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Bulk-mediated surface diffusion: return probability in an infinite system

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Abstract

We analyse the dynamics of adsorbed molecules within the *bulk-mediated surface diffusion* framework. We consider that the particle's desorption mechanism is characterized by a non-Markovian process, while the particle's motion in the bulk is governed by Markovian dynamics, and also include the effect of a Markovian absorption probability on the surface. We study this system for the diffusion of particles in a semi-infinite lattice, analysing the return probability to the reference absorptive plane as well as the mean return time to such a surface. Comparisons with numerical simulations show an excellent agreement.

1. Introduction

Among the many problems studied in material science, the dynamics of adsorbed molecules at an adsorbing surface is a fundamental issue in interface science and is crucial to a number of emerging technologies [1] (for instance, see [2–6] and references therein). Recently, the mechanism called *bulk-mediated surface diffusion* has been identified and explored [7, 8]. The importance of bulk–surface exchange in relaxing homogeneous surface density perturbations is experimentally well established [9–15]). This mechanism typically arises at interfaces separating a liquid bulk phase and a second phase which may be either solid, liquid, or gaseous. Whenever the adsorbed species is soluble in the liquid bulk, adsorption–desorption processes occur continuously, generating a surface displacement because desorbed molecules undergo Fickian diffusion in the liquid's bulk, and are later re-adsorbed elsewhere. When this process is repeated many times, an effective diffusion results for the molecules on the surface.

Usually the studies performed in this type of system are done within the framework of a master equation scheme [7, 8, 16], where the particle's motion through the bulk and the

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adsorption–desorption processes are Markovian. In a series of recent papers we have shown some of the most important features of this phenomenon (however, it must be stressed that this study corresponds to the low particle density limit) [2–6]. In particular, by studying the variance $\langle r^2(t)\rangle_{\text{plane}}$ of the position $\vec{r} \equiv (x, y)$ on the interface, or the conditional probability $P(z = 1; t) \equiv \sum_{x,y} P(x, y, z = 1; t|0, 0, 1; t = 0)$ to find the particle on the interface at time t, if it was initially at $(0, 0, 1)$, through both analytical and numerical methods, the following results were obtained. For the case of a semi-infinite or unbounded bulk [2]

- for $t \to \infty$, the effective diffusion on the interface (first layer of the lattice) is always *sub-diffusive* (the variance of the position grows as $t^{1/2}$) *regardless* of the desorption rate δ. Similarly, the probability of finding the particle on the interface at time t decays as $t^{-1/2}$, independently of δ;
- at *finite* times, the growth of the variance can be fitted by a t^{ϵ} law. The exponent ϵ depends on the range of time considered and the values of the adsorption and diffusion constants, increasing rapidly as δ decreases and saturating at a value compatible with the one reported in [7, 8].

For the finite or bounded bulk case [3], we have investigated the transition from the multilayered to unbounded bulk regime, and found that

- there exists an optimal number of layers that maximizes $\langle r^2(t)\rangle_{\text{plane}}$ on the interface (which is a measure of the effective diffusivity), and up to about that thickness, the long-time effective diffusivity on the interface has *normal* character, and crosses over abruptly towards a sub-diffusive behaviour as the number of layers increases further.

It is worth remarking here that for an arbitrary (finite) number of layers, due to the highly complicated dependence of the functions on s, the Laplace transform usually cannot be analytically inverted. This forced us to apply numerical inversion methods whose efficacy has been tested—with excellent results—not only against analytically solvable cases, like the bilayer one, but also against Monte Carlo simulations.

For the finite and infinite bulk cases, we have also investigated the situation when the particle's desorption is characterized by a non-Markovian process, while the particle's adsorption and its motion in the bulk are governed by a Markovian dynamics. We have also analysed the effect of a biased behaviour for the motion along the vertical axis, that is, the effect of some external field normal to the interface. We have found that [4–6]

- for any non-Markovian desorption waiting time density with a **finite first moment**, the long-time behaviour of both $\langle r^2(t)\rangle_{\text{plane}}$ and $P(z = 1, t)$ is the same as in the Markovian case and only depends on the first moment of the waiting time function $\psi(t)$;
- it was analytically shown that, when the waiting time density for desorption has an *infinite* first moment, an asymptotic **sub-diffusive** regime appears for all values of ν (a parameter that characterizes the behaviour of the 'tail' of $\psi(t)$, $0 < \nu < 1$), except for $\nu = \frac{1}{2}$, where **normal diffusion** takes place;
- the asymptotic behaviour under the presence of an external bias was obtained in two cases: a desorption waiting time density with a **finite** or an **infinite first moment**. Asymptotic **sub-diffusive** regimes, or cases where **normal diffusion** takes place, have been observed. However, from our analysis we have not obtained any kind of super-diffusive behaviour.

In this work we address the dynamics of adsorbed molecules when, in addition to the particle's desorption mechanism being characterized by a non-Markovian process (while the particle's motion in the bulk is governed by a Markovian dynamics), there is a biased behaviour

for the motion along the vertical axis (that is, we consider the effect of some external field normal to the interface) and we consider the effect of an **absorption probability**. This is probably the most simple way to take account of the interaction with the surface leading to adsorption within the master equation framework. Diffusion in the presence of a biasing field is of great interest in several areas such as positron tomography [17], where the addition of a strong electric field perpendicular to the surface leads to greater sample penetration, the analysis of wetting layer growth under the action of a uniform gravitational field [18], particle segregation due to shaking in a gravitational field [19], and the steady-state regime due to a small field in two-dimensional diffusing reactants [20]. It is well known that a non-Markovian desorption process can occur when the surfaces contains 'deep traps', for capture and re-emission from surfaces that contain sites with several internal states such as the 'ladder trapping model', in proteins with active sites deep inside the matrix, etc [21, 22].

It is worth remarking that, when non-Markovian processes are present, it is necessary to resort to *generalized master equations*. These equations are characterized by a 'memory kernel' and may be related univocally with a continuous time random walk scheme (for instance, see the paper by Montroll in [23]). In addition, the absorption probability is, in general, different from the diffusive constant in the bulk, and takes into account the interaction between the particle and the surface.

The main goal of the present work is to study the influence of such an absorption probability—in addition to the non-Markovian desorption and together with the indicated biased dynamics—on the return probability to the interface $z = 1$ as well as the mean return time. The *first passage time density* (FPTD) and the related *first return time density* (FRTD) are examples of properties that were first analysed by Polya within the context of a lattice random walk [24]. Recently, various generalizations of the original *Polya problem* have been solved in a large number of areas of statistical physics [25], including diffusion in local and global fluctuating systems [22, 26–30], optimal search strategies [31], and many others.

Here, we present an evaluation of the FRTD to the original ($z = 1$) plane. For that purpose we calculate the temporal evolution of $P(z = 1, t)$, which (as indicated above) is the conditional probability of finding the particle on the surface at time t since the particle was there at $t = 0$. However, we reduce the previously exploited set of master equations governing the behaviour of $P(z = 1, t)$ (that is, the probability of finding the particle on the interface at time t, if it was initially at $z = 1$ at time $t = 0$), eliminating the detailed information about the diffusion on each plane.

In the next section we formally present the model, in terms of a generalized master equation which describes the particle's dynamics through the bulk and surface, and its desorption. We indicate the differences that are introduced into the formalism respect to the previous studies. In the following section we discuss the obtention of the return probability and mean return time as well as some asymptotic results. After that, we present some numerical results for the return probability and the conditional probability of finding the particle on the surface, and its comparison with numerical simulations. Finally, in the last section we discuss the results and present some conclusions.

2. The adsorption–desorption model

2.1. Generalized master equation

We consider our model for the case of biased behaviour, non-Markovian desorption, and a given Markovian adsorption probability. We use the same framework as in [4–6], writing for $P(n, m, z = 1; t|0, 0, 1; t = 0)$; the probability of finding the particle on the interface at time t

if it was initially at (0, 0, 1), that we indicate by $P(n, m, 1; t)$; the following generalized master equation

$$\begin{aligned}
\dot{P}(n,m,1;t) &= \delta_1 P(n,m,2;t) - \int_0^t \mathrm{d}t'\, K(t')P(n,m,1;t-t'),\\
&\quad + \alpha_1[P(n-1,m,1;t) + P(n+1,m,1;t) - 2P(n,m,1;t)]\\
&\quad + \beta_1[P(n,m-1,1;t) + P(n,m+1,1;t) - 2P(n,m,1;t)], \qquad \text{for } l = 1\\
\dot{P}(n,m,2;t) &= \int_0^t \mathrm{d}t'\, K(t')P(n,m,1;t-t')\\
&\quad + \gamma_1 P(n,m,3;t) - \gamma_2 P(n,m,2;t) - \delta_1 P(n,m,2;t)\\
&\quad + \alpha[P(n-1,m,2;t) + P(n+1,m,2;t) - 2P(n,m,2;t)]\\
&\quad + \beta[P(n,m-1,2;t) + P(n,m+1,2;t) - 2P(n,m,2;t)], \qquad \text{for } l = 2\\
\dot{P}(n,m,l;t) &= \alpha[P(n-1,m,l;t) + P(n+1,m,l;t) - 2P(n,m,l;t)]\\
&\quad + \beta[P(n,m-1,l;t) + P(n,m+1,l;t) - 2P(n,m,l;t)]\\
&\quad + \gamma_1[P(n,m,l+1;t) - P(n,m,l;t)]\\
&\quad + \gamma_2[P(n,m,l-1;t) - P(n,m,l;t)], \qquad \text{for } l \geqslant 3
\end{aligned} \tag{1}$$

where α and β are the transition probabilities per unit time through the bulk in the x, y directions respectively; δ_1 is the transition probability from any site on plane $z = 2$ to the plane $z = 1$ (in other words, the *'adsorption' probability*); while γ_1 and γ_2 are the transition probabilities, per unit time, from any point of the planes $z = l + 1$ (with $l = 2, 3, \ldots$) to the plane $z = l$, and from plane $z = l$ (with $l = 2, 3, \ldots$) to the plane $z = l + 1$, respectively. The case $\gamma_1 \neq \gamma_2$ indicates a biased behaviour, that is, the presence of an external field.

It is important to note that the model presented in equation (1) allows for the possibility that the particles can move in the plane $z = 1$ with temporal frequencies α_1 in the x-direction and β_1 in the y-direction. If these temporal frequencies are equal to zero, the motion through the $z = 1$ plane is exclusively due to the dynamics across the bulk. $K(t)$ represents the memory kernel for desorption at all sites over the $z = 1$ surface (that is for $(n, m, l = 1)$). It is clear that, when $\delta_1 = \gamma_1 = \gamma_2 = \gamma$ (and $\alpha_1 = \beta_1 = 0$), we recover the same set of equations used in [4–6]. Also, if in addition we have that $K(t) \to \theta\, \delta(t)$, where $\delta(t)$ is the Dirac delta function, the system of Markovian equations used in [2, 3] is recovered.

Taking the Fourier transform with respect to the x and y variables and the Laplace transform with respect to the time t in the above equations, we obtain

$$\begin{aligned}
sG(k_x,k_y,1;s) - P(k_x,k_y,1,t=0) &= \delta_1 G(k_x,k_y,2;s) + A_1(k_x,k_y)G(k_x,k_y,1;s)\\
&\quad - K(s)G(k_x,k_y,1;s), \qquad \text{for } l = 1\\
sG(k_x,k_y,2;s) - P(k_x,k_y,2,t=0) &= A(k_x,k_y)G(k_x,k_y,2;s) + K(s)G(k_x,k_y,1;s)\\
&\quad - \delta_1 G(k_x,k_y,2;s) + \gamma_1 G(k_x,k_y,3;s) - \gamma_2 G(k_x,k_y,2;s), \qquad \text{for } l = 2\\
sG(k_x,k_y,l;s) - P(k_x,k_y,l,t=0) &= A(k_x,k_y)G(k_x,k_y,l;s) + \gamma_1[G(k_x,k_y,l+1;s)\\
&\quad - G(k_x,k_y,l;s)] + \gamma_2[G(k_x,k_y,l-1;s) - G(k_x,k_y,l;s)], \qquad \text{for } l \geqslant 3.
\end{aligned} \tag{2}$$

Here we have used the same definitions as in [2–5], and also

$$\begin{aligned}
A(k_x,k_y) &= 2\alpha[\cos(k_x) - 1] + 2\beta[\cos(k_y) - 1],\\
A_1(k_x,k_y) &= 2\alpha_1[\cos(k_x) - 1] + 2\beta_1[\cos(k_y) - 1].
\end{aligned}$$

Clearly, the above equations for $G(k_x, k_y, l; s)]$ are similar to equation (2) in [3], with $K(s)$ instead of δ, the adsorption probability δ_1, and the unbiased γ replaced by γ_1 and γ_2. Therefore all results obtained in [2, 3] remain valid for a non-Markovian dynamics when δ is replaced by $K(s)$, and the bias and the desorption probability are adequately included.

As our aim is to obtain information about the return probability to the plane $z = 1$, we evaluate equations (2) at $k_x = k_y = 0$, or equivalently we sum over all sites of each z plane. Hence we reduce the indicated system to

$$\begin{aligned}
&sG(0,0,1;s) - P(0,0,1,t=0) = \delta_1 G(0,0,2;s) - K(s)G(0,0,1;s), \qquad \text{for } l = 1\\
&sG(0,0,2;s) - P(0,0,2,t=0) = K(s)G(0,0,1;s) - \delta_1 G(0,0,2;s)\\
&\qquad + \gamma_1 G(0,0,3;s) - \gamma_2 G(0,0,2;s), \qquad \text{for } l = 2\\
&sG(0,0,l;s) - P(0,0,l,t=0) = \gamma_1[G(0,0,l+1;s) - G(0,0,l;s)]\\
&\qquad + \gamma_2[G(0,0,l-1;s) - G(0,0,l;s)], \qquad \text{for } l \geqslant 3
\end{aligned} \tag{3}$$

were we used that $A(0,0) = A_1(0,0) = 0$.

Through the previous equations, we can now define $P(z = j, t)$, the probability of being on the plane $z = j$ at time t, due to the fact that at $z = 1$ plane at time $t = 0$. However, we can do more. With a slight change in the equations, we can generalize and work with $P(z = l; t|l_o; t = 0)$, the probability of finding the particle at a point on $z = 1$ at time t, if it was initially at $z = l_o$ at time $t = 0$, $\hat{P}(z = 1, s|l_o; t = 0)$ being its Laplace transform. Hence, the equations governing this probability are

$$\begin{aligned}
&s\hat{P}(z=1,s|l_o;t=0) - P(z=l_o,t=0) = \delta_1\, \hat{P}(z=2,s|l_o;t=0)\\
&\qquad - K(s)\hat{P}(z=1,s|l_o;t=0), \qquad \text{for } l = 1\\
&s\hat{P}(z=2,s|l_o;t=0) - P(z=l_o,t=0) = K(s)\hat{P}(z=1,s|l_o;t=0)\\
&\qquad - \delta_1\hat{P}(z=2,s|l_o;t=0) + \gamma_1\hat{P}(z=3,s|l_o;t=0)\\
&\qquad - \gamma_2\hat{P}(z=2,s|l_o;t=0), \qquad \text{for } l = 2\\
&s\hat{P}(z=l,s|l_o;t=0) - P(z=l_o,t=0) = \gamma_1[\hat{P}(z=l+1,s|l_o;t=0)\\
&\qquad - \hat{P}(z=l,s|l_o;t=0)] + \gamma_2[\hat{P}(z=l-1,s|l_o;t=0)\\
&\qquad - \hat{P}(z=l,s|l_o;t=0)] \qquad \text{for } l \geqslant 3.
\end{aligned} \tag{4}$$

As in our previous works, we can solve this set of equations by reiteratively using Dyson's formula.

2.2. Return probability and return time

As indicated in section 1, we are interested in the problem of return to the reference plane ($z = 1$). In order to study such a problem, we define $f_{\text{ret}}(t)$, the return probability to the $z = 1$ plane *for the first time* within the interval $(t, t + \mathrm{d}t)$, as the walker started on the reference plane $z = 1$ at $t = 0$. Similarly to what has been done in [2], we write $f_{\text{ret}}(t)$ as the convolution of two functions

$$f_{\text{ret}}(t) = \int_0^t \psi(t')\, f_{2\to 1}(t - t')\, \mathrm{d}t', \tag{5}$$

where $f_{2\to 1}(t)\,\mathrm{d}t$ is the probability of arrival *for the first time* at the plane $z = 1$ between $(t, t + \mathrm{d}t)$, due to the fact that the walker was at the plane $z = 2$ at $t = 0$; and $\psi(t)$ is the probability of jumping from plane $z = 1$ to plane $z = 2$ (in our case, for both Markovian and non-Markovian situations, it is the desorption probability).

Exploiting Siegert's formula [25, 32] we obtain

$$f_{2\to 1}(s) = \frac{\hat{P}(z=1,s|z=2;t=0)}{\hat{P}(z=1,s|z=1;t=0)}. \tag{6}$$

Let us remark that, as was indicated before, $\hat{P}(z=1,s|z=2;t=0)$ could be obtained through a reiterative application of Dyson's formula. The result for $f_{2\to 1}(s)$ is

$$f_{2\to 1}(s) = \frac{2\,\delta_1}{2\,\delta_1 - \gamma_1 + \gamma_2 + s + \left[(\gamma_1+\gamma_2+s)^2 - 4\,\gamma_1\gamma_2\right]^{\frac{1}{2}}}. \tag{7}$$

Let us remember that δ_1 is the transition probability from any site on plane $z=2$ to the plane $z=1$, or the *'adsorption' probability*, while γ_1 and γ_2 are the transition probabilities, per unit time, from any point of the plane $z=l+1$ (with $l=2,3,\ldots$) to the plane $z=l$, and from plane $z=l$ (with $l=2,3,\ldots$) to the plane $z=l+1$, respectively.

The mean return time to the $z=1$ plane, $\langle t\rangle_{\rm frt}$, is the sum of two contributions. The first one is the desorption time, that results from $\psi(t)$:

$$\langle t\rangle_{\rm des} = \int_o^\infty t\,\psi(t)\,{\rm d}t, \tag{8}$$

while the second, which is given by

$$\langle t\rangle_{2\to 1} = \frac{\gamma_1}{\delta_1(\gamma_1-\gamma_2)}, \tag{9}$$

corresponds to the mean time to jump from the plane $z=2$ to the plane $z=1$.

2.3. Asymptotic results

Here we show the results of asymptotic long-time system behaviour that, as is usual, are obtained by resorting to Tauberian theorems [32]. Such results are obtained for two cases: when the waiting time function has a short-time or a long-time tail. We assume that, when $s\ll 1$, $\psi(s)\sim 1-Bs^\nu$ with $0<\nu<1$ for the case of a *long tail*, and $\nu=1$ for the *short tail* case. In the case of short-tail waiting time densities we have $B=\langle t\rangle_{\rm des}$. Consequently, in this limit $K(s)\sim \frac{1}{B}s^{1-\nu}$. In this expression we can obtain the asymptotic behaviour for the density probability of finding the walker on the reference plane. This can be achieved by means of Siegert's formula when both the initial and the final planes are the same:

$$f_{\rm ret}(s) = 1 - \frac{1-\psi(s)}{s}\,\frac{1}{\hat{P}(z=1,s|z=1;t=0)}. \tag{10}$$

We can also compute the average number of times that the particle returns to the $z=1$ reference plane. In order to obtain such an average we start by considering the probability that the particle returns exactly n times to the reference plane at time t. In Laplace space this is given by

$$\Omega_n(s) = (f_{\rm ret}(s))^n\left(\frac{1-f_{\rm ret}(s)}{s}\right). \tag{11}$$

Hence, also in Laplace space, the average number of returns to the reference plane is given by

$$\langle n(s)\rangle = \frac{1}{s}\left(\frac{f_{\rm ret}(s)}{1-f_{\rm ret}(s)}\right). \tag{12}$$

Considering the different possibilities we have two cases: (i) $\boldsymbol{\gamma_1 > \gamma_2}$; and (ii) $\boldsymbol{\gamma_1 = \gamma_2 = \gamma}$.

2.3.1. Short tail

- $\boldsymbol{\gamma_1 > \gamma_2}$

$$P(z=1,t|z=1;t=0) \to \left\{1+\frac{\gamma_1}{B\delta_1\,(\gamma_1-\gamma_2)}\right\}^{-1} \tag{13}$$

$$\langle n(t)\rangle \to \left(B+\frac{\gamma_1}{\delta_1\,(\gamma_1-\gamma_2)}\right)^{-1} t; \tag{14}$$

- $\boldsymbol{\gamma_1 = \gamma_2 = \gamma}$

$$P(z=1,t|z=1;t=0) \to \frac{B\,\delta_1}{\sqrt{\pi\,\gamma}}\,t^{-\frac{1}{2}}, \tag{15}$$

$$\langle n(t)\rangle \to \frac{\delta_1}{\sqrt{\pi\,\gamma}}\,t^{\frac{1}{2}}. \tag{16}$$

The above results are the expected ones for a short-tail case. Clearly, for $\gamma_1 < \gamma_2$, $\hat{P}(z = 1, t|z = 1; t = 0)$ decays to zero (exponentially), while for $\gamma_1 = \gamma_2$ it also decays, but much slower (potentially).

2.3.2. Long tail

- $\boldsymbol{\gamma_1 > \gamma_2}$

$$P(z=1,t|z=1;t=0) \to 1, \tag{17}$$

$$\langle n(t)\rangle \to \frac{\delta_1}{B\,\Gamma(\nu+1)}\,t^{\nu}. \tag{18}$$

- $\boldsymbol{\gamma_1 = \gamma_2 = \gamma}$
  Here we have different asymptotic behaviours depending on the range of values of ν.

$$P(z=1,t|z=1;t=0) \to \begin{cases} 1 & 0<\nu<\frac{1}{2} \\ \dfrac{B\delta_1}{(B\delta_1+\sqrt{\gamma})}, & \nu=\frac{1}{2} \\ \dfrac{B\delta_1}{\sqrt{\gamma}\,\Gamma(\frac{3}{2}-\nu)}t^{\frac{1}{2}-\nu}, & \frac{1}{2}<\nu<1, \end{cases} \tag{19}$$

$$\langle n(t)\rangle \to \begin{cases} \dfrac{\delta_1}{B\,\Gamma(\nu+1)}\,t^{\nu}, & 0<\nu<\frac{1}{2} \\ \dfrac{1}{(B\delta_1+\sqrt{\gamma})\,\sqrt{\pi}}\,t^{\frac{1}{2}}, & \nu=\frac{1}{2} \\ \dfrac{\delta_1}{\sqrt{\gamma\,\pi}}\,t^{\frac{1}{2}}, & \frac{1}{2}<\nu<1. \end{cases} \tag{20}$$

In general, we observe the same time dependence for $P(z = 1, t|z = 1; t = 0)$ as in [6], but with different coefficients and, if $\delta_1 = \gamma_1$, we recover the previous results. However, if for any reason we need to describe the adsorption phenomenon by a non-Markovian process, it is clear that we should expect changes in the time dependence.

3. Results

In this section we show the results obtained making both the Laplace transform of the previously indicated expressions for $f_{\rm ret}(s)$ and $\hat{P}(z = 1, s|z = l_0; t = 0)$, as well as Monte Carlo simulations. As was discussed in previous works [2–6], for a general case, the Laplace

transform of the relevant quantities usually cannot be analytically inverted. This occurs for $f_{\rm ret}(s)$ and $\hat{P}(z=1,s|z=l_0;t=0)$ in the present case; hence we have been forced to employ a numerical inversion method [33]. The efficacy of such a method was established in [2–6], where it was shown that it is a reliable tool and that we can trust the results in those cases where analytical results are not accessible.

3.1. Desorption dynamics

In order to describe the desorption dynamics from the surface, as in [6], we have used two families of waiting time densities ($\psi(t)$). The first one has been extensively exploited in modelling non-Markovian situations (see also [32]). The reasons for its wide use are its versatile functional form and its simplicity that allows one to take into account a spread of transition rates in a controllable way [34]. When only one transition rate is present a Markovian description is reobtained: the memory kernel becomes a Dirac δ-function. The form is

$$\psi(t) = \theta a \frac{(\theta a t)^{(a-1)}}{\Gamma(a)} {\rm e}^{-\theta a t}, \tag{21}$$

where a is a positive integer and $\Gamma(a)$ is the *gamma* or *factorial function*. It is worth remarking here on two important facts about this family of functions. First, as can be seen from equation (21), there are two parameters which characterize the function. The parameter a, called the *Markovianicity parameter*, defines the departure from the Markovian behaviour or degree of non-Markovianicity of the function ($a = 1$ corresponds to the Markovian case while $a \neq 1$ corresponds to the non-Markovian one), while the parameter θ is the 'average desorption rate'. Second, as shown in [35], the mean value of these waiting time densities is

$$\langle t \rangle = \int_0^\infty t\psi(t)\,{\rm d}t = \theta^{-1}, \tag{22}$$

that is the 'average desorption time' does not depend on the a parameter, but is only function of the desorption rate. For the form of this family of functions, see figure 1 in [35].

In order to analyse the long-time tail case, we used a second family of desorption waiting time density functions that, defined in the Laplace domain [36], has the form

$$\psi(s) = \frac{1}{1+(\frac{s}{\phi})^\nu}, \qquad 0 < \nu < 1. \tag{23}$$

However, as ϕ amounts to only a change in the time scale, we adopted $\phi = 1$. We have also fixed the parameters α, β, and γ_1, all equal to one.

3.2. Numerical transformation and simulation results

Figures 1 and 2 show the time dependence of $f_{\rm ret}(t)$ for several cases with the short-time tail distribution indicated in equation (21). In figure 1 we have the comparison between the results of Monte Carlo simulations against the numerical Laplace inversion [33] of $f_{\rm ret}(s)$, with the same good agreement we have found in previous works [2–6]. The theoretical results are only for non-Markovian desorption ($a \neq 1$) and the adsorption probability is different from the bias. In all cases we have averaged over 10^6 realizations.

In figure 2 we have shown the time dependence of $f_{\rm ret}(t)$ for different situations. Here we have cases where the bias in the bulk is larger or smaller than the bias for adsorption. However, there is only a small difference between the different situations.

In both figures a transient oscillatory behaviour is apparent. The origin of such oscillations has been explained in [5] and also arose in [6], and has been shown to be related with θ, the desorption rate. It was indicated that the oscillations only appear in the non-Markovian case

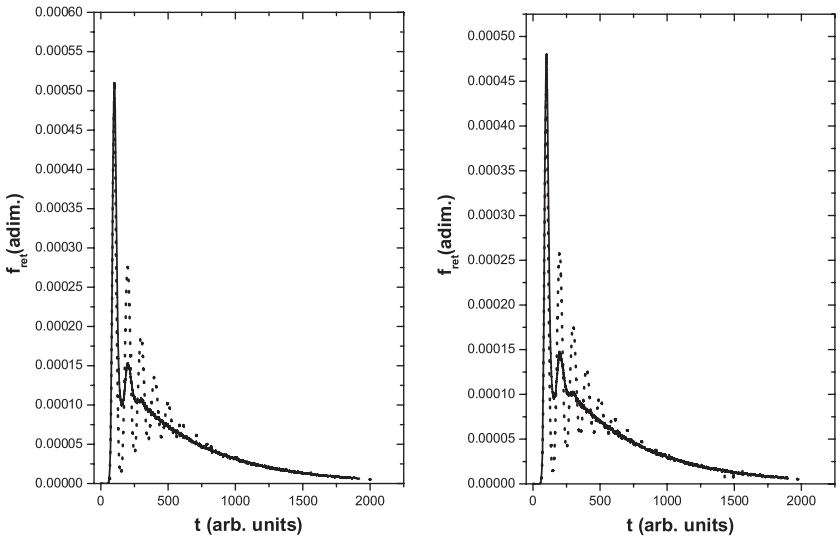

Figure 1. Temporal evolution of $f_{\rm ret}(t)$, the return probability distribution to the plane $z = 1$, for the case of a short-tail distribution. Here we have adopted $\alpha = \beta = 1$, $\theta = 0.01$, $a = 50$, $\delta_1 = 3$ and $\gamma_1 = 1$. In the left panel we have the case $\gamma_2 = 0.3333$, while in the right panel $\gamma_2 = 1.222\,22$. The continuous line corresponds to simulations, while the dotted line corresponds to numerical Laplace transformation of the theoretical one.

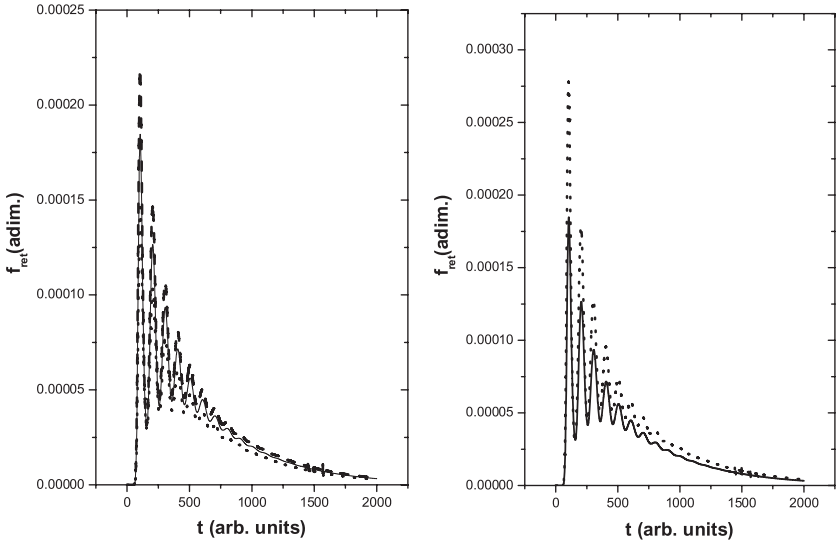

Figure 2. Theoretical temporal evolution of $f_{\rm ret}(t)$, the return probability distribution to the plane $z = 1$, for the case of a short-tail distribution. Here we have adopted $\alpha = \beta = 1$, $\theta = 0.01$, $a = 50$, $\gamma_1 = 1$. In the left panel we have $\gamma_2 = 0.428\,57$; the dashed line corresponds to $\delta_1 = 3.857\,13$, the continuous one to $\delta_1 = 1$, and the dotted to $\delta_1 = 0.285\,71$. In the right panel the dotted line corresponds to $\gamma_2 = 0.428\,57$ and $\delta_1 = 5.666\,66$, and the continuous line to $\gamma_2 = 3.2222$ and $\delta_1 = 2.6363$.

and are due to the particular behaviour of the family of waiting time densities defined above. When the Markovianicity parameter tends to infinity, $a \gg 1$, it is well known that $\psi(t)$ tends

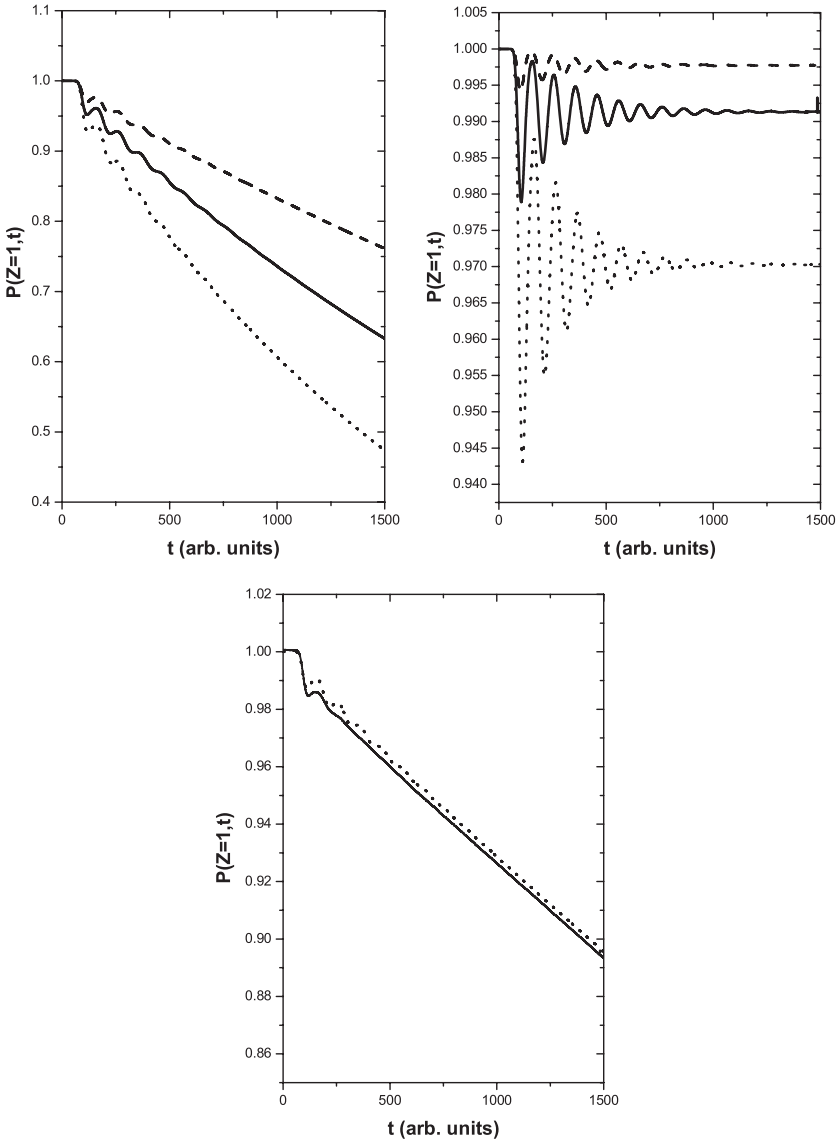

Figure 3. Theoretical temporal evolution of $P(z = 1, t)$, the probability distribution of finding the particle on the plane $z = 1$, for the case of a short-tail distribution. Here we have adopted $\alpha = \beta = 1$, $\theta = 0.01$, $a = 50$ and $\gamma_1 = 1$. On the top left panel $\gamma_2 = 1.222\,22$. The dashed line corresponds to $\delta_1 = 1.833$, the continuous one to $\delta_1 = 1$, and the dotted one to $\delta_1 = 0.5238$. On the top right panel $\gamma_2 = 0.428\,57$. The dashed line corresponds to $\delta_1 = 3.857\,13$, the continuous one to $\delta_1 = 1$, and the dotted one to $\delta_1 = 0.285\,71$. For the lower panel we have $\delta_1 = 4.888\,88$. The dotted line corresponds to the numerical Laplace transform, while the continuous one is the numerical simulation.

towards a Dirac δ function: $\psi(t) \to \delta(t - \theta^{-1})$. This fact implies a kind of 'periodicity', as, on average, there is a desorption after each elapsed $\Delta t \simeq \theta^{-1}$ period.

In figure 3 we depict several different situations for the behaviour of $P(z = 1, t)$. In the lower panel the good agreement between the numerical Laplace transform and Monte Carlo

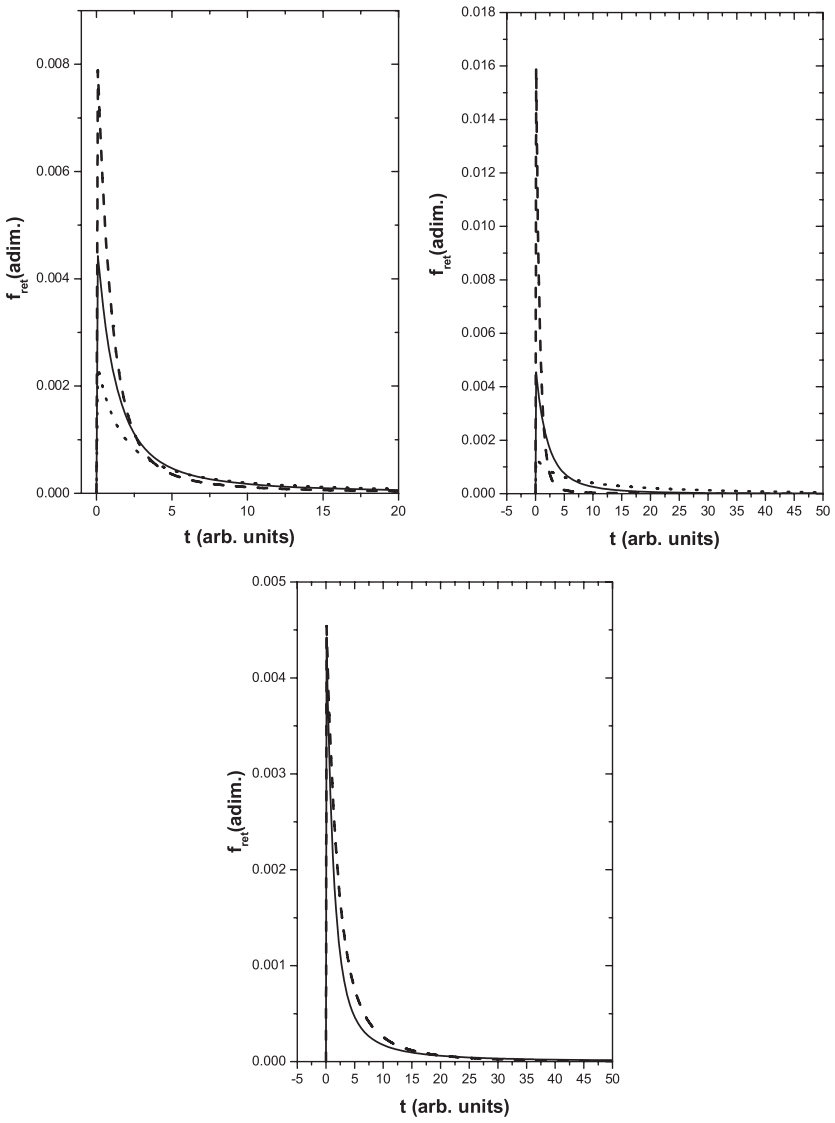

Figure 4. Theoretical temporal evolution of $f_{\mathrm{ret}}(t)$, the return probability distribution to the plane $z = 1$, for the case of a long-tail distribution. Here we have adopted $\alpha = \beta = 1$, $\theta = 0.01$, $\nu = 0.9$ and $\gamma_1 = 1$. In the left top panel we have $\gamma_2 = 1.222\,22$. The dashed line corresponds to $\delta_1 = 1.833\,33$, the continuous one to $\delta_1 = 1$, and the dotted one to $\delta_1 = 0.5238$. For the top right panel we have $\gamma_2 = 0.428\,57$. The dashed line corresponds to $\delta_1 = 3.857\,13$, the continuous one to $\delta_1 = 1$, and the dotted one to $\delta_1 = 0.285\,71$. In the lower panel, the dashed line corresponds to $\gamma_2 = 2.428\,57$ and $\delta_1 = 5.666\,66$, while the continuous one corresponds to $\gamma_2 = 3.2222$ and $\delta_1 = 2.6363$.

simulations is again apparent. In the upper panels we see the differences between the different cases (with lower or larger bulk bias than the adsorption one). It is clear that those cases show the possibility of detecting the differences between them.

Figures 4 and 5 show the cases of long-time tails, as given in equation (23). In these cases it is not possible to compare with simulations. However, due to the good agreement

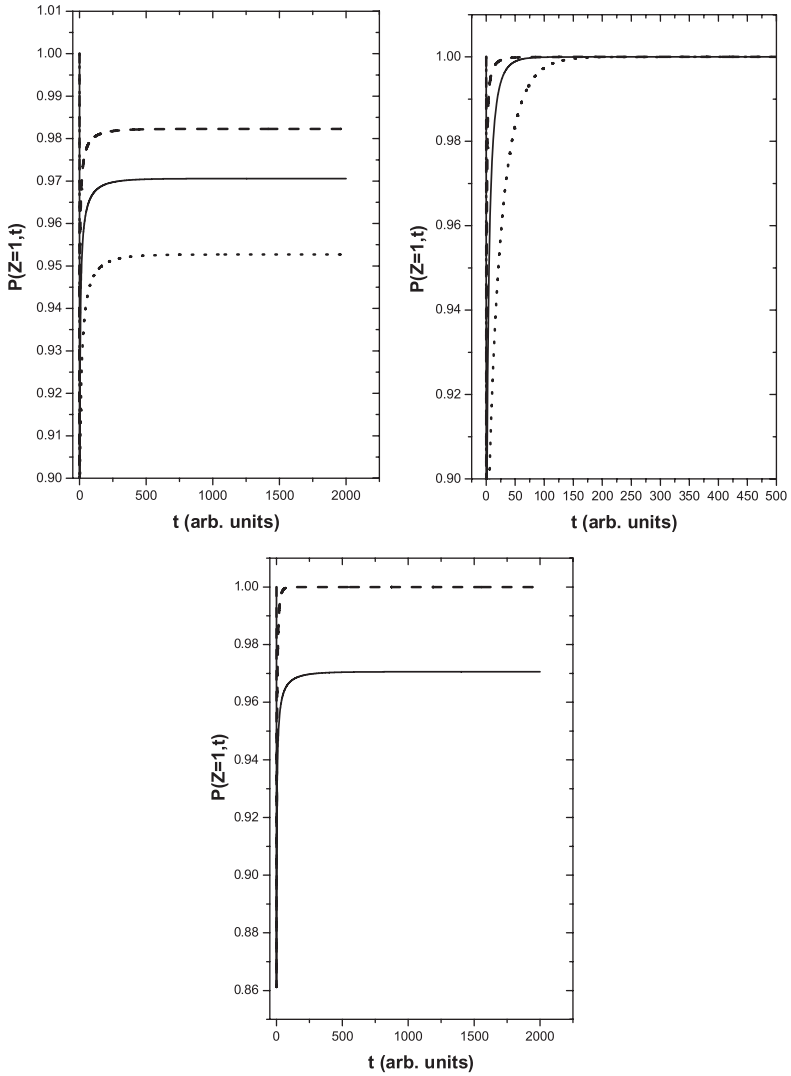

Figure 5. Theoretical temporal evolution of $P(z = 1, t)$, the probability distribution of finding the particle on the plane $z = 1$, for the case of a long-tail distribution. Here we have adopted $\alpha = \beta = 1$, $\theta = 0.01$, $\nu = 0.9$ and $\gamma_1 = 1$. In the top left panel we have $\gamma_2 = 1.222\,22$. The dashed line corresponds to $\delta_1 = 1.833$, the continuous one to $\delta_1 = 1$, and the dotted one to $\delta_1 = 0.5238$. In the top right panel we have $\gamma_2 = 0.428\,57$. The dashed line corresponds to $\delta_1 = 3.857\,13$, the continuous one to $\delta_1 = 1$, and the dotted one to $\delta_1 = 0.285\,71$. In the lower panel we have that the dashed line corresponds to the case $\gamma_2 = 2.428\,57$ and $\delta_1 = 5.666\,666$, while the continuous one corresponds to $\gamma_2 = 3.222\,222$ and $\delta_1 = 2.6363$.

found before, and as indicated previously, we can trust the numerical method for obtaining the Laplace transform. Again, for the case of $f_{\mathrm{ret}}(t)$ there are only small differences between the different cases, but in the case of $P(z = 1, t)$ (figure 5) there are possibilities of detecting differences due to the changes of the adsorption probability.

In addition to the previously indicated results, in all cases we have verified that the asymptotic behaviour for those quantities is fulfilled.

4. Conclusions

We have studied the evolution of particles making an effective diffusion on a surface. The diffusion is actually performed both on the surface and across the bulk surrounding the surface, resulting in the so-called *bulk-mediated surface diffusion* phenomenon. The relevant feature of this work was to present an analytical model for non-Markovian desorption from the surface also including the effect of an external (normal to the surface) field, through a biased behaviour in the normal direction. In addition we have considered the influence of a Markovian absorption probability. For the bulk that surrounds the surface we have considered that it is semi-infinite, the particles undergoing a Markovian motion there. The main goal of the present work was to study the influence of the indicated aspects on $f_{\rm ret}(t)$, the return probability to the interface $z = 1$, as well as $\langle t\rangle_{\rm frt}$, the mean return time.

We presented an evaluation of the *first passage time density* to the original ($z = 1$) plane through the evaluation of the temporal evolution of $P(z = 1, t)$, the conditional probability of finding the particle on the surface at time t since the particle was at $z = l_o$ at $t = 0$, as well as for $f_{\rm ret}(t)$, the return probability. In order to do such an evaluation we have reduced the previously exploited set of master equations eliminating the detailed information about the diffusion on each plane. Let us stress that, as is apparent from equations (8) and (9), the mean return time to the $z = 1$ plane is finite only if both the mean desorption time $\langle t\rangle_{\rm des}$ and the mean adsorption time $\langle t\rangle_{\rm ads}$ are finite. As for unbiased infinite systems the mean adsorption time is always infinite, no matter what the value of the adsorption probability δ_1 is, the results obtained by different theoretical models based on a finite waiting time between successive bulk excursions [7, 8] should be understood as stated in section 1 and in [2–6]. We also want to remark that the inclusion of a Markovian adsorption (characterized by δ_1) has the effect of changing (increasing or reducing) the percentage of particles that asymptotically remain at the plane $z = 1$. Such a percentage is determined by the competition between the desorption and the excursions in the bulk. A remarkable aspect is the oscillatory behaviour found for the case of short-time tail distribution.

It is worth remarking here on an important aspect of the present approach. Through the above results we have shown that the behaviour of $f_{\rm ret}(t)$ and of $P(z = 1, t)$ are strongly dependent on both the desorption mechanism and the effect of bias. As the effective dispersion and the percentage of particles that remain in $z = 1$ are measurable magnitudes [8], they may be used to investigate the characteristic and fundamental parameters of the desorption processes under the effect of a field.

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