Commun Nonlinear Sci Numer Simulat 90 (2020) 105411

Contents lists available at ScienceDirect

Commun Nonlinear Sci Numer Simulat

journal homepage: www.elsevier.com/locate/cnsns

Research paper

Anomalous diffusion and sorption-desorption process in complex fluid systems

F.W. Tavares[a], P.M. Ndiaye[a], E.K. Lenzi[b,*], L.R. Evangelista[c], H.V. Ribeiro[c], R.S. Zola[c,d]

[a] Departamento de Engenharia Química, Escola de Química, Universidade Federal do Rio de Janeiro - Rio de Janeiro, RJ 21941-909, Brazil
[b] Departamento de Física, Universidade Estadual de Ponta Grossa - Ponta Grossa, PR 84030-900, 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

ARTICLE INFO

Article history:
Received 20 April 2020
Revised 12 June 2020
Accepted 15 June 2020
Available online 17 June 2020

Keywords:
Diffusion processes
Fractional dynamics
Sorption-desorption

ABSTRACT

Diffusion processes occurring in a myriad of systems sparkle great interest in understanding their general properties and applications. In this work, we investigate a broad set of diffusive systems that can be governed by a generalized diffusion equation and subjected to a surface that can promote sorption and, consequently, desorption, thus releasing the particles to the bulk. The general bulk equation used here can reproduce different diffusive regimes, among them, those described by the Cattaneo equation or by a fractional, anomalous diffusion. The equation related to the processes on the surface incorporates non-Debye relaxations which can be used to model non-exponential relaxations commonly found in biological or fractal systems. The solutions are obtained by using the Green function approach and show a rich class of behavior that can be related to anomalous diffusion.

1. Introduction

The experiments performed by Robert Brown, of the particles suspense in the fluid, were essential to start the comprehension of one of the most fascinating fields of science, namely, diffusion, in terms of the random motion of the particles. Explanations for this motion can be found in pioneering works of Einstein [1], Smoluchowski [2], and Langevin [3], where elegant arguments have shown how it is possible to model this phenomenon. The main feature related to this random motion is the linear time dependence manifested by the mean square displacement, i.e., $\langle(\Delta x)^2\rangle \sim t$, which has been related to the Markovian and ergodic properties of these systems. However, several experimental scenarios have reported effects which are not suitable described in terms of the standard diffusion such as driven colloids [4], high-speed thermal transients [5], high-speed energy transportation, diffusion on fractals [6,7], microswimmers [8], dispersion in amorphous solids [9], and among others. These situations have motivated the extension of the standard approaches used to describe the diffusion processes to obtain a suitable description of the experimental scenario. One of these extensions is the fractional Fokker - Planck equations [10–19], which essentially incorporate fractional differential operators [18,20] in the usual approach. Interesting points about them concerns the relation with other approaches such as generalized Langevin equations [21–23] and continuous-time random walks and the simplicity of incorporating external fields and conditions on the

* Corresponding author.
E-mail address: eklenzi@uepg.br (E.K. Lenzi).

https://doi.org/10.1016/j.cnsns.2020.105411
1007-5704/

boundaries. They have been successfully applied, for example, in drying of concrete [24], molecular crowding [25], kinetic of surfaces, in membrane cells [26,27], subdiffusion in thin membranes [28], fractal structure [29], electrical response [30–33], and sorption-desorption process [18,34]. It is worth mentioning that the boundary condition [35–37] plays an important role in obtaining a suitable description of these phenomena in connection with the specific processes undergone by particles in the vicinity and on the system surface. In particular, when the sorption - desorption processes are connected to the effects of the surface of the systems through the boundary conditions, several applications can be found in engineering processes by connecting the microscopy behavior of the particles and the experimental data.

Here, we investigate a diffusion process in one dimension governed by a generalized diffusion equation with boundary conditions which may be used to describe sorption – desorption process and, consequently, related to unusual relaxations. Such systems, that involve anomalous diffusion and unusual surface relaxations, which include diffusion of and in biological materials [38,39], diffusion in porous media [40] and several industrially applied separation process [41], are the main goal of producing the general model here presented. This development is performed in Section 2 and Section 3, a summary of the results and our conclusions are presented.

2. Diffusion and surface dynamics

Let us start our analysis by defining the medium, where the diffusion occurs in the presence of a surface that can adsorb-desorb particles. It is defined in the non-negative region of the x-direction with the surface located at the origin. The diffusion of the particles will be governed by a generalized evolution equation in the bulk and the vicinity of the surface, sorption-desorption processes may occur, usually described in terms of a kinetic equation. In particular, we consider the diffusion of particles described in terms of the following equation:

$$\frac{\partial}{\partial t}\rho(x,t) = \mathcal{F}_t\left\{\frac{\partial^2}{\partial x^2}\rho(x,t)\right\} \tag{1}$$

where $\rho(x, t)$ is the density of particles and the fractional operator $\mathcal{F}_t\{\cdots\}$ is defined as follows:

$$\mathcal{F}_t\{\rho(x,t)\} = {}_0\mathcal{D}_t^{1-\alpha}\left\{\int_0^t dt' \mathcal{K}(t-t')\rho(x,t')\right\}. \tag{2}$$

In Eq. (2), ${}_0\mathcal{D}_t^{1-\alpha}\{\cdots\}$ is the Riemann-Liouville fractional differential operator, which is defined as follows:

$${}_0\mathcal{D}_t^{1-\alpha}\{\rho(x,t)\} = \frac{1}{\Gamma(\alpha)}\frac{\partial}{\partial t}\int_0^t dt' \frac{\rho(x,t')}{(t-t')^{1-\alpha}} \tag{3}$$

for $0 < \alpha \leq 1$ and the kernel $\mathcal{K}(t)$ is related to memory effects present in bulk, which are not suitably described by fractional differential operators such as, for example, the phase velocity, among others. Other operators [42–44] have been used to extend diffusion equations. In particular, the operator $\int_0^t \mathcal{K}_i(t-t')\rho(x,t')\,dt'$ has been considered by Sokolov [42] for identifying memory kernels that lead to non-negative solutions and others where this condition is not guaranteed. In this sense, the cases analyzed here verify the conditions discussed in Refs. [45,46] for obtaining non-negative solutions. In this way, we are considering, in the same approach, effects that require different changes in the standard diffusion equation and may be connected to different regimes of diffusion present in a system. For example, the fractional diffusion equation and the Cattaneo equation are particular choices of Eq. (2), by considering the kernel $\mathcal{K}(t) = \mathcal{K}\delta(t)$ with $0 < \alpha < 1$ and $\mathcal{K}(t) = \mathcal{K}e^{-t/\tau_c}/\tau_c$ (τ_c is a relaxation time [47]) with $\alpha = 1$ (for further discussion, see Ref. [42]). The last choice connects Eq. (1) with the Cattaneo's equation and leads us to a persistent motion for small times, i.e., $t \ll \tau_c$, and a Brownian motion for long times, i.e., $t \gg \tau_c$.

It is also interesting to note that Eq. (1) can be derived from the continuous time random walk (CTRW) approach [48,49], depending on the choice performed for the kernel, by considering a suitable choice for the probability density function (pdf) related to the dynamics of the walkers. In fact, for a suitable (well behaved) kernel $\mathcal{K}(t)$, essentially related to diffusion processes, e.g., kernel related to power-laws or fractional time derivatives of distributed order,we may consider the CTRW approach with a separable pdf, i.e., $\psi(x,t) = \lambda(x)\omega(t)$, where $\lambda(x)$ is the jumping probability density function and $\omega(t)$ is the waiting time probability density function. By using the balance equation [49],

$$\eta(x,t) = \varphi(x)\delta(t) + \int_{-\infty}^{\infty} dx' \int_0^t dt' \psi(x-x', t-t')\eta(x',t') \,, \tag{4}$$

which relates $\eta(x, t)$, the pdf of just having arrived at position x at time t, with the pdf $\eta(x', t')$ of having just arrived at x' at time t', for the initial condition $\rho(x, 0) = \varphi(x)$. By using Eq. (4) and the equation$\rho(x,t) = \int_0^t dt' \Phi(t')\eta(x,t')$, where $\Phi(t) = 1 - \int_0^t dt'\omega(t')$, it is possible to relate Eq. (1) with the CTRW approach by considering $\lambda(k) = 1 - \sigma^2 k^2$ and $\omega(s) = s^{1-\gamma}\tilde{\mathcal{K}}(s)/(s + s^{1-\gamma}\tilde{\mathcal{K}}(s))$, where $\tilde{\mathcal{K}}(s) = \mathcal{K}(s)/\left(\sigma^2\tau\right)$ and $\sigma^2\tau$ is a constant. For the kernels related to the Cattaneo equation, i.e., a persistent random walk, we may investigate this scenario by taking the approach present in Ref. [50,51] into account, which considers arbitrary density functions.

It is worth to mention that the exponential choice for $\mathcal{K}(t)$ introduces a finite phase velocity [47] which plays an important role in describing fast processes such as, for example, shock waves in rigid heat conductors, in the theory of diffusion in

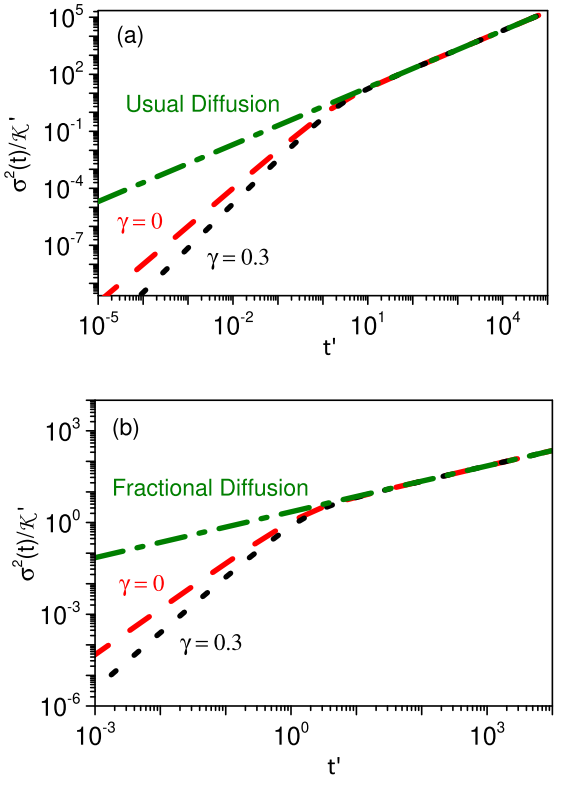

Fig. 1. Behavior of Eq. (5) versus t' (with $t' = t/\tau_c$ and $\mathcal{K}' = \mathcal{K}\tau_c$) by considering $\mathcal{K}(t) = \mathcal{K}\left(t^{\gamma-1}/\Gamma(\gamma)\right)e^{-t/\tau_c}/\tau_c$ for different values of α, γ, and τ_c. In Fig. 1a, we show the behavior of Eq. (5) for $\alpha = 1.0$ and in Fig. 1b the case $\alpha = 0.5$ is illustrated. The black dotted line was obtained by considering $\gamma = 0.3$ for both figures.

crystalline solids, among others. Another choice for the kernel is $\mathcal{K}(t) = \mathcal{K}t^{\gamma-1}/\Gamma(\gamma)$ with $\alpha \neq 1$, which can be connected to anomalous diffusion. It is also possible to consider mixing among different kernels such as $\mathcal{K}(t) = \mathcal{K}\left(t^{\gamma-1}/\Gamma(\gamma)\right)e^{-t/\tau_c}/\tau_c$, which combines the previous cases described above. The choice of the parameters α and the kernel $\mathcal{K}(t)$ have a direct influence on the spreading of the system, thus leading to either anomalous diffusion or diffusion with different regimes, which may be characterized by crossover times. For example, for a free diffusion ($\rho(\pm\infty, t) = 0$) with $\rho(x, 0) = \delta(x)$, we have that the mean square displacement is given by

$$\begin{aligned}\sigma_f^2(t) &= \left\langle (x - \langle x\rangle)^2 \right\rangle \\ &= \frac{2}{\Gamma(1+\alpha)} \int_0^t dt'(t-t')^{\alpha}\mathcal{K}(t')\,,\end{aligned} \tag{5}$$

where f means the free diffusion. Fig. 1 illustrates the behavior of Eq. (5) for the previous kernel, $\mathcal{K}(t) = \mathcal{K}\left(t^{\gamma-1}/\Gamma(\gamma)\right)$ $e^{-t/\tau_c}/\tau_c$ on the free diffusion process, by taking into account different choices of α, γ, and τ_c. Fig. 1a is calculated with $\alpha = 1.0$ (usual diffusion for $\tau_c = 0.0$), and the case with $\gamma = 0.0$ (red) and $\gamma = 0.3$ (black) are compared with the usual diffusion case. Fig. 1b uses $\alpha = 0.5$ (which, for $\tau_c = 0$ results in fractional diffusion) for the same values of γ, and compared to fractional diffusion. Both figures show a pronounced effect for small times, as a consequence of Cattaneo's equation, and the fractional differential operator governs the behavior for long times.

The surface effects strongly influence the properties and, consequently, the behavior of the systems where the diffusion proceeds [52]. In general, these effects produced by the surfaces stem from the interplay of their morphology and chemical properties. We couple these effects with the diffusion process through the boundary conditions, which will connect the kinetic processes of the sorption-desorption process present at the vicinity of the surface with the diffusion equation. In this sense, we consider Eq. (1) subjected to the boundary conditions

$$\mathcal{F}_t\left\{\frac{\partial}{\partial x}\rho(x,t)\right\}\Big|_{x=0} = \frac{d}{dt}\mathcal{C}_{surf}(t), \tag{6}$$

which connects the flux through the surface with the changes due to the processes undergone by particles in the vicinity and

$$\mathcal{F}_t\left\{\frac{\partial}{\partial x}\rho(x,t)\right\}\Big|_{x=\infty} = 0. \tag{7}$$

Thus, the surface will change the spreading of the system, in contrast with the free diffusion case. For the processes present on the surface, we consider that

$$\mathcal{C}_{surf}(t) = \mathcal{C}(t) + \int_0^t dt' \kappa(t-t')\,\rho(x,t')\big|_{x=0}\,, \tag{8}$$

where $\mathcal{C}(t)$ can be related to an arbitrary initial condition and the kernel $\kappa(t)$ is related to the kinetic aspects displayed on the surface. Thus, the results obtained here will extend the ones obtained in Refs. [35–37] to a broad scenario, where different processes on the surface may be considered. Typical choices for the kernel are $\kappa(t) = constant$ and $\kappa(t) = (k/\tau)exp(-t/\tau)$. The first choice leads us to a reaction process of particles with the surface, where the surface adsorb (absorb) the particles. The second one can be related to an adsorption – desorption process with a characteristic time τ. In particular, this case can be directly related to a kinetic process of first-order, i.e.,

$$\frac{d}{dt}\mathcal{C}_{surf}(t) = k\rho(0,t) - \frac{1}{\tau}\mathcal{C}_{surf}(t)\,, \tag{9}$$

where $k\tau$ may be related to a thickness that defines the region of interaction between the surface and bulk, in which the particles in front of the surface can be adsorbed. Other choices for $\kappa(t)$ may also be performed leading us to different kinetic processes. For example, the case $\kappa(t) = \int_0^t dt' \zeta(t') e^{-(t-t')/\tau}/\tau$ with $\zeta(t) = k(t) - \kappa(0)\delta(t)$ which implies in considering the equation

$$\frac{d}{dt}\mathcal{C}_{surf}(t) = \int_0^t dt' k(t')\rho(0,t') - \frac{1}{\tau}\mathcal{C}_{surf}(t)\,, \tag{10}$$

with the kernel $k(t)$ representing a memory effect, which produces an anomalous relaxation process, i.e., a non-Debye relaxation. From the previous results, it is also possible to show that

$$\mathcal{C}_{surf}(t) + \int_0^\infty dx \rho(x,t) = const\,, \tag{11}$$

where the first term on the left-hand side is connected to the particles present on the surface, the second term is connected to the particles present in bulk. It is also interesting to note that Eq. (6) may be modified in order to describe scenarios characterized by the injection of particles into the system or reaction-diffusion processes by incorporating reaction terms in Eq. (1).

3. Time dependent solutions

Let us focus our attention on the time-dependent solutions for Eq. (1), when the previous boundary conditions are considered. We start by considering that the initial condition of the system is given by $\rho(x,0) = \varphi(x)$ and $\mathcal{C}_{surf}(0) = \mathcal{C}(0) = constant$, in order to cover a general situation characterized by the presence of a substance in bulk, on the surface or a situation in which the particles are somehow distributed in bulk and surfaces. The adsorption-desorption processes depend on the characteristics presented by the surface and the choice performed for the kernel $\mathcal{K}(t)$ related to the memory effects present in the bulk. We also consider the Green function approach and the Laplace transform ($\mathcal{L}\{\rho(x,t)\} = \overline{\rho}(x,s)$ and $\mathcal{L}^{-1}\{\overline{\rho}(x,s)\} = \rho(x,t)$) to analyze the solution of Eq. (1), which enables us to incorporate, in a suitable way, the contributions from the boundary conditions given by Eqs. (6) and (7) to the solution.

With the Green function approach, it is possible to show that the solution for the bulk density of particles ($\rho(x,\,t)$ is given by

$$\rho(x,t) = \int_0^\infty dx' \varphi(x') \mathcal{G}(x,x';t) - \int_0^t dt' \mathcal{G}(0,x;t-t')\frac{d}{dt'}\mathcal{C}_{surf}(t'), \tag{12}$$

with Green function defined by the equation

$$\frac{\partial}{\partial t}\mathcal{G}(x,x';t) - \mathcal{F}_t\left\{\frac{\partial^2}{\partial x^2}\mathcal{G}(x,x';t')\right\} = \delta(x-x')\delta(t), \tag{13}$$

with initial condition $\mathcal{G}(x,x';t) = 0$ for $t < 0$ and the boundary condition

$$\frac{\partial}{\partial x}\mathcal{G}(x,x';t)\bigg|_{x=0} = \frac{\partial}{\partial x}\mathcal{G}(x,x';t)\bigg|_{x=\infty} = 0. \tag{14}$$

The solution for Eq. (13) subjected to the previous conditions can be found in the Laplace space by considering an arbitrary time dependence for $\mathcal{K}(t)$. In particular, it is possible to show that it is given by

$$\bar{\mathcal{G}}(x,x';s) = \frac{1}{2s\sqrt{\bar{\mathcal{K}}(s)/s^\alpha}}\left(e^{-\sqrt{\frac{s^\alpha}{\bar{\mathcal{K}}(s)}}|x-x'|} + e^{-\sqrt{\frac{s^\alpha}{\bar{\mathcal{K}}(s)}}|x+x'|}\right). \tag{15}$$

It is worth mentioning that performing the inverse Laplace transform for an arbitrary kernel leads us to a complex situation with cumbersome calculations. For this reason, before applying the Laplace transform, we need to choose the

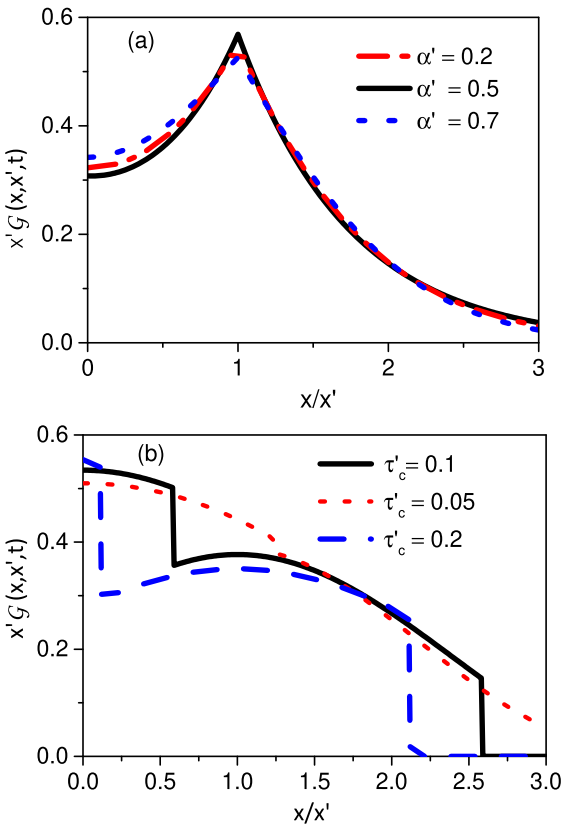

Fig. 2. In Fig. 2a, the behavior of $x'\mathcal{G}(x,x',t)$ versus x/x' obtained from Eq. (16) for different values of α' (where, $\alpha' = \alpha + \gamma$) with $t = \left(x'^2/\mathcal{K}\right)^{1/(\alpha+\gamma)}/2$. In Fig. 2b, the behavior of $x'\mathcal{G}(x,x',t)$ versus x/x' obtained from Eq. (18) for different values of $\tau_c = \left(x'^2/\mathcal{K}\right)\tau_c'$ with $t = 50\tau_c$.

time dependence present on $\mathcal{K}(t)$. In this sense, we consider two behaviors for the fractional operator by considering two different choices for $\mathcal{K}(t)$ and α. The first one is a power-law, i.e., $\mathcal{K}(t) = \mathcal{K}t^{\gamma-1}/\Gamma(\gamma)$ with $\alpha \neq 1$, and the second one is an exponential behavior, i.e., $\mathcal{K}(t) = \mathcal{K}e^{-t/\tau_c}/\tau_c$ with $\alpha = 1$, as mentioned before.

For the first case, the inverse Laplace transform yields

$$\mathcal{G}(x,x';t) = \frac{1}{\sqrt{4\pi\,\mathcal{K}t^{\alpha+\gamma}}}\left(H_{1,1}^{1,0}\left[\frac{|x-x'|}{\sqrt{\mathcal{K}t^{\alpha+\gamma}}}\middle|\begin{matrix}(1-\frac{\alpha+\gamma}{2},\frac{\alpha+\gamma}{2})\\(0,1)\end{matrix}\right]+H_{1,1}^{1,0}\left[\frac{|x+x'|}{\sqrt{\mathcal{K}t^{\alpha+\gamma}}}\middle|\begin{matrix}(1-\frac{\alpha+\gamma}{2},\frac{\alpha+\gamma}{2})\\(0,1)\end{matrix}\right]\right), \tag{16}$$

where $H_{p,q}^{m,n}\left[x\middle|\begin{matrix}(a,A)\\(b,B)\end{matrix}\right]$ is the H Fox function [53]. Fig. 2a illustrates Eq. (16) for different values of $\alpha' = \alpha + \gamma$, where considerable change in the distribution occurs as different values of α' are used. Note that Eq. (16) was obtained by using the result

$$\mathcal{L}^{-1}\left\{s^{-\alpha}e^{-as^{\sigma}}\right\} = t^{\alpha-1}H_{1,1}^{1,0}\left[at^{-\sigma}\middle|\begin{matrix}(\alpha,\sigma)\\(0,1)\end{matrix}\right]. \tag{17}$$

For the kernel $\mathcal{K}(t) = \mathcal{K}e^{-t/\tau_c}/\tau_c$, we have

$$\mathcal{G}(x,x';t) = \mathcal{G}_1(x-x';t) + \mathcal{G}_1(x+x';t) \tag{18}$$

with

$$\mathcal{G}_1(x;t) = \frac{1}{4}\sqrt{\frac{\tau_c}{\mathcal{K}}}e^{-\frac{t}{2\tau_c}}I_0\left(\frac{1}{2\tau_c}\sqrt{t^2-\frac{\tau_c}{\mathcal{K}}|x|^2}\right)\theta\left(t-\sqrt{\frac{\tau_c}{\mathcal{K}}}|x|\right)$$
$$+\sqrt{\frac{\tau_c}{4\mathcal{K}}}e^{-\frac{t}{2\tau_c}}\left\{\delta\left(t-\sqrt{\frac{\tau_c}{\mathcal{K}}}|x|\right)+\frac{t}{2\tau_c}\frac{I_1\left(\frac{1}{2\tau_c}\sqrt{t^2-\frac{\tau_c}{\mathcal{K}}|x|^2}\right)}{\sqrt{t^2-\frac{\tau_c}{\mathcal{K}}|x|^2}}\theta\left(t-\sqrt{\frac{\tau_c}{\mathcal{K}}}|x|\right)\right\}, \tag{19}$$

where $\theta(x)$ is the Heaviside function and $I_n(x)$ is the Bessel function of modified argument. Fig. 2b illustrates Eq. (19) for different values of τ_c. It is worth mentioning that the effect of the finite phase velocity on the behavior of spreading the

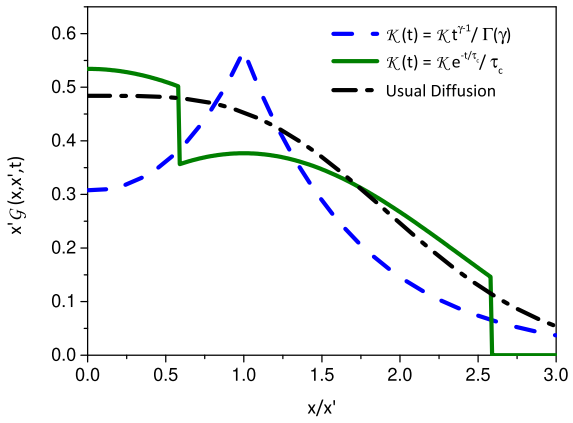

Fig. 3. This figure compares the behavior of the Green functions obtained in Fig. 2a and b with the standard one. The green solid line corresponds to the case $\alpha = 1$ with the exponential kernel and $\tau_c' = 0.1$. The dashed line is the case $\alpha' = 0.5$ with the power-law kernel. The black dashed-dotted line is the standard case with $t = x'^2/(2\mathcal{K})$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

distribution is very pronounced. It is clear by observing the substancial change in the distribution that is caused by small increments on τ_c. In addition, Eq. (19) was obtained by using the results [54]:

$$\mathcal{L}^{-1}\left\{\frac{1}{\sqrt{s^2-a^2}}F\left(\sqrt{s^2-a^2}\right)\right\} = \int_0^t dt' f(t') I_0\left(a\sqrt{t^2-t'^2}\right), \tag{20}$$

and

$$\mathcal{L}^{-1}\left\{\frac{s}{\sqrt{s^2-a^2}}F\left(\sqrt{s^2-a^2}\right)\right\} = f(t) + at\int_0^t \frac{dt'}{\sqrt{t^2-t'^2}} f(t') I_1\left(a\sqrt{t^2-t'^2}\right) \tag{21}$$

where $\mathcal{L}^{-1}\{F(s)\} = f(t)$.

Both equations recover the standard result

$$\mathcal{G}(x,x';t) = \frac{1}{\sqrt{4\pi\mathcal{K}t}}\left\{\exp\left(-\frac{(x-x')^2}{4\mathcal{K}t}\right) + \exp\left(-\frac{(x+x')^2}{4\mathcal{K}t}\right)\right\}, \tag{22}$$

by taking into account, for each case, suitable limits. In fact, Eq. (16) with $\alpha+\gamma = 1$ and Eq. (18) with $t \gg \tau_c$ recover Eq. (22). To illustrate the difference between the various solutions and the broadness of the equation presented here, Fig. 3 shows the Green function for the usual case (Eq. 22), the fractional diffusion case (Eq. 16) and the Cattaneo's case (Eq. 18) in order to evidence the differences obtained for each kernel on the spreading of the distribution. By using the previous result, it is possible to show, in the Laplace space, that

$$\bar{\rho}(0,s) = \frac{1}{1+\sqrt{s^\alpha/\bar{\mathcal{K}}(s)}\bar{\kappa}(s)}\int_0^\infty dx\,\bar{\mathcal{G}}(x,0;s)\varphi(x), \tag{23}$$

which implies that

$$\bar{\mathcal{C}}_{surf}(s) = \frac{\bar{\kappa}(s)}{1+\sqrt{s^\alpha/\bar{\mathcal{K}}(s)}\bar{\kappa}(s)}\int_0^\infty dx\,\bar{\mathcal{G}}(x,0;s)\varphi(x). \tag{24}$$

Thus, the behavior of sorbed particles, i.e., $\mathcal{C}_{surf}(t)$, depends on the choice of $\bar{\kappa}(s)$ and $\bar{\mathcal{K}}(s)$. From this result, it is also possible to show that

$$\bar{\mathcal{S}}(s) = \frac{1}{s} - \frac{\bar{\kappa}(s)}{1+\sqrt{s^\alpha/\bar{\mathcal{K}}(s)}\bar{\kappa}(s)}\int_0^\infty dx\,\bar{\mathcal{G}}(x,0;s)\varphi(x), \tag{25}$$

where $\mathcal{S}(t) = \int_0^\infty dx\rho(x,t)$ (survival probability) is connected to the quantity of substance present in the bulk. By considering, for simplicity, that the surface kernels is given by $\kappa(t) = \kappa = const$, the inverse Laplace transform of Eq. (24) yields, after applying the convolution theorem,

$$\mathcal{C}_{surf}(t) = \int_0^t dt'\,\Lambda(t-t')\int_0^\infty dx\,\mathcal{G}(x,0;t')\varphi(x), \tag{26}$$

with

$$\Lambda(t) = \sqrt{\mathcal{K}}t^{\alpha'-1}E_{\alpha',\alpha'}\left(-\sqrt{\mathcal{K}}t^{\alpha'}/\kappa\right) \tag{27}$$

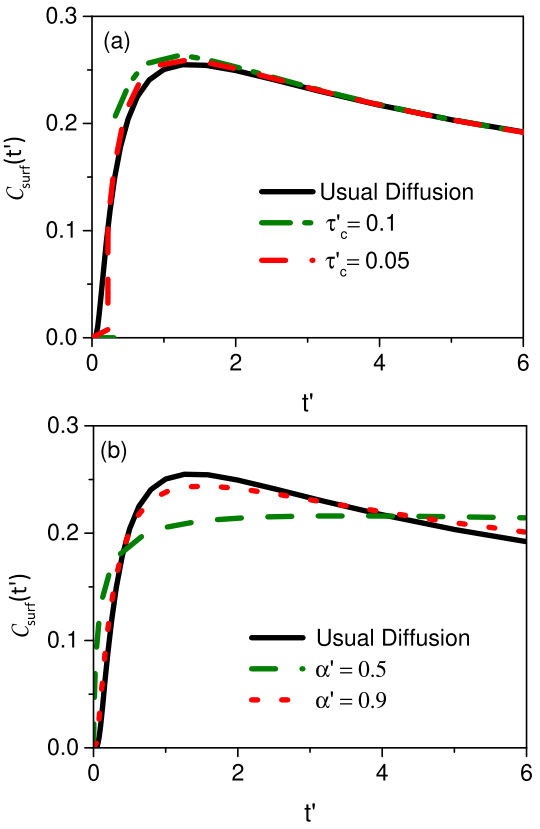

Fig. 4. In Fig. 4a the behavior of $\mathcal{C}_{surf}(t')$ versus $t' = \left(\mathcal{K}/\kappa'^2\right)t$ by considering the kernel with $\mathcal{K}(t) = \mathcal{K}e^{-t/\tau_c}/\tau_c$ is illustrated for different τ_c. We consider, for simplicity, $\tau_c = \left(\mathcal{K}/\kappa'^2\right)\tau'_c$ and $\kappa' = \kappa/\kappa'$. Fig. 4b shows the behavior of $\mathcal{C}_{surf}(t')$ versus t' (with $t' = (\mathcal{K}/\kappa'^2)^{1/(\alpha+\gamma)}t$) by considering the kernel with $\mathcal{K}(t) = \mathcal{K}t^{\gamma-1}/\Gamma(\gamma)$ with $\alpha + \gamma = \alpha' < 1$ and $\kappa/\kappa' = 1$.

for $\bar{\mathcal{K}}(s) = \mathcal{K}/s^{\gamma}$, i.e., $\mathcal{K}(t) = \mathcal{K}t^{\gamma-1}/\Gamma(\gamma)$, where $\alpha' = (\alpha+\gamma)/2$ and $E_{\alpha,\beta}(x)$ is the generalized Mittag-Leffler function [20], defined as $E_{\alpha,\beta}(x) = \sum_{n=0}^{\infty} x^n/\Gamma(\beta+\alpha n)$. In order to obtain Eq. (27), we have used the result [20]:

$$\mathcal{L}^{-1}\left\{\frac{s^{\alpha-\beta}}{(s^{\alpha}+a)^{k+1}}\right\} = \frac{1}{\Gamma(1+k)}t^{\alpha k+\beta-1}E^{(k)}_{\alpha,\beta}(-at^{\alpha}), \tag{28}$$

where $E^{(k)}_{\alpha,\beta}(x)$ is the kth derivative of the generalized Mittag-Leffler, i.e., $E^{(k)}_{\alpha,\beta}(x) = \frac{d^k}{dt^k}E_{\alpha,\beta}(x)$. For $\bar{\mathcal{K}}(s) = \mathcal{K}/(1+\tau_c s)$, i.e., $\mathcal{K}(t) = \mathcal{K}e^{-t/\tau_c}/\tau_c$, and by using the result [54]

$$\mathcal{L}^{-1}\left\{F\left(\sqrt{s^2-a^2}\right)\right\} = f(t) + a\int_0^t dt' \frac{t' f(t')}{\sqrt{t^2-t'^2}} I_1\left(a\sqrt{t^2-t'^2}\right) \tag{29}$$

with $\mathcal{L}^{-1}\{F(s)\} = f(t)$, we have that

$$\Lambda(t) = e^{-\frac{t}{2\tau_c}}\left[f(t) + \frac{1}{2\tau_c}\int_0^t dt' \frac{t' f(t')}{\sqrt{t^2-t'^2}} I_1\left(\frac{1}{2\tau_c}\sqrt{t^2-t'^2}\right)\right], \tag{30}$$

with $f(t) = \sqrt{\mathcal{K}/\tau_c}\exp\left[-(t/\kappa)\sqrt{\mathcal{K}/\tau_c}\right]$. Eq. (26) is illustrated in Fig. 4, by considering the previous cases, i.e., the different choices performed for the kernel and the parameter α (Eqs. (30) and (27)). In Fig. 4a, we show the case represented by Cattaneo's equation for different values of τ_c. Note that, in Fig. 4a, for long times, it recovers the usual behavior, as expected. In contrast, the fractional case is shown in Fig. 4b, where the relaxation process is slower than the usual one and the curves follow different behaviors for long times. For both cases, $\mathcal{C}_{surf}(t) \to 0$ for $t \to \infty$, which implies that the substance is initially sorbed and, after some time, is desorbed from surface to the bulk.

By using the previous equations, it is possible to obtain the mean square displacement for the processes described above. In particular, it is possible to show that

$$\sigma^2(t) = \langle x^2\rangle(t) - (1+\mathcal{C}_{surf}(t))\langle x\rangle^2(t) \tag{31}$$

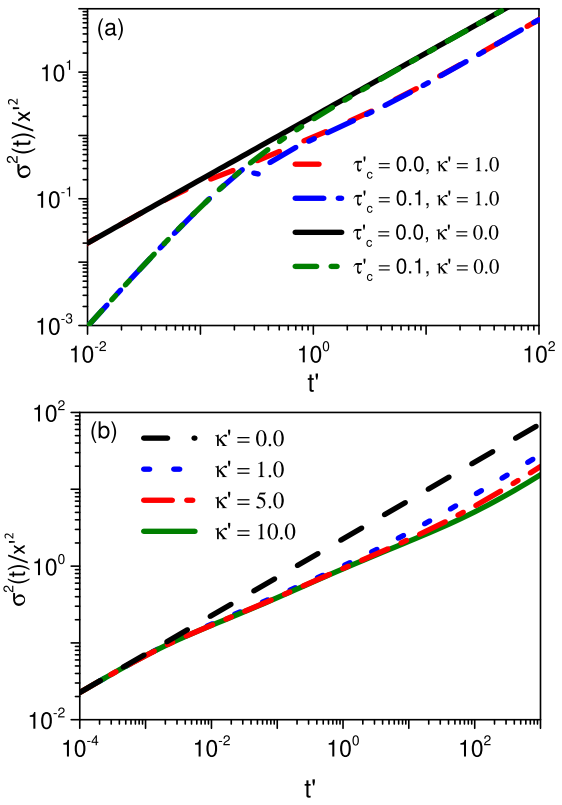

Fig. 5. In Fig. 5a the behavior of $\sigma^2(t')/x'^2$ versus t' (with $t' = \left(\mathcal{K}/x'^2\right)t$) by considering the kernel with $\mathcal{K}(t) = \mathcal{K}e^{-t/\tau_c}/\tau_c$ is illustrated for different τ_c. We consider, for simplicity, $\tau'_c = \left(\mathcal{K}/x'^2\right)\tau_c$ and $\kappa' = \kappa/x'$. Fig. 5b shows the behavior of $\sigma^2(t')/x'^2$ versus t' (with $t' = (\mathcal{K}/x'^2)^{1/(\alpha+\gamma)}t$) by considering the kernel with $\mathcal{K}(t) = \mathcal{K}t^{\gamma-1}/\Gamma(\gamma)$ with $\alpha + \gamma = \alpha' < 1$ and $\kappa/x' = 1$.

with

$$\langle x^2\rangle = x'^2 + \sigma_f^2(t) - \frac{1}{\Gamma(\alpha)}\int_0^t dt'(t-t')^{\alpha-1}\int_0^{t'} dt''\mathcal{K}(t'-t'')\mathcal{C}_{surf}(t'') \tag{32}$$

and

$$\langle x\rangle = x' + \frac{1}{\Gamma(\alpha)}\int_0^t dt'(t-t')^{\alpha-1}\int_0^{t'} dt''\mathcal{K}(t'-t'')\rho(0,t''). \tag{33}$$

Eq. (31) shows how the mean square displacement depends on surface effects. Fig. 5a and b illustrate the behavior of Eq. (31) for the cases previously analyzed. In Fig. 5a, it is possible to observe that, for short times, the Cattaneo and standard cases have a different behavior and for long times exhibit the same behavior. In Fig. 5b, the fractional case is illustrated for different values of κ in order to show the influence of the surface on the fractional case and different regimes of diffusion. Thus, from these figures, we observe that, for short times, $\sigma^2(t) \approx \sigma_f^2(t)$ (where $\sigma_f(t)$ is defined by Eq. (5)) and, for long times, $\sigma^2(t) \approx \sigma_f^2(t)$ if $\mathcal{C}_{surf}(t) \to 0$ for $t \to \infty$. In particular, for the cases discussed above, we have that $\sigma^2(t) \sim t^{1+\gamma}$ and $\sigma^2(t) \sim t$ in the asymptotic limit of $t \to \infty$.

Now, it is pertinent to discuss the broadness of the model presented here briefly. In the general approach taken here, we started from a general diffusion equation, which simultaneously combines ordinary diffusion, fractional diffusion, and Cattaneo's equation; with a kinetic equation capable of describing several adsorption-desorption dynamics, including memory effects. In this sense, the model presented here can be applied in situations that go far beyond ordinary diffusion in the presence of simple adsorption kinetics. Indeed, such non-ordinary cases are in the limelight of scientific attention since they can be used to describe anomalous situations where molecular crowding [55,56], traps [57], diffusion through distinct geometries [58] and many others are present. In particular, this is often the case of diffusion in porous [40] and biological media [38,39]. Furthermore, our model can also combine phase velocity, from Cattaneo's equations and distinct surface dynamics into play, as it is the case in several adsorption processes such as chemisorption and physisorption [34,52], often used in the separation process industrial application [41,59]. We hope that, in the foreseeable future, the results produced in this paper can be applied in the systems discussed above and be used to predict new scenarios that can enlighten the knowledge about diffusion in the various fields of science and industry.

4. Conclusions

We have investigated a generalized diffusion equation, which can be related to several contexts depending on the choice of the kernel $\mathcal{K}(t)$ and index α present in the time fractional derivative. For an arbitrary kernel, we have obtained a solution in the Laplace domain and considered two cases. One of them given in terms of a power - law and another characterized by an exponential, which is related to a diffusion-wave phenomenon, i.e., the Cattaneo equation. For both cases, we have obtained the solution in terms of the Green function. This approach has been used to shown the behavior of the quantity of particles sorbed by the surface and the behavior of the mean square displacement was also obtained for each case. For the kernel in terms of a power-law, we have an anomalous spreading of the particles. For the exponential one a usual process characterized by a linear time dependence is obtained in the asymptotic limit of long times. Note also that the results obtained here also has, as a particular case, the scenarios reported in the literature [35,36], which can be obtained with a suitable choice of the kernel. Finally, we hope that the results presented here can be useful for the discussion of the sorption-desorption processes and anomalous diffusion in the various fields of science and industry.

Declaration of Competing Interest

The authors declare that they do not have any financial or nonfinancial conflict of interests.

CRediT authorship contribution statement

F.W. Tavares: Conceptualization, Methodology, Writing - original draft. **P.M. Ndiaye:** Conceptualization, Methodology, Writing - original draft. **E.K. Lenzi:** Conceptualization, Methodology, Writing - original draft. **L.R. Evangelista:** Conceptualization, Methodology, Writing - original draft. **H.V. Ribeiro:** Conceptualization, Methodology, Writing - original draft. **R.S. Zola:** Conceptualization, Methodology, Writing - original draft.

Acknowledgments

E.K.L. thanks the Lab-ATOMOS/UFRJ for the hospitality and support. This work was partially supported by the National Institutes of Science and Technology of Complex Fluids – INCT-FCx (L.R.E. and R.S.Z.) and Complex Systems – INCT-SC (E.K.L.). E.K.L. acknowledges the support of the CNPq (Grant No. 302983/2018-0). R.S.Z. acknowledges the support of the CNPq (Grant No. 305717/2017-0). L. R. E. acknowledges the support of the CNPq (Grant No. 302981/2018-7). HVR acknowledges the support of CNPq (Grants Nos. 440650/2014-3 and 303642/2014-9).

References

[1] Einstein A. Ann Phys 1905;322:549.
[2] von Smoluchowski M. Ann Phys 1906;326:756.
[3] Langevin P. C R Acad Sci (Paris) 1908;146:530.
[4] Wilson G, Bahadori AA, Bindra H. J App Phys 2019;126:124308.
[5] Rana S, Kanesan J, Reza AW, Ramiah H. Sci World J 2014;2014:671619.
[6] O'Shaughnessy B, Procaccia I. Phys Rev Lett 1985;54:455.
[7] O'Shaughnessy B, Procaccia I. Phys Rev A 1985;32:3073.
[8] Debnath D, Ghosh PK, Li Y, Marchesoni F, Li B. Soft Matter 2016;12:2017.
[9] Scher H, Montroll EW. Phys Rev B 1975;12:2455.
[10] Barkai E, Silbey RJ. J Phys Chem B 2000;104:3866.
[11] Barkai E. Phys Rev E 2001;63:046118.
[12] Barkai E. Chem Phys 2002;284:13.
[13] Barkai E, Metzler R, Klafter J. Phys Rev E 2000;61:132.
[14] Shlesinger MF. J Stat Phys 1974;10:421.
[15] Klafter J, Blumen A, Shlesinger MF. Phys Rev A 1987;35:3081.
[16] Hilfer R, Anton L. Phys Rev E 1995;51:R848–51.
[17] Compte A. Phys Rev E 1996;53:4191.
[18] Evangelista LR, Lenzi EK. Fractional diffusion equations and anomalous diffusion. Cambridge University Press; 2018.
[19] Sandev T, Tomovski Z. Fractional Equations and Models: Theory and Applications.Developments in Mathematics 61. 1st ed. Springer International Publishing; 2019. ISBN 978-3-030-29613-1,978-3-030-29614-8
[20] Podlubny I. Fractional differential equations. Academic Press; 1999.
[21] Sandev T, Živorad Tomovski, Dubbeldam JL. Physica A 2011;390:3627.
[22] Sandev T. Mathematics 2017;5.
[23] Tateishi AA, Lenzi EK, da Silva LR, Ribeiro HV, Picoli S, Mendes RS. Phys Rev E 2012;85:011147.
[24] Zhang L, Ren Q, Li Z, Zhang G. J Mater Civil Eng 2019;31:04019010.
[25] Sokolov IM. Soft Matter 2012;8:9043.
[26] Caputo M, Cametti C, Ruggero V. Physica A 2008;387:2010.
[27] Caputo M, Cametti C. J Phys D 2009;42:125505.
[28] Kosztołowicz T, Dworecki K, Lewandowska KD. Phys Rev E 2012;86:021123.
[29] Weigel AV, Simon B, Tamkun MM, Krapf D. P Natl Acad Sci USA 2011;108:6438.
[30] Lenzi EK, de Paula JL, Silva FRGB, Evangelista LR. J Phys Chem C 2013;117:23685.
[31] Ciuchi F, Mazzulla A, Scaramuzza N, Lenzi EK, Evangelista LR. J Phys Chem C 2012;116:8773.
[32] Lenzi E, Zola R, Rossato R, Ribeiro H, Vieira D, Evangelista L. Electrochim Acta 2017;226:40.
[33] Lenzi EK, Fernandes PRG, Petrucci T, Mukai H, Ribeiro HV. Phys Rev E 2011;84:041128.

[34] Zola RS, Lenzi EK, Evangelista LR, Barbero G. Phys Rev E 2007;75:042601.
[35] Lenzi EK, Evangelista LR, Barbero G, Mantegazza F. EPL (Europhysics Letters) 2009;85:28004.
[36] Lenzi EK, Yednak CAR, Evangelista LR. Phys Rev E 2010;81:011116.
[37] Guimarães VG, Ribeiro HV, Li Q, Evangelista LR, Lenzi EK, Zola RS. Soft Matter 2015;11:1658.
[38] Chipot C, Comer J. Sci Rep 2016;6:35913.
[39] Berrod Q, Hanot S, Guillermo A, Mossa S, Lyonnard S. Sci Rep 2017;7:8326.
[40] Gerber G, Bensouda M, Weitz DA, Coussot P. Phys Rev Lett 2019;123:158005.
[41] Nugent P, Belmabkhout Y, Burd SD, Cairns AJ, Luebke R, Forrest K, et al. Nature 2013;495:80. https://www.nature.com/articles/nature11893#supplementary-information
[42] Sokolov IM. Phys Rev E 2002;66:041101.
[43] Lenzi EK, Yednak CAR, Evangelista LR. Phys Rev E 2010;81:011116.
[44] Chechkin AV, Gorenflo R, Sokolov IM. Phys Rev E 2002;66:046129.
[45] Sandev T, Tomovski Z, Dubbeldam JLA, Chechkin A. J Phys A 2018;52:015201.
[46] Mainardi F, Luchko Y, Pagnini G. Fract Calc Appl Anal 2001;4:153.
[47] Jagher PD. Physica A 1980;101:629.
[48] Klafter J SI. First steps in random walks: from tools to applications. Oxford University Press; 2011.
[49] Metzler R, Klafter J. Phys Rep 2000;339:1.
[50] Masoliver J, Lindenberg K, Weiss GH. Physica A 1989;157:891.
[51] Masoliver J, Lindenberg K. Eur Phys J B 2017;90:107.
[52] Recanello M, Lenzi E, Martins A, Li Q, Zola R. Int J Heat Mass Transf 2020;151:119433.
[53] Mathai AM, Saxena RK, Haubold HJ. The H-function. Springer-Verlag New York; 2010.
[54] Prudnikov AP, Brychkov YA, Marichev OI. Integrals and series, volume 5: inverse laplace transforms. Gordon and Breach Science Publishers; 1992.
[55] Höfling F, Franosch T. Rep Prog Phys 2013;76:046602.
[56] Saxton MJ. Biophys J 2007;92:1178.
[57] Murase K, Fujiwara T, Umemura Y, Suzuki K, Iino R, Yamashita H, et al. Biophys J 2004;86:4075.
[58] Cao A, van Raak RJH, Broer DJ. Soft Matter 2019;15:4737.
[59] Liascukiene I, Amselem G, Gunes DZ, Baroud CN. Soft Matter 2018;14:992.