{z}{|z|} \omega(z, \alpha) \right\}, \quad (\text{A4})$$

where  $\alpha, \beta, \gamma, c$  are constants ( $\gamma$  is any real number,  $0 < \alpha \leq 2$ ,  $-1 < \beta < 1$ , and  $c > 0$ ), and

$$\omega(z, \alpha) = \begin{cases} \tan \frac{\pi\alpha}{2}, & \text{if } \alpha \neq 1 \\ \frac{2}{\pi} \log |z|, & \text{if } \alpha = 1. \end{cases} \quad (\text{A5})$$

From Eq. (A4) it follows that the limiting case  $\alpha = 2$  corresponds to the Gaussian normal distribution governed by the central limit theorem. For  $\beta = 0$ , the distribution is symmetric.  $\gamma$  translates the distribution, and  $c$  is a scaling factor for  $X$ . Thus,  $\gamma$  and  $c$  are not essential parameters; if we disregard them, the characteristic function fulfills

$$|\varphi(z)| = e^{-|z|^\alpha}, \quad \alpha \neq 1. \quad (\text{A6})$$

Thus, one can write

$$\psi(z) = -|z|^\alpha \exp\left(i \frac{\pi\beta}{2} \text{sign}(z)\right) \tag{A7}$$

with the new centering constant  $\beta$  that is restricted in the following region:

$$|\beta| \leq \begin{cases} \alpha, & \text{if } 0 < \alpha < 1 \\ 2 - \alpha, & \text{if } 1 < \alpha < 2. \end{cases} \tag{A8}$$

The pdf  $f_{\alpha,\beta}(x)$  is the Fourier transform of  $\varphi(z)$ , defined by Eq. (A7):

$$f_{\alpha,\beta}(x) = \frac{1}{\pi} \text{Re} \int_0^\infty \exp\left(-ixz - z^\alpha \exp\left(i \frac{\pi\beta}{2}\right)\right) dz. \tag{A9}$$

Thus,

$$f_{\alpha,\beta}(x) = f_{\alpha,-\beta}(-x) \tag{A10}$$

so that

$$f_{\alpha,0}(x) = f_{\alpha,0}(-x) \tag{A11}$$

is symmetric in  $x$ .

The asymptotic behavior of a Lévy stable distribution follows the inverse power-law

$$f_{\alpha,\beta}(x) \sim \frac{A_{\alpha,\beta}}{|x|^{1+\alpha}}, \quad \alpha < 2; \tag{A12}$$

consequently, for all Lévy stable laws with  $0 < \mu < 2$ , the variance diverges:

$$\langle x^2 \rangle \rightarrow \infty. \tag{A13}$$

Special cases include the Cauchy or Lorenz distribution

$$f_{1,0}(x) = \frac{a}{\pi(a^2 + x^2)} \tag{A14}$$

for  $\alpha = 1$  and  $\beta = 0$ , as well as the one-sided or completely asymmetric distribution  $\mathbf{L}_\alpha^+(x) \equiv f_{\alpha,-\alpha}(x)$  if  $0 < \alpha < 1$  and  $\beta = -\alpha$ . For instance, the one-sided stable density for  $\alpha = 1/2$  and  $\beta = -1/2$  is given by

$$\mathbf{L}_{1/2}^+(x) = \frac{1}{2\sqrt{\pi}} x^{-3/2} e^{-1/4x}. \tag{A15}$$

To obtain the characteristic function of a one-sided stable law, one calculates the Laplace transform.

Let us examine the one-sided Lévy distribution  $dF(X) \equiv \mathbf{L}_\alpha^+(t/\tau)$  with the characteristic function

$$\varphi(u) \equiv \langle e^{-Xu} \rangle = \int_0^\infty e^{-Xu} dF(X) = \exp(-(u\tau)^\alpha) \quad (\text{A16})$$

in more detail. Identification with the corresponding Fox function [55, 56],

$$\mathbf{L}_\alpha^+(u\tau) = H_{0,1}^{1,0} \left[ (t/\tau)^\alpha \middle| \begin{matrix} (1, \alpha) \\ (0, 1) \end{matrix} \right], \quad (\text{A17})$$

allows for the direct Laplace inversion, resulting in [56, 84]

$$\mathbf{L}_\alpha^+(t/\tau) = \frac{1}{\tau} H_{1,1}^{1,0} \left[ \left( \frac{\tau}{t} \right)^\alpha \middle| \begin{matrix} (1, \alpha) \\ (1/\alpha, 1) \end{matrix} \right] \quad (\text{A18})$$

with the corresponding series expansion

$$\mathbf{L}_\alpha^+(t/\tau) = \frac{1}{\tau} \sum_{n=1}^{\infty} \frac{(-1)^n}{n! \Gamma(-\alpha n)} \left( \frac{\tau}{t} \right)^{1+\alpha n} \quad (\text{A19})$$

from which we find the asymptotic behavior

$$\mathbf{L}_\alpha^+(t/\tau) \sim A_\alpha \frac{\tau^\alpha}{t^{1+\alpha}}, \quad (\text{A20})$$

with  $A_\alpha \equiv 1/|\Gamma(-\alpha)|$ , for  $0 < \alpha < 1$ . For short times  $t \ll \tau$ , the one-sided Lévy distribution  $\mathbf{L}_\alpha^+(t/\tau)$  becomes exponentially small (compare the discussion of nonexponential relaxation in Ref. 86).

## APPENDIX B: THE UBIQUITOUS MITTAG-LEFFLER FUNCTION

The Mittag-Leffler function [44–46] can be viewed as a natural generalization of the exponential function. Within fractional dynamics, it replaces the traditional exponential relaxation patterns of moments, modes, or of the Kramers survival. It is an entire function that decays completely monotonically for  $0 < \alpha < 1$ . It is the exact relaxation function for the underlying multiscale process, and it leads to the Cole–Cole behavior for the complex

susceptibility, which is broadly used to describe experimental results. It can be decomposed into single Debye processes, the relaxation time distribution of which is given by a one-sided Lévy distribution [80].

The Mittag-Leffler function is defined through the inverse Laplace transform

$$E_\alpha(-(t/\tau)^\alpha) = \mathcal{L}^{-1}\left\{\frac{1}{u + \tau^{-\alpha}u^{1-\alpha}}\right\}, \tag{B1}$$

from which the series expansion

$$E_\alpha(-(t/\tau)^\alpha) = \sum_{n=0}^{\infty} \frac{(-(t/\tau)^\alpha)^n}{\Gamma(1 + \alpha n)} \tag{B2}$$

can be deduced. The asymptotic behavior is

$$E_\alpha(-(t/\tau)^\alpha) \sim ((t/\tau)^\alpha \Gamma(1 - \alpha))^{-1} \tag{B3}$$

for  $t \gg \tau$ ,  $0 < \alpha < 1$ . Special cases of the Mittag-Leffler function are the exponential function

$$E_1(-t/\tau) = e^{-t/\tau} \tag{B4}$$

and the product of the exponential and the complementary error function

$$E_{1/2}\left(- (t/\tau)^{1/2}\right) = e^{t/\tau} \operatorname{erfc}\left((t/\tau)^{1/2}\right). \tag{B5}$$

We note in passing that the Mittag-Leffler function is the solution of the fractional relaxation equation [84]

$$\frac{df(t)}{dt} = -\tau^{-\alpha} {}_0D_t^{1-\alpha} f(t). \tag{B6}$$

The Mittag-Leffler function interpolates between the initial stretched exponential form

$$E_\alpha(-(t/\tau)^\alpha) \sim \exp\left(-\frac{(t/\tau)^\alpha}{\Gamma(1 + \alpha)}\right) \tag{B7}$$

and the long-time inverse power-law behavior (B3). For  $\alpha > 1$ , the Mittag-Leffler function shows oscillations [44–46].

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