Solutions for a sorption process governed by a fractional diffusion equation

E.K. Lenzi [a,b,*], M.A.F. dos Santos [a], D.S. Vieira [c], R.S. Zola [c,d], H.V. Ribeiro [c,d]

[a] *Departamento de Física, Universidade Estadual de Ponta Grossa - Ponta Grossa, PR 87030-900, Brazil*
[b] *National Institute of Science and Technology for Complex Systems - Rio de Janeiro, RJ 22290-180, Brazil*
[c] *Departamento de Física, Universidade Estadual de Maringá - Maringá, PR 87020-900, Brazil*
[d] *Departamento de Física, Universidade Tecnológica Federal do Paraná - Apucarana, PR 86812-460, Brazil*

HIGHLIGHTS

- Solutions for a fractional diffusion equation and anomalous diffusion.
- Sorption process governed by a generalized kinetic equation.
- Exact solutions for a fractional diffusion equation with the Green function approach.
- Analytical solutions for the mean square displacement and survival probability.

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ABSTRACT

We investigate a sorption process where one substance spreads out through another having possibility of chemical reaction between them. So as to describe this process, we have considered the bulk dynamics governed by a fractional diffusion equation, where the reaction term may describe an irreversible or a reversible process. This reaction term represents a generalization of the first order kinetic equation taking memory effects into account. The analytical solutions for the mean square displacement, survival probability and probability density of the particles we have obtained show a rich class of behaviors connected to anomalous diffusion.

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1. Introduction

Nowadays, anomalous diffusion plays an important role in several fields of science, ranging from physics to biology. For instance, protein motion in living cells [1], passive movements of biomolecules or vesicles in cells, diffusion of water and other substances in muscles [2], cardiac electrical propagation [3], electrical response [4,5], and transport properties of particles on complex structures [6]. One of the main characteristics present in this phenomenon is the non-linear time dependence exhibited by the mean square displacement. This behavior is often modeled as a power-law dependence [7,8]. In this context, continuous time random walk [9], generalized Langevin equations and fractional diffusion equations (see Refs. [10–18]) have been analyzed and applied in several situations, such as molecular diffusion *in vivo* [10,19], in membrane cells [20,21], subdiffusion in thin membranes [22] and chemotaxis diffusion [23]. For these situations, the mean-square displacement, in general, is characterized by $\sigma_x^2(t) \sim t^\alpha$, being the superdiffusion ($\alpha > 1$) commonly related, for example,

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* Corresponding author at: Departamento de Física, Universidade Estadual de Ponta Grossa - Ponta Grossa, PR 87030-900, Brazil.
E-mail address: ervinkaminskilenzi@gmail.com (E.K. Lenzi).

to active transport [24–27], while the subdiffusive behavior ($\alpha < 1$) may be related to the molecular crowding [28] and fractal structure [29]. Thus, the comprehension of the formal aspects present in these formalisms is a relevant point to establish connections between models and experimental results.

Here, we investigate a sorption process where one substance spreads out through another having also the possibility of chemically reacting by considering a general situation which can be related to a random walk with a long tailed distributions, i.e., the waiting time and the jumping probability distributions are asymptotically characterized by a power-law behavior. A random walk with this characteristic leads, as reported in Refs. [11,12], to fractional diffusion equations usually applied in anomalous diffusion. Thus, this analysis enables one to investigate, by incorporating this behavior, processes connected to anomalous diffusion which are not suitable described in term of the usual approach. In particular, it has been used to investigate diffusion, adsorption kinetics, and the effect on the molecular rearrangement of the anisotropic molecules on the surface [30]. It can also be applied to biological systems [31] such as for living cells, where chemical reactions and diffusion take place in crowded environment [32], thus, justifying the anomalous behavior [33] embedded in our system. For this, we consider that the density of particles is governed by the following fractional diffusion equation,

$$\frac{\partial}{\partial t}\rho(x,t) = \mathcal{K}_\gamma {}_0\mathcal{D}_t^{1-\gamma}\left(\frac{\partial^\mu}{\partial|x|^\mu}\rho(x,t)\right) - \frac{\partial}{\partial t}\Gamma(x,t) \tag{1}$$

where $\mathcal{K}_\gamma$ is the diffusion coefficient, $0 < \gamma \le 1$ (for $\gamma = 1$ usual diffusion, $0 < \gamma < 1$ subdiffusion), and the fractional time derivative is the Riemann–Liouville [34]. The spatial fractional derivative is considered in the Riesz–Weyl representation [34] with $1 < \mu \le 2$. In Eq. (1), $\rho(x,t)$ represents the density of diffusing particles whereas $\Gamma(x,t)$ is connected to the density of absorbed particles. The last term may represent the process of a substance being absorbed by another as well as the possibility of these substances reacting chemically. This process can thus be understood either as diffusion in which part of the substance becomes immobilized or as a chemical kinetics problem in which the rate of reaction depends on the supply rate of one of the reactants by diffusion. Examples involving diffusion into living cells and microorganisms can be found in biology and biochemistry [35]. In order to accomplish these contexts, we consider, for $\Gamma(x,t)$, the following general kinetic equation:

$$\frac{\partial}{\partial t}\Gamma(x,t) = \int_0^t k_f(t-t')\rho(x,t')\mathrm{d}t' - \int_0^t k_b(t-t')\Gamma(x,t')\mathrm{d}t', \tag{2}$$

where $k_f(t)$ and $k_b(t)$, respectively, are the rate of the forward and backward reactions. Thus, the immobilized solute is formed at a rate proportional to the concentration of solute free to diffuse, and disappears at a rate proportional to its own concentration. This feature lead us to an alternance between periods of diffusive transport and resting times which are governed by $k_f(t)$ and $k_b(t)$. Eq. (2) has as particular case several situations worked out in Refs. [36,37] and, from a phenomenological point of view, the choice of kernel in Eq. (2) could be related, for example, to surface irregularities [38], which is an important factor in adsorption–desorption, diffusion, and catalysis processes. In addition, Eqs. (1) and (2) generalize the ones used in the fluorescence recovery after photobleaching (FRAP), a widely used experimental method to explore binding interactions in cells both in vitro and in vivo [39].

2. Fractional diffusion equation and solutions

We start discussing the time dependent solutions of Eq. (1) subjected to the previous boundary conditions. In order to solve this problem, we use the Laplace ($\mathcal{L}\{\rho(x,t)\} = \overline{\rho}(x,s)$ and $\mathcal{L}^{-1}\{\overline{\rho}(x,s)\} = \rho(x,t)$) and Fourier ($\mathcal{F}\{\rho(x,t)\} = \tilde{\rho}(k,t)$ and the $\mathcal{F}^{-1}\{\tilde{\rho}(k,t)\} = \rho(x,t)$) transforms. Applying the Fourier transform, Eqs. (1) and (2) can be written as

$$-\mathcal{K}_\gamma|k|^\mu {}_0\mathcal{D}_t^{1-\gamma}\left(\tilde{\rho}(k,t)\right) - \frac{\partial}{\partial t}\tilde{\Gamma}(k,t) = \frac{\partial}{\partial t}\tilde{\rho}(k,t) \tag{3}$$

and

$$\frac{\partial}{\partial t}\tilde{\Gamma}(k,t) = \int_0^t k_f(t-t')\tilde{\rho}(k,t')\mathrm{d}t' - \int_0^t k_b(t-t')\tilde{\Gamma}(k,t')\mathrm{d}t'. \tag{4}$$

Now by using the Laplace transform

$$\overline{\tilde{\rho}}(k,s) = \left(\tilde{\rho}(k) + \frac{k_b(s)}{s+k_b(s)}\tilde{\Gamma}(k,0)\right)\overline{\tilde{\mathcal{G}}}(k,s), \tag{5}$$

$$\overline{\tilde{\mathcal{G}}}(k,s) = \frac{1}{s+\mathcal{K}_\gamma s^{1-\gamma}|k|^\mu + \overline{\Upsilon}(s)}, \tag{6}$$

where $\overline{\tilde{\mathcal{G}}}(k,s)$ represents the Green function in the Fourier–Laplace space of Eq. (1) and

$$\overline{\tilde{\Gamma}}(k,s) = \frac{1}{s+\overline{k}_b(s)}\left(\overline{k}_f(s)\overline{\tilde{\rho}}(k,s) + \tilde{\Gamma}(k,0)\right), \tag{7}$$