Diffusion-controlled bimolecular reactions: Long- and intermediate-time regimes with imperfect trapping within a Galanin approach

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We study a model for the $A+B\rightarrow B$ diffusion-reaction system in one dimension, in which the reaction sites are modeled by a Markovian stochastic process. Mean values of the A particle density are obtained, exactly for "dilute" B systems and approximately for "dense" ones. Results are compared with numerical simulations and show good agreement in the short-, intermediate-, and long-time regimes.

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I. INTRODUCTION

The study of irreversible bimolecular diffusion-reaction systems within the diffusion-controlled regime (i.e., when the reaction time is negligible in comparison with the diffusion time) has been receiving great interest for well over a decade. This was motivated by the "anomalous" kinetic laws that govern the evolution of these chemical reactions, as, in low-dimensional systems, they depart from the standard mean-field rate equations [1–17]. Although exact solutions are difficult to obtain, several asymptotic results for the particle-concentration decay have been obtained by means of simulations and/or analytical procedures, through heuristic arguments or by scaling analysis. So far, the different aspects studied cover the influence of dimensionality, conservation laws, segregation properties [6,8,10,11], statistics of nearest-neighbor distances [9,14,15], effects of noise and/or disorder [13,17], etc. Some review articles covering these and other aspects are listed in Ref. [18]. As has been indicated in almost all references, this process could be used to model several different physical and chemical systems: electron trapping and recombination, exciton trapping, defect recombination, bioenzymatic and membrane reactions, surface catalysis, soliton-antisoliton recombination, and so forth.

In this article we focus our attention on the extensively studied $A+B\rightarrow B$ reaction in one dimension. Our aim is to use this simple reaction as a benchmark in order to introduce an alternative and flexible scheme to study diffusion-controlled reactions. This scheme, which, as will be shown, corresponds to the diffusion-controlled limit, was initially introduced to study neutron-diffusion problems with absorption by "small" (and mobile) absorbers [19,20].

The main characteristics of this model are as follows.

(i) It naturally includes the possibility of imperfect reactions or imperfect trapping [15,21].

(ii) It is the continuous limit of the corresponding master equation usually employed in simulations.

(iii) It is an appropriate framework to obtain analytic, exact or approximate, results.

(iv) It offers the possibility of analyzing not only the asymptotic long-time regime, but also the short- and intermediate-time regimes.

Our interest in the study of the short-time behavior and the imperfect-trapping problem, in addition to the natural interests of chemists and material scientists, was motivated by a recent simulation [21] showing a peculiar short-time behavior and the effect of a low reaction probability, as well as by an experimental realization of a one-dimensional system [22]. Previous results of this scheme, together with a path-integral approach to it, have been presented in Ref. [23].

In the present paper we investigate, by means of this scheme, the behavior of the $A+B\rightarrow B$ reaction in one dimension, including cases in which only one of the species (A or B) moves as well as cases in which both species are mobile. In Sec. II, we present the model for the case of one trap, its method of solution, and its relation to simulations as the continuous limit of the associated master equation. Results for different situations are compared with simulations. In Sec. III we consider the case of several traps, considering different orders of approximation and its comparison with simulations. Finally, a general discussion, including the possibility of extending this scheme to higher-dimensional systems and other kind of reactions, is given in Sec. IV.

II. THE SCHEME FOR THE SINGLE-TRAP CASE

We start this section repeating, for sake of completeness, some results of Ref. [20]. As was indicated in the Introduction, we consider the one-dimensional $A+B\rightarrow B$ reaction. In this process, B plays the role of an absorber (or a catalyzer) and then the system can be

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modeled by the Galanin theory [19,20]. Within this scheme, the kinetic equation for the density $N(x,t)$ of the A particles can be written as

$$\frac{\partial}{\partial t}N(x,t)=D_A\frac{\partial^2}{\partial x^2}N(x,t)-\gamma\delta[x-\epsilon(t)]N(x,t)\ . \qquad (1)$$

Here D is the diffusion of the A particles, γ is the Galanin constant which measures the reaction probability, and $\epsilon(t)$ indicates the (random) position of the B (trapping) particle. Before discussing the procedure for solving this equation, we are going to show the connection of Eq. (1) with the discrete master equation used in standard simulations.

A. Connection with simulations

The master equation corresponding to the process $A+B\rightarrow B$, for a B particle fixed in a given lattice point (for instance, the origin) and A particles (indicated by the index α) doing a random walk on a one-dimensional lattice (with sites indicated by the index n), and with a reaction (absorption) rate β each time one of them meets the B particle, is given by

$$\frac{\partial}{\partial t}P_{\alpha,n}(t)=\lambda P_{\alpha,n-1}(t)+\lambda P_{\alpha,n+1}(t)-(2\lambda+\beta\delta_{n,0})P_{\alpha,n}(t)\ , \qquad (2)$$

where $P_{\alpha,n}(t)$ indicates the probability density of finding the αth A particle at site n and at time t, and λ is the jump probability. Then, the probability of absorption of an A particle arriving at the origin (where the B particle is located) is $p=\beta(2\lambda+\beta)^{-1}$. This means that $\beta\rightarrow 0$ corresponds to no absorption while $\beta\rightarrow\infty\,(p\rightarrow 1)$ corresponds to perfect absorption. In order to consider the continuous limit we make the distance between adjacent sites Δ go to zero in such a way that $x=n\Delta$, thus obtaining from Eq. (2)

$$\frac{\partial}{\partial t}P_\alpha(x,t)=D_A\frac{\partial^2}{\partial x^2}P_\alpha(x,t)-\gamma\delta(x)P_\alpha(x,t)\,, \qquad (3)$$

where

$$D_A=\lim_{\Delta\rightarrow 0,\lambda\rightarrow\infty}\Delta^2\lambda\ ,\quad \gamma=\lim_{\Delta\rightarrow 0,\beta\rightarrow\infty}\Delta\beta\ ,$$

$$\delta(x)=\lim_{\Delta\rightarrow 0}\frac{\delta_{i,0}}{\Delta}\ .$$

This limit is exact and could be analyzed from the point of view of the absorption. It is clear that $p\approx D^{-1}\gamma\Delta\rightarrow 0$, indicating weak absorption. Let us consider, however, the meaning of the limit $\gamma\rightarrow\infty$. For instance, if $\gamma\rightarrow\infty$ as $D\Delta^{-1}$, we have the limit $p=1$, corresponding to perfect absorption. This aspect is clearly seen through the analysis of the solution of Eq. (3). Calling $G^{(0)}(x,t|x',t')$ the free-diffusion propagator and $x_0^{(\alpha)}$ the initial coordinate (at $t=0$) of the αth A particle, we have

$$P_\alpha(x,t)=G^{(0)}(x,t|x_0^{(\alpha)},0)-\gamma\int_0^t dt'G^{(0)}(x,t|0,t')P_\alpha(0,t')\ . \qquad (4)$$

Laplace transforming Eq. (4) we obtain

$$P_\alpha(0,s)=G^{(0)}(0|x_0^{(\alpha)},s)[1-\gamma G^{(0)}(0|0,s)]^{-1}\ , \qquad (5)$$

which, when $\gamma\rightarrow\infty$, implies $P_\alpha(0,s)=0$, which is the boundary condition of an absorbing barrier at the origin, which corresponds to a perfect absorber [14,15,16,18(g)]. It is clear that intermediate values of γ $(0<\gamma<\infty)$ will correspond to an imperfect trap, and from the point of view of boundary conditions it corresponds to something intermediate between an absorbing barrier (Dirichlet boundary conditions) and no absorption or total reflection (Neuman boundary condition). Such a case can be described by "albedo" boundary conditions (see below) [24,15].

Going back to Eq. (2), for the case of a moving B particle, it is enough to replace $\delta_{n,0}$ by $\delta_{n,n(t)}$ inside the equation, take the same limit as before, and obtain the Galanin model as given by Eq. (1). Now $n(t)$ is the position of the moving A particle at time t.

B. Solution of the model

The only hypothesis that is necessary to take into account in order to find a solution of Eq. (1) is the Markov character of the process $\epsilon(t)$ [25]. We are interested in calculating $n(x,t)=\langle N(x,t)\rangle$, that is, the averaged particle density, where the average is taken over realizations of $\epsilon(t)$. Taking averages in Eq. (1) we obtain

$$\frac{\partial}{\partial t}n(x,t)=D_A\frac{\partial^2}{\partial x^2}n(x,t)-\gamma\mathcal{A}(x,t)\ , \qquad (6)$$

where $\mathcal{A}(x,t)=\langle\delta(x-\epsilon(t))N(x,t)\rangle$. The effect of the reactant B on A is completely specified by $\mathcal{A}(x,t)$; the knowledge of this quantity makes it simple to evaluate $n(x,t)$. Let us consider the integral form of Eq. (1):

$$N(x,t)=\int_{-\infty}^{\infty}dx'G^{(0)}(x,t|x',0)N(x',0)-\gamma\int_0^t dt'\int_{-\infty}^{\infty}dx'G^{(0)}(x,t|x',t')\times\delta(x'-\epsilon(t'))N(x',t')\ , \qquad (7)$$

$N(x',0)$ being the initial distribution of A particles. Iterating Eq. (7), multiplying by $\delta(x-\epsilon(t))$, and taking averages, we find an infinite expansion whose first two terms read

$$\mathcal{A}(x,t)=\langle\delta(x-\epsilon(t))N(x,t)\rangle$$
$$=\int_0^t dt'\int_{-\infty}^{\infty}dx'G^{(0)}(x,t|x',t')\langle\delta(x-\epsilon(t))\rangle S(x',t')$$
$$-\gamma\int_0^t dt'\int_{-\infty}^{\infty}dx'\int_0^{t'}dt''\int_{-\infty}^{\infty}dx''\langle\delta(x-\epsilon(t))\delta(x'-\epsilon(t'))\rangle\times G^{(0)}(x,t|x',t')G^{(0)}(x',t'|x'',t'')S(x'',t'')+\cdots\ , \qquad (8)$$

where we have called $S(x,t)=N(x,0)\delta(t)$. As we have assumed that ϵ is a Markov process, we have

$$\langle \delta(x-\epsilon(t))\rangle = \int_{-\infty}^{\infty} \delta(x-\epsilon)P(\epsilon,t)d\epsilon = P(x,t)$$
$$= \int_{-\infty}^{\infty} W(x,t|x_0,0)P(x_0)dx_0 ,$$
$$\langle \delta(x-\epsilon(t))\delta(x'-\epsilon(t'))\rangle$$
$$= P(x,t;x',t')$$
$$= W(x,t|x',t') \times \int_{-\infty}^{\infty} W(x',t'|x_0,0)P(x_0)dx_0 ,$$
$$\langle \delta(x-\epsilon))\delta(x'-\epsilon(t'))\delta(x''-\epsilon(t''))\rangle$$
$$= P(x,t;x',t';x'',t'')$$
$$= W(x,t|x',t')W(x',t'|x'',t'') \times \int_{-\infty}^{\infty} W(x'',t''|x_0,0)P(x_0)dx_0 ,$$

and similarly for higher-order correlations. Here we have used the standard notation [25] for the point and the initial probability distribution $P(x_0)$, and $W(x,t|x',t')$ is the conditional probability for the process ϵ. Substitution of these mean values into Eq. (8) leads us to another (infinite) expansion which can be summed as the following closed (exact) integral equation for $\mathcal{A}(x,t)$:

$$\mathcal{A}(x,t) = \int_0^t dt' \int_{-\infty}^{\infty} dx' G^{(0)}(x,t|x',t')S(x',t') \times \int_{-\infty}^{\infty} W(x,t|x_0,0)P(x_0)dx_0 - \gamma \int_0^t dt' \int_{-\infty}^{\infty} dx' G^{(0)}(x,t|x',t') \times W(x,t|x',t')\mathcal{A}(x',t') . \quad (9)$$

With this result in hand, we are, in principle, able to solve Eq. (6) for $n(x,t)$. Such a solution is obtained as

$$n(x,t) = \int_{-\infty}^{\infty} dx' G^{(0)}(x,t|x',t')N(x',0) - \gamma \int_0^t dt' \int_{-\infty}^{\infty} dx' G^{(0)}(x,t|x',t')\mathcal{A}(x',t') . \quad (10)$$

In the following we consider some examples.

C. Examples

The cases to be considered here are the following: (i) the trap (B) fixed and the particles (A) mobile; (ii) the trap mobile and the particles fixed (target problem); (iii) both mobile. In all cases the analytical results are going to be compared with simulations. It is worthwhile to remark that all these results are exact.

1. Fixed trap

Due to the translation invariance, we assume that the trap is fixed at the origin. As the B particle is immobile $W(x,t|x',t')=\delta(x-x')$, hence Eqs. (1) and (7) reduce to [here $N(x,t)\equiv n(x,t)$]

$$\frac{\partial}{\partial t} n(x,t) = D_A \frac{\partial^2}{\partial x^2} n(x,t) - \gamma \delta(x) n(x,t) , \quad (11)$$

$$n(x,t) = \int_{-\infty}^{\infty} dx' G^{(0)}(x,t|x',0)n(x',0) - \gamma \int_0^t dt' \int_{-\infty}^{\infty} dx' G^{(0)}(x,t|x',t') \times \delta(x')n(x',t') . \quad (12)$$

Assuming a uniform initial distribution of A, $n(x,0)=n_0$, and using the Gaussian form of the free diffusion propagator, Eq. (12) reduces to

$$n(x,t) = n_0 - \gamma \int_0^t dt' \frac{e^{-[x^2/4D_A(t-t')]}}{\sqrt{4\pi D_A(t-t')}} n(0,t') . \quad (13)$$

The use of Laplace transformation renders

$$n(x,p) = n_0 \left\{ p^{-1} - \frac{\gamma}{2\sqrt{D_A}} \frac{e^{-(|x|/\sqrt{D_A})p^{1/2}}}{p\left[p^{1/2} + \frac{\gamma}{2\sqrt{D_A}}\right]} \right\} . \quad (14)$$

By doing the inverse Laplace transform we have

$$n(x,t) = n_0 \left\{ \operatorname{erf}\left[\frac{|x|}{2\sqrt{D_A}} t^{-1/2}\right] + e^{|x|(\gamma/2D_A)+(\gamma^2/4D_A^2)t^2} \times \operatorname{erfc}\left[\frac{|x|}{2\sqrt{D_A}} t^{-1/2} + \frac{\gamma}{2\sqrt{D_A}} t^{1/2}\right] \right\} . \quad (15)$$

When considering the limit $\gamma \to \infty$, we recover the solution for a perfect trap [26].

At this point, it is worth remembering the connection about boundary conditions for the fixed-trap case, done after Eq. (5). Let us look at this problem, considering an albedo boundary condition at the origin (also called "radiation" boundary conditions) [24]:

$$\left.\frac{\partial}{\partial x} n(x,t)\right|_{x=0} = \kappa n(x,t)|_{x=0} . \quad (16)$$

If $\kappa \equiv 0$, we have Neuman boundary conditions implying total reflection; $\kappa \to \infty$ corresponds to Dirichlet boundary conditions which imply an absorption barrier. The case $0<\kappa<\infty$, which corresponds to albedo boundary conditions, implies a partial reflection. The solution of this problem turns out to be completely equivalent to the previous one, if we make the identification $\kappa=\gamma/(2D_A)$ which relates the reflection coefficient to the reaction parameter [15].

An aspect largely studied in relation to the fixed-trap problem is the time dependence of the nearest-neighbor distance. It is obtained as

$$\int_0^{x_1} n(x,t)dx = 1 . \quad (17)$$

This turns out to be simpler to calculate in the Laplace space as

$$\int_0^{x_1} n(x,p)dx = p^{-1} = n_0 \left\{ \frac{x_1}{p} + \frac{\gamma}{2p^{3/2}\left[\frac{\gamma}{2\sqrt{D_A}}+p\right]} \times \left[e^{-x_1 p^{1/2}/\sqrt{D_A}}-1\right] \right\} . \quad (18)$$

Using the scaled variables and parameters, $\tau=\gamma^2 t/D_A$, $y=\gamma x/D_A$, $\alpha=2D_A n_0/\gamma$, and making the inverse Laplace transformation of Eq. (18) we find

$$\alpha\left\{ y_1 + \frac{\tau^{1/2}}{\sqrt{\pi}} e^{-y_1^2/4\tau}(y_1+1)\text{efrc}\left[\frac{y_1}{2}\tau^{-1/2}\right] + e^{y_1/2+\tau/4}\text{erfc}\left[\frac{y_1}{2}\tau^{-1/2}+\frac{\tau^{1/2}}{4}\right] - \frac{\tau^{1/2}}{\sqrt{\pi}} - e^{\tau/4}\text{erfc}\left[\frac{\tau^{-1/2}}{2}\right]+1 \right\} = 1 . \quad (19)$$

From this expression it is in principle possible to obtain the value of $y_1(x_1)$ at all times. However, it is simpler to look for the asymptotic behavior (that is, $\tau\to\infty$). In this long-time limit we find that

$$x_1 \sim \left[\frac{2}{n_0}\right]^{1/2} (\pi D_A t)^{1/4} , \quad (20)$$

a result that is coincident with the one obtained by previous authors [26]. We see that x_1 becomes independent of γ.

2. "Target" problem

In this case the A particles are fixed at the origin while the B traps are mobile. Then we have that $G^{(0)}(x,t|x',t')=\delta(x-x')$ (or equivalently $D_A\equiv 0$), $n(x,0)=n_0\delta(x)$, and assuming a diffusive motion for the trap,

$$W(x,t|x',t')=[4\pi D_B(t-t')]^{-1/2}\exp\left[-\frac{(x-x')^2}{4D_B(t-t')}\right] .$$

We also assume that the initial location of the trap is random. Hence Eqs. (6) and (10) take the form

$$\partial_t n(t) = -\gamma \mathcal{A}(0,t) , \quad (21)$$

$$\mathcal{A}(0,t) = \frac{n_0}{\sqrt{D_B t}} - \gamma\int_0^t dt'[4\pi D_B(t-t')]^{1/2}\mathcal{A}(0,t') , \quad (22)$$

and the solution for $n(t)$ is ($\tau=\gamma^2 t/D_B$, $\alpha=2D_B n_0/\gamma$)

$$n(\tau) = n_0 e^{\tau/4}\text{erfc}(\tfrac{1}{2}\tau^{1/2}) . \quad (23)$$

At long times it reduces to

$$n(\tau\gg 1)\sim 2\frac{n_0}{\sqrt{\pi}}\tau^{-1/2} . \quad (24)$$

The asymptotic behavior has the known $\tau^{-1/2}$ dependence.

3. Both particles mobile

In this case we consider that both particles move diffusively. We will assume that both particles are initially located at the origin. In this case we have to use the full form of Eqs. (6) and (10). The result for the absorption function $\mathcal{A}(x\cdot t)$ is

$$\mathcal{A}(x,t) = n_0\left[\frac{\pi}{4(D_A+D_B)}\right]^{1/2}\frac{e^{-x^2/4\beta t}}{\sqrt{4\pi\beta}} \times \left\{\frac{1}{\sqrt{\pi t}} - \alpha e^{\alpha^2 t}\text{erfc}(\alpha\sqrt{t})\right\} , \quad (25)$$

where $\alpha=\gamma/\sqrt{8(D_A+D_B)}$, n_0 the initial number of particles, and D_A and D_B the diffusion constants of A and B particles, respectively. The global (integrated over x) evolution of the number of A particles is given by

$$n(t) = n_0 e^{\alpha^2 t}\text{erfc}(\alpha\sqrt{t}) , \quad (26)$$

which gives, in the asymptotic (long-time) regime,

$$n(t) \underset{t\to\infty}{\sim} \frac{n_0}{\alpha} t^{-1/2} , \quad (27)$$

as could be expected.

III. SEVERAL-TRAPS CASE

So far we have considered the effect of only one trap (or B particle). It is clear that in the more interesting case of considering simultaneously several B particles, we will find different dynamics in the A particle density. The combined effects of diffusion and absorption by each B particle cause a depression in the A particle density extended in space. Each depression will influence other B particles close to the one that has caused it (affecting not *their* dynamics but A's, since the net absorption is proportional to the A particle density). Assume, for example, that there are only two B particles, initially far away from each other (i.e., the integral of the A particle density between both positions is larger than one, indicating the presence of several A particles between them). There is an initial transient period (its duration depending on the diffusion coefficients and the reaction rate) during which we could consider the effect of each B particle as independent from the others'. After some time has elapsed, the depression in the A particle density caused by one of the B particles influence the other, and vice versa. At this time we are no longer allowed to consider the B particles as independent, and it is necessary to resort to more elaborate schemes, appropriate to describe a *dense* B system and the interference effects referred to above.

In order to consider this case we extend the Galanin model introduced in Eq. (1) in the following form:

$$\frac{\partial}{\partial t}N(x,t)=D_A\frac{\partial^2}{\partial x^2}N(x,t)-\gamma\sum_{j=1}^{M}\delta(x-\epsilon_j(t))N(x,t)\ , \tag{28}$$

where we have considered that there are M of the B particles randomly distributed in the volume V. The integral form of this equation corresponding to Eq. (8) is

$$N(x,t)=G^{(0)}(x,t|x_0,0)-\gamma\sum_{i=1}^{M}\int_0^t dt'G^{(0)}(x,t|x',t')\times\delta(x'-\epsilon_i(t'))N(x',t')\ . \tag{29}$$

Here, in order to simplify the notation, we have considered only one A particle initially located at x_0. The extension to a larger number of A particles is trivial. Multiplying Eq. (29) by $\sum_{j=1}^{M}\delta(x-\epsilon_j(t))$ and iterating, we get

$$\sum_{i=1}^{M}\delta(x-\epsilon_i(t))N(x,t)=\sum_{i}^{M}\delta(x-\epsilon_i(t))G^{(0)}(x,t|x_0,0)-\gamma\sum_{i,j}^{M}\delta(x-\epsilon_i(t))\int_0^t dt_1\int_{-\infty}^{\infty}dx_1G^{(0)}(x,t|x_1,t_1)\delta(x_1-\epsilon_j(t_1))G^{(0)}(x,t|x_0,0)+\cdots\ . \tag{30}$$

In order to simplify the notation, we rewrite this equation in a shorthand notation:

$$\sum_{i=1}^{M}\delta(x-\epsilon_i(t))N(x,t)=\sum_{i=1}^{M}\delta_i(x)G_{x\underline{x}_0}-\gamma\sum_{i,j}^{M}\delta_i(x)G_{x\underline{x}_1}\delta_j(x_1)G_{\underline{x}_1\underline{x}_0}+\gamma^2\sum_{i,j,k}^{M}\delta_i(x)G_{x\underline{x}_1}\delta_j(x_1)G_{\underline{x}_1\underline{x}_2}\delta_k(x_1)G_{\underline{x}_2\underline{x}_0}+\cdots\ , \tag{31}$$

where we denote by x_i the pair (x_i,t_i), $\underline{x}_i$ indicates integration over the pair (x_i,t_i) for all functions containing these variables, and $G_{x,x'}=G^{(0)}(x,t|x',t')$. Equation (31) can be rewritten in a more compact notation as

$$\sum_{i=1}^{M}\delta(x-\epsilon_i(t))N(x,t)=\sum_{i}T_i(x,x_0)-\gamma\sum_{\substack{i,j\\(i\neq j)}}^{M}T_i(x,\underline{x}_i)T_j(x_1,x_0)+\gamma^2\sum_{i,j,k(i\neq j\neq k)}^{M}T_i(x,\underline{x}_1)T_j(x_1,\underline{x}_2)T_k(x_2,x_0)+\cdots\ , \tag{32}$$

where

$$T_i(x,x')=T_i(x,t|x',t')=\sum_{n=1}^{\infty}(-\gamma)^{n-1}\delta_i(x)G_{x\underline{x}_1}\delta_i(x_1)G_{\underline{x}_1\underline{x}_2}\cdots\delta_i(x_{n-1})G_{\underline{x}_{n-1}x'}\ . \tag{33}$$

In Eq. (33) we have summed up over equal indices.

At this point, as we have done before, we must average over the realizations of B particle trajectories, keeping in mind the assumption that the process ϵ is Markovian. We also need to average over initial conditions considering the limits $M\to\infty$ and $V\to\infty$ in such a way that $n_B=M/V=$const. Calling as before $\mathcal{A}(x,t)$ the (averaged) absorption function, we obtain

$$\mathcal{A}(x,t)=n_B\hat{T}(x,x_0)-\gamma n_B^2\hat{T}(x,\underline{x}_1)\hat{T}(x_1,x_0)+\gamma^2\hat{T}(x,\underline{x}_1)\hat{T}(x_1,\underline{x}_2)\hat{T}(x_2,x_0)[n_B^3+n_BW(x_1,x_2)]-\gamma^3\hat{T}(x,\underline{x}_1)\hat{T}(x_1,\underline{x}_2)\hat{T}(x_2,\underline{x}_3)\hat{T}(x_3,x_0)\times\{n_B^4+n_B^2[W(x_1,x_2)+W(x_2,x_3)+W(x_1,x_3)]+n_BW(x_1,x_2)W(x_2,x_3)\}+\cdots\ , \tag{34}$$

where

$$\hat{T}(x,x')=\sum_{n=1}^{\infty}(-\gamma)^{n-1}G_{x\underline{x}_1}W_{x\underline{x}_1}G_{\underline{x}_1\underline{x}_2}W_{\underline{x}_1\underline{x}_2}\times\cdots G_{\underline{x}_{n-2}\underline{x}_{n-1}}W_{\underline{x}_{n-2}\underline{x}_{n-1}}G_{\underline{x}_{n-1}x'} \tag{35}$$

and the short notation $G_{x,x'}$ also holds for $W_{x,x'}$. Now, since $G_{x,x'}$ and $W_{x,x'}$ are only dependent on the difference of their arguments $G_{x-x'}$ and $W_{x-x'}$, we make a Fourier-Laplace transform. For those terms which do not contain W_{x_i,x_j}, this is trivial as they have a convoluted form. However, the other cases present much difficulty. What results is

$$\mathcal{A}(k,p)=n_BT(k,p)-\gamma n_B^2T(k,p)^2+\gamma^2n_B^3T(k,p)^3-\cdots+\gamma^{s-1}n_B^sT(k,p)^s+\cdots+\gamma^2n_B^3T_{3,1}(k,p)-\gamma^3n_B^4[3T_{4,1}(k,p)+T_{4,2}(k,p)]+\cdots\ , \tag{36}$$

where

$$T(k,p)=G^0(k,p)[1+\gamma GW(k,p)]^{-1}\ , \tag{37}$$

with $GW(k,p)$ defined as the Laplace-Fourier transform of $G_x W_x$, which is coincident with the one-B-particle contribution, and the meaning of $T_{3,1}(k,p)$, $T_{4,1}(k,p)$, $T_{4,2}(k,p),\ldots,$ is clear. [For example, $T_{3,1}(k,p)=T(k,p)^3W(k,p)^1$.] If we neglect higher-order contributions in Eq. (36), we recover the *dilute* approximation corresponding to only one B particle. However, it is possible to sum up all the contributions of the form $\gamma^{s-1}[n_B T(k,p)]^s$, rendering

$$\mathcal{A}(k,p)=\frac{n_B T(k,p)}{1+\gamma n_B T(k,p)}+\gamma^2 n_B^3 T_{3,1}(k,p)+\cdots\ . \tag{38}$$

The first term becomes a *manageable* approximation for dense systems. The rest of the (crossed) terms represent a much more difficult problem, which we will not consider here. Then as our approximation for dense systems we will adopt the form

$$\mathcal{A}(k,p)\sim n_B\frac{T(k,p)}{1+\gamma n_B T(k,p)}\ . \tag{39}$$

The naive approximation of assuming that $\mathcal{A}(k,p)\sim n_B T(k,p)$, corresponding to the dilute system, will be valid as long as $\gamma n_B T(0,p)\ll 1$, which gives us a time scale during which such a naive approximation will be valid. Taking into account the above indicated approximation of $\mathcal{A}(k,p)$ for dense B systems [Eq. (39)], we get the following result for the global ($k=0$) dependence of the A density:

$$n_A(t)=-\frac{\gamma n_0}{\sqrt{2\pi}}\frac{\gamma^2}{16\pi(D_A+D_B)} -\left[\frac{\gamma n_b}{\sqrt{2\pi}}\right]^{-1/2}\mathrm{Im}\left\{\frac{e^{S_+^2 t}}{S_+}\mathrm{erfc}(-S_+\sqrt{t}\,)\right\}, \tag{40}$$

where

$$S_\pm=-\frac{\gamma}{\sqrt{\pi(D_A+D_B)}} \pm\left[\frac{\gamma^2}{16\pi(D_A+D_B)}-\frac{\gamma n_b}{\sqrt{2\pi}}\right]^{1/2}. \tag{41}$$

In the long-time limit we find that $n_A(t)\sim t^{-1/2}$, as could be expected, in agreement with previous results.

IV. COMPARISON WITH SIMULATIONS

As a test of the results found in the preceding sections within this Galanin-like model we have compared them with several simulations.

Simulations are carried out in a one-dimensional network where particles jump to their neighbor site with a probability $P_\pm^{A,B}$ (A or B for A or B particles, + to the right, − to the left). When two particles A and B are coincident on the same site we consider a probability P_{ABS} to react; in such a case the A particle disappears. In one time step all particles are updated with the above-mentioned processes and probabilities. Then, simulation of the master equation (2) is accomplished by taking z as the time between steps, $t=nz$ as the time of the nth step, $P_\pm^A=\lambda z$, and $P_{ABS}=\beta z$. Taking into account the continuous limit from Eq. (2) to Eq. (3) as explained in Sec. III, we conclude that simulations of Galanin equations can be performed doing the above-mentioned processes with $P_\pm^{A,B}=D_{A,B}z/\Delta^2$ and $P_{ABS}=\gamma z/\Delta$.

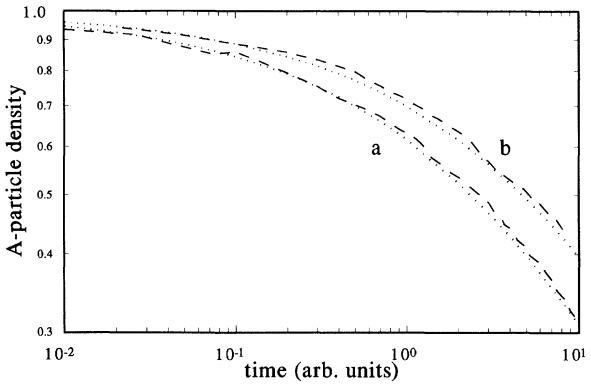

FIG. 1. Probability of survival of one A particle and one trap placed at the origin at $t=0$. The parameters are $\Delta=0.01$, $z=0.001$, $D_A=\gamma=1$. The dashed lines show the result of the simulation done for 1000 realizations. The dotted lines show the theoretical result of Eq. (23). (a) $D_B=0$; (b) $D_B=1$.

In Fig. 1 we plot the probability of survival $n_A(t)/n_A(0)$ in the case of only one particle A and B placed at the origin at $t=0$. We have taken as values of parameters $\Delta=0.01$, $z=0.001$, and $D_A=\gamma=1$ and we have done 1000 realizations. Simulations are compared with the analytical results of Eq. (23). As expected, both results are in a very good agreement for all times. In fact they must coincide in the limits $z\to 0$, and $\Delta\to 0$ since Eq. (23) is an exact result. Figure 2 is the same for a case

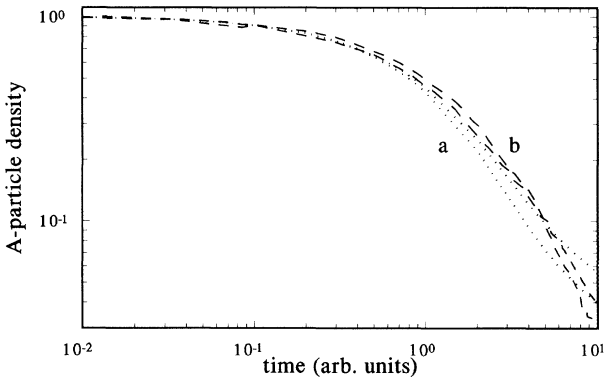

FIG. 2. Probability of survival $n_A(t)/n_A(0)$ for a uniformly distributed set of B particles and the A particle initially at the origin. The parameters are the same as in Fig. 1. The dotted lines show the theoretical result of Eq. 40. (a) $D_B=0$; (b) $D_B=1$.

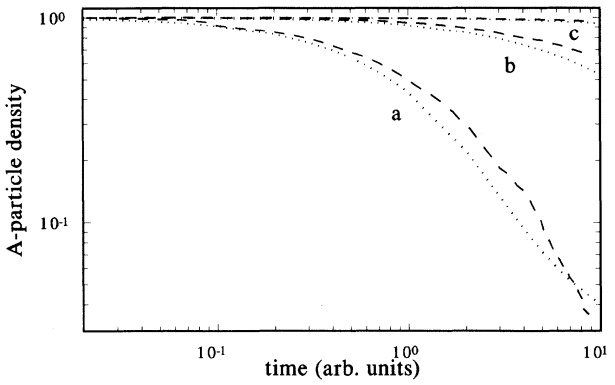

FIG. 3. The same system as that shown in Fig. 2, but for different densities of B particles. (a) $n_B=1$; (b) $n_B=0.1$; (c) $n_B=0.01$.

of many trapping particles. We consider a uniformly distributed set of B particles with only one A particle placed at the origin as an initial condition. Simulations and analytical results given by Eq. (40) are in good agreement for short and intermediate times. For long times differences are mainly due to two reasons. On one hand, our approximation for dense systems is more sensitive at long times. On the other hand, simulations are also more imprecise. Finally, in Fig. 3 we show results for systems with different densities of B particles.

V. CONCLUSIONS

In the present work we have introduced an alternative and flexible scheme to study diffusion-limited reactions. This scheme, which is based on the Galanin model for neutron-diffusion problems, was shown to have several interesting features: it is the continuous limit of the corresponding master equation employed in simulations; it includes the possibility of imperfect reactions; and it offers the possibility of getting analytic (exact or approximate) results covering the whole time range. We have focused on the $A+B\rightarrow B$ reaction in one dimension in order to use it as a benchmark for the model. Initially we have considered the case of only one B particle, discussing cases where only one of the species (A or B) moves (trapping or target problems), as well as the case when both species are mobile. The comparison with the simulations shows rather satisfactory agreement, supporting the goodness of the model. Among others, for the trapping case, we have recovered results for nearest-neighbor distances obtained by others authors [14]. However, we were able to include the effect of imperfect trapping, connecting it with special boundary conditions. In the case of *dense B* systems we have obtained approximate expressions also in good agreement with simulations.

There are several directions in which we can extend the present scheme

(i) Include source terms, adequately introducing them in the master equation.

(ii) Consider higher-dimensional situations. For instance, this can be done by changing the reaction terms to include the finite size of the particles in order to avoid divergences.

(iii) Consider other kinds of problems, for instance, the dynamics of reaction fronts [27], by considering as the initial condition two semispaces with A and B particles, respectively. We could also consider reactions in finite systems, imposing adequate boundary conditions.

(iv) Discuss other kind of reactions. Of particular interest are the cases $A+A\rightarrow 0$ and $A+B\rightarrow 0$. In such situations the model must be rewritten as a self-consistent equation, or as a set of coupled equations, for the particle densities.

All these points are the subject of further work and will be discussed elsewhere [28].

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