Subdiffusive transport close to thermal equilibrium: From the Langevin equation to fractional diffusion

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Subdiffusion in the presence or absence of an external force field is established on the basis of an extension of conventional Langevin dynamics to include long-tailed trapping events. It is demonstrated how the presence of the trapping events leads to the macroscopic observation of fractional diffusion, described by a fractional Klein-Kramers equation.

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In his treatment of the Brownian motion of a scalar test particle in a bath of smaller atoms or molecules exerting random collisions upon that particle, Langevin [1] amended Newton's law of motion with a fluctuating force. On the basis of the resulting Langevin equation, the corresponding fluctuation-averaged phase space dynamics is governed by the Klein-Kramers equation [2–5]. Its solution, the probability density function (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. Thereby, two limiting cases can be distinguished, these being the Rayleigh equation controlling the velocity distribution $W(v,t)$ in the force-free limit, and the Fokker-Planck equation from which the PDF $W(x,t)$ can be derived.

Brownian transport processes are intimately related to the validity of the central limit theorem [6–8]. The latter is ensured by the existence of the first and second moments $\overline{X}$ and $\overline{X^2}$ of the step lengths, as well as the mean jump time Δt of the transfer statistics which govern the random motion under consideration. Such systems are characterized by the mean velocity $V\equiv\overline{X}/\Delta t$ and the diffusion coefficient $K\equiv[\overline{X^2}-\overline{X}^2]/(2\Delta t)$ [6,7].

There exist systems in which not all of these moments are finite [7–10]. This may come about if Lévy stable distributions replace the transfer statistics of the above Brownian process. Accordingly, the associated process drops out of the basin of attraction of the central limit theorem. Instead, the Lévy-Gnedenko generalized central limit theorem takes over and guarantees the existence of a limit distribution which determines the macroscopic dynamics of the system [7,9]. The description of such non-Brownian diffusion in terms of fractional equations has recently been extensively studied in the presence as well as absence of an external force field [10–22].

Lévy flights, on the one hand, are ruled by broad distributions of the jump lengths, leading to the divergence of $\overline{X^2}$. In the presence of an external force field, they are described by fractional Fokker-Planck or fractional Klein-Kramers equations [16–19]. Lévy flights are Markovian processes, and it has been shown that they can be derived from a Langevin equation with Lévy noise [16,17,23].

Subdiffusion, on the other hand, is characterized by the sublinear power-law dependence $\langle x^2\rangle\propto t^\alpha, 0<\alpha<1$, of the force-free mean square displacement, a situation where no finite mean jump time Δt exists [10]. In the long-time limit, subdiffusion with and without an external force field has been described by fractional diffusion equations [11,12], fractional diffusion-advection equations [13,14], and fractional Fokker-Planck equations [20,21]. Although these can be derived from the generalized master equations or continuous time random walk models [21], a foundation on microscopic dynamics within the Langevin picture has not yet been established. On the footing of a Langevin equation, a three-stage description of subdiffusion is developed which allows for a physical interpretation of the crossover to macroscopic fractional dynamics.

These three stages comprise the fundamental Newtonian motion of the scalar test particle experiencing a random force; its combination with trapping events which leads to temporary immobilization in between Langevin-dominated motion events; and the averaged macroscopic predominance of subdiffusion, respectively. In the course of the derivation, fractional analogs of the Klein-Kramers, the Rayleigh, and the Fokker-Planck equations emerge which are close to thermal equilibrium, i.e., they approach the Maxwell- or Gibbs-Boltzmann distributions. This temporal approach is slower than predicted by Brownian statistics, and follows the Mittag-Leffler pattern [10,21]. Moreover, the origin of the generalized transport coefficients and the existence of the generalized Einstein relations are shown to be a direct outcome of the competition between long-tailed trapping events and the Langevin dynamics. In this competition, the generalized central limit theorem ensures that the long-tailed trapping mechanism wins out asymptotically, bringing about the fractional dynamics.

First stage. On this stage, the motion of the particle is Brownian. Thereby, the Langevin equation of the test particle of mass m in the external force field $F(x)=-\Phi'(x)$,

$$m\frac{d^2x}{dt^2}=-m\eta v+F(x)+m\Gamma(t),\quad v=\frac{dx}{dt} \tag{1}$$

describes the ongoing erroneous bombardment through small surrounding atoms or molecules via the fluctuating, δ-correlated Gaussian noise $\Gamma(t)$. The velocity-proportional damping caused by effective interactions with the environ-

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ment, is characterized by the friction constant η. Averaging out the fluctuations, one finds the moments of the mean velocity increments [3]

$$\langle \Delta v \rangle = \left(\eta v - \frac{F(x)}{m} \right) \Delta t,$$

$$\langle (\Delta v)^2 \rangle = \frac{2 \eta k_B T}{m} \Delta t + O([\Delta t]^2) \tag{2}$$

from the Langevin equation (1). Note the proportionality of both moments to the mean jump time Δt. Furthermore, the noise-averaged Eq. (1), $m\langle \ddot{x} \rangle_\Gamma = -m\eta \langle v \rangle_\Gamma + F(x)$, corresponds to Newton's law of motion.

In the usual derivations of the Klein-Kramers equation, the moments of the velocity increments, Eq. (2), are taken as expansion coefficients in the Chapman-Kolmogorov equation [3]. 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 [24]. In order to derive an evolution equation which itself is nonlocal in time, a generalization of the picture based on the Langevin equation (1) is introduced. This generalization is of stochastic origin and produces the fractional operator in the resulting evolution equations, i.e., the inclusion of memory.

Second stage. To this end, trapping events are superimposed to the Langevin dynamics. Trapping describes the occasional immobilization of the random walking test particle for a waiting time which defines 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 $w(t)$. Here we assume that following a trapping event the particle is released with the same velocity which it had prior to the immobilization. Trapping has been recognized as the mechanism underlying the dispersive charge carrier transport in amorphous semiconductors [25,26], the motion of excess electrons in liquids [27], and it occurs in the phase space dynamics of chaotic Hamiltonian systems [28]. It has also been conjectured as the source for the nonstandard dynamics encountered in protein folding in a generalized master equation description [29].

Choosing a waiting time PDF $w(t)$ with a finite first moment, the characteristic waiting time $T \equiv \int_0^\infty dt\, t w(t), T < \infty$, one can show that the following model reduces to the Brownian picture as described by the standard Klein-Kramers equation. It is only for such cases where the characteristic waiting time diverges $T \to \infty$, that a different situation arises which is finally observable as fractional dynamics, manifested as subdiffusion. This divergence of T comes about by a Lévy-type waiting time PDF with the long-tail behavior $w(t) \sim \tau^\alpha / t^{1+\alpha}$, $0 < \alpha < 1$ [30] where τ is an intrinsic time scale of the waiting process.

In addition to trapping, it is supposed 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 underly the standard Brownian counterpart. Each of these motion events after release from the trap, is supposed to endure for the mean time τ^*. This means that while not being trapped, the test particle features a Markov behavior described by the Langevin equation (1). The immobilizing-release-walking scenario therefore combines trapping periods and Langevin dynamics in a sequential manner The combined process is basically the multiple trapping model [25]. Note that, due to the relatively sharply peaked velocity distribution, the average distance $x^* = v\tau^*$ covered during one of these motion events is a measure for the distance between adjacent traps.

Third stage. The last step concerns the task of drawing the macroscopic limit of this multistage process. After straightforward calculations based on the continuous time version of the Chapman-Kolmogorov equation [31,32] which are valid in the long-time limit $t \gg \max\{\tau, \tau^*\}$, one obtains the fractional Klein-Kramers equation

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\alpha} \left[-v^* \frac{\partial}{\partial x} + \frac{\partial}{\partial v} \left(\eta^* v - \frac{F^*(x)}{m} \right) + \eta^* \frac{k_B T}{m} \frac{\partial^2}{\partial v^2} \right] W(x,v,t). \tag{3}$$

Hereby, the Klein-Kramers operator in the square brackets has the same structure as in the Brownian case, except for the occurrence of the starred quantities which are defined through $v^* \equiv v\vartheta$, $\eta^* \equiv \eta\vartheta$, and $F^*(x) \equiv F(x)\vartheta$ whereby the factor ϑ is the ratio $\vartheta \equiv \tau^*/\tau^\alpha$ of the intertrapping time scale τ^* and the internal waiting time scale τ. The fractional Riemann-Liouville operator ${}_0D_t^{1-\alpha} = (\partial/\partial t)\, {}_0D_t^{-\alpha}$ is defined through

$$ {}_0D_t^{-\alpha} W(x,v,t) = \frac{1}{\Gamma(\alpha)} \int_0^t dt' \frac{W(x,v,t')}{(t-t')^{1-\alpha}}. \tag{4}$$

The Riemann-Liouville operator introduces a convolution integral into Eq. (3) with the power-law kernel $K(t) = t^{\alpha-1}$. Therefore, the fractional Klein-Kramers equation (3) involves a slowly decaying memory so that the present state $W(x,v,t)$ of the system depends strongly on its history $W(x,v,t'), t' < t$, in contrast to the Brownian counterpart which is local in time. The stationary solution of the fractional Klein-Kramers equation, Eq. (3), $W_{\mathrm{st}}(x,v) \equiv \lim_{t\to\infty} W(x,v,t)$ is given by the Gibbs-Boltzmann equilibrium distribution $W_{\mathrm{st}}(x,v) = N \exp\{-\beta E\}$ where $\beta \equiv (k_B T)^{-1}$ denotes the Boltzmann factor, $E = \frac{1}{2} m v^2 + \Phi(x)$, and N is the appropriate normalization constant. In the limit $\alpha \to 1$, Eq. (3) reduces to the Brownian Klein-Kramers equation.

The Klein-Kramers equation is central to the modeling of particle escape over a barrier, and to various other processes including Josephson junctions [5]. Thus, the fractional Klein-Kramers equation (3) derived here, is of broad interest for the wide range of systems which display slow dynamics [8,25–27,37].

Integration of Eq. (3) over velocity, and of v times Eq. (3) over velocity results in two equations which together lead to the fractional equation [32]

$$\frac{\partial W}{\partial t} + {}_0D_t^{1+\alpha} \frac{1}{\eta^*} W = {}_0D_t^{1-\alpha} \left[-\frac{\partial}{\partial x} \frac{F(x)}{m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2} \right] W(x,t). \tag{5}$$

Equation (5) reduces to the telegrapher's type equation found in the Brownian limit $\alpha=1$ [33]. In the usual high-friction or long-time limit, one recovers the fractional Fokker-Planck equation

$$\frac{\partial W}{\partial t}={}_0D_t^{1-\alpha}\left[-\frac{\partial}{\partial x}\frac{F(x)}{m\eta_\alpha}+K_\alpha\frac{\partial^2}{\partial x^2}\right]W(x,t) \qquad (6)$$

which was discussed in detail in Ref. [20]. Equation (6) was also derived from a generalized master equation and a nonhomogeneous continuous time random walk, in Refs. [21]. The generalized friction and diffusion coefficients in Eq. (6) are defined by $\eta_\alpha\equiv\eta/\vartheta$ and $K_\alpha\equiv k_BT/[m\eta_\alpha]$ [32] and are thus to be understood as a rescaled version of the physical quantities η and K. Moreover, the generalized Einstein-Stokes relation [20,38] connecting the generalized coefficients η_α and K_α has now been obtained as a direct consequence of the interplay between the Langevin diffusion with the long-tailed trapping process. Note that there is experimental support for the validity of this relation in cases of subdiffusion [34]. The fractional Fokker-Planck equation (6) also fulfills the generalized Einstein relation $\langle x\rangle_F=\frac{1}{2}(F\langle x^2\rangle/k_BT)$ connecting the first moment $\langle x\rangle_F$ in presence of the constant force F with the second moment $\langle x^2\rangle=K_\alpha t^\alpha/\Gamma(1+\alpha)$ in absence of F as demonstrated in Ref. [26]. The stationary solution of the fractional Fokker-Planck equation (6) equals the Gibbs-Boltzmann form $W_{\rm st}(x)=N\exp\{-\beta\Phi(x)\}$. In the Brownian limit $\alpha\to1$, Eq. (6) reduces to the standard Fokker-Planck equation.

The integration of the fractional Klein-Kramers equation (3) over the position coordinate, leads in the force-free limit to the fractional Rayleigh equation

$$\frac{\partial W}{\partial t}={}_0D_t^{1-\alpha}\eta^*\left[\frac{\partial}{\partial v}v+\frac{k_BT}{m}\frac{\partial^2}{\partial v^2}\right]W(v,t). \qquad (7)$$

Its solution, the PDF $W(v,t)$, describes the equilibration of the velocity distribution towards the Maxwell distribution $W_{\rm st}(v)=\sqrt{(\beta m/2\pi)}\exp\{-\beta(m/2)v^2\}$.

In Laplace space [35], the generalization leading to Eqs. (3), (6), or (7) involving the fractional Riemann-Liouville operator looks more ''natural,'' due to the relation $\mathcal{L}\{{}_0D_t^{-\alpha}W(x,v,t)\}=u^{-\alpha}W(x,v,u)$. As for the mathematical properties of this operator, the fractional evolution equations can be solved in a similar way as the standard equations, and they are thus a convenient model for the description of dynamics in complex systems [10].

On the macroscopic level, the dynamics is governed by the fractional Riemann-Liouville operator, Eq. (4). This is the origin for the subexponential relaxation of the Klein-Kramers, Fokker-Planck and Rayleigh modes according to the Mittag-Leffler pattern [10,20,21,32]

$$T_n(t)=E_\alpha(-\lambda_{n,\alpha}t^\alpha)\equiv\sum_{n=0}^{\infty}\frac{(-\lambda_{n,\alpha}t^\alpha)^n}{\Gamma(1+\alpha n)}, \qquad (8)$$

where $\lambda_{n,\alpha}$ is an eigenvalue of the respective equations (3), (6), or (7). This relation is obtained from the temporal eigenequation $(d/dt)T_n=-\lambda_{n,\alpha}\,{}_0D_t^{1-\alpha}T_n(t)$ which can be obtained by the separation ansatz $W(x,v,t)=T(t)\varphi(x,v)$ [10,14,20,21]. The interesting property of the Mittag-Leffler function (8) is its interpolation between an initial stretched exponential behavior $T_n\sim\exp\{-\lambda_{n,\alpha}t^\alpha/\Gamma(1+\alpha)\}$ and an inverse power-law pattern $T_n\sim[\lambda_{n,\alpha}t^\alpha\Gamma(1-\alpha)]^{-1}$ at long times.

The presented model for subdiffusion in the external force field $F(x)=-\Phi'(x)$ provides a basis for fractional evolution equations, starting from Langevin dynamics which 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 τ^* which is basically equivalent to a multiple of the mean jump time Δt in Eq. (2). If the characteristic waiting time is finite, $T<\infty$, the trapping mechanism also possesses its characteristic time scale. Therefore, the second stage brings two processes together, and the macroscopic process defined as the long-time limit in respect to τ^* or T is determined by the standard Klein-Kramers equation. Conversely, if $T\to\infty$ diverges, the time scales of the microscopic Brownian motion τ^* separates from the combined immobilization-release 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 which 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. (3). Physically, this causes the rescaling of the fundamental quantity η by the scaling factor ϑ, to result in the generalized friction constant $\eta_\alpha=\eta/\vartheta$. It is interesting to note that a similar process depicting a force-free trapping-walk scenario on a kinematics level was described in Ref. [27] in (x,t) coordinates, revealing the subdiffusive mean square displacement $\langle x^2\rangle\propto t^\alpha$.

The Langevin picture rules the Markov motion parts in between successive trapping states. On this Ist stage the test particle consequently obeys Newton's law, in the noise-averaged sense defined above. Conversely, averaging the fractional Klein-Kramers equation (3) over velocity and position, one recovers the memory relation $(d/dt)\langle\langle x\rangle\rangle=\vartheta_0D_t^{1-\alpha}\langle\langle v\rangle\rangle$ between the mean position $\langle\langle x\rangle\rangle$ and the mean velocity $\langle\langle v\rangle\rangle$. This ''violation'' is only due to the additional waiting time averaging which camouflages the Newtonian, Langevin-dominated motion events.

The stationary solutions of the fractional evolution equations (3), (6), and (7) are given by the Maxwell or Gibbs-Boltzmann equilibrium distributions. Thus, the presented model for subdiffusion in the external force field $F(x)$ is close to thermal equilibrium, and it is fundamentally different to those models of anomalous transport which are based on Tsallis q thermostatistics and which lead to nonlinear transport equations [36].

It has been shown how the interplay between the Langevin diffusion and the trapping process which is governed by a Lévy-type waiting time PDF gives rise to the fractional dynamics, preserving the existence of (generalized) Einstein relations and revealing the physical origin of the generalized transport coefficients.

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[1] P. Langevin, Comptes Rendus **146**, 530 (1908).
[2] O. Klein, Ark. Mat., Astron. Fys. **16**, 5 (1922); H.A. Kramers, Physica (Amsterdam) **7**, 284 (1940).
[3] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[4] N. G. van Kampen *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
[5] H. Risken *The Fokker-Planck Equation* (Springer-Verlag, Berlin, 1989).
[6] P. Lévy *Processus Stochastiques et Mouvement Brownien* (Gauthier-Villars, Paris, 1965).
[7] J.-P. Bouchaud and A. Georges Phys. Rep. **195**, 12 (1990).
[8] J. Klafter and M.F. Shlesinger, Phys. Today **49**(2), 33 (1996).
[9] P. Lévy *Théorie de L'addition des Variables Aléatoires* (Gauthier-Villars, Paris, 1954); B. V. Gnedenko and A. N. Kolmogorov, *Limit Distributions for Sums of Random Variables* (Addison-Wesley, Reading, 1954).
[10] R. Metzler and J. Klafter, Phys. Rep. (to be published).
[11] R. Hilfer, Fractals **3**, 211 (1995); R. Metzler, W.G. Glöckle, and T.F. Nonnenmacher, Physica A **211**, 13 (1994); W.R. Schneider and W. Wyss, J. Math. Phys. **30**, 134 (1989).
[12] A. Compte, Phys. Rev. E **53**, 4191 (1996).
[13] A. Compte and M.O. Càceres, Phys. Rev. Lett. **81**, 3140 (1998); A. Compte, R. Metzler, and J. Camacho, Phys. Rev. E **56**, 1445 (1997).
[14] R. Metzler, J. Klafter, and I. Sokolov, Phys. Rev. E **58**, 1621 (1998).
[15] M. Buiatti, P. Grigolini, and A. Montagnini, Phys. Rev. Lett. **82**, 3383 (1999).
[16] F. Peseckis, Phys. Rev. A **36**, 892 (1987).
[17] H.C. Fogedby, Phys. Rev. Lett. **73**, 2517 (1994); Phys. Rev. E **50**, 1657 (1994); *ibid.* **58**, 1690 (1998); S. Jespersen, R. Metzler, and H.C. Fogedby, *ibid.* **59**, 2736 (1999); J. Honkonen, *ibid.* **53**, 327 (1996).
[18] G.M. Zaslavsky, M. Edelman, and B.A. Niyazov, Chaos **7**, 159 (1997).
[19] D. Kusnezov, A. Bulgac, and G.D. Dang, Phys. Rev. Lett. **82**, 1136 (1999).
[20] R. Metzler, E. Barkai, and J. Klafter, Phys. Rev. Lett. **82**, 3563 (1999).
[21] R. Metzler, E. Barkai, and J. Klafter, Europhys. Lett. **46**, 431 (1999); E. Barkai, R. Metzler, and J. Klafter, Phys. Rev. E **61**, 132 (2000).
[22] E. Barkai and R. Silbey, J. Phys. Chem. B **104**, 3866 (2000).
[23] B.J. West and V. Seshadri, Physica A **113**, 203 (1982).
[24] K.G. Wang *et al.*, Physica A **203**, 53 (1994); K.G. Wang and M. Tokuyama, *ibid.* **265**, 341 (1999).
[25] G. Pfister and H. Scher, Adv. Phys. **27**, 747 (1978).
[26] Q. Gu, E.A. Schiff, S. Grebner, and R. Schwartz, Phys. Rev. Lett. **76**, 3196 (1996).
[27] M.F. Shlesinger and J. Klafter, J. Phys. Chem. **93**, 7023 (1989).
[28] J. Klafter and G. Zumofen, Phys. Rev. E **49**, 4873 (1994); L. Kuznetsov and G.M. Zaslavsky, *ibid.* **58**, 7330 (1998); S. Benkadda *et al.*, *ibid.* **55**, 4909 (1997).
[29] S.S. Plotkin and P.G. Wolynes, Phys. Rev. Lett. **80**, 5015 (1998); J. D. Bryngelson and P. G. Wolynes, J. Phys. Chem. **93**, 6902 (1989).
[30] Note that the corresponding Lévy stable law for $\alpha=1$ is $w(t)=\delta(t-\tau)$ from which $T=\tau$ follows.
[31] V.M. Kenkre, E.W. Montroll, and M.F. Shlesinger, J. Stat. Phys. **9**, 45 (1973) see Eq. (11).
[32] R. Metzler and J. Klafter, J. Phys. Chem. B **104**, 3851 (2000).
[33] R.W. Davies, Phys. Rev. **93**, 1169 (1954).
[34] F. Amblard *et al.*, Phys. Rev. Lett. **77**, 4470 (1996); **81**, 1135 (1998); E. Barkai and J. Klafter, *ibid.* **81**, 1134 (1998).
[35] $f(u)\equiv\mathcal{L}\{f(t)\}=\int_0^\infty dte^{-ut}f(t)$.
[36] C. Tsallis and D.J. Bukman, Phys. Rev. E **54**, R2197 (1996); L. Borland, *ibid.* **57**, 6634 (1998); C. Tsallis *et al.*, Phys. Rev. Lett. **75**, 3589 (1995); D.H. Zanette and P.A. Alemany, *ibid.* **75**, 366 (1995).
[37] R. Metzler and J. Klafter, Chem. Phys. Lett. **321**, 238 (2000).
[38] E. Barkai and V. N. Fleurov, Phys. Rev. E **58**, 1296 (1998).