Annihilation reaction $A + A \rightarrow 0$ with diffusion and interaction between particles in disordered structures

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We performed numerical simulations of the bimolecular annihilation reaction $A + A \rightarrow 0$ with diffusion and short range interactions. We used the two-dimensional percolation cluster at probability p ($p_c \leq p \leq 1$, where p_c is the critical probability) as the substratum over which the particles diffuse, and studied the particle density ρ as a function of time t. We analyzed the effects of (i) repulsive nearest neighbor interaction, and (ii) repulsive nearest neighbor with attractive next nearest neighbor interactions. These effects become relevant at short times. We propose a crude approximation for $\rho(t)$ for each case and for $p \geq p_c$, which works reasonably well at short times. The crossover from short times to asymptotic regimes is analyzed for case (i). Asymptotic behaviors for $\rho(t)$, which are independent of the interactions, are expected at very long times.

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I. INTRODUCTION

Recently, much effort has been dedicated to the study of diffusion-reaction systems, see, e.g., Refs. [1–3]. This is mainly due to the anomalous behavior that appears when the diffusion occurs on nonhomogeneous substrata (e.g., fractals [4, 5] and multifractals [6]) or on one-dimensional systems. This behavior cannot be predicted by mean-field approximations.

We consider the annihilation reaction $A + A \rightarrow 0$. The particles diffuse independently and react instantaneously and irreversibly when two of them are at nearest neighbors (NN).

In the classic mean-field approach, one assumes that the law of mass-action holds, i.e., that the variation of the particle density ρ with time t is proportional to ρ^2. The process is then described by $d\rho/dt = -k\rho^2$, where k is a constant. This approximation is valid in the reaction-limited case, when the reaction rate is sufficiently low and many collisions occur before a particle reacts. One has $\rho(t) \sim t^{-1}$.

On the other hand, if the diffusion time is much larger than the reaction time, then diffusion governs the process and we have the diffusion-limited case. In this case, the density behaves as [3, 5, 7],

$$\rho \sim t^{\gamma}, \quad \gamma = \min(d_s/2, 1), \tag{1}$$

where d_s is the spectral dimension [8] of the substratum. For some fractal structures, $d_s < 2$ and for d dimensional euclidean lattices, $d_s = d$.

We used the two-dimensional percolation cluster [9] as the substratum over which the particles diffuse. A parameter that characterizes the percolation cluster is the lattice covering probability p; if p is equal to a critical value $p_c = 0.593$ (for the square lattice), the percolation cluster is fractal, and if $p_c < p < 1$ it is not fractal, but it is still a disordered structure. All of these cases are interesting from the experimental point of view, because they are related to actual situations in heterogeneous strutures (see, e.g., Ref [2]). The spectral dimension of the percolation cluster at critical probability is $d_s = 4/3$ [3]. Then, the density behaves as $\rho(t) \sim t^{-2/3}$ at long times.

In the present work, the particles interact with potentials U' at NN and W' at next nearest neighbor (NNN) sites [10]. We define the adimensional potentials $U = U'/k_BT$ and $W = W'/k_BT$. In many physical and chemical processes, the short range interactions are present. This is the motivation for the introduction of U and W into the model. The aim is to analyze the influence of these interactions and to obtain the approximate behavior of $\rho(t)$ at short times.

II. THE MODEL AND THE MONTE CARLO SIMULATION

In the model the particles perform random walks between NN sites of percolation clusters, which percolate in both directions of a 700×700 square lattice. Periodic boundary conditions were used.

The particle density ρ is defined as the number of particles per cluster site and the reaction takes place between NN occupied sites. The initial configuration of particles has no pairs of NN occupied sites. To do this, we take a set of all NNN sites that belong to the percolation cluster and we occupy each of these sites with probability $2\rho_0$. Then, the initial density is ρ_0. After that the diffusion starts.

The energy of a given configuration can be written as $H/k_BT = \frac{1}{2}\sum'_{ij} U n_i n_j + \frac{1}{2}\sum''_{ij} W n_i n_j$, where n_i is the occupation number of site i; $n_i = 1$ if site i is occupied and $n_i = 0$ otherwise. Primed sum and double primed sum symbols denote sums over NN and NNN sites, respectively.

At each Monte Carlo step one of the $N(t)$ particles, randomly chosen, attempts to jump to any of the four NN sites with equal probability. The following situations

may occur.

(1) The chosen site does not belong to the cluster and the jump is not performed.

(2) The chosen site belongs to the cluster, the jump is performed with probability $w = \min\{1, \exp(-\Delta H/k_B T)\}$, where ΔH is the energy change in the movement of the selected particle to the chosen site. If the jump is performed and the chosen site is NN of a second particle, both particles react and $N(t)$ is reduced to $N(t) - 2$.

After each jump attempt, time is increased by $1/N(t)$. This model is known as *the blind ant*, because particles try to jump to any of the four NN sites regardless of whether they belong to the cluster or not. There is another model, *the myopic ant*, in which particles try to jump only to sites that belong to the cluster. We also made simulations with the myopic ant model and did not find relevant differences.

III. RESULTS

A. With repulsive NN interaction

Let us start by considering the case of repulsive NN interaction ($U > 0$, $W = 0$). Due to the repulsive potential, many attempts of reaction occur before a pair of particles finally reacts regardless of the substratum type. Then, at short times (large density and small distances between particles) a mixing effect appears and we expect a random distribution of particles over the substratum with the restriction of no NN occupied sites (remember that the reaction takes place at NN sites).

Let $P(N \to N-2)$ be the probability for a reaction to take place in a Monte Carlo step. In an annihilation reaction the change of the density in a reaction is $\delta\rho = -2/s$, where s is the number of sites in the cluster, and the time increases by $\delta t = 1/N$. Then one has $d\rho/dt = (\delta\rho/\delta t)P(N \to N-2)$. Now let us consider the configuration of Fig. 1(a). The probability of choosing a particle a in a Monte Carlo step is $1/N$. Now the probability that particle a jumps to site 1 and reacts with b is $\exp(-U)/4$. As there are four possibilities of jumping with reaction (particle a or b jumps to site 1 or 2), the probability of reaction is $\exp(-U)/N$. If all the configurations were as shown in Fig. 1(a), one has $P(N \to N-2) = m\exp(-U)/N$, where m is the number of these configurations. Then $d\rho/dt = -2m\exp(-U)/s$. If the particles were distributed at random on the cluster with no NN occupied sites, we have the mean-field approximation $m/s = \rho^2(1-\rho)^4$. Assuming small values of ρ [$(1-\rho)^4 \simeq 1$], one finally has

$$-\frac{d\rho}{dt} = 2e^{-U}\rho^2. \tag{2}$$

Let us stress that Eq. (2) is a crude approximation because other configurations different from Fig. 1(a) can appear. For example, in the configuration shown in Fig. 1(b) the particles cannot jump to site 2 because this site does not belong to the cluster. In the configuration of Fig. 1(c), the probability that particle a (or b) jumps to site 1 is $\exp(-2U)/4$. The contribution of this jumping attempt to $-d\rho/dt$ is of the order of $\rho^3\exp(-2U) \ll \rho^2\exp(-U)$, which is the contribution of distribution of Fig. 1(a) [assuming $\exp(U) \gg 1$ and small ρ].

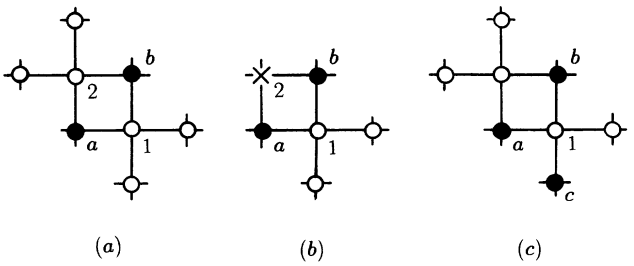

FIG. 1. Some configurations of particles on a percolation cluster. Full circles denote occupied sites, open circles denote empty sites, and crosses denote sites which do not belong to the percolation cluster.

The structure of the percolation cluster at $p = p_c$ is strongly heterogeneous and the exact contribution to $-d\rho/dt$ of all configurations is very difficult to obtain. The alternative that we use is to propose Eq. (2) as a first approximation to the problem and to check how well it works. Let us note that even when $p = 1$ where there are no holes (the percolation cluster corresponds to the complete square lattice), Eq. (2) is also an approximation because configurations as the one shown in Fig. 1(c) can appear. We will use Eq. (2) for all p ($p_c \le p \le 1$). Integrating Eq. (2) we have

$$R \equiv \left(\frac{1}{\rho} - \frac{1}{\rho_0}\right)^{-1} = \frac{1}{2e^{-U}t}. \tag{3}$$

In Fig. 2 we plot $\log_{10} R$ versus $\log_{10} t$ for different values of interaction U and $p = p_c$. The straight lines correspond to Eq. (3); the agreement with the numerical results at short times is apparent. At very short times there is a small deviation of the numerical results with

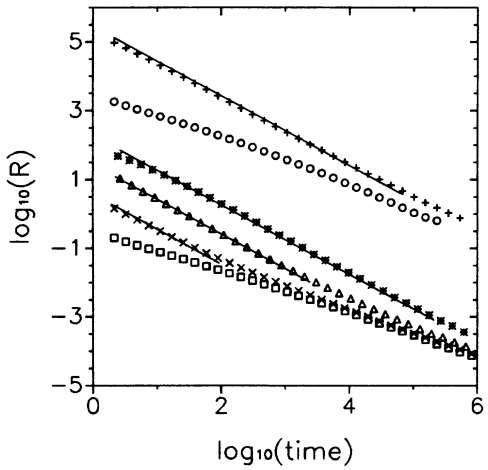

FIG. 2. $\log_{10} R$ as a function of $\log_{10} t$ in the percolation cluster at $p = p_c = 0.593$ for different values of U (and $W = 0$): $U = 0$ (□), $U = 2$ (×), $U = 4$ (△), and $U = 6$ (∗). There are also plotted the results for $p = 0.65$ for the interactions $U = 0$ (○) and $U = 4$ (+). For the sake of clarity, the results for $p = 0.65$ have been shifted on the ordinate axis four higher. The straight lines correspond to the approximation given by Eq. (3). A value of $\rho_0 = 0.2$ was used in all cases.

respect to the lines. This is due possibly to the crude approximation used in Eq. (2). In Fig. 2 we also plot the results for $p = 0.65$ and different values of U; the results are shifted for clarity. We can see that the approximation of Eq. (3) for short times also holds in this case.

At long times the density is low, the particles are spread out and we do not expect a mixing effect. The reaction is diffusion limited and the asymptotic anomalous behavior $\rho(t) \sim t^{-2/3}$ for $p = p_c$ coincides with the case of no interaction regardless of the value of U for $p = p_c$. It is well known that at $p = 1$ and $U = 0$, $\rho \sim (t/\log t)^{-1}$ in the asymptotic regime [11]. Due to the lack of mixing effect this same behavior is expected to hold for all $U > 0$. For $p_c < p < 1$ the percolation cluster at large scales behaves as a two-dimensional substratum. Then we expect that $\rho \sim (t/\log t)^{-1}$ when $t \to \infty$ for all $U \geq 0$ and $p > p_c$.

Let us consider the case $p = p_c$ and compare the mean-field behavior of Eq. (3) with the anomalous behavior at long times ($\rho \sim t^{-2/3}$). We define the crossover time t_1 as the time at which the intersection of these behaviors occurs and the crossover density ρ_c as the density at this time. Assuming $2\rho_0 \exp(-U)t_1 \gg 1$ one has $t_1 \sim \exp(3U)$ and $\rho_c \sim \exp(-2U)$. As expected, the length of the time interval where the mean field approximation holds ($0 < t \ll t_1$) increases as U increases. Defining $R_c = (1/\rho_c - 1/\rho_0)^{-1}$ (as $\rho_c \ll \rho_0$, $R_c \sim \rho_c \sim e^{-2U}$), we expect that R/R_c will be a function of t/t_1 only, independent of the values of U. In order to analyze this universal behavior, in Fig. 3 we plot $\log_{10}(R/e^{-2U})$ against $\log_{10}(t/e^{3U})$. As expected this approximate scaling works reasonably well for large values of U. For small values of U the mixing effect does not appear and Eq. (3) does not hold, for this reason the data for $U = 0$ do not collapse with the results for other cases.

Now, comparing the mean-field behavior of Eq. (3) with the asymptotic behavior $\rho \sim (t/\log t)^{-1}$ for $p > p_c$, one obtains that the crossover time and the crossover density behave as $t_1 \sim \exp(e^U)$ and $\rho_c \sim \exp(-e^U)$. Let us note that in this case the crossover is very smooth [from $\rho \sim t^{-1}$ to $\rho \sim (t/\log t)^{-1}$] and time t_1 increases very fast with a double exponential in U. We were not able to check this crossover with simulations due to the lack of enough computational capacity.

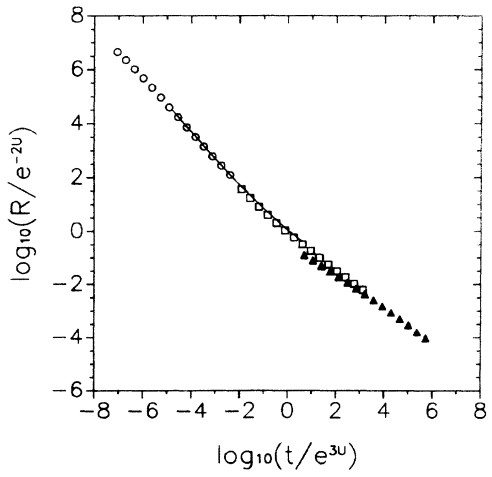

FIG. 3. $\log_{10}(R/e^{-2U})$ versus $\log_{10}(t/e^{3U})$, scaling of the data in Fig. 2 for $p = p_c$. The interactions used are $U = 0$ (full triangles), $U = 2$ (□), $U = 4$ (line), and $U = 6$ (○).

B. With repulsive NN and attractive NNN interactions

We consider the case with repulsive NN potential ($U > 0$) and attractive NNN potential ($W < 0$). This combination of interactions produces a particular distribution of particles at short times. The most energetically favorable configuration of two particles is when they form a pair of NNN occupied sites. The system tends to form groups of particles separated by NNN distances. This behavior has been checked by simulations.

As the reaction takes place at NN sites, it is expected that [12]

$$-\frac{d\rho}{dt} \sim \Gamma_2, \tag{4}$$

where Γ_2 is the correlation at NNN sites, i.e., the probability of finding a pair of NNN occupied sites. In Eq. (2) Γ_2 was assumed to be equal to ρ^2. Let us now consider the value of Γ_2 for the present case. At short times, when we have groups of NNN particles, Γ_2 is the probability of finding a particle at a given site, which is ρ, times the probability of finding another particle in a NNN site to that given site, which is, in this case, of the order of 1. So $\Gamma_2 \sim \rho$ and we have $-d\rho/dt \sim \rho$, which means an exponential decay,

$$\rho \sim e^{-\alpha t}, \tag{5}$$

where α is a parameter that depends on the values of U, W, and the probability of the percolation cluster p ($p_c \leq p \leq 1$).

In Fig. 4 we plot $\log_{10}\rho$ versus t for $U = 4$ and

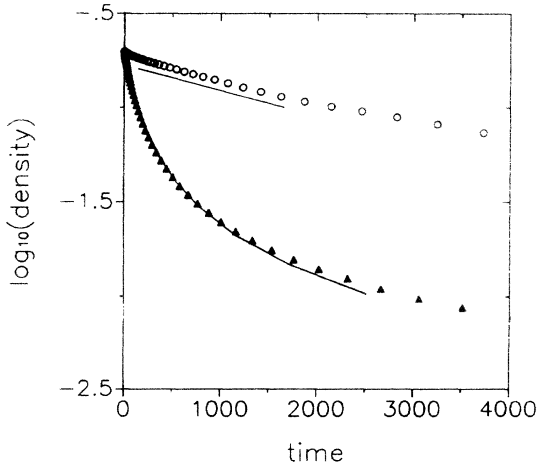

FIG. 4. $\log_{10}\rho$ versus t in the percolation cluster at p_c for interactions $U = 4$, $W = -3$ (○), and $U = 4$, $W = 0$ (full triangles). The upper straight line denotes the linear behavior present when an attractive NNN interaction is used, see Eq. (5). The lower continuous line is the approximation of Eq. (3).

$W = -3$ for the percolation cluster at p_c (other cases, with $W = 0$, are plotted for comparison). We can see at short times (in a range of approximately three decades in t) a linear behavior as predicted by Eq. (5). For long times, the groups of NNN particles disintegrate and the asymptotic behavior without interaction, $\rho \sim t^{-2/3}$, is obtained. Similar results are obtained for the percolation cluster at $p > p_c$.

IV. CONCLUSIONS

We analyzed the behavior of the particle density in the annihilation reaction $A + A \rightarrow 0$ in the percolation cluster with probability p ($p_c \leq p \leq 1$). The particles diffuse coupled by NN and NNN interactions.

As is well known, the asymptotic behaviors [Eq. (1)] are not modified by the introduction of short range interactions between particles [3,10].

At short times the effect of the repulsive NN potential ($U > 0$, $W = 0$) is to favor the particle mixing so that the particles are randomly distributed over the substratum. This allows the application of the mean-field approximation (2) that yields the behavior given by Eq. (3). Such behavior is independent of the substratum type and is present at short times. The lapse during which the effect of the interaction is present increases as the value of the potential U increases. Specifically this time interval extends to $t \ll t_1$, where t_1 behaves as $t_1 \sim \exp(3U)$ for $p = p_c$ and $t_1 \sim \exp(e^U)$ for $p > p_c$.

For the case of repulsive NN interaction ($U > 0$) with attractive NNN interaction ($W < 0$), configurations with pairs of NNN occupied sites appear at short times and the exponential decay approximation of Eq. (5) holds for $p \geq p_c$.

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