Kinetics of Trapping Reactions with a Time Dependent Density of Traps

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We study a trapping process where the traps (particles B), besides being mobile, have a variable number. We analyze two cases related with the coupled reactions: $A + B \rightarrow B$, $B + C \rightarrow C$, and $A + B \rightarrow B$, $B + C \rightarrow 0$. It is shown that the time evolution of the traps strongly influences the kinetics of the trapping process, yielding qualitatively different behavior in both cases. The results of a model, adapted from one used before for trapping and annihilation in a one dimensional diffusion-limited system, have been compared with simulations yielding good qualitative agreement. [S0031-9007(97)02752-X]

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The important role played by diffusion-controlled reactions in the most diverse branches of chemistry, physics, and biology has attracted the interest of researchers into the study of these problems during the last couple of decades [1]. This interest was motivated by the so-called "anomalous" kinetic laws that govern the evolution of these chemical reactions as in low dimensional systems ($d \leq 2$); they depart from the standard mean field rate equations [1,2]. In general, the kind of problems that have been studied include coalescence and annihilation reactions in one or two-species systems [1,2]. Such systems show a remarkable sensitivity in the kinetics of the recombination process and segregation to changes on initial conditions, presence of sources, disorder, external forces, etc. [1–4]. Most of the recent literature is devoted to the analysis of these phenomena under the assumption that some kinds of rate equations are valid, considering the case of perfect reactions and, with lesser emphasis, in systems of partially absorbing media, which are of particular interest in many problems of attenuation in biological and physical problems [5–8].

In this Letter we address the problem of a trapping reaction (symbolically written $A + B \rightarrow B$) in a one dimensional system of diffusing A particles and B traps, but in the case where the number of traps is time dependent. This dependence can arise because the traps participate in another reaction or because they are externally controlled. Such a situation, which has not been treated previously in the scientific literature, besides its interest in relation with several problems related to heterogeneous reactions and catalysis, shows some peculiarities that makes relevant its study on its own right. Here we will consider the following two related situations: (a) $A + B \rightarrow B$, $B + C \rightarrow C$ (double trapping). (b) $A + B \rightarrow B$, $B + C \rightarrow 0$ (trapping with annihilated traps). In both cases it is clear that the second reaction will not be affected at all by the first one. This allows us to exploit known results for trapping and annihilation. In case (b), as usual, we restrict ourselves to equal initial densities of B and C particles in the annihilation reaction.

In the present work, we show the results of Monte Carlo simulations made for both cases, and comparisons with the result of a mean field evaluation and with another theoretical model, which is a version of the Galanin model [8–11], adapted to the present situation.

First we present the mean field results in both situations. In case (a) the solution is given by

$$n_B(t) = n_{B0} \exp(-\gamma_{BC} n_C t), \tag{1}$$

$$n_A(t) = n_{A0} \exp\left[-\frac{\gamma_{AB}\ n_{B0}}{\gamma_{BC}\ n_C}(1 - e^{-\gamma_{BC} n_C t})\right]. \tag{2}$$

For case (b), the solution is

$$n_B(t) = n_{B0}(1 + \gamma_{BC} n_{B0} t)^{-1}, \tag{3}$$

$$n_A(t) = n_{A0}(1 + \gamma_{BC} n_{B0} t)^{-\gamma_{AB}/\gamma_{BC}}. \tag{4}$$

Here $\gamma_{AB,BC}$ are the reaction rates of each reaction, $n_{A0,B0}$ the initial densities of A, B particles, and n_C the (fixed) C density for the case (a).

It is worth remarking that the qualitative behavior of the indicated solutions is clearly different. The most remarkable aspect is that asymptotically they reach completely different limits. In the first case we have

$$n_A(t \rightarrow \infty) = n_{A0} \exp\left(-\frac{\gamma_{AB} n_{B0}}{\gamma_{BC} n_C}\right). \tag{5}$$

This finite value is in contrast with the second case where we have total extinction [$n_A(t \rightarrow \infty) \propto t^{-\gamma_{AB}/\gamma_{BC}}$] for A particles.

For the Galanin description we have adapted the model that was introduced for the annihilation case [9]. We will not go into the details of the model (discussed, in particular, in [8,9]), but only exploit the results of our previous work. The general result for n_A, the density of A particles, is

$$\frac{d}{dt} n_A(t) = -\gamma_{AB} n_A(t) n_B(t) + \int_0^t dt'\, C(t - t') n_A(t') n_B(t'), \tag{6}$$

where $C(t) = \alpha\gamma_{AB}[(\pi t)^{-1/2} - \alpha \exp(\alpha^2 t)\,\mathrm{erfc}(\alpha\sqrt{t})]$ with $\alpha = \gamma_{AB}/\sqrt{4(D_A + D_B)}$; D_A and D_B are the diffusivities of particles A and B, respectively, and $n_B(t)$ is the (variable) density of B particles. Even though this equation was originally derived for a simple annihilation process, it can be proved to be correct for the general case of variable $n_B(t)$. For our particular cases this density comes from a trapping [case (a)] or an annihilation [case (b)] process.

The indicated integrodifferential equation must be solved numerically. However, the asymptotic analysis can be done analytically by means of Laplace transformation procedures yielding for the double trapping case the final value reached for A density

$$n_{Af} = n_A(t \to \infty) = n_{A0}\left(1 + \frac{n_{B0}}{n_C}\sqrt{\frac{D_A + D_B}{D_B + D_C}}\right)^{-1}. \tag{7}$$

This, again, is a finite value that contrasts with the second case where we have potentially a decay to zero $n_A(t \to \infty) \propto t^{-1/4}$. In the most general way, the asymptotic analysis within this model predicts that, if we assume a long time behavior $n_B(t) \propto t^{\beta}$, for $-1/2 < \beta \le 0, n_A$ will have a potential decay to zero, with an exponent $-(1/2 + \beta)$. On the contrary, as indicated in the double trapping case, when $\beta = -1/2$, n_A reaches a finite value. Hence, we can expect that for $\beta < -1/2, n_A$ will also reach a finite asymptotic value.

We give here a short description of the algorithm we have used in the simulations. These were made on a one dimensional lattice with periodic boundary conditions. We choose a particle at random and update this particle in the following way: we consider the possibility of a jump in either direction with a probability $q_{A,B,C}$. For A or B particles, if the particle does not jump and there is some trap (B or C, respectively) at the same site, then we consider the possibility of reaction with a probability $\min(1, pN_{B,C})$ [12], where $N_{B,C}$ is the number of traps in the site. After that, the time is increased in $(n_A + n_B + n_C)^{-1}$. If we call the space and time increments Δx and Δt, we can establish a relation between simulation and macroscopic parameters through the master equation for the process [13]. These relations are $D_{A,B,C} = q_{A,B,C}\,(\Delta x)^2/\Delta t$ and $\gamma_{AB,BC} = p_{AB,BC}(1 - 2\,q_{A,B})\Delta x/\Delta t$. We have taken $\Delta x = \Delta t = 1$ in all the cases.

In Fig. 1 we show the result of simulations, the Galanin model and the mean field for the density of A particles for two different values of γ_{AB}. Note that in order to keep a constant macroscopic rate γ we must change the microscopic absorption probability p whenever we change the jump probability q. It is clear that the Galanin model offers a better description of the problem than mean field approach although both give a qualitative good description for short times.

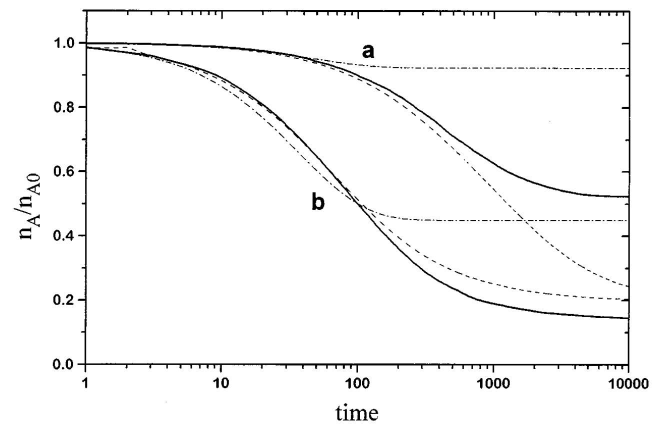

FIG. 1. Temporal evolution of the density of A particles for a double trapping system. The solid line corresponds to simulations, the dashed one to the Galanin model (numerical integration) and the dashed-dot one to mean field results. The simulation (10 realizations) was performed in a 1000 sites lattice with periodic boundary conditions. The common parameters are $n_{A0} = 1000$, $n_{B0} = 200$, $n_C = 50$, $q_A = q_B = q_C = 0.1$, $\gamma_{BC} = 0.4$, while $\gamma_{AB} = 0.008$ for (a) and 0.08 for (b). The final value n_{Af}/n_{A0} for the Galanin model is 0.2 in both cases.

Figures 2 and 3 show a study of the asymptotic value dependence with the diffusivities and the macroscopic absorption rate, respectively. The error bars indicate the standard deviation of values. For computing the final value we waited until $n_b = 0$ in each realization. In Fig. 2 we include the theoretical expression (7) in order to compare with simulations. In both figures we restricted ourselves to the case where $D_B = D_C$. We can see that the dependence of the asymptotic value of n_A on the

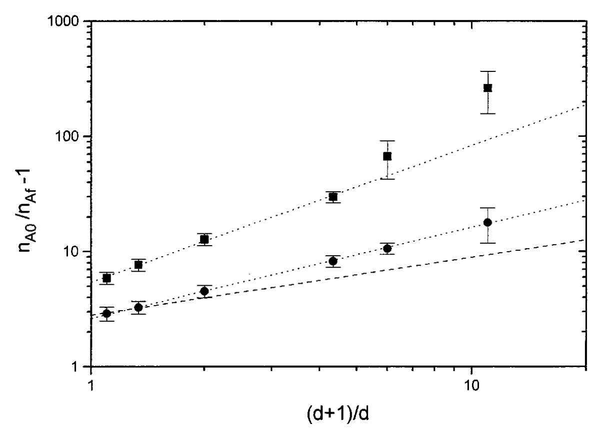

FIG. 2. Variation of the final value n_{Af} as function of $d = D_B/D_A$. Here we choose the same initial densities and lattice size as in Fig. 1. The diffusivities are $D_B = D_C = 0.03$ in all the cases. The parameters are $\gamma_{AB} = 0.2$ (squares) and 0.02 (circles), and $\gamma_{BC} = 0.2$ for both cases. The dashed line indicates the Galanin result [Eq. (7)]. The corresponding (constant) values for the mean field model are 53.6 (squares) and 0.5 (circles). The dotted lines correspond to a fitting of the simulation results.

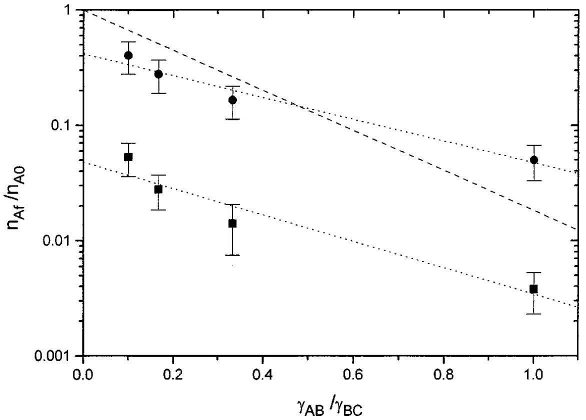

FIG. 3. Variation of final value n_{Af} as function of γ_{BC}/γ_{AB}. Here we have chosen the same initial densities and lattice size as in Fig. 1. The parameters are $D_B = 0.3$ (circles) and 0.03 (squares) while $\gamma_{BC} = 0.2$, $D_A = 0.3$ in both cases. The dashed line corresponds to mean field result [Eq. (5)]. The (constant) Galanin values are 0.2 (circles) and 0.96 (squares). The dotted lines correspond to a fitting of the simulation results.

diffusivity is qualitatively well described by the Galanin model, while it does not depend at all on the diffusivities for the mean field description. However, the Galanin expression does not show any dependence on the γ's though it is qualitatively well described by the mean field. Matching both theoretical results we expect that the diffusivity dependence will appear only on the ratio $d = D_B/D_A$ while the reaction rates dependence will appear as the ratio γ_{BC}/γ_{AB}. We have computed n_{Af} in some simulations, with results that confirm (at least approximately) this guess.

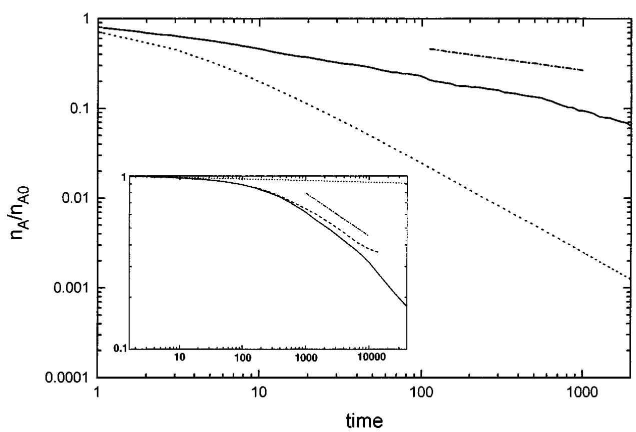

FIG. 4. Temporal evolution of the density of A particles for a trapping with annihilated traps. The solid line corresponds to simulations, and the dots to mean field results. The dot-dashed line indicates the $t^{-1/4}$ slope. The simulations (10 realizations or more) were performed in a lattice of 100 sites with periodic boundary conditions. The parameters are $n_{A0} = 100$, $n_{B0} = n_{C0} = 50$, $q_A = q_B = q_C = 0.1$, and $\gamma_{BC} = \gamma_{AB} = 0.8$. The inset shows the dependence with the lattice size: a 100-site lattice (dashed, $n_{Af}/n_{A0} = 0.35 \pm 0.06$) and a 200-site lattice (solid, $n_{Af}/n_{A0} = 0.16 \pm 0.06$); keeping the same density and the same parameters except that $\gamma_{AB} = 0.008$.

In Fig. 4 we show results for the annihilation case. It is worth remarking here that the result of n_A reaching a zero value is only valid for an infinite lattice. For a finite one we can, for example, reduce γ_{AB} until the trapping reaction becomes so slow that all the traps can be annihilated before they can trap all A particles. This is shown in the inset of Fig. 4.

Summarizing, we have shown that, for the reaction $A + B \rightarrow B$, the time evolution of the number of traps (B) can strongly influence the time evolution of the trapping process. Even more, there is a critical exponent $[n_B(t \rightarrow \infty) \propto t^{\beta}, \beta_c = -1/2]$ separating different qualitative asymptotic behaviors for n_A: for $-1/2 < \beta \leq 0$ we have complete extinction, while for $\beta \leq -1/2$ we obtain the asymptotic survival of the A particles. In the double trapping case, matching mean field, and Galanin results, we have seen that the n_{Af} dependence on diffusivities and reaction rates comes through the ratios D_B/D_A and γ_{BC}/γ_{AB}. The adapted Galanin model gives a much better agreement with simulations than mean field, with a better qualitative prediction of the parameter dependence. However, it needs further improvement in order to obtain a still better quantitative agreement with simulations. This last point will be the subject of further work.

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