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Non-Markovian diffusion and the adsorption-desorption process

E. K. Lenzi,[1,2] C. A. R. Yednak,[1,2] and L. R. Evangelista[1]
[1]*Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, PR, Brazil*
[2]*Dipartimento di Fisica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*

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The non-Markovian diffusion of dispersed particles in a semi-infinite cell of an isotropic fluid limited by an adsorbing-desorbing surface is theoretically investigated. The density of dispersed particles in the bulk is a time dependent function and the time dependent density of surface particles is governed by a modified kinetic equation with a time dependent kernel. In this framework, the densities of bulk and surface particles are analytically determined, taking into account the conservation of the number of particles immersed in the sample. This system exhibits anomalous diffusion behavior as well as memory effects in the adsorption-desorption process. The results obtained here are expected to be useful to investigate the adsorption-desorption phenomena of neutral as well as charged particles in an isotropic fluid in contact with a solid substrate when the anomalous diffusion is present.

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I. INTRODUCTION

One of the most common phenomena in the nature is the diffusion which may be describe in terms of an stochastic process. The kind of the diffusion process is related to the properties of the medium and depends on the conditions imposed to the system. This manner, the diffusion may have an usual behavior where the main characteristic is the square mean displacement with a linear dependence on time, i.e., $\langle (z-\langle z\rangle)^2\rangle \sim t$ [1], which reflects the Markovian nature of this process or an anomalous behavior [2]. The last case usually occurs when the system present non-Markovian aspects such as, for example, memory effects [3,4], long-range correlations, and long-range interactions [5–7]. A direct consequence is an anomalous spreading of the system manifested by the square mean displacement which has not linear dependence on time or, in the case of Lévy distributions [8], is not finite. These situations can be found, for instance, in atom deposition into a porous substrate [9], diffusion of high molecular weight polyisopropylacrylamide in nanopores [10], highly confined hard disk fluid mixtures [11], fluctuating particle fluxes [12], diffusion on fractals [13], ferrofluid [14], and colloids [15]. Different diffusive behaviors may also be exhibited by these systems such as the ones found in [6,7], for the case of long-range interaction, and in [16,17], for active intracellular transport. This rich variety of situations may be investigated by several formalisms [2–4,18–20], in particular, by extensions of the diffusion equation such as the fractional diffusion equations [3,4,21] or by incorporating spatial and time dependence on the diffusion coefficient. The conditions imposed to the system may also lead us to an anomalous diffusion [22]. A typical situation may be found in adsorption-desorption process by a surface, governed by a typical balance equation characterizing a chemical reaction of first kind (Langmuir's approximation), when the conservation of the number of particles is imposed [22–24]. For this case, the results for the momentum distribution [22] show that the system exhibits anomalous diffusion [2] behavior, according to the values of the characteristic times entering the problem. More precisely, not only a single subdiffusive or superdiffusive motion can be found, but the system presents a multiple behavior that includes both modes of subdiffusion and superdiffusion and, for large times, the normal diffusive behavior. A system presenting similar behavior can be found in the dynamics of vesicles driven by adhesion gradients of a Langmuir monolayer [25]. In this scenario, the diffusion process of suspended or dispersed particles in an anisotropic media like liquid crystals [26] may be found suitable description. In fact, dispersions of particles in an anisotropic host medium such as nematic liquid crystals are responsible for a series of different physical scenarios deserving a more fundamental explanation [26]. Among the systems recently considered, it is worth mentioning the suspension of magnetic grains [27], silica spheres [28], latex particles [29], oil droplets [30]. All the bulk effects in these systems have been object of attention in the last few years.

In this paper, we investigate the adsorption-desorption process of a system governed by an unusual diffusion equation which may recover, by suitable choice, several situations such as the fractional diffusion equations [2–4], fractional diffusion equations of distributed order [31,32] and Cattaneo equation [33,34]. We also consider here a modified kinetic equation in which by a suitable choice for a temporal kernel in the desorption rate can account for the relative importance of physisorption or of chemisorption [23,24], according to the time scale governing the adsorption phenomena. Indeed, more realistic descriptions of the kinetics at the interface in the framework of a first-order chemical reaction should be developed by taking into account both the chemisorption and the physisorption processes, because the actual position of the molecule on the surface can have a memory of its incoming state, eventually modifying the adsorption-desorption rates. For this context, we found exact solutions in the Laplace space and analyzed some representative situations. These developments are performed in Sec. II while in Sec. III our discussions and conclusions are presented.

II. PROBLEM

To mathematically formulate the problem we consider a typical geometry for the sample such that the Cartesian reference frame has the z axis perpendicular to the bounding surface, located at $z=0$. If the system is a nematic liquid crystal, we can consider that in this geometry the sample is homeotropically oriented. In the general case of other host medium, it is enough to consider that the bulk density of particles $\rho(z,t)$ is governed by the diffusion equation

$$\frac{\partial}{\partial t}\rho(z,t)=\int_0^t d\bar{t}\mathcal{D}(t-\bar{t})\frac{\partial^2}{\partial z^2}\rho(z,\bar{t}), \tag{1}$$

where $\mathcal{D}(t)$ is a generic time dependent diffusion coefficient. The bulk density of particles is subjected to the conditions: $\rho(\infty,t)=0$ and $\rho(z,0)=\bar{\rho}(z)$. This equation may be connected to several cases such as the fractional diffusion equations [3,4], fractional diffusion equation of distributed order [31,32], and depending on the choice for the diffusion coefficient it may incorporate a finite collision time, which is not present in the usual diffusion equation. Indeed, the usual diffusion equation is an approximation valid only on time scales which are large compared to the time scale at which the diffusion-causing collisions takes place. One of the most striking nonphysical properties of the diffusion equation is an infinite velocity of information propagation. However, the inclusion of the finite collision frequency in the system may create additional difficulties to treat the problem; an approximation which makes the problem more tractable is discussed by Bourret [35] and leads to an integral equation similar to Eq. (1) with a correlation function in the kernel [34]. This equation may be obtained from a stochastic differential equation related to a two state process [33]. In this case, the kernel of the diffusive term $\mathcal{D}(t)$ is connected to the two-time correlation function of this two state process, i.e., $\mathcal{D}(t)=\langle\xi(0)\xi(t)\rangle/\langle\xi^2\rangle$ [33]. Other situations related to the above equation are discussed in Ref. [36]. In addition, it is interesting to note that Eq. (1) may also be connected to the situations discussed in Refs. [37,38] which are essentially non-Markovian. Also, in Ref. [39] more non-Markovian situations may be found.

The boundary condition of $\rho(z,t)$ on the surface $z=0$ is defined in terms of the surface density of particles, $\sigma(t)$, by the kinetic equation

$$\frac{d}{dt}\sigma(t)+\int_0^t d\bar{t}\mathcal{K}(t-\bar{t})\sigma(\bar{t})=\kappa\rho(0,t), \tag{2}$$

where κ and τ are parameters describing the adsorption phenomenon. In Eq. (2), a temporal kernel $\mathcal{K}(t)$ was introduced to keep the approach as general as possible and to account for memory effects in the adsorption-desorption process. In Refs. [23,24], it was shown that a suitable choice of the kernel can underline the relative importance of physisorption or chemisorption process according to the time scale governing the adsorption phenomena. Other condition to be imposed to the system is the conservation of the number of particles

$$\sigma(t)+\int_0^\infty dz\rho(z,t)=\Phi(t), \tag{3}$$

where $\Phi(t)$ represents the instantaneous amount of dispersed particles in the bulk. Again, we have chosen a time dependent function to represent this quantity to keep the approach in a general perspective. However, a term of this kind can be interpreted as an external source or sink of particles connected with the system. Furthermore, in the case of doped systems, a term like this one has to be considered to account for the possibility of recombination or transformation in the molecular structures. Some organic materials, such as azobenzenes, which also may exhibit liquid crystalline properties, undergo, upon light illumination, a trans-to cis-isomerisation, i.e., they are photosensitive materials. In the initial state of this photosensitive material, all the molecules are in the trans state. If one considers the selective adsorption process (e.g., the adsorption-desorption of only trans-isomers) in a sample doped with this material, upon light illumination the quantity $\Phi(t)$ may represent the actual amount of one of the components of the dyes dispersed in the host medium. Before to proceed, it can be helpful to note that while the first term of Eq. (3) gives the quantity of particle adsorbed by the surface, the second term gives the quantity of particles present in the bulk and is known as survival probability $\mathcal{S}(t)$, i.e., $\mathcal{S}(t)=\int_0^\infty dz\rho(z,t)$.

In order to solve Eq. (1) subjected to the conditions stated above, we use the Green's function approach and integral (Laplace and Fourier) transforms. We start by applying in Eq. (1) the Laplace transform ($\mathcal{L}\{\cdots\}=\int_0^\infty dte^{-st}\cdots$ and $\mathcal{L}^{-1}\{\cdots\}=\frac{1}{2\pi i}\int_{-i\infty+c}^{i\infty+c}dse^{st}\cdots$) on the variable t. This permits us to reduce Eq. (1) to the ordinary differential equation

$$\mathcal{D}(s)\frac{d^2}{dz^2}\rho(z,s)=s\rho(z,s)-\rho(z,0). \tag{4}$$

The solution for Eq. (4) may be formally given by

$$\rho(z,s)=-\int_0^\infty dz\rho(z,0)\mathcal{G}(z,z';s) - \mathcal{D}(s)\rho(0,s)\frac{d}{dz'}\mathcal{G}(z,z';s)\Big|_{z'=0}, \tag{5}$$

with the Green's function obtained from the equation

$$\mathcal{D}(s)\frac{d^2}{dz^2}\mathcal{G}(z,z';s)-s\mathcal{G}(z,z';s)=\delta(z-z'), \tag{6}$$

whose solution, after some calculations using the Fourier transform ($\mathcal{F}_s\{\cdots\}=\sqrt{\frac{2}{\pi}}\int_0^\infty dk\,\sin(kz)\cdots$ and $\mathcal{F}_s^{-1}\{\cdots\}=\sqrt{\frac{2}{\pi}}\int_0^\infty dk\,\sin(kz)\cdots$), may be written as follows:

$$\mathcal{G}(z,z';s)=-\frac{1}{2\sqrt{s\mathcal{D}(s)}}\left(e^{-\sqrt{s/\mathcal{D}(s)}|z-z'|}-e^{-\sqrt{s/\mathcal{D}(s)}|z+z'|}\right). \tag{7}$$

It is interesting to mention that the last term of Eq. (5) gives the contribution of the surface for the time evolution of the initial condition and is directly connected to the adsorption-desorption process. Now, the Laplace transform of Eq. (2) gives $s\sigma(s)-\sigma(0)+\mathcal{K}(s)\sigma(s)=\kappa\rho(0,s)$ which, when substituted in the transformed Eq. (3), i.e., $\sigma(s)+\int_0^\infty dz\rho(z,s)=\Phi(s)$, leads us to write

$$\sigma(s)=\frac{1}{1+\sqrt{\frac{\mathcal{D}(s)}{s\kappa^2}}[s+\mathcal{K}(s)]}\Bigg[\Phi(s)-\mathcal{M}+\frac{1}{s}\int_0^\infty dz'\rho(z',0)e^{-\sqrt{s/\mathcal{D}(s)}z'}+\sqrt{\frac{\mathcal{D}(s)}{s\kappa^2}}\sigma(0)\Bigg], \quad (8)$$

where $\mathcal{M}=(1/s)\int_0^\infty dz\rho(z,0)$. In this framework, the problem is formally solved in the s space. The analysis of significant cases can be carried on in this space and the inverse of Eq. (8) can be then searched to give, respectively, the distribution of particles in the surface.

The first case we consider is such that $\Phi(s)=1/s$, $\int_0^\infty dz\rho(z,0)=1$, $\sigma(0)=0$ and $\mathcal{K}(s)=1/\tau$. Note that the choice for $\mathcal{D}(s)$ will be done later on. This approach may be useful to describe the diffusion process of a given amount of dispersed particles in the bulk followed by the adsorption-desorption process at a surface that initially is empty. This adsorption-desorption process is governed by the kernel $\mathcal{K}(t)$ present in the kinetic equation, whose characteristic time is τ. Since τ has the dimension of time and κ of a length/time, it is possible to introduce characteristics times connected with these quantities to fully describe the adsorption-desorption process at the interface. These quantities, together with a diffusion time of the form τ_{D}, form the time scales governing the dynamical behavior of dispersed particles in the medium when the adsorption phenomenon is taken into account [40,41]. In particular, the quantity $\overline{\tau}=\mathcal{D}/\kappa^2$, where $\mathcal{D}$ is the diffusion coefficient of an isotropic system, involves the characteristic parameters connected with the dynamics of the diffusion process and the kinetics of the adsorption phenomenon in the sample [22]. If we consider, furthermore, a diffusion coefficient in the form $\mathcal{D}(s)=\mathcal{D}s^{1-\gamma}$, the diffusive process here described is a fractional diffusion process, i.e., it is equivalent to solve a fractional diffusion equation of order γ in the time derivative. In this case, Eq. (8) becomes

$$\sigma(s)=\frac{s^{\gamma/2-1}}{s^{\gamma/2}+\sqrt{\overline{\tau}}(s+1/\tau)}\int_0^\infty dz\rho(z,0)e^{-\sqrt{s/\mathcal{D}(s)}z}. \quad (9)$$

It is possible to obtain the inverse Laplace transform of Eq. (9) if a judicious choice for the contour of integration C is performed [42]. After some calculations, one obtains

$$\sigma(t)=\int_0^\infty d\overline{z}\rho(\overline{z},0)\int_0^t dt'\Pi(t-t')\Psi(\overline{z},t), \quad (10)$$

with

$$\Pi(t)=\frac{1}{\pi}\sin\left(\frac{\pi}{2}\gamma\right)\int_0^\infty d\eta\frac{\eta^{\gamma/2}e^{-\eta t}}{\eta^\gamma+\overline{\tau}(1/\tau-\eta)^2}, \quad (11)$$

and

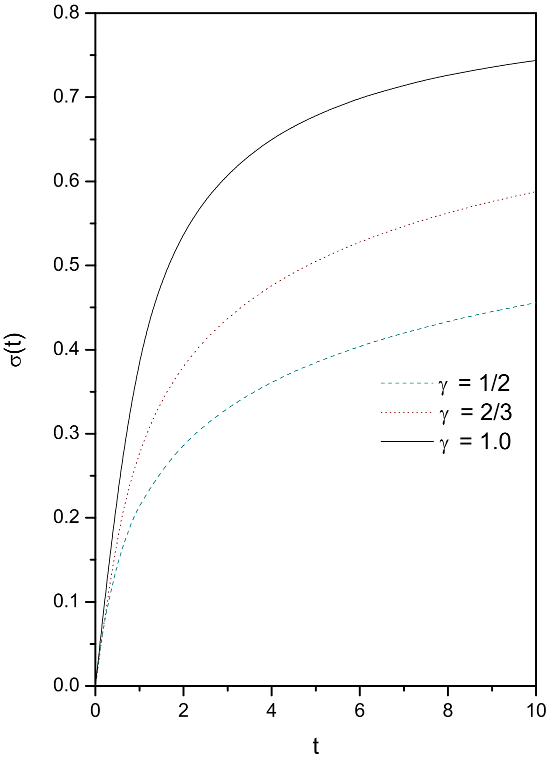

FIG. 1. (Color online) Behavior of $\sigma(t)$ versus t for different values of γ in order to illustrate Eq. (10). We consider, for simplicity, $\tau=10$, $\kappa=5$, $\mathcal{D}=1$, and the initial condition $\rho(z,0)=\delta(z-1)$.

$$\Psi(z,t)=\frac{1}{t^{\gamma/2}}\mathrm{H}_{1,1}^{1,0}\left[\frac{z}{\sqrt{\mathcal{D}t^\gamma}}\,\middle|\,\begin{matrix}(1-\gamma/2,\gamma/2)\\(0,1)\end{matrix}\right], \quad (12)$$

where $\mathrm{H}_{p,q}^{m,n}\left[x\middle|\begin{smallmatrix}(a_1,A_1),\cdots,(a_p,A_p)\\(b_1,B_1),\cdots,(b_q,B_q)\end{smallmatrix}\right]$ is the Fox H function [43]. In this manner, the time dependent distribution of particles on the surface is exactly obtained. Figure 1 shows the behavior of $\sigma(t)$ versus t for different values of γ in order to illustrate how a subdiffusive process governed by a fractional-diffusion-like equation changes the adsorption process. In this direction, it evidences that for the diffusion process governed by the usual case, i.e., $\mathcal{D}(s)=\mathcal{D}=\mathrm{const}$, the quantity of adsorbed particles is greater than in the fractional case represented by the choice $\mathcal{D}(s)=\mathcal{D}s^{1-\gamma}$. This feature also indicates how the spreading of the system (or distribution) may influence the adsorption process at the surface $z=0$. In fact, the values of γ considered here are essentially related to the subdiffusive case that makes the system to spread slower than the usual case.

In this context, other representative situation is characterized by $\mathcal{D}(t)=\mathcal{D}e^{-t/\tau_C}/\tau_C$ $[\mathcal{D}(s)=\mathcal{D}/(1+\tau_C s)]$ which corresponds to the Cattaneo equation [34]. For this case Eq. (8) is given by

$$\sigma(s)=\frac{\sqrt{s(s+1/\tau_c)}}{\sqrt{s(s+1/\tau_c)}+\sqrt{\overline{\tau}}(s+1/\tau)}\frac{1}{s}\int_0^\infty d\overline{z}\rho(\overline{z},0)e^{-\sqrt{s/\mathcal{D}(1+\tau_c s)}\overline{z}}. \quad (13)$$

By performing the inverse Laplace transform, we obtain that the adsorption is given by

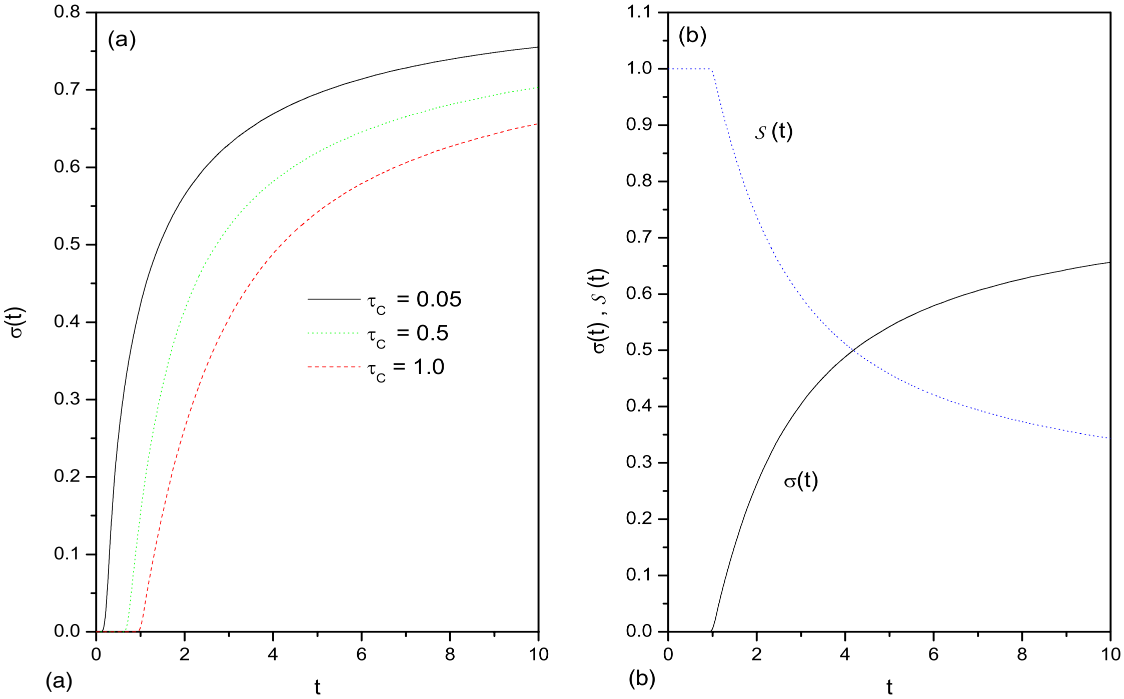

FIG. 2. (Color online) Behavior of $\sigma(t)$ versus t for different values of τ_c in order to illustrate in Fig. 2(a) Eq. (14). Figure 2(b) shows $\sigma(t)$ and $\mathcal{S}(t)$ versus t for a typical values of τ_c. Note that the particles are not immediately adsorbed, in contrast to the case characterized by the usual diffusion. This feature is related to finite phase velocity of propagation of the system which is related to τ_c. We consider, for simplicity, $\tau=5$, $\kappa=10$, $\mathcal{D}=1$, and the initial condition $\rho(z,0)=\delta(z-1)$ in both figures.

$$\sigma(t) = \int_0^\infty d\bar{z}\rho(\bar{z},0)\int_0^t d\bar{t}\Lambda(\bar{z},t-\bar{t})e^{-\bar{t}/2\tau_c}I_0\left(\frac{\bar{t}}{2\tau_c}\right)$$

$$\Lambda(z,t) = \frac{2}{\pi\tau_c}\Theta\left(t-\sqrt{\frac{\tau_c}{\mathcal{D}}}z\right)\int_0^1 d\eta\frac{\eta(1-\eta^2)e^{-\eta^2 t/\tau_c}}{\eta^2(1-\eta^2)+\bar{\tau}\left(\frac{\tau_c}{\tau}-\eta^2\right)^2}$$
$$\times\left[\eta\sqrt{1-\eta^2}\times\cos\left(\frac{z\eta}{\sqrt{\mathcal{D}\tau_c}}\sqrt{1-\eta^2}\right)+\sqrt{\bar{\tau}}\left(\frac{\tau_c}{\tau}-\eta^2\right)\sin\left(\frac{z\eta}{\sqrt{\mathcal{D}\tau_c}}\sqrt{1-\eta^2}\right)\right], \tag{14}$$

where $\Theta(t)$ is the step function and $I_0(x)$ is a Bessel function of modified argument. Note that the adsorption process for this case starts after a characteristic time related to the quantity $\sqrt{\tau_c/\mathcal{D}}z$, which is connected to the necessary time for the initial particles arrive to the surface $z=0$, where the adsorption-desorption will occur. This feature may be evidenced by choosing as initial condition $\rho(z,0)=\delta(z-z')$ which results for the characteristic time $\sqrt{\tau_c/\mathcal{D}}z'$ indicating that the adsorption process starts after this time. This behavior for $\sigma(t)$ is consistent with the finite phase velocity (related to a finite collision time) which is introduced with this choice for the diffusion coefficient. Figure 2(a) illustrates the behavior of $\sigma(t)$ versus t for different values of τ_c in order to show the effect of this term on the adsorption process. It is also interesting to note that for $\tau_c\to 0$ the usual case is recovered. Figure 2(b) shows the behavior of the survival probability $[\mathcal{S}(t)=\int_0^\infty dz\rho(z,t)]$ and the quantity of adsorbed particles for a typical value of τ_c. It evidences the presence of finite phase velocity since the adsorption process starts after a finite time, in contrast to the case governed by the usual diffusion equation.

The situations previously analyzed are essentially characterized by the particles initially in the bulk and the surface in absence of particles. Now, we consider an opposite situation, i.e., the particles initially adsorbed by the surface and the bulk without particles, in order to investigate a typical process governed by desorption of particles. For simplicity, for this case we consider $\Phi(s)=1/s$, $\mathcal{M}=0$, $\sigma(0)=1$, $\mathcal{K}(s)=1/\tau$, and $\mathcal{D}(s)=\mathcal{D}(s)$. This choice represents a usual diffusive process in which a given amount of dispersed particles is initially adsorbed on the surface as mentioned before. Also, we consider for this scenario $\mathcal{D}(s)=\mathcal{D}s^{1-\gamma}$, $\mathcal{D}(s)=\mathcal{D}/(1+\tau_c s)$ and $\mathcal{D}(s)=\mathcal{D}=\text{const}$ which represents the usual diffusion equation. For the first case, Eq. (8) becomes

$$\sigma(s) = \frac{1}{s}\left(1-\frac{\sqrt{\bar{\tau}}/\tau}{s^{\gamma/2}+\sqrt{\bar{\tau}(s+1/\tau)}}\right). \tag{15}$$

Performing the inverse Laplace transform, we obtain that

$$\sigma(t) = 1-\frac{\sqrt{\bar{\tau}}}{\tau\pi}\sin\left(\frac{\pi}{2}\gamma\right)\int_0^\infty d\eta(1-e^{-\eta t})\frac{\eta^{\gamma/2-1}}{\eta^\gamma+\bar{\tau}(1/\tau-\eta)^2}, \tag{16}$$

(see Fig. 3). Note that similarly to the previous case, this choice for the diffusion coefficient is related to the subdiffusive process and makes the system to spread slower than the

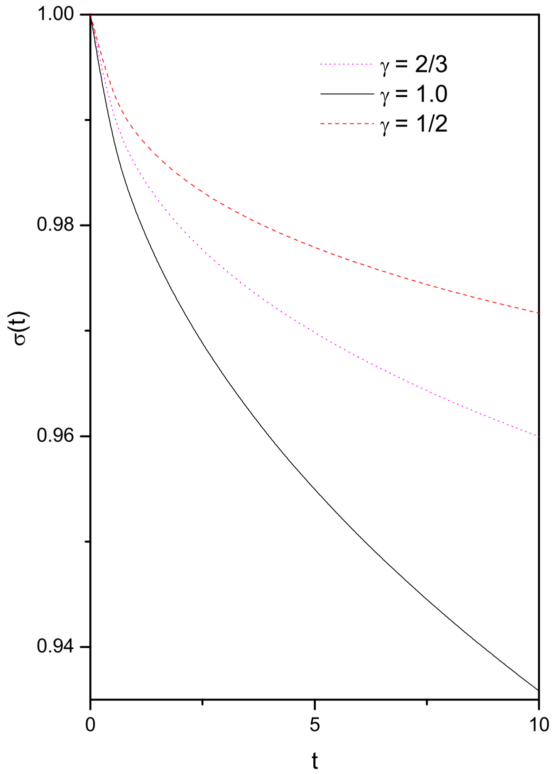

FIG. 3. (Color online) Behavior of $\sigma(t)$ versus t for different values of γ in order to illustrate Eq. (16). We consider, for simplicity, $\tau=10$, $\kappa=5$, $\mathcal{D}=1$, and the initial condition $\rho(z,0)=\delta(z-1)$.

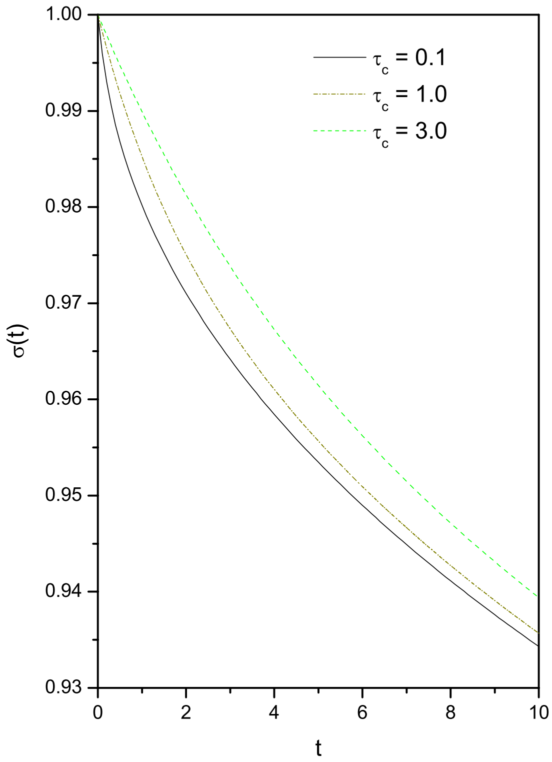

FIG. 4. (Color online) Behavior of $\sigma(t)$ versus t for different values of τ_c in order to illustrate Eq. (17). We consider, for simplicity, $\tau=5$, $\kappa=10$, $\mathcal{D}=1$, and the initial condition $\rho(z,0)=\delta(z-1)$.

usual one. This is also evidenced in Fig. 3 by the behavior of $\sigma(t)$ which decays slower for $\gamma<1$ indicating that the desorption process is related to the spreading of the system. Now let us consider the case which has $\mathcal{D}(s)=\mathcal{D}/(1+\tau_c s)$. For this case we obtain, after substituting the diffusion coefficient in Eq. (8) and performing the inverse Laplace transform, that the adsorption is given by

$$\sigma(t) = 1 - \frac{1}{\tau}\sqrt{\frac{\bar{\tau}}{\tau_c}}\left\{\int_0^t dt'[\Omega(t-t')\Sigma(t') - \Upsilon(t')]\right\}, \tag{17}$$

with

$$\Omega(t) = \frac{e^{-(\omega+\lambda)t/2\nu\tau^2\tau_c}}{2\nu\lambda}[(2\mathcal{R}_c^2\tau(\tau-\tau_c)-\tau^2)(1-e^{t\lambda/\nu\tau^2\tau_c}) - \lambda(1+e^{t\lambda/\nu\tau^2\tau_c})],$$

$$\Sigma(t) = e^{-t/(2\tau_c)}I_0[t/(2\tau_c)], \quad \text{and} \tag{18}$$

$$\Upsilon(t) = \frac{e^{-(\omega+\lambda)t/2\nu\tau^2\tau_c}}{2\nu\lambda}[(\tau^2-2\tau\tau_c)(1-e^{t\lambda/\nu\tau^2\tau_c}) - \lambda(1+e^{t\lambda/\nu\tau^2\tau_c})], \tag{19}$$

where $\omega=2R_c^2\tau_c\tau-\tau^2$, $\nu=\mathcal{R}_c^2-1$, $\mathcal{R}_c=\sqrt{\bar{\tau}/\tau_c}$ $\lambda=\tau\sqrt{\tau^2-4\bar{\tau}(\tau-\tau_c)}$ (see Fig. 4) By employing for the case $\mathcal{D}(s)=\mathcal{D}=$const the previous procedure, we have that

$$\sigma(t) = 1 - \sqrt{\frac{\bar{\tau}}{\tau^2-4\bar{\tau}\tau}}\left\{\frac{1}{\gamma_-}[1-e^{\gamma_-^2 t}\operatorname{erfc}(\gamma_-\sqrt{t})] - \frac{1}{\gamma_+}[1-e^{\gamma_+^2 t}\operatorname{erfc}(\gamma_+\sqrt{t})]\right\}, \tag{20}$$

where $\gamma_\pm=1/(2\sqrt{\bar{\tau}})\pm\sqrt{1/(4\bar{\tau})-1/\tau}$ and $\operatorname{erfc}(x)$ is the complementary error function. Equation (20) may also be obtained from Eq. (16) by taking the limit $\gamma\rightarrow 0$ or from Eq. (17) in the limit $\tau_c\rightarrow 0$. Figure 5 shows the behavior of Eqs. (16), (17), and (20) in order to illustrate the effect of γ and τ_c on the desorption process. In addition, it also is interesting to note from this figure that depending on the choice of the time dependence of the diffusion coefficient, which is related to the diffusive process presented by the system, different behaviors for $\sigma(t)$ may be obtained.

III. DISCUSSIONS AND CONCLUSIONS

We have analyzed the adsorption-desorption process of a system governed by a generalized diffusion equation which may be related to representative diffusion equations by a suitable choice of the diffusion coefficient. In addition, we also consider an unusual form the kinetic equation which depending on the choice of $\mathcal{K}(t)$ may aggregate memory effects of different kinds related to adsorption-desorption process. Another aspect of the results presented here is the constraint given by Eq. (3), which represents a number of components in the system. In particular, for this constraint

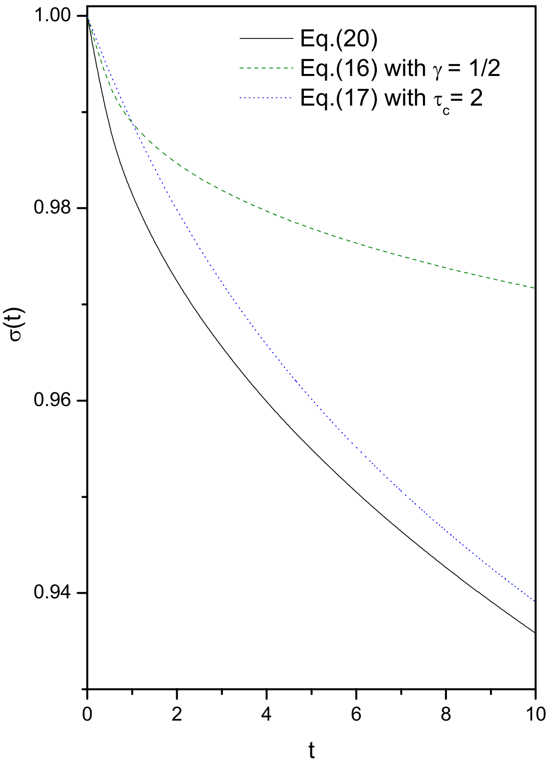

FIG. 5. (Color online) Behavior of $\sigma(t)$ versus t for a typical value of γ and τ_c in order to illustrate the effect of different time dependences on the diffusion coefficient. We consider, for simplicity, $\tau=10$, $\kappa=5$, $\mathcal{D}=1$, and the initial condition $\rho(z,0)=\delta(z-1)$. Note that in both cases when have a different behavior from the usual one for $\sigma(t)$.

we admit a time dependence in order to cover others processes in which the number of components of the system may change, as previously discussed. In order to show how the adsorption-desorption process may change by incorporating the extensions investigated here two representative cases were worked out. The first one consists in considering the system initially in the bulk and the surface without particles. In this context, we investigate the effect produced by a diffusion coefficient in the form $\mathcal{D}(t)=\mathcal{D}t^{\gamma-2}/\Gamma(\gamma-2)$ and $\mathcal{D}(t)=\mathcal{D}e^{t/\tau_c}/\tau_c$. The power law time dependence for the diffusion coefficient enable us to relate Eq. (1) with the time fractional diffusion equation and the exponential dependence for the diffusion coefficient leads us to obtain the Cattaneo equation from Eq. (1). The results obtained for these cases, when compared to the ones obtained for the usual diffusion equation, show differences which are connected to the subdiffusive regime of the diffusion process or by the presence of a finite phase velocity. The second situation is characterized by the particles on the surface and the bulk without particles. This case is typically governed by desorption process which exhibits, for the situations worked out, a different behavior from the usual one. These feature indicate that the diffusion process of the system and, consequently, the spreading of the system, plays an important role on the adsorption-desorption process present at the surface $z=0$. Other choices for the diffusion coefficient $\mathcal{D}(t)$ may imply different behaviors for the $\sigma(t)$. Indeed, they are related to the diffusion equation which governs the diffusive process of the system. Finally, we hope that the results presented here may be useful to investigate the adsorption-desorption process when the anomalous diffusion is present.

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