

# Boundary value problems for fractional diffusion equations

Ralf Metzler\*, Joseph Klafter

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

Received 29 October 1999

---

## Abstract

The fractional diffusion equation is solved for different boundary value problems, these being absorbing and reflecting boundaries in half-space and in a box. Thereby, the method of images and the Fourier–Laplace transformation technique are employed. The separation of variables is studied for a fractional diffusion equation with a potential term, describing a generalisation of an escape problem through a fluctuating bottleneck. The results lead to a further understanding of the fractional framework in the description of complex systems which exhibit anomalous diffusion. © 2000 Elsevier Science B.V. All rights reserved.

*PACS:* 05.40.–a; 05.40.Fb; 02.50.Ey; 05.10.–a

*Keywords:* Fractional diffusion equation; Boundary value problems; Mittag–Leffler relaxation; Anomalous diffusion; Anomalous relaxation

---

## 1. Introduction

The mathematical properties of the diffusion equation

$$\frac{\partial W}{\partial t} = K_1 \frac{\partial^2}{\partial x^2} W(x, t) \quad (1)$$

have been extensively studied [1–5] so that numerous methods exist for the solution of boundary value problems, and for diffusion under the influence of an external potential [1–8]. Loosely speaking, an external potential leading to a non-trivial stationary solution is also a boundary value problem with a discrete set of eigenvalues, and we refer to both cases as boundary value problems in this loose sense. In the present paper, similar

---

\* Corresponding author. Fax: +972-3-640-6466.

*E-mail address:* metzler@post.tau.ac.il (R. Metzler)

conditions are imposed on the fractional diffusion equation (FDE) [9–11]

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\gamma} K_\gamma \frac{\partial^2}{\partial x^2} W(x, t) \quad (2)$$

with  $0 < \gamma < 1$ , which describes a non-Markovian diffusion process with a memory [12–15]. Originally, Schneider and Wyss [9] considered the equivalent fractional integral equation

$$W(x, t) - W_0(x) = {}_0D_t^{-\gamma} K_\gamma \frac{\partial^2}{\partial x^2} W(x, t), \quad (3)$$

where the initial value  $W_0(x) \equiv \lim_{t \rightarrow 0^+} W(x, t)$  is directly incorporated. Thus, Eq. (2) is obtained by differentiating Eq. (3) with respect to time. The fractional Riemann–Liouville operator in Eq. (2) is defined through [16]

$${}_0D_t^{1-\gamma} W(x, t) = \frac{1}{\Gamma(\gamma)} \frac{\partial}{\partial t} \int_0^t dt' \frac{W(x, t')}{(t-t')^{1-\gamma}}. \quad (4)$$

Some properties of this fractional operator are listed in Appendix A. The fractional differentiation  ${}_0D_t^{1-\gamma}$  contains a convolution integral with a slowly decaying power-law kernel  $M(t) = t^{\gamma-1}/\Gamma(\gamma)$ . In Fourier–Laplace space, the solution of the FDE (2) for natural boundary conditions  $\lim_{|x| \rightarrow \infty} W(x, t) = 0$  and for a sharp initial condition  $W_0(x) = \delta(x)$  reads [9–11,15,17,18]

$$W(k, u) = u^{\gamma-1} \frac{1}{u^\gamma + K_\gamma k^2}, \quad (5)$$

from which the mean square displacement

$$\langle x^2 \rangle = \frac{2K_\gamma}{\Gamma(1+\gamma)} t^\gamma \quad (6)$$

can be derived by  $\langle x^2 \rangle(u) = -\lim_{k \rightarrow 0} (\partial^2/\partial k^2) W(k, u)$  and Laplace inversion. Alternatively, this result is obtained from Eq. (2) or Eq. (3) via integration by parts and making use of Eq. (A.7). Eqs. (2), (3) and (6) contain the generalised diffusion coefficient of dimension  $[K_\gamma] = \text{cm}^2 \text{s}^{-\gamma}$ . Eq. (6) deviates from the linear time dependence  $\langle x^2 \rangle = 2K_1 t$  which is the hallmark of Brownian motion [1,3–5,8]. The FDE, Eq. (2), for  $0 < \gamma < 1$  describes anomalous subdiffusive processes [19–22]. Subdiffusion is encountered, for instance, in highly ramified media like porous systems [23], percolation clusters [24], exact fractals [25], in the motion of a bead in a polymer network [26,27], or in the charge carrier transport in amorphous semiconductors [28–30].

The FDE, Eq. (2), and fractional Fokker–Planck equations [13,14,31–36] are closely related to generalised Lévy-type statistics [22,37,38] and can be derived from continuous time random walk models, or their extensions [8,13–15,17,18,28,29,36,39–41], or from a Langevin equation [31,32,42,43]. Complementing to random walks, or to the generalised master equation approach [13,14,44], the FDE and the fractional Fokker–Planck equations constitute an additional framework to describe diffusion in complex systems. Here we demonstrate that fractional equations make it possible to calculate,

in a straightforward manner and in analogy to the techniques used in the Brownian limit, explicit solutions for boundary value problems, and in the presence of external potential fields.

Firstly, reflecting and absorbing boundaries in half-space and in a box of finite size are solved by the method of images. The results feature deviations from the corresponding Brownian limiting cases. Subsequently, we consider the escape problem through a fluctuating bottleneck in the presence of a slowly decaying memory which is formally equivalent to anomalous diffusion in an external field. This leads to the description in terms of a fractional Smoluchowski-type equation with a discrete set of eigenvalues. Using the method of separation of variables, a solution in terms of a series involving the Mittag-Leffler function and the Hermite polynomials is obtained. As demonstrated by the plotted results, the fractional equations produce quite different behaviours in comparison to their Brownian counterparts.

## 2. Reflecting and absorbing boundaries

Subdiffusion described through Eq. (2) corresponds to a situation in the random walk picture where the jumps are characterised by a finite jump length variance [8,13–15,41]. The non-Markovian character of the FDE (2) can be shown to come about in a random walk picture where the time elapsing between successive jumps is drawn from a waiting time distribution which allows for long waiting times such that the characteristic waiting time diverges [13,39–41]. Consequently, the method of images [4,45] can be applied to subdiffusion, in contrary to the case of Lévy flights [46,47].

### 2.1. Half-space problem

The half-space problem concerns the diffusion on a line which is terminated at one point by a boundary which can be either of reflecting or absorbing nature.

#### 2.1.1. Reflecting condition

Suppose that a reflecting boundary is placed at the origin of the  $x$ -axis on which the diffusing particle moves. This condition is defined as a von Neumann problem in the form  $\partial Q(x,t)/\partial x|_{x=0} = 0$  where  $Q$ , specified below, denotes the image solution of this boundary value problem. If the initial condition is a sharp distribution at the position  $x_0$ ,  $W_0(x) = \delta(x - x_0)$ ,<sup>1</sup> the free solution can be “folded” along a line through the origin, perpendicular to the  $x$ -axis, i.e., the unrestricted solution is taken, and the portion which spreads to the space region opposite to  $x_0$ , with respect to the origin, is

<sup>1</sup> This condition, up to a translation, is equivalent to having a boundary at the position  $-x_0$ , and the sharp initial condition  $W_0(x) = \delta(x)$ .

reflected at this line; the final result fulfils the von Neumann condition. The solution is thus given by the function [4]<sup>2</sup>

$$Q(x, t|x_0) = W(x - x_0, t) + W(-x - x_0, t), \tag{7}$$

where  $W(x, t)$  denotes the solution of the FDE (2), for natural boundary conditions. The reasoning in terms of the image method, in analogy to the presentation of Feller [4], chosen to illustrate the coming about of Eq. (7) is not necessary, and some readers may find Eq. (7) as such more intuitive. To construct the image solution  $Q(x, t|x_0)$ , Eq. (7), we need to develop some preparing considerations. Thus, note that according to Eq. (5), the different modes of the FDE, Eq. (2), decay according to the Mittag-Leffler pattern  $E_\gamma$  (see Appendix B)

$$W(k, t) = E_\gamma(-K_\gamma k^2 t^\gamma) \tag{8}$$

with the asymptotic power-law behaviour  $W(k, t) \sim [K_\gamma \Gamma(1 - \gamma) k^2 t^\gamma]^{-1}$ . The solution in position space,  $W(x, t)$ , is given in terms of the Fox function  $H_{1,2}^{2,0}$  [9–11,48,49],

$$W(x, t) = \frac{1}{\sqrt{4\pi K_\gamma t^\gamma}} H_{1,2}^{2,0} \left[ \frac{x^2}{4K_\gamma t^\gamma} \left| \begin{matrix} (1 - \frac{\gamma}{2}, \gamma) \\ (0, 1), (\frac{1}{2}, 1) \end{matrix} \right. \right] \tag{9}$$

or by the alternative representation, using  $H_{1,1}^{1,0}$ ,

$$W(x, t) = \frac{1}{\sqrt{4K_\gamma t^\gamma}} H_{1,1}^{1,0} \left[ \frac{|x|}{\sqrt{K_\gamma t^\gamma}} \left| \begin{matrix} (1 - \frac{\gamma}{2}, \frac{\gamma}{2}) \\ (0, 1) \end{matrix} \right. \right], \tag{10}$$

with the asymptotic stretched Gaussian behaviour

$$W(x, t) \sim \frac{1}{\sqrt{4\pi K_\gamma t^\gamma}} \sqrt{\frac{1}{2 - \gamma}} \left(\frac{2}{\gamma}\right)^{(1-\gamma)/(2-\gamma)} \left(\frac{|x|}{\sqrt{K_\gamma t^\gamma}}\right)^{-(1-\gamma)/(2-\gamma)} \times \exp\left(-\frac{2 - \gamma}{2} \left(\frac{\gamma}{2}\right)^{\gamma/(2-\gamma)} \left[\frac{|x|}{\sqrt{K_\gamma t^\gamma}}\right]^{1/(1-\gamma/2)}\right). \tag{11}$$

In the Brownian limit  $\gamma \rightarrow 1$  both Eqs. (9) and (10), as well as Eq. (11), reduce to the well-known Gaussian propagator

$$W(x, t) = \frac{1}{\sqrt{4\pi K_1 t}} \exp\left(-\frac{x^2}{4K_1 t}\right) \tag{12}$$

which is valid for all  $x$  and  $t$ . Note that in Eq. (11), the stretching exponent  $1/(1 - \gamma/2)$  and the power in front of the exponential are similar to the asymptotic result reported in Refs. [50,51]. As an example, for  $\gamma = \frac{1}{2}$ , the propagator (9) can be rewritten in terms

<sup>2</sup> It is easily checked that the von Neumann condition is fulfilled:

$$\frac{\partial Q}{\partial x} \Big|_{x=0} = \frac{\partial W}{\partial x}(-x_0, t) - \frac{\partial W}{\partial x}(-x_0, t).$$

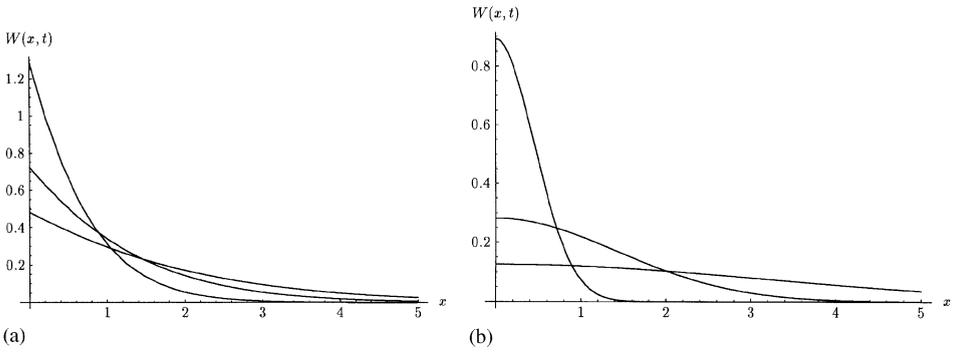


Fig. 1. Probability density function  $W(x, t)$ . Left: The subdiffusive result for  $\gamma = \frac{1}{2}$ . Right: The Brownian case, the Gaussian solution. Both plots are for the times  $t = 0.1, 1$  and  $5$ . The broader tail and the sharper behaviour close to the origin for the subdiffusive solution is distinct.

of Meijer’s  $G$ -function as follows:

$$\begin{aligned}
 W(x, t) &= \frac{1}{\sqrt{2\pi^2 K_{1/2} t^{1/2}}} H_{0,2}^{2,0} \left[ \frac{x^2}{8K_{1/2} t^{1/2}} \middle| \frac{\text{---}}{(0, 1), (\frac{1}{4}, \frac{1}{2})} \right] \\
 &= \frac{1}{\sqrt{8\pi^3 K_{1/2} t^{1/2}}} H_{0,3}^{3,0} \left[ \frac{1}{16} \left( \frac{x^2}{4K_{1/2} t^{1/2}} \right)^2 \middle| \frac{\text{---}}{(0, 1), (\frac{1}{4}, 1), (\frac{1}{2}, 1)} \right] \\
 &= \frac{1}{\sqrt{8\pi^3 K_{1/2} t^{1/2}}} G_{0,3}^{3,0} \left[ \frac{1}{16} \left( \frac{x^2}{4K_{1/2} t^{1/2}} \right)^2 \middle| \frac{\text{---}}{0, \frac{1}{4}, \frac{1}{2}} \right]
 \end{aligned} \tag{13}$$

by twice using the duplication formulae of the Gamma function in the Mellin–Barnes-type integral defining the Fox function [48]. This representation is useful, as the Meijer  $G$ -function belongs to the implemented special functions of Mathematica where the syntax for the  $G$ -function in Eq. (13) is `MeijerG[{{}, {}}, {{0, 1/4, 1/2}}, {{}}, x^4 / (16^2 t)]` for  $K_{1/2} \equiv 1$ . Fig. 1 shows the subdiffusive solution (13) alongside the Brownian solution. Similar reductions of the Fox function to sums of Meijer  $G$ -functions are possible for rational values of the anomalous diffusion exponent  $\gamma$ .

Let us now come back to the boundary value problem. Basing on the Meijer  $G$ -representation (13), the half-space solution  $Q(x, t|x_0)$ , Eq. (7), is drawn in Fig. 2, featuring the slow spread in time of the distinct cusps, i.e., the relatively strong memory to the initial condition. The second moment in half-space,

$$\langle x^2 \rangle_h = \int_0^\infty dx x^2 Q(x, t|x_0), \tag{14}$$

can be calculated on the basis of the Fourier inversion of the propagator in Eq. (5),

$$W(x, u) = \frac{u^{\gamma/2-1}}{\sqrt{4K_\gamma}} e^{-\sqrt{u/K_\gamma}|x|}. \tag{15}$$

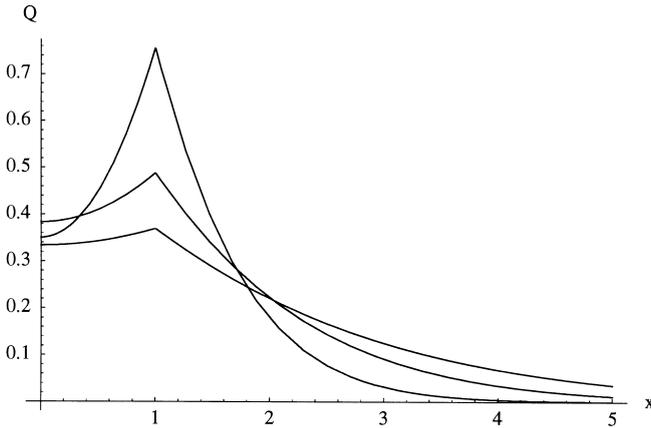


Fig. 2. Half-space solution  $Q(x, t|x_0)$ , Eq. (7), for the initial condition  $x_0 = 1$  and  $\gamma = \frac{1}{2}$ , drawn at the times  $t = 0.1, 1$  and  $5$ . A closer inspection of the behaviour in the vicinity of  $x = 0$  shows that the subdiffusive solution also possesses a horizontal asymptote, i.e., the condition  $(\partial/\partial x)Q(x, t|x_0)|_{x=0}$  following from the von Neumann condition is fulfilled.

According to Eqs. (5) and (7), the probability density function in Laplace space,

$$Q(x, u|x_0) = \frac{u^{\gamma/2-1}}{\sqrt{4K_\gamma}} (e^{\sqrt{u^{\gamma/2}/K_\gamma}(x-x_0)} [\Theta(x) - \Theta(x-x_0)] + e^{-\sqrt{u^{\gamma/2}/K_\gamma}(x-x_0)} \Theta(x-x_0) + e^{-\sqrt{u^{\gamma/2}/K_\gamma}(x+x_0)}) \tag{16}$$

is obtained, where  $\Theta(x)$  denotes the Heaviside function. This leads to the second moment

$$\langle x^2 \rangle_h = \frac{x_0^2}{u} + 2u^{-1-\gamma} K_\gamma \tag{17}$$

and by Laplace inversion,

$$\langle x^2 \rangle_h = x_0^2 + \frac{2K_\gamma t^\gamma}{\Gamma(1+\gamma)} \tag{18}$$

which is a direct generalisation of the standard result for  $\gamma = 1$ . Conversely, it corresponds exactly to the case of natural boundary conditions, and initial condition  $W_0(x) = \delta(\pm x_0)$ . This insensitivity to the one boundary at  $x = 0$  might be an a priori surprising result. Physically, it means that the dispersion (variance) of a passive scalar on the semi-infinite line has the very same time evolution as on the full line. However, the mean square displacement, Eq. (24), calculated below includes the directional information. Note that the result (18) is due to the fact that  $\langle x^2 \rangle_h$  is measured with respect to  $x = 0$ , and not to  $x = x_0$ . Mathematically, the result is therefore implied by the fact that  $x^2$  is direction independent, i.e.,  $(-x)^2 \equiv x^2$ . In order to study the directionality of this half-space problem, consider the first moment,  $\langle x \rangle_h$ . The first moment is obtained in a like manner as the second moment, the result being

$$\langle x \rangle_h = x_0 \left( 1 + H_{1,1}^{1,0} \left[ \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \middle| \begin{matrix} (1, \frac{\gamma}{2}) \\ (-1, 1) \end{matrix} \right] \right) . \tag{19}$$

The Fox function occurring in Eq. (19) has the series expansion

$$H_{1,1}^{1,0} \left[ \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \left| \begin{matrix} (1, \frac{\gamma}{2}) \\ (-1, 1) \end{matrix} \right. \right] = \sum_{\nu=0}^{\infty} \frac{(-1)^\nu}{\Gamma(1 + \gamma/2[1 - \nu])\nu!} \left( \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \right)^{\nu-1} \tag{20}$$

which is valid for large  $t$ . For short  $t$ , it becomes exponentially small,

$$H_{1,1}^{1,0} \left[ \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \left| \begin{matrix} (1, \frac{\gamma}{2}) \\ (-1, 1) \end{matrix} \right. \right] \sim \frac{1}{\sqrt{2\pi}} \left( \frac{\gamma}{2} \right)^{-(1+\gamma)/(2-\gamma)} \frac{1}{\sqrt{1-\gamma/2}} \left( \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \right)^{-3/(2-\gamma)} \\ \times \exp \left\{ - \left( 1 - \frac{\gamma}{2} \right) \left( \frac{\gamma}{2} \right)^{1/(2/\gamma-1)} \left( \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \right)^{1/(1-\gamma/2)} \right\}. \tag{21}$$

Thus, for long times  $t \gg (x_0/\sqrt{K_\gamma})^{2/\gamma}$ , the first moment grows in time like

$$\langle x \rangle_h \sim \frac{\sqrt{K_\gamma}}{\Gamma(1 + \gamma/2)} t^{\gamma/2} + \frac{x_0^2}{2\Gamma(1 - \gamma/2)\sqrt{K_\gamma t^\gamma}} - O\left(\frac{x_0^3}{K_\gamma t^\gamma}\right), \tag{22}$$

i.e., it is, to leading order, independent of  $x_0$ . The short-time behaviour,

$$\langle x \rangle_h \sim x_0 + O(\exp), \quad t \ll \left( \frac{x_0}{\sqrt{K_\gamma}} \right)^{2/\gamma}, \tag{23}$$

on the contrary, is dominated by the initial value, where  $O(\exp)$  abbreviates the asymptotic form found in Eq. (21). Thus, in the half-space problem, the first moment reflects the directionality whereas the second moment is not sensitive to the asymmetry of the process. The mean square displacement, for short times,

$$\langle (\Delta x) \rangle_h \equiv \langle x^2 \rangle_h - \langle x \rangle_h^2 \sim \frac{2K_\gamma}{\Gamma(1 + \gamma)} t^\gamma + O(\exp), \tag{24}$$

is given to first order through the “free” contribution  $2K_\gamma t^\gamma/\Gamma(1 + \gamma)$  whereas, due to the influence of the reflecting boundary, the expression depends, in a non-trivial manner, on  $x_0$  for longer times. If the initial condition is chosen to be  $W_0(x) = \delta(x)$ ,  $\langle x \rangle_h = \sqrt{K_\gamma t^\gamma}/(x_0 \Gamma(1 + \gamma/2))$  and  $\langle x^2 \rangle_h = 2K_\gamma t^\gamma/\Gamma(1 + \gamma)$ . From the point of view of the method of images, this situation corresponds to the inversion symmetry of this special case.

### 2.1.2. Absorbing condition

An absorbing boundary is defined via the Dirichlet condition  $Q(x_0, t) = 0$ . In this case, the half-space solution for the sharp initial condition  $W_0(x) = \delta(x_0)$  takes on the form

$$Q(x, t|x_0) = W(x - x_0, t) - W(-x - x_0, t). \tag{25}$$

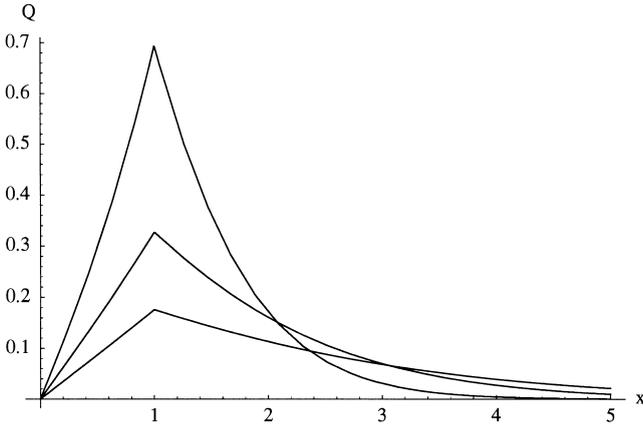


Fig. 3. Half-space solution  $Q(x, t|x_0)$ , Eq. (25), for the initial condition  $x_0 = 1$  and  $\gamma = \frac{1}{2}$ , drawn at the times  $t = 0.1, 1$  and  $5$ . As it should, the probability density function vanishes at the origin.

Obviously,  $Q(0, t|x_0) = 0$ . In Fig. 3, the half-space solution, Eq. (25), for the absorbing conditions is displayed for various times. Again, note the distinct cusps in the distribution.

For the absorbing condition, it is interesting to calculate the integrated survival probability

$$w_h(t) = \int_0^\infty dx Q(x, t|x_0) \tag{26}$$

which defines that portion of the initial probability which has not yet been absorbed. Combining the definitions, Eqs. (25) and (26), with Eq. (15), one arrives at

$$w_h(u) = \frac{1}{u} (1 - e^{-x_0 \sqrt{u/K_\gamma}}) \tag{27}$$

in Laplace space. By use of the Fox function  $H_{0,1}^{1,0}$ , it is possible to calculate the Laplace inversion in the form

$$w_h(t) = 1 - H_{1,1}^{1,0} \left[ \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \left| \begin{matrix} (1, \gamma/2) \\ (0, 1) \end{matrix} \right. \right]. \tag{28}$$

This Fox function  $H_{1,1}^{1,0}$  becomes exponentially small for  $t \ll (x_0/\sqrt{K_\gamma})^{2/\gamma}$ , i.e., for large argument [48],

$$H_{1,1}^{1,0} \left[ \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \left| \begin{matrix} (1, \gamma/2) \\ (0, 1) \end{matrix} \right. \right] \sim \frac{1}{\sqrt{2\pi}} \left( \frac{\gamma \sqrt{K_\gamma t^\gamma}}{2x_0} \right)^{1/(2-\gamma)} \frac{1}{\sqrt{1-\gamma/2}} \times \exp \left\{ - \left( \frac{\gamma}{2} \right)^{1/(2/\gamma-1)} \left( 1 - \frac{\gamma}{2} \right) \left( \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \right)^{1/(1-\gamma/2)} \right\} \tag{29}$$

and has the series representation [48]

$$H_{1,1}^{1,0} \left[ \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \middle| \begin{matrix} (1, \gamma/2) \\ (0, 1) \end{matrix} \right] = \sum_{v=0}^{\infty} \frac{(-1)^v}{\Gamma(1 - \gamma v/2)v!} \left( \frac{x_0}{\sqrt{K_\gamma t^\gamma}} \right)^v \tag{30}$$

for long times  $t \gg (x_0/\sqrt{K_\gamma})^{2/\gamma}$ . We therefore recover the following behaviour:

$$w_h(t) \sim \begin{cases} 1 - O(\exp), & t \ll \left( \frac{\sqrt{K_\gamma}}{x_0} \right)^{2/\gamma}, \\ \frac{x_0}{\Gamma(1 - \gamma/2)\sqrt{K_\gamma t^\gamma}}, & t \gg \left( \Gamma(1 - \gamma/2) \frac{\sqrt{K_\gamma}}{x_0} \right)^{2/\gamma}. \end{cases} \tag{31}$$

The exponential corrections in the short-time behaviour are defined in Eq. (29). In this limit, the probability is still concentrated around the initial point  $x_0$ , and no significant portion has reached the absorbing boundary. On the other hand, for long times, the decrease of the total probability is dominated by the probability of reaching a site which is a distance  $|x_0|$  away from the starting point. Note that the time scale distinguishing the two régimes in Eq. (31) is proportional to  $x_0/\sqrt{K_\gamma}$ , i.e., it includes the starting point  $x_0$ , as it should: the farther the starting point is from the origin, the slower is the decay of the total probability.

In the limit  $\gamma = 1$ , the integrated survival probability

$$w_h(t) = 1 - \operatorname{erfc} \left( \frac{x_0}{2\sqrt{K_1 t}} \right) = \operatorname{erf} \left( \frac{x_0}{2\sqrt{K_1 t}} \right), \tag{32}$$

involves the error function  $\operatorname{erf}(z)$  [63].

### 2.2. Diffusion in a box

As shown in Feller [4], the propagator  $W(x, t)$  also suffices to determine the boundary value problem of two absorbing or two reflecting boundaries which are supposed to lie at  $x = \pm a$ . Then, the free solution with the initial value problem  $W_0(x) = \delta(x)$  is successively folded along the lines through  $x = \pm a$ , perpendicular to the  $x$ -axis, i.e., the exact solution is constructed with increasing accuracy according to the method of images, to result in the boundary value solution [4,45]

$$Q(x, t) = \sum_{m=-\infty}^{\infty} [W(x + 4ma, t) \mp W(4ma - x + 2a, t)], \tag{33}$$

where the minus sign stands for absorbing, the plus sign for reflecting boundaries at  $x = \pm a$ . We note that the solution for the mixed condition of one absorbing and one reflecting boundary is obtained via a final folding at the origin of the solution for two absorbing boundaries.

Employing the relation<sup>3</sup>

$$\sum_{m=-\infty}^{\infty} e^{-ikm} = e^{-ik/2} \sum_{m=-\infty}^{\infty} (-1)^m \delta\left(m + \frac{k}{2\pi}\right), \tag{34}$$

we rewrite Eq. (33), after an additional Laplace transform, as

$$Q(x, u) = (4a)^{-1} \sum_{m=-\infty}^{\infty} e^{i\pi mx/(2a)} \left[ W\left(k = \frac{m\pi}{2a}, u\right) \mp (-1)^m W\left(k = -\frac{m\pi}{2a}, u\right) \right]. \tag{35}$$

Making use of Eq. (5), the sums can be simplified, and the following results are obtained for the cases of absorbing and reflecting boundaries, respectively.

### 2.2.1. Absorbing boundaries

In the case of absorbing boundaries at  $x = \pm a$  we get

$$Q(x, u) = u^{\gamma-1} a^{-1} \sum_{m=0}^{\infty} e^{\pi i(2m+1)x/(2a)} \frac{1}{u^{\gamma} + K_{\gamma}(2m+1)^2 \pi^2 / 4a^2}. \tag{36}$$

Backtransformed into time space, the result becomes

$$Q(x, t) = a^{-1} \sum_{m=0}^{\infty} e^{\pi i(2m+1)x/(2a)} E_{\gamma}\left(-K_{\gamma} \frac{(2m+1)^2 \pi^2}{4a^2} t^{\gamma}\right) \tag{37}$$

and again involves the Mittag–Leffler function  $E_{\gamma}$  which for  $\gamma=1$  reduces to the standard exponential function, see Appendix B. In the special case  $\gamma = \frac{1}{2}$ , we get via (B.5)

$$Q(x, t) = a^{-1} \sum_{m=0}^{\infty} e^{\pi i(2m+1)x/(2a)} \exp\left(K_{\gamma} \frac{(2m+1)^4 \pi^4}{16a^4} t\right) \times \operatorname{erfc}\left(K_{\gamma} \frac{(2m+1)^2 \pi^2}{4a^2} \sqrt{t}\right). \tag{38}$$

The probability density function  $Q(x, t)$  is shown in Fig. 4 for  $a=1$  and different times. Note that the cusp shape of the subdiffusive solution is due to the slower flux from

<sup>3</sup> This relation can be easily proved by the Poisson summation formula [52]

$$\sum_{k=-\infty}^{\infty} f(k) = \sum_{m=-\infty}^{\infty} \int_{-\infty}^{\infty} dx f(x) e^{2\pi i m x}$$

and the integral definition of the delta function [53]

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ik(x-x')},$$

as well as some resummations.

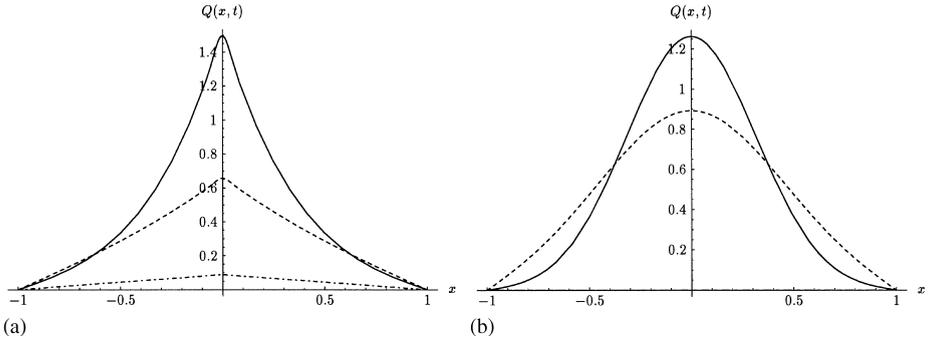


Fig. 4. Probability density function  $Q(x, t)$  for absorbing boundaries in  $x = \pm 1$ . Left: The subdiffusive case,  $\gamma = \frac{1}{2}$ . Right: The Brownian case,  $\gamma = 1$ . The curves are drawn for the times  $t = 0.005, 0.1$  and  $10$  on the left, and for  $t = 0.05, 0.1$  and  $10$  on the right. 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.

the origin to the wings, encountered in subdiffusion. The integrated survival probability defined through

$$w_a(t) = \int_{-a}^a dx Q(x, t) \tag{39}$$

becomes

$$w_a(t) = \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{(-1)^m}{2m+1} E_{\gamma} \left( -K_{\gamma} \frac{(2m+1)^2 \pi^2}{4a^2} t^{\gamma} \right) \tag{40}$$

which has the long-time behaviour  $w_a(t) \sim \text{const.} \cdot t^{-\gamma}$ . The integrated survival probability  $w_a(t)$  is plotted in Fig. 5 together with the Brownian counterpart. For long times, the slow decay of the subdiffusive solution in comparison to the Brownian result is obvious.

### 2.2.2. Reflecting boundaries

Similarly, for reflecting boundaries the result for the image solution is

$$Q(x, t) = \frac{1}{2a} + \frac{1}{a} \sum_{m=1}^{\infty} e^{\pi i m x/a} E_{\gamma} \left( -K_{\gamma} \frac{\pi^2 m^2}{a^2} t^{\gamma} \right) \tag{41}$$

which is shown in Fig. 6. In the limit of long times, an equidistribution is reached, as expected. This is also manifested in the mean square displacement for which we find

$$\langle x^2 \rangle_a = \frac{a^2}{3} + \frac{4a^2}{\pi^2} \sum_{m=1}^{\infty} \frac{(-1)^m}{m^2} E_{\gamma} \left( -K_{\gamma} \frac{m^2 \pi^2}{a^2} t^{\gamma} \right). \tag{42}$$

For long times, the saturation value  $a^2/3$  is reached. The result is displayed in Fig. 7.

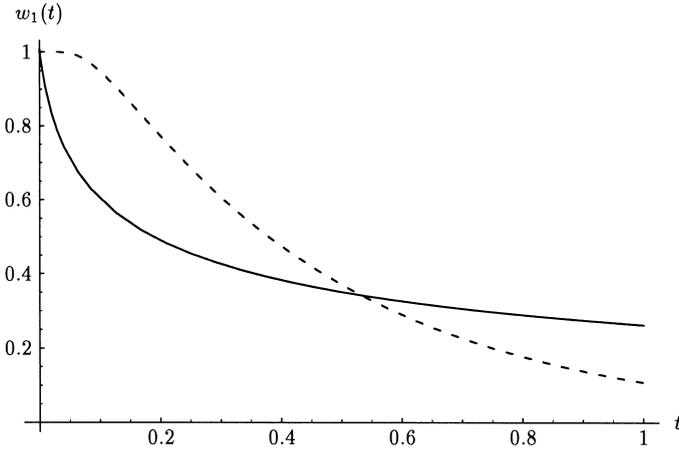


Fig. 5. Survival probability, Eq. (40), for absorbing boundary conditions, plotted for  $\gamma = \frac{1}{2}$  and  $\gamma = 1$  (dashed). For longer times, the faster (exponential) decay of the Brownian solution, in comparison to the power-law asymptotic of the Mittag–Leffler behaviour, is obvious. Closer inspection shows that the subdiffusive survival probability distribution also has a horizontal asymptote for short times, i.e., the short-time behaviour is dominated by the initial value: only a negligible amount of the initial probability released in the origin has travelled to the boundaries.

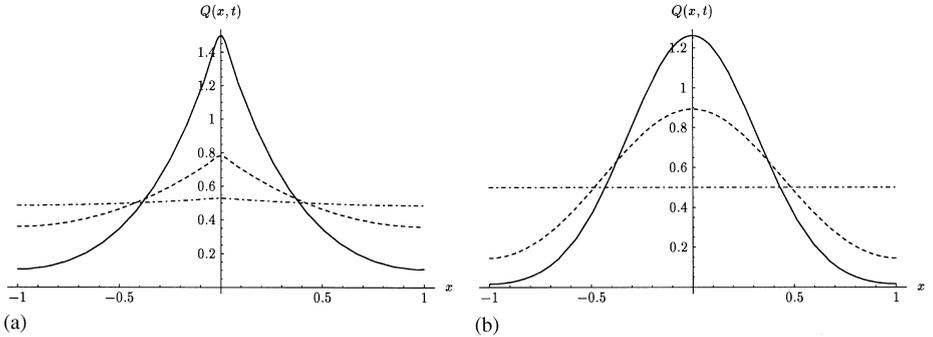


Fig. 6. Probability density function  $Q(x,t)$  for reflecting boundaries at  $x = \pm 1$ . Left: The subdiffusive case,  $\gamma = \frac{1}{2}$ . Right: The Brownian case,  $\gamma = 1$ . Note, again, the cusp shape of the subdiffusive solution. The curves are shown for the times  $t = 0.005, 0.1$  and  $10$  on the left and  $t = 0.05, 0.1$  and  $10$  on the right. The broad wings in the left graph are due to the stretched Gaussian shape of the free propagator in the subdiffusive régime.

### 3. A set of eigenvalues — the separation ansatz

The method of images is limited to special spatial symmetries. More versatile is the approach based on the separation of variables which is addressed now. It has first been applied to fractional equations in Refs. [13–15,33,35] in a harmonic potential. In general, extensions of Eq. (2) to study cases such as the fractional diffusion–advection

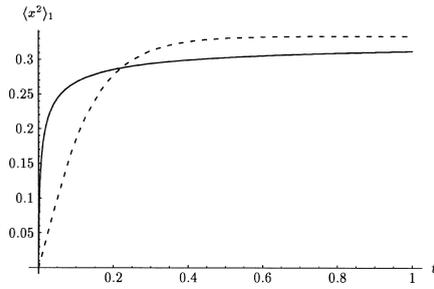


Fig. 7. Mean square displacement for reflecting boundaries, drawn for the subdiffusive ( $\gamma = \frac{1}{2}$ ) and Brownian ( $\gamma = 1$ , dashed) cases. Both curves saturate in the asymptotic value  $\lim_{t \rightarrow \infty} \langle x^2 \rangle_t = \frac{1}{3}$ . Note the slow approaching of the saturation value in the subdiffusive case.

equation [15]

$$\frac{\partial W}{\partial t} + v \frac{\partial W}{\partial x} = {}_0D_t^{1-\gamma} K_\gamma \frac{\partial^2}{\partial x^2} W(x, t) \tag{43}$$

or the fractional equation

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\gamma} L(x)W(x, t), \tag{44}$$

with a linear operator  $L(x)$  can be solved through the separation of variables. In Eq. (44), the linear operator might be the Fokker–Planck operator which has been investigated in Refs. [13–15,31–35].

Consider the fractional diffusion-type equation (44), in combination with the separation ansatz

$$W(x, t) = X(x)T(t). \tag{45}$$

The resulting equation

$$\frac{dT(t)}{dt} ({}_0D_t^{1-\gamma} T)^{-1} = \frac{L(x)X}{X} = -\lambda \tag{46}$$

can then be decoupled into the pair of eigenequations [13–15,33,35]

$${}_0D_t^\gamma T(t) - \frac{t^{-\gamma} T_0}{\Gamma(1-\gamma)} = -\lambda_{n,\gamma} T, \tag{47}$$

$$L(x)X(x) = -\lambda_{n,\gamma} X \tag{48}$$

for an eigenvalue  $\lambda_{n,\gamma}$  of  $L(x)$ .

Given the eigenvalue  $\lambda_{n,\gamma}$ , the corresponding temporal eigensolution, Eq. (47), is

$$T_n(t) = T_0 E_\gamma(-\lambda_{n,\gamma} t^\gamma). \tag{49}$$

The normal exponential decay of the modes thus gets replaced by the slow Mittag–Leffler relaxation, as was already observed for the diffusion modes in Eq. (8). In the case of the reflecting boundary conditions discussed above, its temporal part is to be augmented with the spatial solution (trigonometric functions), and summed over all

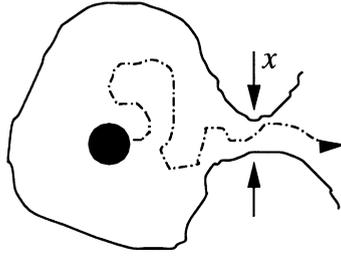


Fig. 8. Escape of the trapped molecule, from the pocket formed by the configuration of the macromolecule, through the bottleneck, the cross-section of which is characterised by the fluctuating radius  $x$ .

eigenvalues, leading back to the result (41). In what follows,  $T_0 = 1$  is assumed. The full solution is then the sum  $\sum_n X_n(x) T_n(t)$  over all eigensolutions.

Although the following considerations in respect to the separation of variables are valid on a more general level, an interesting application of fractional equations can be discussed for the case of an escape through a fluctuating bottleneck which mimics a molecule initially trapped in a protein cul-de-sac [“pocket”], which can only escape through a bottleneck which fluctuates in time, as drawn schematically in Fig. 8. The standard problem for a  $\delta$ -correlated Gaussian noise discussed by Zwanzig [56], and Eizenberg and Klafter [57,58] is based on the coupling of the rate equation for the ligand concentration in the pocket, and a Langevin equation describing the fluctuating bottleneck dynamics. Thus, the concentration obeys the rate equation

$$\frac{dC}{dt} = -K(x)C, \quad (50)$$

where the rate  $K(x) = kx^2$  is assumed to be proportional to the bottleneck cross-section. The fluctuations of the bottleneck radius  $x$  are supposed to follow the Langevin equation

$$\frac{dx}{dt} = -\lambda x + F(t) \quad (51)$$

with the white noise term  $F(t)$ .  $\lambda$  is the decay rate of the fluctuations [56]. The equilibrium second moment of the radius be  $\langle x^2 \rangle_{\text{eq}} = \theta$ . From this approach, the deterministic equation of the Fokker–Planck–Smoluchowski type

$$\frac{\partial C}{\partial t} = -kx^2 C + \lambda \theta \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} + \frac{x}{\theta} C \right) \quad (52)$$

can be deduced [56] where the quantity  $C(x, t)$  is the noise-averaged concentration for a given bottleneck radius  $x$ . In reduced coordinates [59], Eq. (52) can be rewritten in the form

$$\frac{\partial C}{\partial t} = \left[ -\epsilon x^2 + \frac{\partial}{\partial x} x + \frac{\partial^2}{\partial x^2} \right] C. \quad (53)$$

Averaging  $C$  over all possible radii  $x$  gives the concentration  $\langle C \rangle$  in the protein pocket.

In analogy to the fractional diffusion and diffusion-reaction equations considered so far, we now concentrate on a possible fractional generalisation

$$\frac{\partial C}{\partial t} = {}_0D_t^{1-\gamma} \left[ -\varepsilon x^2 + \frac{\partial}{\partial x} x + \frac{\partial^2}{\partial x^2} \right] C \tag{54}$$

of Eq. (53). Eq. (54) corresponds to the fractional Fokker–Planck equation considered in Refs. [13,35], with an additional term proportional to  $x^2$ . The introduction of the fractional operator removes the Markovian character from the bottleneck dynamics, namely the dynamics becomes non-local in time. The generalisation of Eq. (53) in terms of Eq. (54) is not unique. It is based on the observation that in the subdiffusive fractional Fokker–Planck equations which were previously derived from kinematics [13,37,38] and dynamics [42,43] principles, the momentary change  $\partial C/\partial t$  is brought about by force and diffusion terms which are *all* acted upon by the fractional operator. Thus, in Eq. (54), it was assumed that the contribution  $-\varepsilon x^2 C$  also feeds on  $\partial C/\partial t$  through the memory delay which is expressed by the fractional operator. The result obtained below is therefore a physical model which should be checked against further experimental investigations (see also the remarks below).

The separation ansatz  $C(x, t) = X(x)T(t)$  leads to the result

$$C(x, t) = \frac{1}{\Gamma\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{1}{2^n n!} E_{\gamma}(-\lambda_{n,\gamma} t^{\gamma}) \times H_n(0) H_n\left(\frac{x}{\Gamma}\right) \exp\left(-x^2 \left[\frac{1}{4} + \frac{1}{2\Gamma^2}\right]\right), \tag{55}$$

where the eigenvalues are defined via  $\lambda_{n,\gamma} = (2n + 1)\sqrt{\varepsilon + 1/4} - 1/2$ , and we have  $\Gamma = (\varepsilon + 1/4)^{-1/4}$ . The  $H_n(x)$  denote the Hermite polynomials [59,60]. Integrating Eq. (55) over  $x$ , as well as using  $H_n(0) = 2^n \sqrt{\pi}/\Gamma([1 - n]/2)$  and  ${}_2F_1(-n, 1/2; 1/2; a) = (1 - a)^n$ , we arrive at

$$\langle C \rangle(t) = \sum_{n=0}^{\infty} (-1)^n \frac{\Gamma(n + 1/2)}{\sqrt{1 + \Gamma^2/2} \Gamma(1/2 - n)} \frac{2^{2n+1/2}}{(2n)!} \times \left(1 - \frac{2}{1 + \Gamma^2/2}\right)^n E_{\gamma}(-\lambda_{2n,\gamma} t^{\gamma}). \tag{56}$$

This sum converges for all  $t$  due to the observation that  $\sum_0^{\infty} [2^{2n} \Gamma(n+1/2)/(2n)! \Gamma(1/2 - n)](1 - \varepsilon)^n < \infty$ , with the provision that  $0 \leq \varepsilon < 2$ . For long times  $t \gg \lambda_{0,\gamma}^{1/\gamma}$ , the function  $\langle C \rangle(t)$  follows  $t^{-\gamma}$  for  $\gamma \in (0, 1)$ , and decreases exponentially for  $\gamma = 1$ . The latter statement can easily be seen, rewriting Eq. (56) by Mehler’s summation formula to recover Zwanzig’s original result [56,59]. In Fig. 9 we graph  $\langle C \rangle(t)$  for  $\gamma = \frac{1}{2}$ , in comparison to the standard result with  $\gamma = 1$ .

The escape problem discussed here is related to the rebinding of a ligand molecule after dissociation from a protein, e.g., a myoglobin as discussed in Refs. [61,62]. In fact, it is reasonable to assume that the rebinding follows the same dynamics as the bottleneck escape sketched here. For rebinding,  $\langle C \rangle(t)$  describes then the concentration

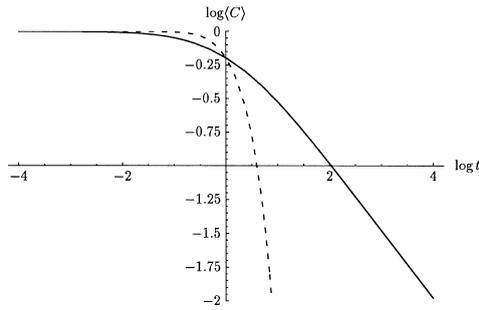


Fig. 9. Survival probability distribution of the molecule in the pocket. The solid line represents the fractional solution for  $\gamma = \frac{1}{2}$ , the dashed line denotes the standard result ( $\gamma = 1$ ). In the  $\log_{10}$ – $\log_{10}$  plot, the slow power-law asymptotic behaviour for the fractional solution is distinct.

of ligands which have not yet rebound after the dissociation. It was shown by Glöckle and Nonnenmacher in Ref. [62] that the experimental data obtained by Iben et al. [61] can be described by a *fractional* relaxation equation leading to a single Mittag–Leffler decay, to a remarkable accuracy. The above result, Eq. (56), combines a discrete, infinite set of Mittag–Leffler decays, and it can be shown that this result  $\langle C \rangle(t)$  has a comparable numerical behaviour as the single Mittag–Leffler pattern from Ref. [62].<sup>4</sup>

#### 4. Conclusions

Most physical systems, in one way or the other, involve boundary conditions, or an external field causes the existence of a set of eigenvalues. In this paper the stage was set for the modelling of such cases in terms of fractional diffusion-type equations. The presented results show a considerably different behaviour in comparison to the corresponding Brownian cases, thus making this approach interesting for the discussion of transport processes in complex system where anomalous diffusion or long-tailed relaxation of modes dominate.

Solutions for the FDE (2) and the more general Eq. (44) have been derived and discussed, imposing certain boundary value conditions upon the system. The discussion used the fact that fractional equations are per se very similar to their Fickian counterparts, except for the occurrence of the fractional operator replacing the first-order time derivative. Therefore, standard methods of solution, such as the Fourier–Laplace technique, the method of images, or the separation of variables can be applied to these generalised equations. The examples treated above demonstrate that the fractional approach is a powerful framework for the description of anomalous transport in complex systems, augmenting the existing toolbox of approaches such as the continuous time random walk scheme, or the master equation framework [6,13,36].

<sup>4</sup> It should indeed be possible to calculate the sum, Eq. (56) in a similar way as in the Markovian case, and the result should be a single Mittag–Leffler function.

## Acknowledgements

RM is supported in part through an Amos de Shalit fellowship from MINERVA, and through a Feodor-Lynen fellowship from the Alexander von Humboldt Stiftung, Bonn am Rhein, Germany. Financial assistance from GIF and the TMR programme of the European Commission is acknowledged as well. RM thanks Norbert Südländ for help with Mathematica, and Israela Becker for helpful comments.

## Appendix A. The Riemann–Liouville fractional operator

In Eq. (4) we defined the Riemann–Liouville fractional differentiation of order  $1 - \gamma$ ,  $0 < \gamma < 1$  through [16]

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

Here we list some interesting properties of this fractional operator.

In general, the Riemann–Liouville fractional operator is defined through the operation of the fractional integration:

$${}_0D_t^{-\gamma}f(t) = \frac{1}{\Gamma(\gamma)} \int_0^t dt' \frac{f(t')}{(t-t')^{1-\gamma}} \tag{A.2}$$

and a subsequent ordinary differentiation, to result in definition (A.1). The integration theorem of Laplace transformation can be shown to hold for fractional integration:

$$\mathcal{L}\{{}_0D_t^{-\gamma}f(t)\} = u^{-\gamma}f(u), \tag{A.3}$$

an important property when dealing with fractional equations. Note that there exists also a generalisation of the differentiation theorem of the Laplace transformation in the form

$$\mathcal{L}\{{}_0D_t^p f(t)\} = u^p f(u) - \sum_{j=0}^{n-1} u^j c_j \tag{A.4}$$

whereby the pseudo-initial values

$$c_j = \lim_{t \rightarrow 0^+} {}_0D_t^{p-1-j} f(t) \tag{A.5}$$

arise, for  $n \geq p > n - 1$ . As in our calculations we start off from the integral version (3) of the fractional diffusion equation, we avoid this somewhat complicated calculation, resting with Eq. (A.3).

A fundamental property of the Riemann–Liouville fractional operator is

$${}_0D_t^\mu t^\nu = \frac{\Gamma(1 + \nu)}{\Gamma(1 + \nu - \mu)} t^{\nu-\mu} \tag{A.6}$$

for all real  $\mu, \nu$ ; especially, one finds for the fractional differentiation of a constant

$${}_0D_t^\mu 1 = \frac{t^{-\mu}}{\Gamma(1 - \mu)}. \tag{A.7}$$

For  $\mu \rightarrow n$ ,  $n$  a natural number, the Gamma function diverges, and the standard result  $d^n 1/dt^n = 0$  is recovered.

## Appendix B. The Mittag–Leffler function

The Mittag–Leffler function [63] is the natural generalisation of the exponential function. It is defined through the inverse Laplace transform

$$E_\gamma(-[t/\tau]^\gamma) = \mathcal{L}^{-1} \left\{ \frac{1}{u + \tau^{-\gamma} u^{1-\gamma}} \right\}, \quad (\text{B.1})$$

from which the series expansion

$$E_\gamma(-[t/\tau]^\gamma) = \sum_{n=0}^{\infty} \frac{(-[t/\tau]^\gamma)^n}{\Gamma(1 + \gamma n)} \quad (\text{B.2})$$

can be deduced. The asymptotic behaviour is

$$E_\gamma(-[t/\tau]^\gamma) \sim ((t/\tau)^\gamma \Gamma(1 - \gamma))^{-1} \quad (\text{B.3})$$

for  $t \gg \tau$ ,  $0 < \gamma < 1$ . Special cases of the Mittag–Leffler function are

$$E_1(-[t/\tau]) = e^{-t/\tau} \quad (\text{B.4})$$

and

$$E_{1/2}(-[t/\tau]^{1/2}) = e^{t/\tau} \operatorname{erfc}([t/\tau]^{1/2}). \quad (\text{B.5})$$

We note in passing that the Mittag–Leffler function is the solution of the fractional relaxation equation [54,55]

$$\frac{d\Phi(t)}{dt} = -\tau^\gamma {}_0D_t^{1-\gamma} \Phi(t). \quad (\text{B.6})$$

## References

- [1] J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1970.
- [2] H.S. Carslaw, J.C. Jaeger, *Conduction of Heat in Solids*, Clarendon Press, Oxford, 1959.
- [3] R. Aris, *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysis*, Vols. I and II, Clarendon Press, Oxford, 1975.
- [4] W. Feller, *An Introduction to Probability Theory and its Applications*, Vol. 2, Wiley, New York, 1971.
- [5] P. Lévy, *Processus stochastiques et mouvement brownien*, Gauthier-Villars, Paris, 1965.
- [6] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North-Holland, Amsterdam, 1981.
- [7] H. Risken, *The Fokker–Planck Equation*, Springer, Berlin, 1989.
- [8] B. Hughes, *Random Walks and Random Environments*, Volume 1: Random Walks, Oxford University Press, Oxford, 1995.
- [9] W.R. Schneider, W. Wyss, *J. Math. Phys.* 30 (1989) 134.
- [10] R. Metzler, W.G. Glöckle, T.F. Nonnenmacher, *Physica A* 211 (1994) 13.
- [11] R. Hilfer, *Fractals* 3 (1995) 211.
- [12] R. Zwanzig, R. Balian, G. Weill (Eds.), *Molecular Fluids*, Gordon and Breach, London, 1976.
- [13] R. Metzler, E. Barkai, J. Klafter, *Europhys. Lett.* 46 (1999) 431.
- [14] R. Metzler, E. Barkai, J. Klafter, *Physica A* 266 (1999) 343.

- [15] R. Metzler, J. Klafter, I. Sokolov, *Phys. Rev. E* 58 (1998) 1621.
- [16] K.B. Oldham, J. Spanier, *The Fractional Calculus*, Academic Press, New York, 1974.
- [17] R. Hilfer, L. Anton, *Phys. Rev. E* 51 (1995) R848.
- [18] A. Compte, *Phys. Rev. E* 53 (1996) 4191.
- [19] A. Blumen, J. Klafter, G. Zumofen, I. Zschokke (Ed.), *Optical Spectroscopy of Glasses*, Reidel, Dordrecht, 1986.
- [20] S. Havlin, D. Ben-Avraham, *Adv. Phys.* 36 (1987) 695.
- [21] M.B. Isichenko, *Rev. Mod. Phys.* 64 (1991) 961.
- [22] J-P. Bouchaud, A. Georges, *Phys. Rep.* 195 (1990) 12.
- [23] F. Klammmler, R. Kimmich, *Croat. Chem. Acta* 65 (1992) 455.
- [24] A. Klemm, H.-P. Müller, R. Kimmich, *Phys. Rev. E* 55 (1997) 4413.
- [25] J. Klafter, G. Zumofen, A. Blumen, *J. Phys. A: Math. Gen.* 25 (1991) 4835.
- [26] F. Amblard, A.C. Maggs, B. Yurke, A.N. Pargellis, S. Leibler, *Phys. Rev. Lett.* 77 (1996) 4470.
- [27] E. Barkai, J. Klafter, *Phys. Rev. Lett.* 81 (1998) 1134.
- [28] E.W. Montroll, H. Scher, *J. Stat. Phys.* 9 (1973) 101.
- [29] H. Scher, E.W. Montroll, *Phys. Rev. B* 7 (1973) 4491.
- [30] Q. Gu, E.A. Schiff, S. Grebner, R. Schwartz, *Phys. Rev. Lett.* 76 (1996) 3196.
- [31] H.C. Fogedby, *Phys. Rev. Lett.* 73 (1994) 2517.
- [32] H.C. Fogedby, *Phys. Rev. E* 50 (1994) 1657.
- [33] S. Jespersen, R. Metzler, H.C. Fogedby, *Phys. Rev. E* 59 (1999) 2736.
- [34] G.M. Zaslavsky, M. Edelman, B.A. Niyazov, *Chaos* 7 (1997) 159.
- [35] R. Metzler, E. Barkai, J. Klafter, *Phys. Rev. Lett.* 82 (1999) 3563.
- [36] E. Barkai, R. Metzler, J. Klafter, *Phys. Rev. E* 61 (2000) 132.
- [37] P. Lévy, *Théorie de l'addition des variables aléatoires*, Gauthier-Villars, Paris, 1954.
- [38] B.V. Gnedenko, A.N. Kolmogorov, *Limit Distributions for Sums of Independent Random Variables*, Addison-Wesley, Reading, 1954.
- [39] E.W. Montroll, G.H. Weiss, *J. Math. Phys.* 6 (1965) 167.
- [40] M.F. Shlesinger, *J. Stat. Phys.* 10 (1974) 55.
- [41] J. Klafter, A. Blumen, M.F. Shlesinger, *Phys. Rev. A* 35 (1987) 3081.
- [42] R. Metzler, J. Klafter, submitted for publication.
- [43] R. Metzler, J. Klafter, *J. Phys. Chem.*, accepted for publication.
- [44] V.M. Kenkre, E.W. Montroll, M.F. Shlesinger, *J. Stat. Phys.* 9 (1973) 45.
- [45] A. Compte, R. Metzler, J. Camacho, *Phys. Rev. E* 56 (1997) 1445.
- [46] G. Zumofen, J. Klafter, *Phys. Rev. E* 51 (1995) 2805.
- [47] P.M. Drysdale, P.A. Robinson, *Phys. Rev. E* 58 (1998) 5382.
- [48] A.M. Mathai, R.K. Saxena, *The H-function with Applications in Statistics and Other Disciplines*, Wiley Eastern Ltd., New Delhi, 1978.
- [49] H.M. Srivastava, K.C. Gupta, S.P. Goyal, *The H-functions of One and Two Variables with Applications*, South Asian Publishers, New Delhi, 1982.
- [50] G. Zumofen, J. Klafter, *Phys. Rev. E* 47 (1993) 851.
- [51] J. Klafter, G. Zumofen, *J. Phys. Chem.* 98 (1994) 7366.
- [52] P.M. Morse, H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, New York, 1953.
- [53] J.D. Jackson, *Classical Electrodynamics*, Wiley, New York, 1975.
- [54] W.G. Glöckle, T.F. Nonnenmacher, *J. Stat. Phys.* 71 (1993) 741.
- [55] W.G. Glöckle, T.F. Nonnenmacher, *Rheol. Acta* 33 (1994) 337.
- [56] R. Zwanzig, *J. Chem. Phys.* 97 (1992) 3587.
- [57] N. Eizenberg, J. Klafter, *Chem. Phys. Lett.* 243 (1996) 9.
- [58] N. Eizenberg, J. Klafter, *J. Chem. Phys.* 104 (1996) 6796.
- [59] G.H. Weiss, *J. Chem. Phys.* 80 (1984) 2880.
- [60] M. Abramowitz, I.E. Stegun, *Handbook of Mathematical Functions*, Dover, New York, 1968.
- [61] I.E.T. Iben, D. Braunstein, W. Doster, H. Frauenfelder, M.K. Hong, J.B. Johnson, S. Luck, P. Ormos, A. Schulte, P.J. Steinbach, A.H. Xie, R.D. Young, *Phys. Rev. Lett.* 62 (1998) 1916.
- [62] W.G. Glöckle, T.F. Nonnenmacher, *Biophys. J.* 68 (1995) 46.
- [63] A. Erdélyi (Ed.), *Tables of Integral Transforms*, Bateman Manuscript Project, Vol. 1, McGraw-Hill, New York, 1954.