Rate equation of the $A + A \rightarrow A$ reaction with probability of reaction and diffusion

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We study the coagulation reaction $A + A \rightarrow A$ with probability p of reaction in a one-dimensional lattice. We show that $d\rho/dt = -p\Gamma_1$, where $\rho(t)$ is the density of particles and $\Gamma_1(t)$ is the density of nearest-neighbor occupied sites. From the analysis of the crossover between the reaction-controlled-reaction and the diffusion-controlled-reaction regimes an approximate scaling ansatz for Γ_1 and ρ for different values of p is proposed. Using this scaling, the collapse of Monte Carlo data improves when p decreases. From this scaling an analytical approximation of the density is found which agrees well with the numerical results of $\rho(t)$ for different values of p.

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I. INTRODUCTION

In the past decade much effort has been dedicated to the study of diffusion-reaction systems, see, e.g., [1,2]. This is mainly due to the anomalous behavior that appears when the diffusion occurs on nonhomogeneous substrata (e.g., fractals [3,4] and multifractals [5]) or on one-dimensional systems. This behavior cannot be predicted by mean-field approximations.

In the coagulation reaction $A + A \rightarrow A$ the particles diffuse independently and react instantaneously and irreversibly when two of them meet. The density ρ of particles as a function of time t behaves, for long times, as [2,4,6],

$$\rho = \begin{cases} t^{-d_s/2} & \text{if } d_s < 2 , \\ t^{-1} & \text{otherwise} , \end{cases} \tag{1}$$

where d_s is the spectral dimension [7] of the substratum where the particles diffuse. For some fractal structures $d_s < 2$ and for d-dimensional Euclidean lattices, $d_s = d$.

Recently extensive numerical studies of the annihilation reaction $A + A \rightarrow 0$, with partial reaction probability were done [8] (for a related model see [9]). We modify the model in the same way, so that when two particles collide they react with probability p ($0 < p \leq 1$, see Sec. II for more details). In many physical and chemical processes, the reaction does not take place instantaneously and the species can collide many times before the reaction occurs. This can be the case when the reaction depends on the orientation of the molecules or when the species must overcome an effective energy barrier to react [10]. This is the motivation for the introduction of p into the model.

In the present work we analyze the behavior of $\rho(t)$ for the reaction $A + A \rightarrow A$ with the probability p of reaction in a one-dimensional lattice.

As we will see below, Eq. (1) holds at very long times independently of the value of p. That is $\rho(t) \sim t^{-1/2}$ when $t \rightarrow \infty$. Therefore we will focus our attention on the short- and intermediate-time regimes, where $\rho(t)$ strongly depends on p.

The paper is organized as follows. In Sec. II we present the model and the Monte Carlo simulation. In Sec. III we obtain the rate equation. This equation shows that the reaction rate, $d\rho/dt$, is proportional to the number Γ_1 of pairs of nearest-neighbor (NN) occupied sites per lattice site. In Sec. IV we analyze the behavior of Γ_1 as a function of ρ. We found that for $p \ll 1$, at short times (large ρ) the reaction is controlled by reaction processes. At very long times (small ρ) the reaction is controlled by diffusion. We also obtain a scaling function of Γ_1 and ρ for all values of ρ and p. Using a simple function which fulfills the scaling form, in Sec. V an approximation of $\rho(t)$ is obtained. We compare this approximation with the Monte Carlo data. Finally, in Sec. VI we state our conclusions.

II. THE MODEL AND THE MONTE CARLO SIMULATION

In the model the particles perform a random walk between NN sites of a one-dimensional lattice of length $L = 100\,000$. We use periodic boundary conditions in order to avoid edge effects.

At $t = 0$ each site of the lattice is occupied by a particle with probability ρ_0 ($\rho_0 \leq 1$), which is the initial particle density. A value of $\rho_0 = 0.8$ was used. After that the diffusion starts.

At each *Monte Carlo step*, one of the $n(t)$ particles present in the lattice at time t, randomly chosen, attempts to jump to any of the NN sites with equal probability $\frac{1}{2}$. The following situations may appear. (i) If the chosen site is empty, the particle jumps. (ii) If the chosen site is occupied by another particle, they react with probability p. If successful, the selected particle is removed from the lattice and the number of particles is decreased by 1, $n(t) \rightarrow n(t) - 1$. (iii) Otherwise the jump is not performed and the selected particle remains at its position. This means that the selected particle jumps to the chosen site, collides with the other particle present at this site, and is

reflected back with probability $(1-p)$ to its original position.

In the simulation, a time interval equal to 1 is defined as the time needed for the $n(t)$ particles to have, on average, one change to jump. Specifically after each Monte Carlo step, time t is increased by $1/n(t)$.

We define the density $\rho(t)$ as the number of particles per lattice site at time t. The function Γ_1 is defined as the number of pairs of NN occupied sites per lattice site at time t. $\rho(t)$ and $\Gamma_1(t)$ are obtained averaging over many (typically 20–30) samples; $d\rho/dt$ is obtained by deriving $\rho(t)$ numerically.

III. THE RATE EQUATION

In this section we will obtain a relation between $d\rho/dt$ and the function Γ_1. Let us denote by $P(n\to n-1)$ the probability for a reaction to take place in a Monte Carlo step. The change of the density in a reaction is $\delta\rho=-1/L$ and the time increases by $\delta t=1/n$. Then one has

$$\frac{d\rho}{dt}=\frac{\delta\rho}{\delta t}P(n\to n-1)\ . \tag{2}$$

Let us consider a given pair of NN occupied sites. The probability for one of these two particles to be selected at random in a Monte Carlo step is $2/n$. The probability for the selected particle to react with the other one is $\frac{1}{2}p$. Then,

$$P(n\to n-1)=\frac{2}{n}\frac{1}{2}pn_1\ , \tag{3}$$

where n_1 is the number of NN pairs present in the system at time t. From Eqs. (2) and (3) one obtains

$$\frac{d\rho}{dt}=-p\Gamma_1\ , \tag{4}$$

where $\Gamma_1\equiv n_1/L$ is the number of pairs of NN occupied sites per lattice site.

It is also possible to obtain Eq. (4) using the master equation of the process. This method is presented in the Appendix.

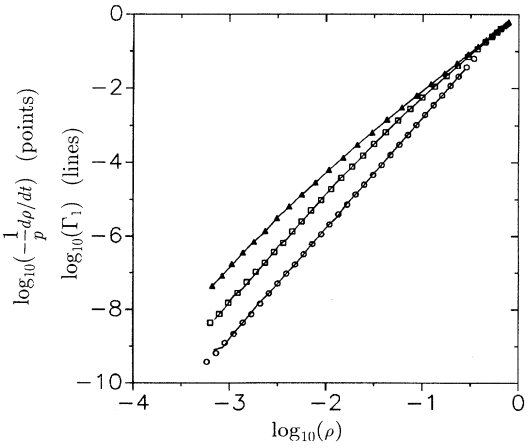

FIG. 1. $\log_{10}[-(1/p)d\rho/dt]$ (points) and $\log_{10}\Gamma_1$ (lines) versus $\log_{10}\rho$, for different values of p: $p=1$ (circles), $p=0.1$ (squares), and $p=0.01$ (full triangles).

Figure 1 shows numerical results of $-(1/p)d\rho/dt$ and Γ_1 versus ρ in log-log scales for different values of p. The superposition of the curves for a given value of p supports the validity of Eq. (4).

IV. THE SCALING FUNCTION

In the simulations we start with a random distribution of particles. In this case,

$$\Gamma_1=\rho^2\ , \tag{5}$$

and then [see Eq. (4)],

$$\frac{d\rho}{dt}=-p\rho^2\ . \tag{6}$$

This is the classical textbook second-order ($d\rho/dt\propto\rho^x$ with $x=2$) reaction which is used in all dimensional systems and for all times [in our case Eq. (6) is strictly valid only at $t=0$, see below]. This classical behavior can be obtained by assuming that the reaction time (the mean time that particles need to react when they are close to each other) is much larger than the diffusion time (the mean time between collisions). In this so-called reaction-controlled reaction (RCR) the diffusion effects are neglected and the mean-field approximation holds.

The anomalous behavior can appear in the so called diffusion-controlled reaction (DCR) when diffusion effects are relevant. This is, for example, the case of Eq. (1) for $d=1$ (and $p=1$), where one obtains a third-order reaction ($d\rho/dt\propto\rho^3$).

In our model, when time increases, the initial random distribution of particles changes. In a work by Doering and ben-Avraham [11] the interparticle distribution function for the reaction $A+A\to A$ is studied, with $p=1$ in one dimension. From this distribution [see Eq. (1.4) of Ref. [11]], for a discrete space (the lattice) and assuming small values of ρ, one can obtain

$$\Gamma_1=\frac{\pi}{2}\rho^3\ ,\quad p=1\ , \tag{7}$$

when $t\to\infty$. Then, from Eq. (4),

$$\frac{d\rho}{dt}=-\frac{\pi}{2}\rho^3\ ,\quad p=1\ . \tag{8}$$

Let us note that this equation is equal to Eq. (1.3) of Ref. [11] [the diffusion coefficient D in Eq. (1.3) is equal to $\frac{1}{2}$ in our discrete model]. This is a verification of Eq. (4).

On the other hand, when $\rho\to 0$ ($t\to\infty$) the average interparticle distance is very large. The diffusion time is much longer than the reaction time. Then one expects that the rate equation would be independent of p. Specifically, in Fig. 4 we plot $\log_{10}\rho$ against $\log_{10}t$. Note that all curves, which corresponds to different values of p, tend to collapse for very long times. As the dependence on p disappears, Eq. (8) must be valid for all p. Then, using Eq. (4), when $t\to\infty$,

$$\Gamma_1=\frac{1}{p}\frac{\pi}{2}\rho^3\ . \tag{9}$$

In summary, it is expected that for very small values of t (large ρ) $\Gamma_1=\rho^2$ [Eq. (5), RCR regime] and for large t (small ρ) Γ_1 is given by Eq. (9) (DCR regime). These behaviors are verified in Fig. 2, where we plot the Monte Carlo data of $\log_{10}\Gamma$ against $\log_{10}\rho$ for $p=0.01$. The intersection of these two asymptotical behaviors occurs at the *crossover* density ρ_c, given by

$$\rho_c=\frac{2}{\pi}p \ . \tag{10}$$

In order to analyze the universal (independent of p) behavior of Γ_1 as a function of ρ, we propose the following ansatz:

$$\frac{\Gamma_1}{\rho_c}=\rho f(\rho/\rho_c) \ , \tag{11}$$

where

$$f(x)=\begin{cases} x & \text{if } x\gg 1 \ , \\ x^2 & \text{if } x\ll 1 \ . \end{cases} \tag{12}$$

In Fig. 3 we plot the Monte Carlo data of $\Gamma_1/(\rho\rho_c)$ against ρ/ρ_c, in log-log scales, for different values of p. The observed data collapse supports the scaling ansatz. But we must make the following comment. In the simulation we start with a random distribution of particles. Then, at $t=0$, one has $(\rho,\Gamma_1)=(\rho_0,\rho_0^2)$. This point is located above the data collapse curve (it is in the asymptotic straight line $\Gamma_1/\rho\rho_c=\rho/\rho_c$ of slope 1). For this reason a small separation of Γ_1 from the data collapse curve appears for large values of ρ. The largest separation occurs for the case $p=1$. For $p=0.1$ and $p=0.01$ this separation is very small and cannot be detected in the scale of Fig. 3.

In general, we expect that the collapse of the data improves when $\rho_0/\rho_c=\rho_0\pi/2p$ increases. That is, if the starting point $x_0=\rho_0/\rho_c\gg 1$, and then the region where $x\gg 1$ really exists [see Eq. (12)], the numerical data will satisfy the scaling ansatz. As $\rho_0\leq 1$, this condition can only be fulfilled for small values of p.

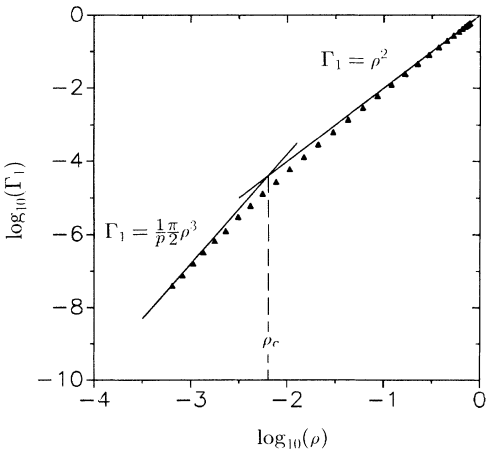

FIG. 2. $\log_{10}\Gamma_1$ versus $\log_{10}\rho$ for $p=0.01$. The crossover point is shown at $\rho=\rho_c$. The asymptotic behaviors of Eqs. (5) and (9) are represented by the straight lines.

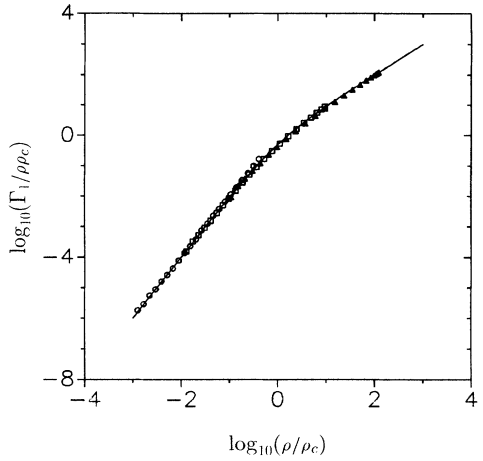

FIG. 3. Scaling of $\log_{10}(\Gamma_1/\rho\rho_c)$ versus $\log_{10}(\rho/\rho_c)$ for different values of p: $p=1$ (circles), $p=0.1$ (squares), and $p=0.01$ (full triangles). The line represents the approximation of Eq. (13).

V. AN APPROXIMATION FOR $\rho(t)$

A simple function which fulfills the scaling form is

$$f(x)=\frac{x^2}{x+1} \ . \tag{13}$$

We will use f as an approximation to the scaling function. From Eqs. (11) and (13) one has

$$\Gamma_1=\frac{\rho^3}{\rho+\rho_c} \ . \tag{14}$$

In Fig. 3 one can see that function Γ_1 agrees approximately with the data collapse curve. Integrating Eq. (4) with Γ_1 given by Eq. (14) one obtains the approximate density ρ_a

$$\rho_a(t)=\rho_c\frac{1+\sqrt{1+2a(t)}}{2a(t)} \ , \tag{15}$$

with

$$a(t)=\frac{\rho_c}{\rho_0}+\frac{1}{2}\left[\frac{\rho_c}{\rho_0}\right]^2+p\rho_c t \ . \tag{16}$$

In Fig. 4 we present $\log_{10}\rho_a$ and the Monte Carlo data of $\log_{10}\rho$ versus $\log_{10}t$ for different values of p. The agreement between ρ_a and ρ is reasonably good. Let us note that the logarithmic scale used is more appropriate than the linear scale for ρ in order to analyze the difference between ρ_a and ρ for a fixed value of t.

It is possible to use other approximations to the scaling function f. For example,

$$f(x)=\frac{x^{3/2}}{(x+1/x+2b)^{1/2}} \ , \tag{17}$$

or

$$f(x)\frac{x^{3/2}}{(x^k+x^{-k})^{1/2k}} \ , \tag{18}$$

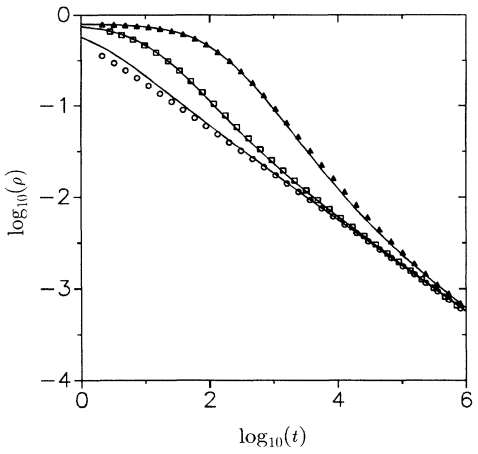

FIG. 4. $\log_{10}\rho$ versus $\log_{10}t$ for different values of p: $p=1$ (circles), $p=0.1$ (squares), and $p=0.01$ (full triangles). The points are numeric results and the curves are the approximation of Eq. (16). A value of $\rho_0=0.8$ was used for all curves.

with $x=\rho/\rho_c$, and where b and k are adjustable parameters. Nevertheless we prefer to use Eq. (13) due to its simplicity and because using this equation one can obtain a close form for the approximate density ρ_a [see Eq. (15)]. Moreover, the ρ_a obtained is a good approximation for the true ρ.

VI. CONCLUSIONS

The main conclusions for the imperfect coagulation reaction $A+A\rightarrow A$ in a one-dimensional lattice are as follows.

(i) The rate equation (4) has been deduced and verified by Monte Carlo data. From this equation one concludes that the behavior of $\rho(t)$ for all t depends on the density of pairs of NN occupied sites, and it is not necessary to know the density of pairs at large distances.

(ii) From the analysis of the behavior of Γ_1 at short times (RCR regime) and at long times (DCR regime), the scaling ansatz of Eqs. (11) and (12) is proposed. The Monte Carlo data supports this scaling, specially when $\rho_0 \gg \rho_c=(2/\pi)p$. Let us stress that from the numerical data we cannot affirm that the exact (and unknown) $\rho_e(t)$ will fulfill the scaling exactly. We only conclude that the scaling ansatz works for our Monte Carlo data, and this approximation improves when ρ_0/ρ_c increases.

(iii) Using a simple function which fulfills the scaling form, we obtain an analytical approximation of the density ρ_a [see Eqs. (15) and (16)]. The agreement between ρ_a and the Monte Carlo data for the density is reasonably good for all times and for different values of p (see Fig. 4).

Very recently an alternative analytical diffusion-equation-type approximation [12] has been developed to study the crossover between the RCR and DCR regimes. Using this method an approximation for $\rho(t)$ is obtained, which improves for large values of p and small initial density ρ_0. Our approximate scaling form [Eqs. (11) and (12)] becomes more accurate in the opposite region, that is, for small values of p and large ρ_0.

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APPENDIX

We present a deduction of Eq. (4) by using the master equation of the process. Let us denote the occupation number of a generic site i by s_i. If site i is occupied then $s_i=1$, otherwise $s_i=0$. If we have at time t any given configuration $\{s\}$, the occupation probability for site i at time $t=\delta t$ is

$$
\begin{aligned}
P_{i\{s\}}(t+\delta t)=&\,s_{i-1}(1-s_i)(1-s_{i+1})/2n \quad \bullet\circ\circ\\
&+(1-s_{i-1})s_i(1-s_{i+1})(1-1/n) \quad \circ\bullet\circ\\
&+(1-s_{i-1})(1-s_i)s_{i+1}/2n \quad \circ\circ\bullet\\
&+s_{i-1}s_i(1-s_{i+1})[(1-p)/2n+1-1/n] \quad \bullet\bullet\circ\\
&+s_{i-1}(1-s_i)s_{i+1}/n \quad \bullet\circ\bullet\\
&+(1-s_{i-1})s_is_{i+1}[(1-p)/2n+1-1/n] \quad \circ\bullet\bullet\\
&+s_{i-1}s_is_{i+1}[(1-p)/n+1-1/n] \quad \bullet\bullet\bullet\,.
\end{aligned}
\tag{A1}
$$

At the right side we show the configuration of sites $(i-1,i,i+1)$ which corresponds to each term of $P_{i\{s\}}(t+\delta t)$. Symbol $\bullet$ ($\circ$) denotes an occupied (empty) site at time t. Remember that $1/n$ is the probability of selecting a particle in a Monte Carlo step and that $\frac{1}{2}$ is the probability of jumping to the right or to the left (see Sec. II). Simplifying Eq. (A1) and averaging over configurations $\{s\}$ we obtain

$$P_i(t+\delta t)=P_i(t)+\frac{1}{2n}[P_{i+1}(t)+P_{i-1}(t)-2P_i(t)] - \frac{p}{2n}\langle s_i(s_{i-1}+s_{i+1})\rangle \ , \quad \text{(A2)}$$

where $P_i(t)=\langle s_i \rangle$.

In the simulations we begin at $t=0$ with random configurations in a lattice with periodic boundary conditions. As there are no privileged sites in the lattice, then on average the particle distribution will be uniform. Therefore $P_i=P_j$ and $\langle s_i s_{i+1}\rangle=\langle s_j s_{j+1}\rangle$ for all i,j. Then,

$$P(t+\delta t)-P(t)=-\frac{p}{n}\langle s_i s_{i+1}\rangle \ . \quad \text{(A3)}$$

The occupation probability per lattice site $P(t)$, now independent of i, is equivalent to the global density $\rho(t)$. Knowing that in the simulations $\delta t=1/n$, we have

$$\frac{d\rho}{dt}=-p\langle s_i s_{i+1}\rangle \ . \quad \text{(A4)}$$

Because there are no privileged sites, averaging $s_i s_{i+1}$ over configurations is equal to averaging over all sites of one configuration,

$$\langle s_i s_{i+1}\rangle=\frac{1}{L}\sum_{j=1}^{L} s_j s_{j+1}=\frac{n_1}{L} \ , \quad \text{(A5)}$$

where $s_{L+1}=s_1$. Then $\Gamma_1=\langle s_i s_{i+1}\rangle$ and Eq. (A4) is equal to Eq. (4).

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