ORIGINAL ARTICLE

Solutions for a fractional diffusion equation: Anomalous diffusion and adsorption–desorption processes

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Abstract We investigate the solutions for a fractional diffusion equation subjected to boundary conditions which can be connected to adsorption–desorption processes. The analytical solutions were obtained using the Green function approach and showed an anomalous spreading which can be connected to an anomalous diffusion.

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1. Introduction

Diffusion is one of the most important phenomena present in nature which has been investigated using several approaches. In general, the description employs stochastic differential equations which are connected to Markovian processes (Crank, 1975) and, consequently, leads us to a linear dependence for the mean square displacement, i.e., $\langle (x - \langle x \rangle)^2 \rangle \propto t$. However, the experimental scenarios characterized by fractality (ben-Avraham and Havlin, 2005; Weigel et al., 2011), molecular diffusion *in vivo* (Leijnse et al., 2012; Robson

et al., 2013), molecular crowding (Sokolov, 2012), chemotaxis diffusion (Langlands and Henry, 2010), and active transport (Caspi et al., 2000; Bruno et al., 2009; Brangwynne et al., 2009; Weber et al., 2012) have evidenced the limitations of the Markovian processes in describing situations where memory effects, long-range correlations, and long-range interactions are present. In order to overcome the limitations present in the usual approach several extensions, for example, involving continuous time random walk (Klafter and Sokolov, 2011), generalized Langevin equations, and fractional diffusion equations (Leijnse et al., 2012; Hilfer et al., 2004; Metzler and Klafter, 2000, 2004; Eliazar and Shlesinger, 2013; Bressloff and Newby, 2013; Condamin et al., 2008; Podlubny, 1999), have been investigated to establish the appropriated links between the models and the experimental results. It is also worth mentioning that Cantor space-time has been used to analyse the diffusion equation and the reported results show the dependence on the fractal dimension order of the differential equation on Cantor space-time

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(Yang et al., 2013; Yang et al., 2015a,b; Yan, 2015). In these extensions, one of the main points is the nonlinear time dependence exhibited by the mean-square displacement which, in general, is characterized by $\langle (x - \langle x \rangle)^2 \rangle \propto t^\alpha$, where $\alpha > 1$ and $\alpha < 1$ correspond to superdiffusion and subdiffusion, respectively (Caputo et al., 2008; Caputo and Cametti, 2009; Kosztolowicz et al., 2012). Here, we investigate the solutions for the fractional diffusion equation (Jiang et al., 2013; Barbero and Evangelista, 2006; Garrod, 1995; Lyklema, 1993)

$$\frac{\partial}{\partial t}\rho(x, t) = {}_0D_t^{1-\gamma}\left(K_\gamma \frac{\partial^2}{\partial x^2}\rho(x, t) - F\frac{\partial}{\partial x}\rho(x, t)\right) \qquad (1)$$

where K_γ is the diffusion coefficient, F is an external force which represents a constant field acting on the system, and fractional time operator is the Riemann–Liouville with $0 < \gamma < 1$. For $\gamma = 1$ Eq. (1) recovers the usual form of the diffusion equation with a constant external force. This equation is subjected to the boundary conditions: $\rho(\infty, t) = 0$,

$$\kappa\tau\rho(0, t') = \tau\frac{d}{dt}\Gamma_0(t) + \Gamma_0(t) \qquad (2)$$

where κ is connected to the characteristics of the surface and

$$\Gamma_0(t) + \int_0^\infty dx'\ \rho(x', t) = \text{const.} \qquad (3)$$

In Eq. (2), $\Gamma_0(t)$ gives the quantity of particles sorbed by the surface, κ represents the sorption rate of the particles from the bulk to the surface, and τ is the relaxation time connected with the desorption process of particles from the surface to the bulk. The quantity $\kappa\tau$ has the dimension of length and represents a thickness which may be related to the interaction of the surface with particles present in the bulk (Garrod, 1995; Lyklema, 1993). Also, Eq. (3) implies that the number of particles in the system is conserved, independently of the nature of surface effects that may occur. In particular, it can be connected to the condition

$$D_t^{1-\gamma}(J(x, t))|_{x=0} = -\frac{d}{dt}\Gamma_0(t) \qquad (4)$$

$$J(x, t) = -K_\gamma\frac{\partial}{\partial x}\rho(x, t) + F\rho(x, t) \qquad (5)$$

where $J(x, t)$ is the current density. Some changes in Eq. (3) by incorporating source or sink terms (Lenzi et al., 2010) are necessary when the processes present in the system lead us to a non-conservation number of particles.

2. Diffusion equation and adsorption–desorption

Let us start our discussion concerning the solutions for Eq. (1) and the implications of the sorption phenomenon on the surface present at $x = 0$. For this, we first apply the Laplace transform and, after, use the Green function approach to investigate the behavior of this system. Following, in the Laplace domain, it can be written as

$$K_\gamma s^{1-\gamma}\frac{\partial^2}{\partial x^2}\rho(x, s) - s^{1-\gamma}F\frac{\partial}{\partial x}\rho(x, s) - s\rho(x, s) = -\varphi(x), \qquad (6)$$

where the initial condition $\rho(x, 0) = \varphi(x)$ was considered, subjected to

$$\kappa\tau\rho(0, s) = (1 + \tau s)\Gamma_0(s) - \Gamma_0(0) \qquad (7)$$

and Eq. (3). The presence of $\Gamma_0(0)$ in the previous equation shows that the surface may initially contain particles which for $t > 0$ can be released to the bulk. A similar situation involving desorption phenomenon can be found in the pharmaceutical scenario concerning the behavior of the drug release in a living organism. In particular, a better understanding of how the system behaves in conditions due to geometry, drug concentration, and drug solubility is important to the development of medications (Siepmann and Siepmann, 2008, 2012; Siepmann and Peppas, 2001). In terms of the Green function approach, the solution for Eq. (6) can formally be written as
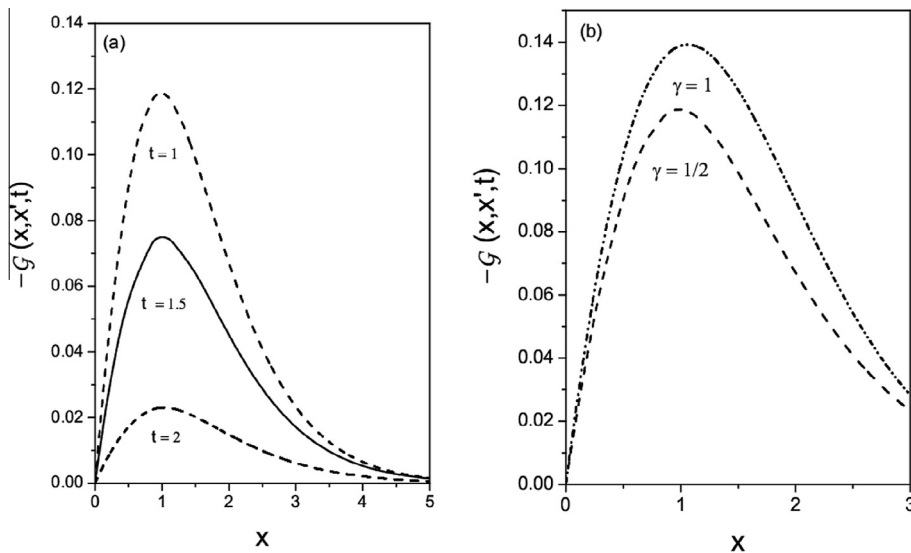

Figure 1 (a and b) shows the behavior of the Green function. (a) Shows the time evolution of the Green function for $\gamma = 1/2$ for three different times to illustrate the effect of the external force. (b) Illustrates the behavior of the Green function for different values of γ. For simplicity, $K_\gamma = 1$ and $F = 1$.

$$\rho(x,s) = -\frac{1}{s^{1-\gamma}}\int_0^\infty dx'\mathcal{G}(x,x';s)\varphi(x') - K_\gamma\rho(0,s)$$

$$\times \frac{\partial}{\partial x'}\mathcal{G}(x,x';s)|_{x'=0} \tag{8}$$

where the last term represents the surface effect on the spreading of the initial condition, which is represented by the first term of this equation. The Green function is obtained by solving the following equation:

$$K_\gamma\frac{\partial^2}{\partial x^2}\mathcal{G}(x,x';s) + F\frac{\partial}{\partial x}\mathcal{G}(x,x';s) - s^\gamma\mathcal{G}(x,x';s) = \delta(x-x') \tag{9}$$

with $\mathcal{G}(0,x';s) = 0$ and $\mathcal{G}(\infty,x';s) = 0$. Before solving this equation for the Green function, it is interesting to perform the change $\mathcal{G}(x,x';s) = e^{-Fx/2K_\gamma}\mathcal{G}'(x,x';s)$ which leads us to

$$K_\gamma\frac{\partial^2}{\partial x^2}\mathcal{G}'(x,x';s) - \left(s^\gamma + \frac{F^2}{4K_\gamma}\right)\mathcal{G}'(x,x';s) = e^{\frac{F}{2K_\gamma}x}\delta(x-x') \tag{10}$$

By solving Eq. (10) with the previous condition, after some calculations, it is possible to show that the solution can be written as

$$\mathcal{G}'(x,x';s) = -\frac{e^{\frac{F}{2K_\gamma}x'}}{\sqrt{F^2 + 4K_\gamma s^\gamma}}\left(e^{-\frac{\sqrt{F^2+4K_\gamma s^\gamma}}{2K_\gamma}|x-x'|} - e^{-\frac{\sqrt{F^2+4K_\gamma s^\gamma}}{2K_\gamma}|x+x'|}\right) \tag{11}$$

Then, the Green function, after performing the inverse Laplace transform, can be written as

$$\mathcal{G}(x,x';t) = -\frac{2}{\pi}t^{\gamma-1}e^{-\frac{F}{2K_\gamma}(x-x')}\int_0^\infty dk\sin(kx)\sin(kx')E_{\gamma,\gamma}$$

$$\times\left[-\left(K_\gamma k^2 + \frac{F^2}{4K_\gamma}\right)t^\gamma\right] \tag{12}$$

where $E_{\gamma,\beta}(x)$ is the generalized Mittag-Leffler function (see, Fig. 1(a) and (b)) and the distribution is given by

$$\rho(x',t) = -\frac{1}{\Gamma(1-\gamma)}\int_0^t\frac{dt'}{(t-t')^\gamma}\int_0^\infty dx\mathcal{G}(x,x';t')\varphi(x')$$

$$- K_\gamma\int_0^t dt'\rho(0,t')\frac{\partial}{\partial x}\mathcal{G}(0,x';t-t') \tag{13}$$

using the previous results, it is possible to obtain the quantity of adsorbed particles by the surface. In particular, in the Laplace domain, it is given by

$$\Gamma_0(s) = \frac{\kappa\tau\left(\sqrt{F^2+4K_\gamma s^\gamma} - F\right)\big/s + 2K_\gamma}{2K_\gamma(1+s\tau) + \kappa\tau(\sqrt{F^2+4K_\gamma s^\gamma} - F)}\Gamma_0(0)$$

$$+ \frac{\kappa\tau\left(\sqrt{F^2+4K_\gamma s^\gamma} - F\right)}{2K_\gamma(1+s\tau) + \kappa\tau\left(\sqrt{F^2+4K_\gamma s^\gamma} - F\right)}\frac{1}{s}$$

$$\int_0^\infty d\tilde{x}\varphi(\tilde{x})e^{\frac{F}{2K_\gamma}\tilde{x}}e^{-\frac{1}{2K_\gamma}\sqrt{F^2+4K_\gamma s^\gamma}\tilde{x}} \tag{14}$$

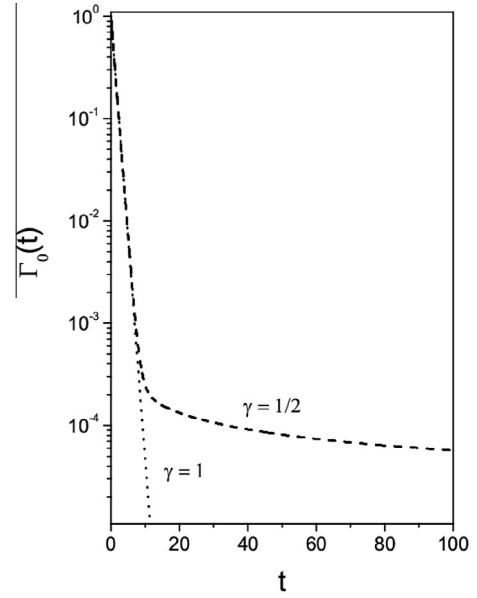This equation, in the asymptotic limit of $|4K_\gamma s^\gamma/F^2| \ll 1$ can be approximated to

Figure 2 This figure shows the behavior of the Eq. (14) for two different values of γ with $\Gamma_0(0) = 1$ and $\varphi(x) = 0$. For simplicity, $K_\gamma = 1$, $F = 10^3$, $\kappa = 1$, and, $\tau = 1$. Note that the effect of $\gamma \neq 1$ is pronounced for long times.
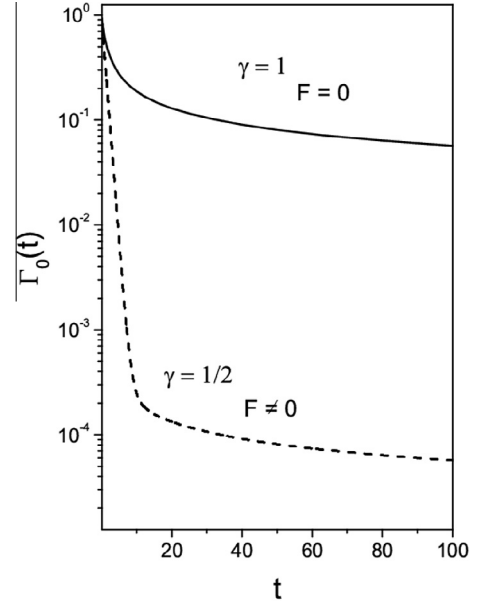

Figure 3 This figure shows the behavior of the Eq. (14) for two different values of γ with $\Gamma_0(0) = 1$ and $\varphi(x) = 0$. For simplicity, $K_\gamma = 1$, $F = 10^3$, $\kappa = 1$, and $\tau = 1$.

$$\Gamma_0(s)\frac{F}{(1+s\tau)F + \kappa\tau s^\gamma}\Gamma_0(0) + \frac{\kappa\tau s^\gamma}{(1+s\tau)F + \kappa\tau s^\gamma}$$

$$\times\frac{1}{s}\left(\Gamma_0(0) + \int_0^\infty d\tilde{x}\phi(\tilde{x})e^{-\frac{s^\gamma}{F}\tilde{x}}\right) \tag{15}$$

and, consequently, for $\gamma \neq 1$ the inverse Laplace transform is given by (Mathai et al., 2009)

$$\Gamma_0(t) \approx \int_0^t dt' \Upsilon(t-t') \left(\Gamma_0(0) + \frac{\kappa\tau}{\Gamma(1-\gamma)} \frac{1}{t'^\gamma} \Gamma_0(0) + \int_0^\infty d\bar{x}\varphi(\bar{x}) H_{1,1}^{1,0} \left[\frac{x}{Ft'^\gamma} \Big|_{(0,1)}^{(1-\gamma,\gamma)} \right] \right)$$

(16)

with

$$\Upsilon(t) = \frac{1}{\tau} e^{-t/\tau} + \frac{1}{\tau} \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{\kappa}{F} \right)^n t^{n(1-\gamma)} E_{1,1-n\gamma}^{(n)}(-t/\tau)$$

(17)

where $E_{\alpha,\beta}^{(n)}(t) \equiv \frac{d^n}{dt^n} E_{\alpha,\beta}(t)$ is the nth time derivative of the generalized Mittag-Leffler function. Fig. 2 shows the behavior of Eq. (14) for a desorption process by considering two different values of γ and Fig. 3 compares the behavior of the desorption process for the cases $\gamma = 1/2$ with $F \neq 0$ (obtained from Eq. (16)) and $\gamma = 1$ with $F = 0$ (obtained from Eq. (14)).

3. Discussion and conclusion

We have investigated the solutions for a fractional diffusion equation subjected to a constant external field with nonusual boundary conditions which can be connected to an adsorption and desorption processes. We obtained exact and approximated analytical solutions in the Laplace domain in order to evidence the effect of the external force. In Fig. 2, we illustrated the effect of the index γ on the desorption process, leading us to an asymptotic behavior different from the exponential. Fig. 3 shows the effect of the external field and index γ. The results presented here may be useful to discuss sorption and desorption processes when nonconventional dynamics aspects are present.

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