Time Fractional Diffusion Equations and Analytical Solvable Models

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Abstract. The anomalous diffusion of a particle that moves in complex environments is analytically studied by means of the time fractional diffusion equation. The influence on the dynamics of a random moving particle caused by a uniform external field is taken into account. We extract analytical solutions in terms either of the Mittag-Leffler functions or of the M-Wright function for the probability distribution, for the velocity autocorrelation function as well as for the mean and the mean square displacement. Discussion of the applicability of the model to real systems is made in order to provide new insight of the medium from the analysis of the motion of a particle embedded in it.

1. Introduction

Diffusion is a non-equilibrium phenomenon. The Einstein-Smoluchowski (ES) equation, $<\vec{r}^2(t)>=2dDt$, describes a diffusive process in homogeneous and isotropic environments, which is called normal diffusion. D is the diffusion coefficient in units (cm^2/s) and d is the dimensionality of the space where the motion evolves. It says that the variance of the displacement of a diffusing particle grows linearly in time. The above description is made in the frame of statistical physics where the probability density function (pdf) and its moments are used to describe the dynamics. For normal diffusion, the pdf is Gaussian, its moments are finite and only the first two of them are necessary to capture the entire dynamics [1]. Experimental evidence, however, in a broad range of phenomena that take place in diverse fields, that is, from physics to biology, and even to social and to economical sciences, indicate deviations from normal diffusion.

Complexity either spatial [2] and/or temporal [3] leads to divergent probability distributions, resulted of different time scales. Heterogeneities, entrapment, crowding, confinements, to name a few phenomena, give rise to individual sequences, which potentially evolve at similar time scales competing each other. In other words, divergence of microscopic time scales may be connected to the anomalous behavior in longer time scales, which means that the system gets some memory over time. The overall outcome reflects on the dynamics that differ radically from normal diffusion. This kind of motion is called anomalous diffusion, and the variance of the displacement, $W(t)=<\vec{r}^2(t)>-<\vec{r}(t)>^2$, grows as a power law of time

$$W(t)=\frac{2dK_a t^a}{\Gamma(1+a)} \qquad (1)$$

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K_a is a generalized diffusion coefficient in units of (cm^2/s^a), $\Gamma()$ is the gamma function and a is the exponent that classifies the motion. For $a = 1$ the motion is truly Brownian and the ES equation is recovered, for $0 < a < 1$ the motion is sub-diffusive, for $1 < a < 2$ it is super-diffusive, and for $a = 2$ it becomes ballistic.

Deviation from normal diffusion mirrored on the pdf, which cannot be described by the classical Gaussian. Finding of exact propagators that incorporate all the interactions with the environment is feasible only under certain circumstances [4-5]. Toy models based on random walks and associated to specific stochastic scenarios have been introduced and describe anomalous diffusion [6-7]. Fractional Brownian motion (FBM) [8-9], continuous time random walk (CTRW) [10-11], Levy flights (LFs), and Levy walks (LWs) [12-13] are the most known. Each of them, and according to stochastic scenario that obeys, may describe diffusion process within complex systems if and only the stochastic mechanism associated to it is the only operative cause, which gives rise to anomalous behavior. Detailed studies showed that more than one stochastic mechanism may govern the motion of a diffusing particle and potentially lead to multifractal behavior. Subordination [14], mixed noises [15-17], confinement either result of an external field or result of environmental constrains [18], are, just to name a few, cases where more than one stochastic mechanisms are present. The method of the generalized moments [19], which has successfully been applied in diverse fields [20-23], is a good diagnostic tool towards distinguishing multifractality [24-25]. One-sided Levy stable distributions, $l_a(x)$, may describe pdf's of multifractal processes [25], and its characteristic function in Laplace space, $L[l_a(x)](s) = \int_0^\infty e^{-sx} l_a(x)dx = e^{-s^a}$, $0 < a < 1$, $s > 0$, is the well-known Kohlraush-Williams-Watts function [26] or stretched exponential. These functions, $l_a(x)$, find applications in many fields and especially in fractional kinetics [27-28]. It has been pointed out that the function $l_a(x)$ is the solution of the fractional Fokker-Planck equation in the force free case [29]. Fractional calculus can describe spatial and temporal complexity; see [30], and references therein, for an introduction to modeling complex phenomena by a fractional point of view. The application of fractional calculus in diffusion is straightforward since deals with fractional derivatives and integrals, which by definition incorporate memory terms that are responsible for anomalous diffusion [13, 29, 31-34].

In the present study we consider the time fractional diffusion equation with an additive term (reaction term) [35-36], which stands for the influence of a uniform external field. Notice that the same methodology may be followed for generalization of non-fractional diffusion model [37]. In each case, we obtain the pdf, the normalized mean and mean square displacement as well as the normalized velocity autocorrelation function. We provide criteria of estimating the generalized diffusion coefficient and the exponent that classifies the motion. The paper is organized as follows; in Section 2 we give the general mathematical framework, in Section 3 we discuss the influence of a uniform external field on a particle's random motion within complex environments, and we conclude in section 4.

2. The Mathematical Framework

The time fractional reaction diffusion equation of order a, $a \in (0,1)$, in the Riemann-Liouville sense, see also Appendix A for definitions, reads

$$\frac{\partial^a P}{\partial t^a} = LP + N(x,t) \tag{2}$$

$P \equiv P(x,x_0;t)$ is the pdf to find the particle at x at time t given that it was at x_0 at t_0. L is the operator that acts on the pdf, and has the form $L = K_a \frac{\partial^2}{\partial x^2} - \frac{K_a}{k_B T} F(x) \frac{\partial}{\partial x}$, where $F(x)$ stands for the force that a potential exerts on the moving particle, $k_B T$ is the Boltzmann's constant times the temperature

of the bath. $N(x,t)$ is the reactive term and models modification on the overall motion of the particle that caused either by an external stimulus or by a conformational change of the particle itself (reaction). Eq. (2) describes the dynamics of a particle within the domain, $-b_1 < x < b_2$ (boundaries), and under the initial condition $P(x,x_0;0) = f(x)$. We apply natural boundary conditions, which mean $b_{1,2} \to \infty$ and $\lim_{x\to\pm\infty} P(x,x_0;t) = 0$. By setting $F(x) = 0$ the solution of eq. (2) in integral form reads

$$P(x,x_0;t) = f(x) + \frac{K_a}{\Gamma(a)}\int_0^t (t-\tau)^{a-1}\frac{\partial^2 P(x,x_0;\tau)}{\partial x^2}d\tau + \frac{1}{\Gamma(a)}\int_0^t (t-\tau)^{a-1}N(x,t-\tau)d\tau \qquad (3)$$

By applying consecutive the integral transforms, $L\{f(t)\} = \int_0^\infty e^{-st}f(t)dt$, for the Laplace, and $F\{f(x)\} = \int_0^\infty e^{-ikx}f(x)dx$, for the Fourier transform, eq. (3) takes the form

$$\bar{\hat{P}}(k,s) = \frac{s^{a-1}\hat{f}(k)}{(s^a + k^2K_a)} + \frac{\bar{\hat{N}}(k,s)}{(s^a + k^2K_a)} \qquad (4)$$

where, the bar/hat stands for the Laplace and the Fourier transform respectively. Eq. (4) is the characteristic function and contains all the information about the dynamics, which the particle followed, by means of the analytical form of all the moments of the pdf in Laplace space. More specifically, the zeroth moment is the normalization factor of the pdf, the first moment describes the un-normalized mean displacement and provides information about directionality of the motion, that is, if it is zero then all directions are equi-probable. The second moment gives the mean square displacement of the particle and classifies the motion either as normal or as sub/super diffusive. Notice that if the zero moment is different than one, then proper normalization is needed. More information about the pdf may be extracted, for example, the skewness and the kurtosis can also be obtained, which means that the third and the fourth moment ought to be obtained.

By considering that $f(x) = \delta(x - x_0)$, we write the moments up to the second order by using eq. (4)

$$m_0(s) = \int \bar{P}(x,s)dx = \bar{\hat{P}}(k,s)\Big|_{k=0} \qquad (5)$$

$$m_1(s) = <(x-x_0)>(s) = i\frac{d\bar{\hat{P}}(k,s)}{dk}\Big|_{k=0} - x_0 m_0(s) \qquad (6)$$

and

$$m_2(s) = <(x-x_0)^2>(s) = i^2\frac{d^2\bar{\hat{P}}(k,s)}{dk^2}\Big|_{k=0} - 2x_0 i\frac{d\bar{\hat{P}}(k,s)}{dk}\Big|_{k=0} + x_0^2 m_0(s) \qquad (7)$$

Furthermore, assuming that the second dissipation fluctuation theorem (DFT) holds true, $W(t) = \frac{k_BT}{M}\int_o^t dt_1\int_0^t C_v(t_1,t_2)dt_2$, then an analytical derivation of the normalized velocity autocorrelation function in Laplace space is feasible through the relation [38]

$$C_v(s) = \frac{M}{2k_BT}s^2W(s) \qquad (8)$$

where *M* is the mass of the particle, see also [39] for scaling Green-Kubo relation applicable to aging systems. By assuming that $N(x,t) = 0$ and by using eqs (4-8) we take; a) $m_0(s) = 1/s$, which means that the pdf is normalized since $L^{-1}(s^{-1}) = 1$, b) $m_1(s) = 0$ and underlines that there is no preferred

direction of motion, c) $m_2(s) = 2K_a s^{-1-a}$, and d) $C_v(s) = \frac{MK_a}{k_B T} s^{1-a}$. Inverting in real space we take $< (x - x_0)^2 > (t) = 2K_a \frac{t^a}{\Gamma(1+a)}$ for the mean square displacement, and $C_v(t) = \frac{MK_a}{k_B T} \frac{t^{-2+a}}{\Gamma(-1+a)}$ for the velocity autocorrelation function. Since, $0<a<1$ the particle performs sub-diffusive motion with anti-correlated steps as the velocity autocorrelation function shows because it goes to zero from negative as t^{-2+a}. The pdf of the diffusing particle is obtained by the inversion of the Fourier transform in eq. (4), which reads $\bar{P}(x,s) = \frac{\exp\left(-\sqrt{\frac{s^a}{K_a}}|x - x_0|\right)}{2K_a^{1/2} s^{1-a/2}}$ and its inversion in real time domain is feasible giving $P(x,x_0;t) = \frac{1}{\sqrt{4K_a t^a}} M_{a/2}\left(\frac{|x - x_0|}{\sqrt{K_a t^a}}\right)$, where $M_{a/2}(\ )$ is the M-Wright function [40]. It should be noticed that the above pdf has also been expressed in closed form either in terms of a Fox function [41] or in terms of a one sided Levy stable distribution [29]. We prefer the use of the M-Wright function since it is the generalization of the Gaussian density function [42].

3. Influence of a uniform external field.

Considering $N(x,t) = uP(x,x_0;t)$ and $f(x) = \delta(x - x_0)$, eq.(2) reads

$$\frac{\partial^a P(x,x_0;t)}{\partial t^a} = K_a \frac{d^2 P(x,x_0;t)}{dx^2} - uP(x,x_0;t) \tag{9}$$

where, from dimensional analysis *u* stands for a generalized frequency term in units (s^{-a}) which alters uniformly the probability distribution, increase/decrease so it can take either negative or positive values and for zero value the original time fractional diffusion equation is recovered. The corresponding to eq. (9) characteristic function reads

$$\hat{\bar{P}}(k,s) = s^{a-1} \frac{\exp(-ikx_0)}{(s^a + u + K_a k^2)} \tag{10}$$

The inverse Fourier transform of eq. (10) delivers

$$\bar{P}(x,s) = \frac{\exp\left(-\sqrt{\frac{s^a+u}{K_a}}|x - x_0|\right)}{2K_a^{1/2} s^{1-a}\sqrt{s^a + u}} \tag{11}$$

By using eqs (5-7) we write

$$m_0(s) = \frac{s^{a-1}}{s^a + u} \tag{12}$$

$$< m_2 > (s) = \frac{2K_a s^{a-1}}{(s^a + u)^2} \tag{13}$$

and $< (x - x_0) > (s) = 0$. The latter is expected since the uniform way that the external stimulus acts on the complex environment cannot produce any preferred direction of motion. Finally, by using eq. (8) we write for the velocity autocorrelation function

$$C_v(s) = \frac{MK_a}{k_B T} \frac{s^{1+a}}{(s^a + u)^2} \tag{14}$$

For u=0 the well-known results discussed in the previous section are recovered. For u different than zero a more attractive physical picture is revealed. For the inversion of eqs (12), (13) and (14) we make use of the relations (A.4) and (A.5) [42], see Appendix A, and we write

$$m_0(t) = E_a(-ut^a) \tag{15}$$

$$< m_2 > (t) = 2K_a t^a E^2_{a,a+1}(-ut^a) \tag{16}$$

and

$$C_v(t) = \frac{MK_a}{k_B T} t^{a-2} E^2_{a,a-1}(-ut^a) \tag{17}$$

where $E_a(x)$, $E_{a,b}(x)$ and $E^k_{a,b}(x)$ are the one, two and three parameter Mittag-Leffler functions, see Appendix A for the definitions. By dividing eq.(16) with eq.(15) we take, $< (x - x_0)^2 >_{norm} (t) = 2K_a t^a E^2_{a,a+1}(-ut^a) / E_a(-ut^a)$, which describes the normalized mean square displacement. The asymptotic behavior of this quantity can be found either by using eq. (A.7) of Appendix A and retaining up to the first two terms of the expansion or by expanding eqs (12) and (13) for $s^a \to 0$ and inverting in real time domain. Both ended up with exactly the same result, which reads

$$\lim_{t\to\infty} < (x - x_0)^2 >_{norm} (t) \approx \frac{2K_a}{u} - \frac{4K_a}{u^2} \frac{\Gamma(1-a)}{\Gamma(1-2a)} t^{-a} \tag{18}$$

By following the same procedure the normalized velocity autocorrelation function is defined as, $C_v^{norm}(t) = \frac{MK_a}{k_B T} t^{a-2} E^2_{a,a-1}(-ut^a) / E_a(-ut^a)$ and in the long time limit its behavior reads

$$\lim_{t\to\infty} C_v^{norm}(t) \approx \frac{1}{u} \frac{\Gamma(1-a)}{\Gamma(-1-a)} t^{-a} \left\{ 1 + \left(2\frac{\Gamma(-1-a)}{\Gamma(-1-2a)} - \frac{\Gamma(1-a)}{\Gamma(1-2a)} \right) \frac{t^{-a}}{u} \right\} \tag{19}$$

The leading term of eq. (18) describes the full confinement of the particle since the mean square displacement reaches a plateau. This behavior is already known [18]. Eq. (18) may be used to estimate the diffusion coefficient of a particle that moves within a complex environment. Before the plateau, eq. (18) changes according to a power law. Therefore, these two terms of eq.(18) describe two different regimes. On the one hand, the value of the plateau corresponds to the ratio K_a / u, generalized diffusion coefficient per generalized frequency imposed by the external field. On the other hand, the second regime can give the exponent that classifies the motion and its slope correlates the exponent with the parameter u. By exploiting both regimes the values of a, K_a, and u can be explicitly given. It should be noticed, however, that confinement could potentially be the result of many factors that affect the diffusing particle. For example, reflected boundaries can lead to confinement [5], which are not taken into account in the current analysis. Additionally, and in order to ensure that the confinement on the motion is result of the uniform external field, the normalized autocorrelation velocity function should satisfy eq. (19).

4. Conclusions

In conclusion, we study the erratic motion of a particle within a complex environment under the influence of a uniform external field. We provide criteria under which properties of the system could be extracted, specifically, the generalized diffusion coefficient as well as the exponent that classifies the motion and the frequency term installed by the field. The mean square displacement in the long time limit indicates the existence of two regimes; the first one goes as a power law before reaches a plateau, where the plateau is the second one. This condition is not enough to ensure the kind of the motion; therefore, experimental evidence should also fulfil the normalized velocity autocorrelation

function, eq.(19). The results presented herein may be helpfully in trying to determine complex systems from experimental results.

Appendix A

The one parameter Mittag-Leffler (M-L) function is defined as [44-45]

$$E_a(x) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(an+1)} \tag{A.1}$$

where $x \in \mathbb{C}$, $\mathbb{R}(a) > 0$. The two parameter M-L function has been introduced and studied quite later [46-47].

$$E_{a,\beta}(x) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(an+\beta)} \tag{A.2}$$

where $x, \beta \in \mathbb{C}$, $\mathbb{R}(a) > 0$. At the early seventies Prabhakar introduced the three parameter M-L function [48]

$$E_{a,\beta}^k(x) = \sum_{n=0}^{\infty} \frac{(k)_n}{\Gamma(an+\beta)} \frac{x^n}{n!} \tag{A.3}$$

$x, \beta, k \in \mathbb{C}$, $\mathbb{R}(a) > 0$ and $(k)_n = \Gamma(k+n)/\Gamma(k)$ is the Pochhammer symbol. From equations (A.1) to (A.3) the following identity, $E_{a,1}^1(x) = E_{a,1}(x) = E_a(x)$, is easily established. The Laplace transform of the two-parameter M-L function [43]

$$L\{t^{\beta-1}E_{a,\beta}(\pm bt^a)\} = \int_0^{\infty} e^{-st} t^{\beta-1} E_{a,\beta}(\pm bt^a) dt = \frac{s^{a-\beta}}{s^a \mp b} \tag{A.4}$$

where $\mathbb{R}(s) > |b|^{1/a}$. The Laplace transform of the three-parameter M-L function [43,48]

$$L\{t^{\beta-1}E_{a,\beta}^k(\pm bt^a)\}(s) = \frac{s^{ak-b}}{(s^a \mp b)^k} \tag{A.5}$$

where $\mathbb{R}(s) > |b|^{1/a}$. The asymptotic expansion for the three-paramater M-L function satisfies the following relations [49]

$$E_{a,b}^k(x) = \sum_{n=0}^{\infty} \frac{\Gamma(k+n)}{\Gamma(k)\Gamma(an+b)} \frac{x^n}{n!}, \quad |x| < 1 \tag{A.6}$$

and

$$E_{a,b}^k(x) = \frac{(-x)^{-k}}{\Gamma(k)} \sum_{n=0}^{\infty} \frac{\Gamma(k+n)}{\Gamma(b-a(k+n))} \frac{(-x)^n}{n!}, \quad |x| > 1 \tag{A.7}$$

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