Diffusion-mediated reactions with a time-dependent absorption rate

Miguel A. Ré* and Carlos E. Budde
Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5010 Córdoba, Argentina
(Received 28 July 1999)

Diffusion-mediated reactions models are particularly useful for the characterization of physical, chemical, and biological problems. In this paper we present a theoretical study of the absorption probability density, survival probability, and reaction rate for diffusion-mediated reactions models with a time-dependent finite absorption rate (an extension of a model usually referred to as the ''imperfect trap model''). The results are obtained by means of the formalism of continuous time random walk on a lattice and considering a general reaction dynamics upon encounter of the reactives. First jump probability densities are included to take initial conditions into account. Previous results presented by Collins and Kimball [J. Colloid. Sci. **4**, 425 (1949)] and Noyes [J. Chem. Phys. **22**, 1349 (1954)] are reobtained for the particular case of a time-independent absorptivity. Short and long time behaviors are analyzed resulting, in particular, in that the long time behavior of the absorption probability density exhibits the same time dependence as the first passage time density. The results obtained are illustrated by considering a one-dimensional model with consequent discussion.

PACS number(s): 05.40.−a, 05.60.−k, 82.20.Fd, 02.50.Ey

I. INTRODUCTION

The dynamics of diffusion-mediated reaction processes has been extensively studied for many years due to its relevance in the description of diverse phenomena in physics, chemistry, and biology [1–4]. A particularly interesting problem is the calculation of the probability density for the time at which a reaction $A+B\rightarrow C$ takes place when the displacement of species A or B (or both) is diffusive. Other related magnitudes such as time-dependent reaction rates or survival probabilities of the reactives can be derived from the mentioned probability distribution. Dielectric relaxation [5–7], capture of ligands after surface diffusion [8], proteins with active sites deep inside the protein matrix [9], and receptor mediated endocytosis for cholesterol homeostasis [10] are examples of the application of the diffusion-mediated reactions scheme.

The first calculation of chemical reaction rates from a model of diffusing particles in the presence of a trap was proposed by Smoluchowski [11]: a single absorbing sphere sorrounded by diffusing particles with an initial uniform concentration. The model assumes an immediate trapping (reaction) upon encounter of the reactives (an extremely short reaction time), a great dilution of one of the species (pseudounimolecular scheme) and normal diffusion with $D=D_A+D_B$, D_A and D_B being the diffusion constants of A and B, respectively [12]. Since the pioneering work of Smoluchowski, different extensions have been proposed to the original model to include diffusion in disordered media [7] or to give a better description of the short time behavior. Among these extensions we mention the dynamic or gated trapping model [13–15], where the reaction progress is modulated by another independent reaction $A\leftrightarrow A^*$ and the imperfect trap model [6,16,17] introducing a finite reaction time upon encounter of the reactives. In both cases of dynamic and imperfect trapping the reactives may also separate without reaction in each encounter. Smoluchowski's original model turns out to be the limit case of infinite absorptivity or unity probability of reaction of the imperfect trap model. In these extensions, as already mentioned in Ref. [14], the asymptotic long time behavior of reaction rates will not be altered, being determined by the first passage time density (FPTD) given by the diffusive model, as will be shown.

Two traditional treatments have been given to the imperfect trap model: one by Collins and Kimball [16] based on considerations of the concentration gradient; the other one by Noyes [17] based on the reactivity of an isolated pair. A comparison between both approaches and a discussion on their validity has been given by Razi Naqvi and co-workers [18,19].

In this paper the imperfect trap model is extended by including a general probability density for the reaction time that allows a better description of the specific reaction process. Examples of application are rotational diffusion in chemical reactions [20] or proteins with active sites deep inside the protein matrix [9]. The equivalence with previous work is obtained when an exponential reaction dynamics and normal diffusion is assumed. The main magnitude to be calculated here is the absorption probability density (APD): the probability density for the absorption (reaction) time of a particle starting at an arbitrary distance from the trap.

The calculation is made by means of the formalism of continuous time random walks (CTRW) on a lattice, considering the trap as a local inhomogeneity [13]. The proposed model is described in Sec. II, introducing a general reaction dynamics in the absence of diffusion. We also define here the ''equivalent problem'' as a CTRW in the absence of trapping; i.e., the usual CTRW scheme. Due attention is given to initial conditions by incorporating first jump probability densities. In Sec. III, the APD is calculated in terms of the FPTD for the equivalent problem. We note here that the FPTD is the APD for the perfect trap or Smoluchowski's model. From the APD, reaction rates and reactives' survival probabilities are derived and comparison is established with Collins and Kimball's and Noyes' results under appropriate

*Electronic mail address: re@roble.fis.uncor.edu

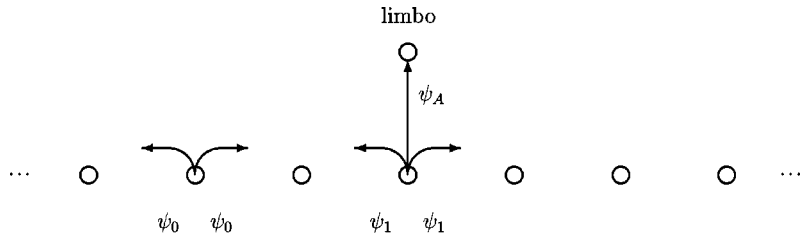

FIG. 1. Random walk on a one-dimensional lattice in the presence of a trap. The reaction is modeled by a jump of the walker into a ''limbo'' state, from where it cannot return. When the walker reaches trap position it can make a jump into the limbo with a probability $\psi_A(t)dt$ between t and $t+dt$ or it can escape to another lattice site with probability $\psi_1(t)dt$.

boundary conditions. The asymptotic behavior of the APD and the reaction rate in the short and long time limits are also considered. In the long time limit, in particular, it is shown that the APD and the FPTD exhibit the same time dependence. Finally in Sec. IV, the results obtained from this proposal are illustrated by considering a simple one-dimensional system, exhibiting the main characteristics predicted.

II. MODEL DESCRIPTION

Let us consider an infinite lattice, a one-dimensional version of which is shown in Fig. 1. Each position in the lattice will be identified by an integer vector $\vec{s}$. We assume that at some instant $t=0$ there is present on the lattice a distribution of noninteracting walkers with concentration $c_0(\vec{s})$ at lattice position $\vec{s}$. Each walker is able to perform a random walk with a probability $\psi_0(\vec{s},\vec{s}';t-t')dt$ for a jump from $\vec{s}'$ to $\vec{s}$ between t and $t+dt$, given that arrival to $\vec{s}'$ was at $t=t'$. As pointed out by Tunaley [21], the CTRW formalism should be completed by incorporating a distinct waiting time density (WTD) for the first jump, $v_0(\vec{s},\vec{s}_0;t)$, which describes the initial condition, with $\vec{s}_0$ the walker position at $t=0$. The point is that even when the walker starts at $\vec{s}_0$, the transition to $\vec{s}_0$ may have occurred some time before $t=0$. We will refer to this CTRW without traps as the ''equivalent problem.''

We include here some general CTRW results. Although most of these results may be found (at least in principle) in the literature, we find it helpful to include them here with our particular problem in mind and also to make consistent the notation used in this paper.

Let $G_h(\vec{s},\vec{s}';t)$ be the probability density that a walker reaches site $\vec{s}$ at time t given that it made a hop to $\vec{s}'$ at $t=0$. This density satisfies the recursive relation

$$G_h(\vec{s},\vec{s}';t)=\delta_{\vec{s},\vec{s}'}\delta(t-0^+)+\int_0^t dt'\sum_{\vec{s}''}\psi_0(\vec{s},\vec{s}'';t-t')\times G_h(\vec{s}'',\vec{s}';t') \tag{2.1}$$

and it is the Green's function for the equivalent problem, indicated by subindex h.

For a walker to be at $\vec{s}$ at time t, it must have arrived to $\vec{s}$ at some time $t'<t$ and stayed there for a time interval greater than $t-t'$. There is also the probability that $\vec{s}=\vec{s}_0$, the starting position, and no transitions occurred at all. Hence the conditional probability of finding a walker at site $\vec{s}$ at time t, given that it started at $\vec{s}_0$, $P_h(\vec{s},\vec{s}_0;t)$, can be obtained in terms of the Green's function by

$$P_h(\vec{s},\vec{s}_0;t)=\Upsilon_0(\vec{s};t)\,\delta_{\vec{s},\vec{s}_0}+\int_0^t dt'\Psi_0(\vec{s};t-t')\times\int_0^{t'}dt''\sum_{\vec{s}'}G_h(\vec{s},\vec{s}';t'-t'')v_0(\vec{s}',\vec{s}_0;t'') \tag{2.2}$$

where

$$\Psi_0(\vec{s};t)=\int_t^\infty dt'\sum_{\vec{s}'}\psi_0(\vec{s}',\vec{s};t') \tag{2.3}$$

is the *sojourn* probability at $\vec{s}$ (the probability that no further transitions occurred at least until time t since the arrival of the walker), and

$$\Upsilon_0(\vec{s};t)=\int_t^\infty dt'\sum_{\vec{s}'}v_0(\vec{s}',\vec{s};t') \tag{2.4}$$

is the *sojourn* probability for the first jump [22].

It is frequently assumed in the literature (although not always explicitly stated) that the instant $t=0$ coincides with the transition of the walker to $\vec{s}_0$. We shall call this particular assumption the ''synchronized condition,'' under which we have two possible choices for the first jump WTD: we may consider the transition at $t=0$ as the first one (as for example in Ref. [7]) so that

$$v_0(\vec{s},\vec{s}_0;t)=\delta_{\vec{s},\vec{s}_0}\delta(t-0^+) \tag{2.5}$$

or alternatively we may consider as the first transition the first occurring at $t>0$ [22] and

$$v_0(\vec{s},\vec{s}_0;t)=\psi_0(\vec{s},\vec{s}_0;t). \tag{2.6}$$

In both cases of Eq. (2.5) or (2.6) we get for the conditional probability of finding a walker at site $\vec{s}$ at time t, given that it arrived to $\vec{s}_0$ at $t=0$ (distinguished by superindex S)

$$P_h^S(\vec{s},\vec{s}_0;t)=\int_0^t dt'\Psi_0(\vec{s};t-t')G_h(\vec{s},\vec{s}_0;t'). \tag{2.7}$$

Of great interest in the CTRW theory, and particularly in applications to diffusion controlled reaction models, is the FPTD, $F_h(\vec{s},\vec{s}_0;t)$, that a walker starting at $\vec{s}_0$, reaches for

the first time site $\vec{s}_1$ at time t. In fact, the time of the first arrival is the time of trapping in the perfect trap or Smoluchowski's model. The FPTD is related to the conditional probability (2.2) by an extension of the renewal equation [22] for a general WTD

$$P_h(\vec{s},\vec{s}_0;t)=\Upsilon_0(\vec{s};t)\,\delta_{\vec{s},\vec{s}_0}+\int_0^t dt' P_h^S(\vec{s},\vec{s};t-t')F_h(\vec{s},\vec{s}_0;t') \tag{2.8}$$

since the probability of finding the walker at $\vec{s}$ at time t is given by the probability of first arrival at $\vec{s}$ between $t'(<t)$ and $t'+dt'$ times the probability of finding the walker at $\vec{s}$ after a time $t-t'$ has elapsed since the first arrival. There is also the probability that the walker was initially at $\vec{s}_0$ and no transition occurred at all, given by the first term of the second member. Notice that the conditional probability under the synchronized condition appears in the right hand side of Eq. (2.8) since we are assuming that the walker arrives for the first time at site $\vec{s}$ at time t'.

The Laplace transformation of Eq. (2.8) yields

$$F_h(\vec{s},\vec{s}_0;u)=\frac{P_h(\vec{s},\vec{s}_0;u)-\Upsilon_0(\vec{s};u)\,\delta_{\vec{s},\vec{s}_0}}{P_h^S(\vec{s},\vec{s};u)}. \tag{2.9}$$

Hereafter we distinguish the Laplace transform of a function by substituting $t\to u$, so that $F_h(\vec{s},\vec{s}_0;u)=\int_0^\infty dt\, e^{-ut}F_h(\vec{s},\vec{s}_0;t)$ and similarly for the other functions. Equation (2.9) is a general relation for a CTRW, since no assumptions as Markovianicity or separable process have been made. Under the synchronized condition, the FPTD is

$$F_h^G(\vec{s},\vec{s}_0;u)=\frac{G_h(\vec{s},\vec{s}_0;u)}{G_h(\vec{s},\vec{s};u)} \tag{2.10}$$

if we assume Eq. (2.5), and

$$F_h^S(\vec{s},\vec{s}_0;u)=\frac{G_h(\vec{s},\vec{s}_0;u)-\delta_{\vec{s},\vec{s}_0}}{G_h(\vec{s},\vec{s};u)} \tag{2.11}$$

if we assume Eq. (2.6), giving for $\vec{s}=\vec{s}_0$ the probability of return to the origin.

Consider now a trap at lattice position $\vec{s}_1$. The reaction $A+B\to C$ is modeled by the trapping of a walker at $\vec{s}_1$ (the walker jumps into a ''limbo'' from where it cannot return [23]). Upon arriving to $\vec{s}_1$ at time t_1 the walker may either be trapped between t and $t+dt$ with probability $\psi_A(t-t_1)dt$ $(t>t_1)$ or it may jump to $\vec{s}$ with probability $\psi_1(\vec{s},\vec{s}_1;t-t_1)dt$. In this way the diffusion of a walker in the presence of a trap differs from that of the equivalent problem because of the substitution of $\psi_0(\vec{s},\vec{s}_1;t-t_1)$ by $\psi_1(\vec{s},\vec{s}_1;t-t_1)$.

We relate now the densities ψ_1 and ψ_A with the dynamics of hopping and reaction when considered as separate processes. The *sojourn* probability at site $\vec{s}_1$ is given by

$$\Psi_1(\vec{s}_1;t)=\int_t^\infty dt'\left[\psi_A(t')+\sum_{\vec{s}}\psi_1(\vec{s},\vec{s}_1;t')\right] \tag{2.12}$$

defining the transition rates

$$B(\vec{s},\vec{s}_1;t)=\frac{\psi_1(\vec{s},\vec{s}_1;t)}{\Psi_1(\vec{s}_1;t)},$$

$$\gamma(t)=\frac{\psi_A(t)}{\Psi_1(\vec{s}_1;t)}, \tag{2.13}$$

i.e., the probability per unit time of making a jump to site $\vec{s}$ and to the limbo, respectively. If transitions to the limbo were not allowed $[\gamma(t)=0]$ the probability density for a jump to $\vec{s}$ would be

$$\psi_0(\vec{s},\vec{s}_1;t)=B(\vec{s},\vec{s}_1;t)\exp[-\Lambda(\vec{s}_1;t)]$$

with

$$\Lambda(\vec{s}_1;t)=\int_0^t dt'\sum_{\vec{s}}B(\vec{s},\vec{s}_1;t') \tag{2.14}$$

i.e., the WTD at $\vec{s}_1$ for the equivalent problem. Similarly, in the absence of diffusion, $B(\vec{s},\vec{s}_1;t)=0\ \ \forall\vec{s}$ the dynamics of reaction is

$$\psi_r(t)=\gamma(t)\exp[-\Gamma(t)],$$

with

$$\Gamma(t)=\int_0^t dt'\,\gamma(t'). \tag{2.15}$$

In this way the following relationships can be established:

$$\Psi_1(\vec{s}_1;t)=\Psi_0(\vec{s}_1;t)\exp[-\Gamma(t)],$$

$$\psi_1(\vec{s},\vec{s}_1;t)=\psi_0(\vec{s},\vec{s}_1;t)e^{-\Gamma(t)}, \tag{2.16}$$

$$\psi_A(t)=\gamma(t)e^{-\Gamma(t)}\Psi_0(\vec{s}_1;t).$$

For the particular case of γ independent of time we get

$$\psi_1(\vec{s},\vec{s}_1;t)=\psi_0(\vec{s},\vec{s}_1;t)e^{-\gamma t},$$

$$\psi_A(t)=\gamma e^{-\gamma t}\Psi_0(\vec{s}_1;t), \tag{2.17}$$

$$\Psi_1(\vec{s}_1;t)=\Psi_0(\vec{s}_1;t)e^{-\gamma t}$$

the usual imperfect trap model as proposed by Condat [6,24] in lattices or by Collins and Kimball [16] in the continuous space. Notice that in the limit $\gamma\to\infty$

$$\psi_1(\vec{s},\vec{s}_1;t)\to 0,$$

$$\psi_A(t)\to\delta(t-0^+), \tag{2.18}$$

$$\Psi_1(\vec{s}_1;t)\to 0,$$

corresponding to an immediate absorption of the walker upon arrival to $\vec{s}_1$ as in the perfect trap model.

To complete the description of the trapping problem, the initial condition should be given through the first jump probability densities, in particular for $\vec{s}_0=\vec{s}_1$. To calculate these first jump probability densities we extend the proposal of Lax and Scher [25] based on conditional probabilities: Consider a regular lattice site $\vec{s}\neq\vec{s}_1$ and suppose that at $t=0$ the walker has sojourned there a time τ. Then the probability that the walker makes a transition to $\vec{s}'$ between t and $t+dt$ is [26,27]

$$\psi_0(\vec{s}',\vec{s};t|\tau)=\frac{\psi_0(\vec{s}',\vec{s};t+\tau)}{\Psi_0(\vec{s};\tau)}. \tag{2.19}$$

Assuming now that the time interval τ is governed by a probability density $\rho_0(\vec{s};\tau)$ (in principle dependent of the site under consideration) we get

$$\upsilon_0(\vec{s}',\vec{s};t)=\int_0^\infty d\tau\,\rho(\vec{s};\tau)\psi_0(\vec{s}',\vec{s};t|\tau). \tag{2.20}$$

The synchronized condition is given by $\rho_0(\vec{s};\tau)=\delta(\tau-0^+)$ resulting in $\upsilon_0=\psi_0$. On the other hand, if there is a finite mean waiting time at each site $\vec{s}$, $\langle t\rangle_{\vec{s}}$, the stationary state is given by $\rho_0(\vec{s};\tau)=\Psi_0(\vec{s};\tau)/\langle t\rangle_{\vec{s}}$ [22,25].

We extend the previous reasoning to site $\vec{s}_1$ and denote by $\rho_1(\vec{s}_1;\tau)$ the probability that at $t=0$ a walker has sojourned a time τ at the trap position obtaining for the first jump

$$\begin{aligned}\upsilon_1(\vec{s},\vec{s}_1;t)&=\int_0^\infty d\tau\,\rho_1(\vec{s}_1;\tau)\frac{\psi_1(\vec{s},\vec{s}_1;t+\tau)}{\Psi_1(\vec{s}_1;\tau)},\\ \upsilon_A(t)&=\int_0^\infty d\tau\,\rho_1(\vec{s}_1;\tau)\frac{\psi_A(t+\tau)}{\Psi_1(\vec{s}_1;\tau)}.\end{aligned} \tag{2.21}$$

The probability that a walker starting at $\vec{s}_1$ sojourns at $\vec{s}_1$ a time greater than t may be calculated from Eq. (2.21)

$$\Upsilon_1(\vec{s}_1;t)=\int_t^\infty dt'\left[\upsilon_A(t')+\sum_{\vec{s}}\upsilon_1(\vec{s},\vec{s}_1;t')\right] \tag{2.22}$$

or, by means of Eq. (2.16),

$$\Upsilon_1(\vec{s}_1;t)=\int_0^\infty d\tau\,\rho_1(\vec{s}_1;\tau)\frac{\Psi_1(\vec{s}_1;t+\tau)}{\Psi_1(\vec{s}_1;\tau)}. \tag{2.23}$$

As an example of the calculation of first jump probability densities, we consider two initial conditions of experimental interest.

(1) *Pair creation.* A pair walker trap is created at $\vec{s}_1$ at $t=0$ as considered by Nadler and Stein (NS) [9]. The initial condition in this case is described by $\rho(\vec{s};\tau)=\delta_{\vec{s},\vec{s}_1}\delta(\tau-0^+)$ since there are no walkers on the lattice for $t<0$, and at $t=0$ the particle appears on $\vec{s}_1$. Under this initial condition

$$\upsilon_0(\vec{s},\vec{s}';t)=0,\quad \vec{s}'\neq\vec{s}_1,$$

$$\upsilon_1(\vec{s},\vec{s}_1;t)=\psi_1(\vec{s},\vec{s}_1;t), \tag{2.24}$$

$$\upsilon_A(t)=\psi_A(t),$$

and the initial walker concentration is obviously $c_0(\vec{s})=\delta_{\vec{s},\vec{s}_1}$.

(2) *Trap creation in a medium with uniform walker concentration.* This initial condition corresponds to the appearance of the trap at $\vec{s}_1$ at $t=0$ in a region free of traps with a uniform walker concentration for $t<0$, as considered by Chuang and Eisenthal (CE) [20]. We will assume here that the trap does not decay (disappear) except when trapping a walker.

Let us consider now a walker that at $t=0$ has sojourned a time τ at $\vec{s}_1$. Extending the previous reasoning leading to Eq. (2.16) we get for the probability densities of making a transition to another lattice site $\vec{s}$ and to the limbo between t and $t+dt$

$$\psi_1(\vec{s},\vec{s}_1;t+\tau)=\begin{cases}\psi_0(\vec{s},\vec{s}_1;t+\tau), & -\tau<t<0\\ e^{-\Gamma(t)}\psi_0(\vec{s},\vec{s}_1;t+\tau), & t>0\end{cases} \tag{2.25}$$

$$\psi_A(t+\tau)=\begin{cases}0, & -\tau<t<0\\ \gamma(t)e^{-\Gamma(t)}\Psi_0(\vec{s}_1;t+\tau), & t>0\end{cases}$$

respectively, since there is no trap for $t<0$. For the same reason, the probability density governing the time interval τ will be the corresponding one to a regular lattice site: $\rho_1(\vec{s}_1;\tau)=\Psi_0(\vec{s}_1;\tau)/\langle t\rangle_{\vec{s}_1}$. Substituting in Eq. (2.21) we finally get

$$\begin{aligned}\upsilon_1(\vec{s},\vec{s}_1;t)&=\upsilon_0(\vec{s},\vec{s}_1;t)e^{-\Gamma(t)},\\ \upsilon_A(t)&=\gamma(t)e^{-\Gamma(t)}\Upsilon_0(\vec{s}_1;t),\\ \Upsilon_1(\vec{s}_1;t)&=e^{-\Gamma(t)}\Upsilon_0(\vec{s}_1;t).\end{aligned} \tag{2.26}$$

For other walkers being at any lattice site $\vec{s}'\neq\vec{s}_1$, the first jump probability density will be as in the stationary case; i.e., $\upsilon_0(\vec{s},\vec{s}';t)$. More general initial conditions may be obtained in a similar way.

III. THE ABSORPTION PROBABILITY DENSITY

We calculate in this section the probability density that a walker starting at $\vec{s}_0$ is absorbed by the trap at $\vec{s}_1$ at time t, denoted here by $A(\vec{s}_0;t)$. Let us consider first the Green's function for the trapping problem, identified by subindex t,

satisfying the recursive relation

$$G_t(\vec{s},\vec{s}_0;t)=\delta_{\vec{s},\vec{s}_0}\delta(t-0^+)+\int_0^t dt'\sum_{\vec{s}'}\psi(\vec{s},\vec{s}';t-t')G_t(\vec{s}',\vec{s}_0;t'). \tag{3.1}$$

Here $G_t(\vec{s},\vec{s}_0;t)$ is the probability density that a walker reaches site $\vec{s}$ at time t given that it made a jump to $\vec{s}_0$ at $t=0$ for the trapping problem. The difference between this equation and recursive relation (2.1) for the equivalent problem, is given by the contribution from $\vec{s}'=\vec{s}_1$ in the sum on the right hand side. Proceeding as in Ref. [13] we get in the Laplace representation

$$G_t(\vec{s},\vec{s}_0;u)=G_h(\vec{s},\vec{s}_0;u)-G_h(\vec{s}_1,\vec{s}_0;u)\frac{G_h(\vec{s},\vec{s}_1;u)-\delta_{\vec{s},\vec{s}_1}-\sum_{\vec{s}'}G_h(\vec{s},\vec{s}';u)\psi_1(\vec{s}',\vec{s}_1;u)}{G_h(\vec{s}_1,\vec{s}_1;u)-\sum_{\vec{s}'}G_h(\vec{s}_1,\vec{s}';u)\psi_1(\vec{s}',\vec{s}_1;u)}, \tag{3.2}$$

where $G_h(\vec{s},\vec{s}_0;u)$ is the Green's function for the equivalent problem satisfying Eq. (2.1).

We are able now to give an expression for the APD in terms of the Green's function, since for a walker to be absorbed at time t by the trap, it must arrive to $\vec{s}_1$ at a time $t'<t$ and then make a transition to the limbo after a time $t-t'$. There is also the probablity that the walker started at $\vec{s}_1$ and jumped into the limbo without leaving $\vec{s}_1$. Hence

$$A(\vec{s}_0;t)=\nu_A(t)\delta_{\vec{s}_0,\vec{s}_1}+\int_0^t dt'\,\psi_A(t-t')\times\int_0^{t'}dt''\sum_{\vec{s}'}G_t(\vec{s},\vec{s}';t'-t'')\nu(\vec{s}',\vec{s}_0;t''). \tag{3.3}$$

Taking Laplace transformation of Eq. (3.3) and substituting Eqs. (2.10) and (3.2) we get

$$A(\vec{s}_0;u)=\nu_A(u)\delta_{\vec{s}_1,\vec{s}_0}+\psi_A(u)\times\frac{\sum_{\vec{s}'}F_h^G(\vec{s}_1,\vec{s}';u)\nu(\vec{s}',\vec{s}_0;u)}{1-\sum_{\vec{s}'}F_h^G(\vec{s}_1,\vec{s}';u)\psi_1(\vec{s}',\vec{s}_1;u)}, \tag{3.4}$$

i.e., the APD is expressed in terms of the FPTD as given by the equivalent problem. Notice that for the perfect trap model ($\gamma\to\infty$) $\psi_1=0$ [Eq. (2.18)] and the APD turns out to be

$$A^P(\vec{s}_0;u)=F_h(\vec{s}_1,\vec{s}_0;u)(1-\delta_{\vec{s}_0,\vec{s}_1}). \tag{3.5}$$

For a walker starting at $\vec{s}_0$, the conditional probability of finding it at site $\vec{s}$ at time t may be expressed in terms of the Green's function through

$$P_t(\vec{s},\vec{s}_0;t)=\Upsilon(\vec{s};t)\delta_{\vec{s},\vec{s}_0}+\int_0^t dt'\,\Psi(\vec{s};t-t')\times\int_0^{t'}dt''\sum_{\vec{s}'}G_t(\vec{s},\vec{s}';t'-t'')\nu(\vec{s}',\vec{s}_0;t'') \tag{3.6}$$

by a similar reasoning to that leading to Eq. (2.2) for the equivalent problem. If we compare this equation at $\vec{s}=\vec{s}_1$ and Eq. (3.3) we find the relation

$$A(\vec{s}_0;u)=\frac{\psi_A(u)}{\Psi_1(\vec{s}_1;u)}P_t(\vec{s}_1,\vec{s}_0;u)+\delta_{\vec{s}_1,\vec{s}_0}\left[\nu_A(u)-\frac{\psi_A(u)}{\Psi_1(\vec{s}_1;u)}\Upsilon_1(\vec{s}_1;u)\right], \tag{3.7}$$

which is a generalization of Collins and Kimball's absorption condition at the trap position for general diffusion and trapping processes. If in particular we assume a constant trapping rate γ we get from Eqs. (2.17), (2.21), and (2.23)

$$A(\vec{s}_0;t)=\gamma P_t(\vec{s}_1,\vec{s}_0;t) \tag{3.8}$$

and the absorption of a walker starting at $\vec{s}_0$ is proportional to the probability of finding it at $\vec{s}_1$.

A rather simpler expression for $A(\vec{s}_0;u)$ is obtained if a separable diffusion process is assumed:

$$\psi_0(\vec{s},\vec{s}';t)=p_{\vec{s},\vec{s}'}\psi_0(t),\qquad \psi_1(\vec{s},\vec{s}_1;t)=p_{\vec{s},\vec{s}_1}\psi_1(t), \tag{3.9}$$

and similar expressions for the WTD for the first jump. Under these assumptions we get from Eqs. (2.9) and (2.11)

$$\sum_{\vec{s}'} F_h^G(\vec{s}_1,\vec{s}';u)p_{\vec{s}',\vec{s}_1}\psi_1(u)=\frac{\psi_1(u)}{\psi_0(u)}F_h^S(\vec{s}_1,\vec{s}_1;u),$$
$$\sum_{\vec{s}'} F_h^G(\vec{s}_1,\vec{s}';u)p_{\vec{s}',\vec{s}_1}v(u)=\frac{v_1(u)}{v_0(u)}F_h(\vec{s}_1,\vec{s}_1;u). \tag{3.10}$$

Substituting in Eq. (3.5) we get for the separable process

$$A(\vec{s}_0;u)=\delta_{\vec{s}_1,\vec{s}_0}v_A(u)+\psi_A(u)\frac{F_h(\vec{s}_1,\vec{s}_0;u)\tilde{v}(\vec{s}_0;u)}{1-\frac{\psi_1(u)}{\psi_0(u)}F_h^S(\vec{s}_1,\vec{s}_1;u)} \tag{3.11}$$

with

$$\tilde{v}(\vec{s}_0;u)=\begin{cases}1, & \vec{s}_0\neq\vec{s}_1\\ \dfrac{v_1(u)}{v_0(u)}, & \vec{s}_0=\vec{s}_1.\end{cases} \tag{3.12}$$

We wish to draw attention on the similitude of this result and the expression obtained by Weiss and Rubin [28] for the absorption generating function in discrete time random walk assuming a probability α for the walker absorption in each visit to the trap

$$A(\vec{r};z)=\frac{\alpha F(\vec{r};z)}{1-(1-\alpha)F(\vec{0};z)}, \tag{3.13}$$

where $F(\vec{r};z)$ is the generating function for the discrete time FPT probability and $\vec{r}$ the initial walker position relative to the trap. Both results can be compared by the usual substitution $z\rightarrow\psi(u)$ with due inclusion of the first jump. In doing so, however, some differences emerge when $\vec{s}_0=\vec{s}_1$ because of the contribution to absorption of those realizations in which the walker is absorbed without leaving $\vec{s}_1$. Besides this, denominators in both expressions of Eqs. (3.11) and (3.13) cannot be simply put into correspondence except when it is assumed a constant rate γ and a Poisson hopping process, in which case it is verified

$$\frac{\psi_1(u)}{\psi_0(u)}=1-\psi_A(u). \tag{3.14}$$

A. Survival probability and reaction rate

Let us consider a walker starting at $\vec{s}_0$. The probability that this walker has not been absorbed by the trap at $\vec{s}_1$ by time t (the one particle survival probability) is

$$S_1(t)=1-\int_0^t dt'\,A(\vec{s}_0;t'). \tag{3.15}$$

Evaluated at $\vec{s}_0=\vec{s}_1$, Eq. (3.15) gives the survival probability under the NS initial condition and is proportional to the fraction of systems walker trap that has not reacted by time t.

Consider now a distribution of walkers with concentration $c_0(\vec{s}_0)$ at $t=0$ in the presence of a trap at $\vec{s}_1$. Assuming that the walkers do not interact among them, the survival probability of the trap $\Phi(t)$ (the probability that no walker has been trapped) is obtained by extending the Bendler and Shlesinger [15] formula

$$\Phi(t)=\exp\left[-\int_0^t dt'\sum_{\vec{s}_0}A(\vec{s}_0;t')c_0(\vec{s}_0)\right]. \tag{3.16}$$

The exponent is the integral of the time-dependent reaction rate, $k(t)=-\partial_t\ln\Phi(t)$,

$$k(t)=\sum_{\vec{s}_0}A(\vec{s}_0;t)c_0(\vec{s}_0) \tag{3.17}$$

and represents the flux of walkers into the trap between t and $t+dt$. An analytic expression may be obtained in the Laplace representation by means of Eq. (3.4)

$$k(u)=v_A(u)c_0(\vec{s}_1)+\psi_A(u)\times\frac{\sum_{\vec{s}',\vec{s}_0}F_h^G(\vec{s}_1,\vec{s}';u)v(\vec{s}',\vec{s}_0;u)c_0(\vec{s}_0)}{1-\sum_{\vec{s}'}F_h^G(\vec{s}_1,\vec{s}';u)\psi_1(\vec{s}',\vec{s}_1;u)}. \tag{3.18}$$

If we substitute Eq. (3.7) in Eq. (3.17) we get in turn

$$k(u)=\frac{\psi_A(u)}{\Psi_1(\vec{s}_1;u)}c(\vec{s}_1;u)+c_0(\vec{s}_1)\times\left[v_A(u)-\frac{\psi_A(u)}{\Psi_1(\vec{s}_1;u)}\Upsilon(\vec{s}_1;u)\right], \tag{3.19}$$

where

$$c(\vec{s}_1;t)=\sum_{\vec{s}_0}P_t(\vec{s},\vec{s}_0;t)c_0(\vec{s}_0) \tag{3.20}$$

is the walker concentration at $\vec{s}_1$.

In this way, a generalization of the absorption condition proposed by Collins and Kimball's results. Besides the contribution from $c(\vec{s}_1;t)$ we note an extra contribution from the initial concentration at $\vec{s}_1$, given by the second term.

For the particular case $\gamma=$ const., independent of time, Collins and Kimball's original absorption condition is obtained

$$k(t)=\gamma c(\vec{s}_1;t). \tag{3.21}$$

If besides $\gamma=$ const., we also assume the CE initial condition; i.e., the initial walker concentration is the stationary distribution for the equivalent problem as discussed in Sec. II, we obtain Noyes' [17] proposal

$$k(t)=\gamma c_0(\vec{s}_1)\left[1-\int_0^t dt'\,A(\vec{s}_1;t')\right] \tag{3.22}$$

with an explicit expression for Noyes' function $h(t)$, the probability density that a pair of reactive particles coinciding at $t=0$ react at time t.

B. Asymptotic limits

We consider here the behavior of the APD and reaction rate in the limits $t\to 0$ and $t\to\infty$ for a separable process (3.9). The calculation of asymptotic limits is carried out starting with the exact expressions (3.11) and (3.18) for the respective Laplace transforms and analyzing the behavior in the corresponding limits $u\to\infty$ and $u\to 0$, as established by Abelian and Tauberian theorems [29].

We start considering the APD in the limit $u\to\infty$ (corresponding to $t\to 0$). Since $F_h(\vec{s},\vec{s}_0;t)\to 0$ for $t\to 0$, by the initial value theorem $F_h(\vec{s},\vec{s}_0;u)\to 0$ at least as u^{-1} when $u\to\infty$. Besides this, by Eq. (2.16) $\psi_1(t)<\psi_0(t)\Rightarrow\psi_1(u)<\psi_0(u)\forall u$ and we may aproximate in the limit $u\to\infty$

$$A(\vec{s}_0;u)\approx v_A(u)\,\delta_{\vec{s}_0,\vec{s}_1}+\psi_A(u)\tilde{v}(\vec{s}_0;u)F_h(\vec{s},\vec{s}_0;u). \tag{3.23}$$

In this way we may conclude that the dominant behavior at short times will be given by the reaction dynamics when $\vec{s}_0=\vec{s}_1$ and by the reaction dynamics convoluted with the FPTD for $\vec{s}_0\neq\vec{s}_1$. In particular under NS initial conditions $v_A=\psi_A$ and $c_0(\vec{s}_0)=\delta_{\vec{s}_0,\vec{s}_1}$, so that $\psi_A(t)$ will be proportional to the number of reactions between t and $t+dt$ at short times.

On the other extreme ($t\to\infty$) we will focus attention on NS initial conditions. We will assume here that the first moment of all transition probability densities ψ_i are finite (ψ_i stands for ψ_A, ψ_1, or ψ_0) so that we can aproximate

$$\psi_i(u)\approx\psi_{i_0}-\overline{t}_i u \tag{3.24}$$

in the limit $u\to 0$, where $\overline{t}_i=\int_0^\infty dt\, t\psi_i(t)$ is the first moment of density ψ_i and $\psi_{i_0}=\int_0^\infty dt\,\psi_i(t)$.

Normalization condition imposes $\psi_{0_0}=1$ while $\psi_{A_0}=\alpha$ is the probability of absorption in each visit and $\psi_{1_0}=1-\alpha$ is the probablity of escaping in each visit. For the particular case of $\gamma=$ const. and a Poisson jumping process as given by $\psi_0=\lambda\exp(-\lambda t)$, we get from Eq. (2.17) the simple relation $\alpha=\gamma/(\gamma+\lambda)$ and $\alpha\to 1$ when $\gamma\to\infty$ (the perfect trap case).

At the same time we will assume a rather general behavior for the FPTD

$$F_h^S(\vec{s}_1,\vec{s}_1;u)\approx f_l-f(u), \tag{3.25}$$

where $0<f_l\leqslant 1$ is the probability of return to the origin and $f(u)>u$ for $u<u_l$, some fixed value [for example, in normal one-dimensional diffusion $f(u)\propto u^{1/2}$]. Using these approximations we get

$$A(\vec{s}_1;u)\approx\frac{\alpha}{1-(1-\alpha)f_l}-\frac{\alpha(1-\alpha)}{[1-(1-\alpha)f_l]^2}f(u) \tag{3.26}$$

and we find that the APD exhibits the same time dependence as the FPTD in the long time limit, although the coefficients of the expansion are modified by the dynamics of reaction. When return to the origin is certain ($f_l=1$), we find the asymptotic behavior

$$A(\vec{s}_1;u)\approx 1-\frac{1-\alpha}{\alpha}f(u) \tag{3.27}$$

so that the walker will certainly be trapped. In this case, for the particular value $\alpha=1/2$, the APD and the probability of return to the origin will be exactly coincidents at long times.

In summary we have found here that at short times ($t\ll\overline{t}_i$) $A(\vec{s}_1;t)$ will behave as the reaction dynamics, while at long times ($t\gg\overline{t}_i$) $A(\vec{s}_1;t)$ will exhibit the same time dependence as the probability of return to the origin. This result can be interpreted in terms of the competition between reaction and diffusion dynamics for a walker starting at $\vec{s}_1$ by realizing that at short times (in particular compared with the mean waiting time at $\vec{s}_1$) most reactions will correspond to particles that have not left $\vec{s}_1$, and in this way the reaction time will not be affected by diffusion. At long times, on the other hand, most surviving particles will have left $\vec{s}_1$, and now $A(\vec{s}_1;t)$ is regulated by the probability of return to the origin.

Let us now turn attention to the reaction rate as given by Eq. (3.18), under CE initial conditions. In the short time limit, by the same considerations leading to Eq. (3.23), we get

$$k(u)\approx c_0(\vec{s}_1)\left[v_A(u)+\frac{\psi_A(u)}{\overline{t}_{0_0}u}\right] \tag{3.28}$$

and, as in the case of the APD, the short time behavior is dominated by the reaction dynamics.

On the other hand, in the long time limit, and making the same assumptions leading to Eq. (3.26), we get

$$k(u)\approx c_0(\vec{s}_1)\frac{\lambda\alpha}{1-(1-\alpha)f_l}\left\{\frac{1-f_l}{u}+\frac{f(u)}{u}\frac{\alpha}{1-(1-\alpha)f_l}\right\} \tag{3.29}$$

and, again as in the case of the APD, the long time behavior for the reaction rate is determined by the probability of return to the origin. In particular, if $f_l=1$, we get the simpler expression

$$k(u)\approx c_0(\vec{s}_1)\frac{\lambda}{u}f(u)\left\{1+f(u)\frac{\psi_{1_0}}{\psi_{A_0}}\right\}. \tag{3.30}$$

The transition from the reactive regime at short times to the diffusive regime at long times exhibited by the reaction rate can be interpreted in similar terms as in the case of the APD: At short times the main contribution to reactions will be given by those walkers initially at $\vec{s}_1$. This will produce a depletion in walker concentration at $\vec{s}_1$ that will be compensated at later times by the diffusion process. In this way, as the concentration of walkers evolves in time, the behavior at the long time limit becomes regulated by the diffusion process.

IV. ONE-DIMENSIONAL RANDOM WALK

We illustrate the results obtained with the proposed treatment for an imperfect trap by considering a one-dimensional

separable random walker with hopping probability density

$$\psi_0(s,s';t)=\frac{1}{2}[\delta_{s,s'+1}+\delta_{s,s'-1}]\lambda e^{-\lambda t} \tag{4.1}$$

where $\lambda^{-1}=\langle t_d\rangle$ is the mean waiting time at any site s'. We are defining in this way the equivalent problem with Green's function

$$G_h(s,s';t)=e^{-\lambda t}\partial_t[I_{|s-s'|}(\lambda t)] \tag{4.2}$$

as is obtained by substituting Eq. (4.1) in recursive relation (2.1).

For the reaction time we assume a generic probability density in the absence of diffusion

$$\psi_r(t)=\frac{(\beta t)^n}{n!}\beta e^{-\beta t} \tag{4.3}$$

i.e., an Erlang density with mean reaction time $\langle t_r\rangle=(n+1)/\beta$ corresponding to a time-dependent absorptivity

$$\gamma(t)=\beta\frac{(\beta t)^n}{\sum_{j=0}^{n}\frac{n!}{j!}(\beta t)^j}. \tag{4.4}$$

The particular value $n=0$ reduces the example to the usual imperfect trap model with a time-independent absorptivity.

The probability densities ψ_1 and ψ_A can now be obtained substituting Eqs. (4.1) and (4.3) in Eq. (2.16), resulting in the Laplace representation

$$\psi_1(s,s_1;u)=\psi_0(s,s_1,u)\left\{1-\left[1+\frac{u+\lambda}{\beta}\right]^{-(n+1)}\right\},$$

$$\psi_A(u)=\left[1+\frac{u+\lambda}{\beta}\right]^{-(n+1)}. \tag{4.5}$$

It remains to give the initial condition in order to define completely the example. We will consider the two already introduced NS and CE initial conditions (Sec. II).

A. Pair creation at $t=0$

This initial condition is introduced in the model through the first jump densities (2.24). With these expressions and making use of Eqs. (2.3), (3.11), and (4.1) we get for the Laplace transform of the APD (3.11)

$$A(s_1;u)=\left\{1+\sqrt{\frac{u(u+2\lambda)}{\beta^2}}\sum_{j=0}^{n}\left(1+\frac{u+\lambda}{\beta}\right)^j\right\}^{-1}. \tag{4.6}$$

The results obtained for $n=0$ and different values of the quotient

$$\kappa=\frac{\langle t_d\rangle}{\langle t_r\rangle} \tag{4.7}$$

are shown in Fig. 2 with time in units of $\langle t_d\rangle$. These values were numerically computed by means of the Laplace inversion algorithm (LAPIN) [30]. It can be appreciated here that the transition from the reaction regime at short times ($t\ll\langle t_d\rangle$) to the diffusive regime for $t\gg\langle t_d\rangle$ was in accordance with the conclusions extracted from the asymptotic behavior analysis. This transition is more evident for values of $\kappa>1$, when $\langle t_r\rangle<\langle t_d\rangle$. The transition between both regimes reflects the fact that at short times as compared to characteristic diffusion time ($\langle t_d\rangle$) no significative fraction of walkers will have escaped from s_1.

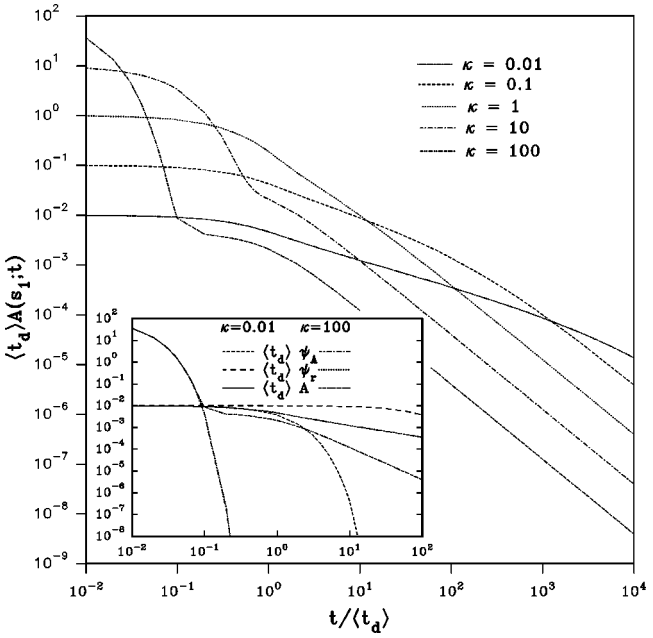

FIG. 2. APD vs $t/\langle t_d\rangle$ for the one-dimensional model under consideration (see text). Shown are the plots for different values of $\kappa=\langle t_d\rangle/\langle t_r\rangle$. Here $\langle t_d\rangle$ is the mean waiting time at any site in the lattice and $\langle t_r\rangle$ is the mean reaction time.

The probability that a walker (initially at s_1) is trapped without leaving s_1 is given by $\psi_A(t)$ under the assumed initial condition. The inset in Fig. 2 shows a comparison among $A(s_1;t)$, $\psi_A(t)$ and $\psi_r(t)$ for $\kappa=0.01$, 100.

On the other hand, the long time behavior exhibits the same time dependence as the probability of return to the origin as predicted by Eq. (3.27), although the time at which the asymptotic behavior is reached depends on the value of κ. As it can be appreciated from Fig. 2, this behavior is reached faster for greater values of κ, when there is a smaller probability of escaping from s_1 in each visit: $1-\alpha=1/(1+\kappa)$.

The dominance of reaction dynamics becomes more evident in Fig. 3, where we have plotted $A(s_1;t)$ for different values of κ and n. The time scale in this plot is given in units of $\langle t_r\rangle$, the mean reaction time. For increasing values of n, the reaction probability density ψ_r [Eq. (4.3)] is more concentrated around the mean value $\langle t_r\rangle$, and this behavior is also observed by the APD. The long time behavior, in turn, exhibits the same time dependence as the probability of return to the origin. Notice in particular that for $\kappa=100$ all curves converge to the same asymptotic behavior, independent of the particular value chosen for n.

The inset in Fig. 3 shows again a comparison among $A(s_1;t)$, $\psi_A(t)$, and $\psi_r(t)$ for two different values of κ. Here the coincidence of APD and $\psi_A(t)$ at short times can again be appreciated.

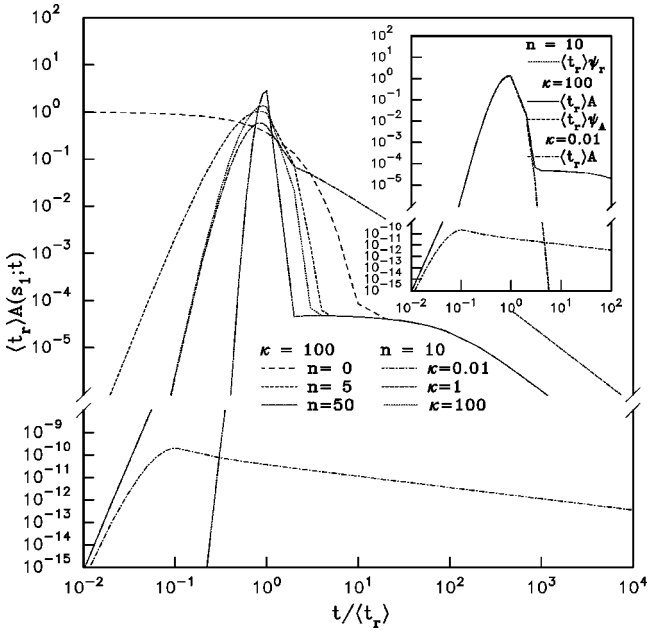

FIG. 3. APD vs $t/\langle t_r\rangle$. Shown are the plots for different values of $\kappa=\langle t_d\rangle/\langle t_r\rangle$ and n is the index of Erlang distribution.

B. Trap creation in a uniform walker concentration

This initial condition, referred to as CE in Sec. II, is described by the first jump densities (2.26). With the particular expressions obtained when substituting Eq. (4.5) in Eq. (2.26) and making use of Eqs. (2.10), (3.11), (3.18), and (4.1) we get for the reaction rate

$$k(u)=c_0\frac{\lambda}{u}\frac{\sqrt{\frac{u}{\lambda}\left(\frac{u}{\lambda}+2\right)}}{1+\sqrt{\frac{u}{\beta}\left(\frac{u}{\beta}+2\frac{\lambda}{\beta}\right)}\sum_{j=0}^{n}\left[1+\frac{u+\lambda}{\beta}\right]^{j}} \tag{4.8}$$

in the Laplace representation. The inset in Fig. 4 shows a plot of $k(t)$ for different choices of the parameters κ and n. In this plot, the time scale is given in units of $\langle t_r\rangle$.

We can appreciate here the transition from the reactive to the diffusive regime as time evolves, as was already discussed when asymptotic behavior was analyzed in Sec. III B. Again the transition becomes more evident for greater values of κ. As in the case of the APD in the previous section, we see that at long times all curves corresponding to a given value of κ converge to the same function, while the time at which the asymptotic regime is reached depends on the value of κ.

The survival probability can be calculated from the reaction rate through

$$\Phi(t)=\exp\left[-\int_0^t dt'k(t')\right]. \tag{4.9}$$

The results obtained for the same values of κ and n already considered are shown in the main plot of Fig. 4, presented as $[\Phi(t)]^{1/c_0}$ vs $t/\langle t_r\rangle$ in order to make the curves independent of the particular value of initial walkers' concentration. The influence of reaction dynamics for short times can also be observed in this plot. For a given value of

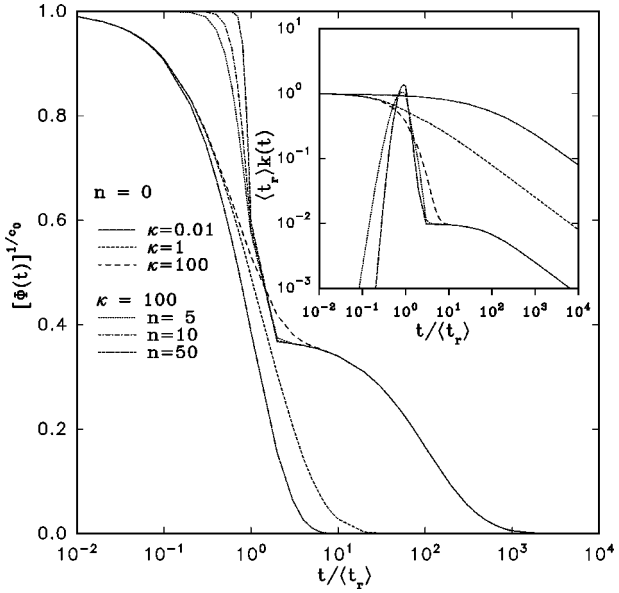

FIG. 4. Survival probability and time-dependent reaction rate vs $t/\langle t_r\rangle$ for the one-dimensional model under consideration (see text). The main figure shows the plots for different values of $\kappa=\langle t_d\rangle/\langle t_r\rangle$ and n is the index of Erlang distribution. The inset shows the corresponding values for the reaction rate for the same set of values for the parameters.

κ, in particular, we can appreciate a delay in walkers' absorption with increasing values of n.

At long times, on the other hand, we observe the behavior predicted by the probability of return to the origin [as this is the dominant behavior of $k(t)$].

The influence of initial walkers' concentration is considered in Fig. 5, where we have plotted the function

$$F(t)=1-\Phi(t) \tag{4.10}$$

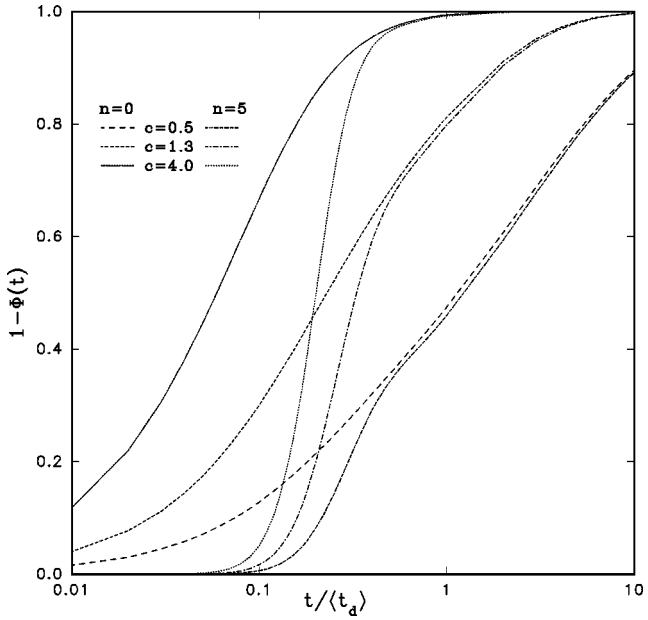

FIG. 5. $F(t)=1-\Phi(t)$ vs $t/\langle t_d\rangle$ for different values of initial walkers' concentration. $F(t)$ is proportional to the number of reactions occurred by time t.

vs time in units of $\langle t_d \rangle$. This function, introduced in Ref. [20], gives the fraction of minority species (the trap) that has reacted by time t; i.e., the number of reactions occurred by time t divided by the initial number of reactive A. We have chosen for comparison two different values of n and a fixed value of $\kappa = 3.2$ as determined from physical parameters in CE. Three different values for the initial concentration of minority species have been selected, also in accordance with CE when the lattice parameter is identified with the reaction radius.

At short times the curves can be grouped according to the value of n, reflecting the dominance of reaction dynamics. On the other extreme, at long times, when the diffusive regime is dominant, the behavior is determined by the initial walkers' concentration. A direct comparison with experimental values reported by CE cannot be established at long times, since we are considering here a one-dimensional model while the CE experiment is three-dimensional. Nevertheless, the short time behavior does not depend on the dimension of diffusion space since it is governed by reaction dynamics. In this way we believe that discrepancies reported at short times by CE could be explained in terms of a more detailed description of the reaction process.

V. DISCUSSION AND CONCLUSIONS

We have presented a theoretical study of diffusion mediated reaction processes that extends previous treatments in order to include the trapping or reaction process (through the reaction probability density). Expressions for magnitudes of experimental interest, the absorption probability density, time-dependent reaction rate, and survival probability, are obtained in terms of the probability densities that characterize the hopping and reaction processes. Our treatment contains as a particular case the so called imperfect trap model first considered by Collins and Kimball [16] on the continuous space and later on by Condat [6] on a lattice. Furthermore, our model remains valid for non-Markovian diffusion. In particular, expression (2.9) for the first passage time density is a generalization of previous results since no particular assumptions such as Markovianicity or separability of the process have been made.

In Sec. II we have characterized the trapping or reaction process by defining a time-dependent transition rate to the limbo $\gamma(t)$ or alternatively by the reaction probability density when diffusion is not allowed, $\psi_r(t)$. Both magnitudes are connected through Eq. (2.15). The imperfect trap model is obtained by assuming a time-independent absorptivity γ and in the limit $\gamma \to \infty$, Smoluchowski's originial model emerges. Due attention has been given to initial conditions by incorporating first jump probability densities that generalize previous results in the literature. Particular examples of experimental interest [9,20] have been discussed and the corresponding expressions for first jump densities have been derived.

The main results of this study were presented in Sec. III, corresponding to expression (3.4) for the APD, Eq. (3.18) for the time-dependent reaction rate, and Eq. (3.16) for the survival probability. In particular, Eq. (3.19) is a generalization of Collins and Kimball's absorption condition when a general diffusion process is considered. For the particular case γ independent of time and assuming an initial walker concentration in equilibrium previous to the appearance of the trap, Noyes' proposal is obtained with an explicit expression for the probability density that a reactive pair coincident at $t = 0$ reacts at time t: the APD with s_1 the initial position of the walker.

The short and long time behavior of the APD and reaction rate were analyzed in Sec. III B. We conclude from this analysis that at short times the behavior of both magnitudes is governed by the reaction dynamics, while at long times the time dependence is that of the probability of return to the origin.

The results obtained were illustrated in Sec. IV by considering a one-dimensional diffusive model. One of the most important consequences predicted by the proposed treatment is that the short time behavior of the relevant magnitudes is governed by reaction dynamics. This behavior is not predicted by Collins and Kimball since it is a consequence of the finite size of the trap implicitely assumed when considering a lattice diffusion. In fact, since the trap is assumed to be a lattice site, its extension is given by the lattice parameter. If we assume a lattice parameter a and we take the limit $a \to 0$ keeping $\lambda a^2/2 = D$ and $\gamma a = k_0$ in expression (4.8), Collins and Kimball's result for the time-dependent reaction rate is reobtained. In this way we think that the proposed treatment may be helpful in particular to analyze the short time behavior of reaction mediated processes and the influence of reaction dynamics.

ACKNOWLEDGMENTS

The authors acknowledge Dr. Domingo Prato for a thorough discussion of this paper. This research has been supported by CONICET (Argentina) through Grant No. PICT 0153/98 and by CONICOR through Grant No. PID 4158/97.

[1] A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses*, edited by I. Zschtkke (Reidel, Dordrecht, 1986).
[2] G. H. Weiss, J. Stat. Phys. **42**, 3 (1986).
[3] N. S. Goel and N. Richter-Dyn, in *Stochastic Models in Biology* (Academic, New York, 1974).
[4] B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts, and J. Watson, *Biología Molecular de la Célula* (Omega, Barcelona, 1992).
[5] S. H. Glarum, J. Chem. Phys. **33**, 1371 (1960).
[6] C. A. Condat, Z. Phys. B **77**, 313 (1989).
[7] J. T. Bendler and M. F. Shlesinger, in *The Wonderful World of Stochastics*, edited by M. F. Shlesinger and G. H. Weiss (Elsevier, Amsterdam, 1985).
[8] D. Wang, S. Gou, and D. Axelrod, Biophys. Chem. **43**, 117 (1992).
[9] W. Nadler and D. L. Stein, J. Chem. Phys. **104**, 1918 (1996).
[10] M. Brown and H. Goldstein, Science **232**, 34 (1986).
[11] R. V. Smoluchowski, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **29**, 129 (1917).

[12] Z. Koza and H. Taitelbaum, Phys. Rev. E **57**, 237 (1998).
[13] M. O. Cáceres, C. E. Budde, and M. A. Ré, Phys. Rev. E **52**, 3462 (1995).
[14] J. L. Spouge, A. Szabo, and G. H. Weiss, Phys. Rev. E **54**, 2248 (1996).
[15] M. A. Ré, C. E. Budde, and M. O. Cáceres, Phys. Rev. E **54**, 4427 (1996).
[16] F. C. Collins and G. E. Kimball, J. Colloid Sci. **4**, 425 (1949).
[17] R. M. Noyes, J. Chem. Phys. **22**, 1349 (1954).
[18] K. Razi Naqvi, K. J. Mork, and S. Walderstrøm, J. Phys. Chem. **84**, 1315 (1980).
[19] K. Razi Naqvi, S. Walderstrøm, and K. J. Mork, J. Phys. Chem. **86**, 4750 (1982).
[20] J. T. Chuang and K. B. Eisenthal, J. Chem. Phys. **62**, 2213 (1975).
[21] J. K. E. Tunaley, Phys. Rev. Lett. **33**, 1037 (1974).
[22] J. W. Haus and K. W. Kehr, Phys. Rep. **150**, 265 (1987).
[23] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
[24] C. A. Condat, Phys. Rev. A **39**, 2112 (1989).
[25] M. Lax and H. Scher, Phys. Rev. Lett. **39**, 781 (1977).
[26] A. Papoulis, *Probablity, Random Variables and Stochastic Processes*, 3rd ed. (McGraw-Hill, Singapore, 1991), p. 166.
[27] N. G. van Kampen, Physica A **96**, 435 (1979).
[28] G. H. Weiss and R. J. Rubin, Adv. Chem. Phys. **52**, 363 (1983).
[29] W. Feller, *An Introduction to Probability Theory* (Wiley, New York, 1967), Vol. II.
[30] G. Honing and U. Hirdes, J. Comput. Appl. Math. **10**, 113 (1984).