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Anomalous transport in disordered systems under the influence of external fields

Ralf Metzler[a], Eli Barkai[b], Joseph Klafter[a]

[a]School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

[b]School of Physics, Tel Aviv University, 69978 Tel Aviv, Israel

Abstract

We discuss two models for the description of anomalous diffusion, these being the *continuous time random walk* scheme, and *fractional diffusion equations*. We show their interrelations, and combine both approaches for the description of anomalous transport in constant external velocity and force fields. For an arbitrary external force $F(x)$, we introduce a fractional Fokker–Planck equation, which generalises the two Einstein relations. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transport in complex systems is intimately related to deviations from the standard Fickean description of Brownian motion [1–4]. *Anomalous diffusion* is usually characterised by the occurrence of a mean squared displacement of the form

$$\langle(\Delta x)^2\rangle \sim t^\gamma\,, \tag{1}$$

where the so-called anomalous diffusion exponent γ covers the following régimes:

$$\gamma < 1 \text{ subdiffusive}$$

$$\gamma = 1 \text{ Brownian}$$

$$\gamma > 1 \text{ enhanced} \begin{cases} 1<\gamma<2 & \text{intermediate}\,, \\ \gamma = 2 & \text{ballistic}\,, \\ \gamma > 2 & \text{“turbulent”}\,. \end{cases}$$

The anomalous behaviour in Eq. (1) is related to deviations from the standard Gaussian evolution of the propagator, caused by memory effects, and generalised Lévy–type statistics [2–6].

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Examples for subdiffusive transport include charge transport in amorphous semiconductors [7–9], NMR diffusometry in disordered materials [10], and the dynamics of a bead in a polymer network [11]. On fractal supports, subdiffusion prevails, due to the lacunarity of the structure, this is, the presence of "holes" of all length scales [3]. Enhanced diffusion is, for example, encountered in arrays of vortices in a rotating flow [12], in layered velocity fields [13], or for Richardson dispersion [14–16].

In the following, we introduce the concepts of fractional diffusion equations (FDE) and the continuous time random walk (CTRW) scheme, and show their interrelations. We then proceed by combining these two approaches for the inclusion of homogeneous external velocity and force fields. Finally, we introduce a fractional Fokker–Planck equation, which describes subdiffusion in arbitrary external force fields $F(x)$.

2. Continuous time random walks and fractional diffusion equations

CTRW processes are characterised by the probability density function $\psi(x,t)$, which determines the length x of the jump, and the waiting time t which elapses after the last jump, until a new jump occurs. For each jump, a new pair of jump length and waiting time is drawn [17–20]. The jump probability density function $\psi(x,t)$ can either be given by the statistically independent product $\psi(x,t)=\lambda(x)\psi(t)$ of jump length and waiting time densities, which leads to subdiffusion for a broad $\psi(t) \sim t^{-1-\gamma}$ and narrow (Gaussian) $\lambda(x)$, or to Lévy flights. Alternatively, it can be given through the coupled expression $\psi(x,t)= p(x|t)\psi(t)$, which is used for the introduction of Lévy walks with a finite velocity of propagation. Here, the conditional probability $p(x|t)$ introduces a time cost for the jumps and thus penalises long jumps [20].

From a generalised master equation approach [20], it can be shown, that the propagator for such a process in Fourier–Laplace space ($x \leftrightarrow k,\ t \leftrightarrow u$) is given by

$$\varrho(k,u)=\frac{1-\psi(u)}{u}\frac{1}{1-\psi(k,u)}\,, \tag{2}$$

where k is the wave vector, and u the Laplace variable complementary to the time t. A CTRW process is characterised by the existence or divergence of a characteristic waiting time $T=\int \mathrm{d}t\, t\psi(t)$, and the second moment $\Sigma^2=\int \mathrm{d}t \int \mathrm{d}x\, x^2\psi(x,t)$ [20].

An alternative description of anomalous diffusion is given by FDEs [21–24]. Schneider and Wyss [21] introduced an equation of the form

$$\varrho(x,t)-\varrho(x,0)=K_\gamma\, {}_0D_t^{-\gamma}\varrho''\,, \tag{3}$$

with the anomalous diffusion coefficient K_γ of dimension $[K_\gamma]=\mathrm{cm}^2\ \mathrm{s}^{-\gamma}$. In Eq. (3), the Riemann–Liouville fractional integral operator ${}_0D_t^{-\gamma}$ is defined through [25]

$${}_0D_t^{-\gamma}\varrho(x,t)=\frac{1}{\Gamma(\gamma)}\int_0^t \mathrm{d}t'\,\frac{\varrho(x,t')}{(t-t')^{1-\gamma}}. \tag{4}$$

The extension to fractional differentiation is given by ${}_0D_t^{\delta}=\mathrm{d}/\mathrm{d}t\,{}_0D_t^{-(1-\delta)}$ for $0<\delta<1$ [25].

Let us now investigate the connections between CTRWs and FDEs. To this end, we consider the case of a broad waiting time distribution $\psi(t) \sim (t/\tau)^{-1-\gamma}$, $0 < \gamma < 1$, i.e. diverging T, but finite Σ^2, for which we find the propagator [20]

$$\varrho(k,u) = \frac{1}{u + Dk^2 u^{1-\gamma}} \,. \tag{5}$$

By means of the definitions of fractional calculus, we infer the corresponding FPE [25–28]

$$\dot{\varrho} = {}_0D_t^{1-\gamma} K_\gamma \varrho'' \,. \tag{6}$$

Using the composition rules of fractional calculus [25], it can be shown, that Eq. (6) is equivalent to Eq. (3), or to

$${}_0D_t^{\gamma}\varrho - \frac{t^{-\gamma}\varrho(x,0)}{\Gamma(1-\gamma)} = K_\gamma \varrho'' \,. \tag{7}$$

Both Eqs. (3) and (7) include the initial value $\varrho(x,0)$. The correspondence of the CTRW description (5) to the FDEs (3), (6) and (7), in the subdiffusive régime of a broad waiting time distribution, is exact. An equation for intermediate transport, similar to Eq. (6), was derived from a dichotomous stochastic process with a long-range velocity–velocity correlation function by West et al. [29,30].

3. Anomalous diffusion in homogeneous velocity and force fields

In this section, we consider the case of anomalous diffusion under the influence of an external homogeneous velocity or force field, see also Ref. [28].

For a uniform velocity field v, we introduce the similarity variable $\xi = x - vt$ for the moving frame. This reduces the problem to the standard CTRW problem which simply has to be transformed to the laboratory frame. In the rest frame of the fluid, the frame moving with velocity v relative to the laboratory frame, the jump distribution is given by the standard CTRW expression, $\psi(x,t)$. Therefore, following the Galilei transformation to the laboratory frame, the jump distribution there, $\phi(x,t)$, can be expressed by

$$\phi(x,t) = \psi(x - vt, t). \tag{8}$$

The corresponding relation in (k,u) space reads

$$\phi(k,u) = \psi(k, u + \mathrm{i}vk) \,. \tag{9}$$

For the Brownian case we choose $\psi(t) = \tau^{-1}e^{-t/\tau}$ and $\lambda(x) = [4\pi\sigma^2]^{-1/2}e^{-x^2/(4\sigma^2)}$, leading to the diffusion-advection equation [1]

$$\dot{\varrho}(x,t) + v\varrho' = K_1\varrho'' \tag{10}$$

with $K_1 = \sigma^2/\tau$. For a broad waiting time distribution $\psi(t) \sim (t/\tau)^{-1-\gamma}$ and $0 < \gamma < 1$, the propagator becomes

$$\varrho(k,u) = \frac{1}{u + \mathrm{i}vk}\,\frac{1}{1 + K_\gamma k^2 u^{-\gamma}} \sim \frac{1}{u + \mathrm{i}vk + K_\gamma k^2 u^{1-\gamma}} \tag{11}$$

in the $k \to 0$ and $u \to 0$ limit, from which the moments follow:

$$\langle x \rangle(t) = vt\,, \tag{12a}$$

$$\langle x^2 \rangle(t) = \frac{2K_\gamma}{\Gamma(1+\gamma)} t^\gamma + v^2 t^2\,, \tag{12b}$$

$$\langle (\Delta x)^2 \rangle(t) = \frac{2K_\gamma}{\Gamma(1+\gamma)} t^\gamma\,. \tag{12c}$$

Thus, we obtain a proper Galilean drift vt, and a mean squared displacement which is the subdiffusive molecular contribution. This is to be compared with the results below, Eqs. (18a)–(18c). The corresponding generalised diffusion equation to the result in Eq. (11) is

$$\dot{\varrho}(x,t) + v\varrho' = K_\gamma\, {}_0D_t^{1-\gamma} \varrho'', \tag{13}$$

where the drift term $v\varrho'$ is not affected by the memory convolution ${}_0D_t^{1-\gamma}$.

For the study of enhanced transport we avoid the occurrence of a diverging second moment, and introduce the Lévy walk model, which is defined by the coupling $\psi(x,t) = C|x|^{-\mu}\delta(|x| - t^\nu)$ [20]. Several interesting cases that stem from the choice of the parameters ν and μ can be distinguished, from which we concentrate on the case for which $1 < \nu\mu < 2$ and $\nu(\mu - 2) < 1$. This choice leads to the propagator in Fourier–Laplace space:

$$\varrho = \frac{1}{u + \mathrm{i}vk} \frac{1}{1 + K_\gamma k^2 u^{-2\nu}} \sim \frac{1}{u + \mathrm{i}vk + K_\gamma k^2 u^{1-2\nu}}\,, \tag{14}$$

in the $k \to 0$, $u \to 0$ limit, which is to be compared with Eq. (43) in Ref. [20].

For the moments we end up with

$$\langle x \rangle(t) = vt\,, \tag{15a}$$

$$\langle x^2 \rangle(t) = \frac{2K_\gamma t^{2\nu}}{\Gamma(1+2\nu)} + v^2 t^2\,, \tag{15b}$$

$$\langle (\Delta x)^2 \rangle(t) = \frac{2K_\gamma t^{2\nu}}{\Gamma(1+2\nu)}\,, \tag{15c}$$

so that in this case we find the two possibilities of subdiffusive and enhanced motion, depending on the value of ν. Finally, the corresponding fractional equation is of the form

$$\dot{\varrho}(x,t) + v\varrho' = K_\gamma\, {}_0D_t^{1-2\nu} \varrho''\,, \tag{16}$$

similar to Eq. (13), where now the RHS can either be a fractional integration or differentiation, according to the value of ν.

We now consider an interesting modification of this model, which we call *partial sticking*, where the Galilean invariance is no longer fulfilled. This might be of relevance for diffusion in porous systems where the tracer particles can get stuck in pores before the next jump, or for modelling sticking in vortices in rotating flows. Partial sticking can be taken into account by choosing $\phi(u) = \phi(k = 0, u)$ [28]. That means, that the particle does not move during the waiting time. For the propagator, we then find $(k \to 0,\ u \to 0)$

$$\varrho(k,u) = \frac{1}{u + \gamma \mathrm{i} v k - \gamma(\gamma-1)/2 v^2 u^{-1} k^2 + K_\gamma u^{1-\gamma} k^2}\,, \tag{17}$$

and the results for the moments are now

$$\langle x\rangle(t) = \gamma v t\,, \tag{18a}$$

$$\langle x^2\rangle(t) = \frac{2K_\gamma}{\Gamma(1+\gamma)} t^\gamma + \frac{\gamma(\gamma+1)}{2} v^2 t^2\,, \tag{18b}$$

$$\langle(\Delta x)^2\rangle(t) = \frac{2K_\gamma}{\Gamma(1+\gamma)} t^\gamma + \frac{\gamma(1-\gamma)}{2} v^2 t^2\,. \tag{18c}$$

In this case, the velocity dependence does not cancel out. Consequently, a ballistic behaviour remains in Eq. (18c), in contrast to the result $\propto t^{2\gamma}$ in Ref. [31]. However, the apparent drift velocity in Eq. (18a) is v scaled by the factor γ, $0 < \gamma < 1$. Regarding the generalised equation corresponding to Eq. (17):

$$\dot{\varrho} + v\varrho' = \frac{\gamma(1-\gamma)}{2} v^2\, {}_0D_t^{-1} \varrho'' + K_\gamma\, {}_0D_t^{1-\gamma} \varrho''\,, \tag{19}$$

we recognise the division of the transport process into two different mechanisms: a subdiffusive part characterised by K_γ, and a "ballistic" part proportional to v^2. In this process, the particles that jump often, are separated more efficiently from those which are stuck for a long time. The significant distinction of Eqs. (18a)–(18c) from Eqs. (12a)–(12c) might also be important for the spreading of pollutants in ground water flows in different media.

We now turn to the problem of a constant force, which leads to different results in the case of anomalous transport. We model this case by a jump distribution $\psi(x,t) = \psi(t)\lambda^{\pm}(x)$ with an asymmetric jump length distribution $\lambda^{\pm} = (\lambda+(x)\Theta(x) + \lambda^-(x)\Theta(-x))$, compare with [12,32,33]. For a broad $\psi(t)$ and narrow jump length distribution given by two Gaussians of inverse width a and b, we find [28]

$$\langle x\rangle(t) = F_\gamma \frac{t^\gamma}{\Gamma(1+\gamma)}\,, \tag{20a}$$

$$\langle x^2\rangle(t) = 2K_\gamma \frac{t^\gamma}{\Gamma(1+\gamma)} + 2F_\gamma^2 \frac{t^{2\gamma}}{\Gamma(1+2\gamma)}\,, \tag{20b}$$

$$\langle(\Delta x)^2\rangle(t) = F_\gamma^2 \frac{2\Gamma^2(1+\gamma) - \Gamma(1+2\gamma)}{\Gamma(1+2\gamma)\Gamma^2(1+\gamma)} t^{2\gamma} + 2K_\gamma \frac{t^\gamma}{\Gamma(1+\gamma)} \tag{20c}$$

for the moments and

$$\dot{\varrho} = {}_0D_t^{1-\gamma}\left(-\frac{\partial F_\gamma \varrho}{\partial x} + \frac{\partial^2 K_\gamma \varrho}{\partial x^2}\right) \tag{21}$$

for the fractional diffusion equation, with the velocity force term $F_\gamma = (\sqrt{a} - \sqrt{b})/[2\tau^\gamma\sqrt{\pi}\sqrt{ab}]$ and the generalised diffusion constant $K_\gamma = (a + b)/[8\tau^\gamma ab]$. From Eq. (20a), we see that now the divergence of the characteristic waiting time T leads to a sublinear time dependence of the first moment. This also causes a $t^{2\gamma}$ behaviour in the mean squared displacement, which is mirrored in the fractional equation (21), where now the force is inside the memory convolution, in contrast to Eq. (13).

4. Fractional Fokker–Planck equation for one variable

In this section, we generalise the above considerations to arbitrary external force fields $F(x) = -V'(x)$ for the subdiffusive case, close to thermal equilibrium. Possible applications include Refs. [7–9,11], or the sedimentation of pollutants under the influence of gravitation.

Usually, diffusion problems in an external force field are modelled by a Fokker–Planck equation (FPE) [34]. Fractional Fokker–Planck equations (FFPE) have been previously discussed for chaotic systems [35], for Lévy flights in random environments [36], or for fractal time spaces [37].

We propose the one-dimensional FFPE for one variable (Smoluchowski equation) [38]

$$\dot{\varrho}(x,t) = {}_0D_t^{1-\gamma} L_{\mathrm{FP}}\varrho \tag{22}$$

for the study of subdiffusive processes, where the linear Fokker–Planck operator, acting upon the probability density function $\varrho(x,t)$, is given by $L_{\mathrm{FP}} = \left[\partial/\partial x V'(x)/m\eta_\gamma + K_\gamma \partial^2/\partial x^2\right]$ with the external potential field $V(x)$ and the generalised friction coefficient η_γ with $[\eta_\gamma] = \sec^{\gamma-2}$.

The RHS of the FFPE (22) is equivalent to $-{}_0D_t^{1-\gamma}\partial S(x,t)/\partial x$, where S is the probability current [34]. If a stationary state is reached, S must be constant. Thus, if $S = 0$ for any x, it vanishes for all x [34], and the stationary solution is given by $V'(x)\varrho_{\mathrm{st}} + K\varrho_{\mathrm{st}}' = 0$. Comparing this expression with the required Boltzmann distribution $\varrho_{\mathrm{st}} \propto \exp(-V(x)/[k_B T])$, we find a generalisation of the Einstein relation, also referred to as Stokes–Einstein–Smoluchowski relation,

$$K_\gamma = \frac{k_B T}{m\eta_\gamma}\,, \tag{23}$$

for the generalised coefficients K_γ and η_γ.

In the presence of a uniform force field, given by $V(x) = -Fx$, a net drift occurs. We calculate the quantity $\langle \dot{x} \rangle_F = \int \mathrm{d}x\, x\dot{\varrho}$ via the FFPE (22), for which we find

$$\langle x \rangle_F = \frac{F}{m\eta_\gamma}\frac{t^\gamma}{\Gamma(1+\gamma)}\,. \tag{24}$$

On the other hand, the mean squared displacement for the FFPE (22) in absence of a force, can be calculated similarly:

$$\langle x^2 \rangle_0 = \frac{2K_\gamma t^\gamma}{\Gamma(1+\gamma)}\,, \tag{25}$$

where the subscripts F and 0 indicate presence and absence of the force field. Using Eq. (23), we finally recover the generalised Einstein relation

$$\langle x \rangle_F = \frac{1}{2}\frac{F\langle x^2 \rangle_0}{k_B T} \tag{26}$$

connecting the first moment in the presence with the second moment in absence of the force, see Refs. [4,39].

From Ref. [11] and the following discussion in Ref. [40], it was shown, that in the subdiffusive case the generalised Einstein relation holds true. The investigation in Ref. [9] revealed, that, up to a factor of 2, which could not be determined exactly, relation (26) is valid.

The FFPE (22) can be solved exactly by a separation ansatz $\varrho_n = T_n(t)\varphi_n(x)$ for a given eigenvalue n, the full result being [38]

$$\begin{aligned}\varrho(x,t|x',0) \\ = e^{\Phi(x')/2-\Phi(x)/2} \sum_n \Psi_n(x)\Psi_n(x')E_\gamma\left(-\alpha_{n,\gamma}t^\gamma\right)\,,\end{aligned} \tag{27}$$

for an initial distribution concentrated in x'. The single modes of this solution correspond to an anomalous Mittag–Leffler relaxation with an asymptotic power–law dependence $\propto t^{-\gamma}$, in contrast to the standard exponential decay. In Eq. (27), the functions $\Psi_n(x) = e^{\Phi(x)/2}\varphi_n(x)$ are related to the eigenfunctions of the Fokker–Planck operator L_{FP}, $\varphi_n(x)$, via the scaled potential $\Phi(x) = V(x)/[k_B T]$. The Ψ_n are eigenfunctions of the Hermitian operator $L = e^{-\Phi}L_{\mathrm{FP}}e^{\Phi}$. L and L_{FP} have the same eigenvalues $\alpha_{n,\gamma} = (\eta_1/\eta_\gamma)\alpha_{n,1}$, where the subscript 1 refers to the standard case $\gamma = 1$ [34].

5. Conclusions

We have shown that the combined approach by FDE and CTRW allows for consistent extensions of equations which describe anomalous diffusion in disordered systems, under the influence of external fields. Especially, the problems of a constant velocity and a constant force field have been discussed. For subdiffusive transport processes under arbitrary external force fields, we introduced a new fractional Fokker–Planck equation, which was shown to relax towards the Boltzmann equilibrium, and to lead to generalisations of the Einstein relations.

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