Nucleation model for diffusion-limited coalescence with finite reaction rates in one dimension

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We study the diffusion-limited coalescence model $A + A \rightarrow A$ with nucleation and a finite reaction rate in one dimension for the particle density decay by means of a Monte Carlo simulation and analytic modeling. In our model, one or more particles in a lattice site act as a nucleus for the particles that diffuse into the site without reacting. The master equation governing the time evolution of local particle number and the rate equation for the particle density are derived. We present an analytic approach for the early time regime (reaction-controlled limit), which is strongly dependent on the initial particle density. In this regime, the particle density decays faster than the classical (or second-order reaction) limit and lower than the exponential decay (or first-order reaction) limit. For the long time regime the diffusion-controlled limit is recovered. We show that the intermediate regime can be obtained as an interpolation between the initial decay and the diffusion limit. The numerical integration results from the analytic approach are compared with computer simulations.

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I. INTRODUCTION

The reaction-diffusion systems in low dimensions have been widely investigated in recent years [1–8]. Most of the research has focused on one-component coalescence coagulation $A + A \rightarrow A$, and annihilation $A + A \rightarrow 0$ in low dimensions. The last two systems were solved exactly in one dimension for diffusion-limited reactions with an infinite rate. These processes show the breakdown of the mean field approximation for reaction kinetics. In this case the diffusion-limited coalescence processs occurs instantaneously. Experimentally, reactions are never instantaneous [8]. This fact can be modeled by introducing a probability of reaction between the particles when they attempt to occupy the same site [3, 4]. If the particles bounce off the model is known as the hard-core model. Simulation and theoretical approach [5, 6] have been performed for one-component coalescence processes in one dimension, with a finite rate. The results show three different regimes: (a) An early time regime where the particles simply diffuse (with a small change in the initial particle density) until they reach the classical limit in which the particle density behavior is $\rho \sim t^{-1}$. (b) A long time diffusion-limited regime where the particle density behavior is $\rho \sim t^{-1/2}$. (c) An intermediate regime, in which the particle density decays slower than the classical regime and faster than the diffusion-limited regime. This last regime is merely a crossover between the classical and the diffusion-controlled limits. For the intermediate regime, an interpolation formula between the classical and diffusion-controlled limits emerges as a natural consequence of the approximation done in [5, 6].

In this paper we study the one-dimensional coalescence model $A + A \rightarrow A$, with nucleation and a finite reaction rate. In our model one or more particles in a finite space region act as a nucleus for the particles that diffuse into the region without reacting. In order to avoid interactions among different nuclei we assume that the average distance between adjacent regions is much larger than the characteristic size of the nucleation region. The attractive interactions between nucleated particles are small enough to allow them to diffuse into neighbor regions. The energy of the nucleated particles is reduced such that the reaction among them is negligible. We associate these physical regions with discrete lattice sites. The mathematical model assumes that one or more particles can coexist in the same site to avoid the extra interaction of the volume effect. The nucleation induces a first-order decay behavior in the early time regime at high particle densities. This is the largest difference between our model and the hard core model. At low densities we recover the same results of hard core, i.e., a second-order-type reaction at short time.

We introduce the nucleation model for the particle density decay by means of a Monte Carlo simulation and an analytic model. The paper is organized as follows. In Sec. II we present our model and a Monte Carlo simulation. In Sec. III, the master equation governing the time evolution of local particle number is derived. Also, the rate equation for the particle density is obtained. In Sec. IV we develop an analytic approach for the time evolution of particle density. The early time regime and diffusion-controlled regime are described. The intermediate regime is obtained by matching the early and the long time regimes. Finally, we conclude with a discussion in Sec. V.

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II. NUCLEATION MODEL AND MONTE CARLO SIMULATION

In this model the particles perform a random walk between nearest-neighbor sites in a one dimensional lattice of lenght L with periodic boundary conditions. The particles are allowed to nucleate in the same position, i.e., this is not a hard-core model. At the initial time, we start with a fixed density of particles ρ_0. The lattice sites are chosen at random to be occupied by one particle until the lattice is filled with $N_0 = L\rho_0$ particles. In our model the probability to choose a site at random is $1/L$. So the random variable J that denotes the number of particles in one site has binomial distribution with parameter $1/L$,

$$P(J=j) = \binom{N_0}{j}\left(\frac{1}{L}\right)^j\left(1-\frac{1}{L}\right)^{N_0-j} .$$

When $L \to +\infty$, $N_0 \to +\infty$, and $N_0/L \to \rho_0$, the Poisson distribution is appropiate to model the random variable J, so that

$$P(J=j) = \frac{e^{-\rho_0}\,\rho_0^j}{j!} . \tag{2.1}$$

Notice that, the probability of any site being occupied is $P(J \geq 1) = \sigma_0 = 1 - e^{-\rho_0}$, where σ_0 is the initial average density of occupied sites.

In the simulation, at each Monte Carlo step, one of the $N(t)$ particles is randomly picked to jump to any of the nearest-neighbor sites with the same probability 1/2. This jump always happens because many particles can coexist in the same site. When the selected site is empty the particle diffuses. If the chosen site is occupied, the selected particle reacts with probability k; if the reaction takes place this particle is removed from de system and the number of particles is decreased by 1 [$N(t) \to N(t) - 1$]. Otherwise, the selected particle stays in the chosen site with probability $(1-k)$. Again, in contrast with the hard-core model, this happens because of the lack of repulsion between particles. When the number of Monte Carlo steps is equal to the actual number of particles in the system, the time is increased by one unity ($t \to t+1$). In other words, after each Monte Carlo step the time is increased by $\delta t = 1/N(t)$. The process is repeated for many unit time steps, typically up to $t = 10^6$ in a lattice with $L = 10^5$.

One outcome of the model is that for all time and finite rates the distribution of the particle number is a departure from Eq. (2.1). When a particle jumps onto an occupied site, the reaction takes place with probability k; otherwise, the particle is nucleated with probability $(1-k)$. For $k = 0$ the particles merely diffuse, so the Poisson distribution Eq. (2.1) holds for all time. When k is very small but finite, one expects a little deviation from Poisson distribution. Figure 1 shows the distribution of the particle number $P(J=j)$ as a function of the average particle number density $\rho(t)$. When k increases this deviation also increases. Thus the reaction rate induces the departure. The early time regime is dominated by the slow reaction rate (reaction-limited case) and nondeparture exists. Then at an early time regime for all k the average occupation number [$\sigma = 1 - P(J=0)$] in our model is

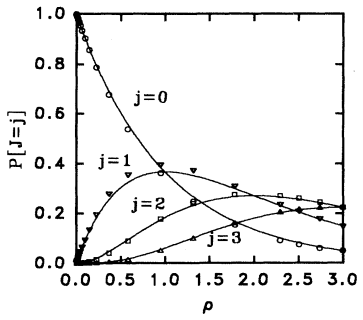

FIG. 1. Probability distribution of the particles number vs particle density. The open symbols correspond to the Monte Carlo simulation for $k = 0.1$ and the solid line to Eq. (2.1).

$$\sigma(t) = 1 - e^{-\rho(t)} . \tag{2.2}$$

For all time Eq. (2.2) holds approximately for $k \ll 1$. Notice that in the hard-core model $\sigma = \rho$ for all k.

Figure 2 displays the occupied sites density $\sigma(t)$ as a function of particle density $\rho(t)$. The symbols correspond to the Monte Carlo simulation results and the solid line to Eq. (2.2). The inset figure displays the mean distance between neighbor occupied sites, ($\langle x \rangle = \sigma^{-1}$) as a function of particle density. The dashed lines ($\sigma = \rho$) correspond to the hard-core model in both figures. In our nucleation model at very high densities ($\rho \gg 1$) the occupied sites density comes near to 1. That means that, on average, any particle has a first neighbor in a large densities interval, therefore enhancing the reaction. In the hard-core model the mean distance between particles is approximately 1 at short density intervals in the high density regime ($\rho \lesssim 1$). The nucleation model and the

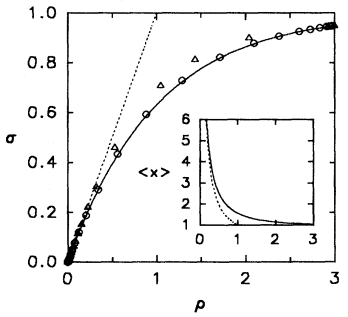

FIG. 2. Occupied sites density vs particle density. The symbols correspond to the Monte Carlo simulation results and the solid line to Eq. (2.2). Here $k = 0.01$ (○) and 0.5 (△). The inset figure displays the mean distance between neighbor occupied sites, i.e., $\langle x \rangle = \sigma^{-1}$, as a function of particle density. In this simulation $\rho_0 = 3$. In both cases the dashed line ($\sigma = \rho$) corresponds to the hard-core model.

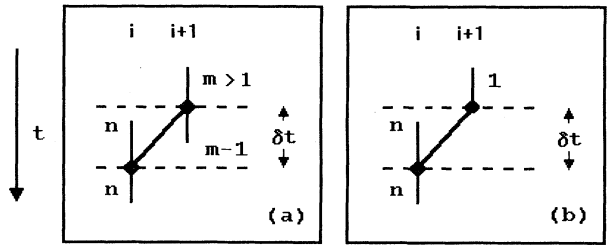

FIG. 3. Schematic representation of the reaction mechanisms in one Monte Carlo step for particles in first-neighbor sites. In case (a) m and n are the particles numbers in the sites $(i+1)$ and i at time t, respectively. In case (b) 1 is one particle in the site $(i+1)$ and n is the particle number in the site i at time t. In both cases the reaction takes place in the i site at time $(t+\delta t)$.

hard-core model at low densities have a similar regime because $\sigma \to \rho$ for all k.

In our model the reaction mechanisms are schematically illustrated in Fig. 3. In both cases ρ decreases. In a Monte Carlo step the mechanisms are as follows:

(a) One particle of a multioccupied site diffuses to a neighbor occupied site and reacts. In this case σ remains constant.

(b) One particle of a single occupied site diffuses to a neighbor occupied site and reacts leaving an empty site. In this case σ decreases.

At high densities the mechanism (a) predominates. As the particle density decreases, the mechanism (a) is attenuate and the mechanism (b) is enhanced. At low densities the mechanism (b) predominates. The competition between both mechanisms can be understood by analyzing Fig. 1. The time evolution of $\rho(t)$ in the initial and intermediate regime exhibits different behavior in both models because the nucleation effects are relevant, as we show in Sec. IV.

III. THE MASTER EQUATION

We consider here the master equation of the process described above. At time t, let us denote by $n_i(t)$ the particles number and by $s_i(t)$ the occupation number of the ith generic site. When this site is occupied $s_i = 1$, otherwise $s_i = 0$. The time evolution equation for the particle number in a Monte Carlo step δt is

$$n_i(t+\delta t) = [n_i(t)+1]\left(\frac{n_{i+1}(t)}{2N(t)} + \frac{n_{i-1}(t)}{2N(t)}\right)[1-ks_i(t)] + [n_i(t)-1]\frac{n_i(t)}{N(t)} + n_i(t)\left[1-\left(\frac{n_{i+1}(t)}{2N(t)} + \frac{n_i(t)}{N(t)} + \frac{n_{i-1}(t)}{2N(t)}\right) + ks_i(t)\left(\frac{n_{i+1}(t)}{2N(t)} + \frac{n_{i-1}(t)}{2N(t)}\right)\right]. \tag{3.1}$$

Notice that $1/N(t)$ is the probability of selecting a particle in Monte Carlo step δt, and $1/2$ is the probability of jumping to each neighbor site. The particle number n_i increases by 1 when a particle occupying a neighbor site is chosen and jumps to the ith without reaction. The nonreaction probability is $1-ks_i$. The other possibility is that n_i decreases by 1 when the ith site selected particle diffuses to a neighbor site. Otherwise, the particle number remains unchanged if one of the following alternatives holds: (a) No particle is chosen from the ith site or from one of its neighbors. (b) A particle from a neighbor site, to the ith site, is chosen to diffuse to this site and reacts with probability k. We remark that any chosen particle always diffuses. Replacing $N(t) = 1/\delta t$ and taking the limit $\delta t \to 0$ Eq. (3.1) becomes $[n_i = n_i(t), s_i = s_i(t)]$,

$$\frac{dn_i}{dt} = \frac{1}{2}(n_{i-1} - 2n_i + n_{i+1}) - \frac{k}{2}s_i(n_{i-1} + n_{i+1}), \tag{3.2}$$

with periodic boundary condition $n_0 = n_L$. Introducing the particle density as

$$\rho(t) = \frac{1}{L}\sum_{j=1}^{L} n_j(t),$$

and averaging Eq. (3.2) over lattice sites results in

$$\frac{d\rho}{dt} = -k\,\Gamma_n, \tag{3.3}$$

where

$$\Gamma_n = \frac{1}{L}\sum_{j=1}^{L} s_j\left(\frac{n_{j-1}+n_{j+1}}{2}\right). \tag{3.4}$$

In other words, if in one Monte Carlo step $\delta t = 1/N(t)$ the reaction is successful, then $\delta\rho = -1/L$. Let j and $j+1$ be the occupied sites, with n_j and n_{j+1} particles, respectively. Then the probability to select one of the n_j's to diffuse to the $(j+1)$th site and react is $s_{j+1}n_j/(2N)$. Similarly, the probability to select one of the n_{j+1}'s to diffuse to the jth site and react is $s_j n_{j+1}/(2N)$. The probability that the number of particles in the system decreases one unit is

$$W(N \to N-1) = k\sum_{j=1}^{L}\frac{s_{j+1}n_j + s_j n_{j+1}}{2N},$$

and taking into account that

$$\frac{d\rho}{dt} = \frac{\delta\rho}{\delta t}W(N \to N-1)$$

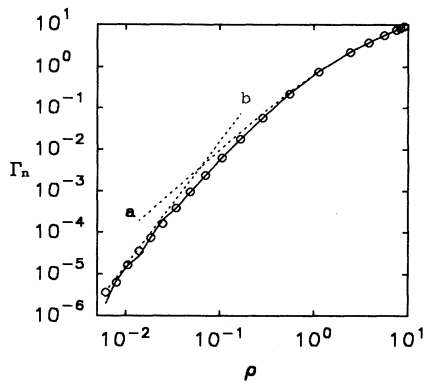

FIG. 4. Monte Carlo simulation results of Γ_n (O), $-\dot{\rho}/k$ (solid line), $\sigma\rho$ (dashed line a), and $\pi\rho^3/(2k)$ (dashed line b) as a function of ρ. In this simulation $\rho_0 = 10$, $k = 0.1$, and $t = 10^5$.

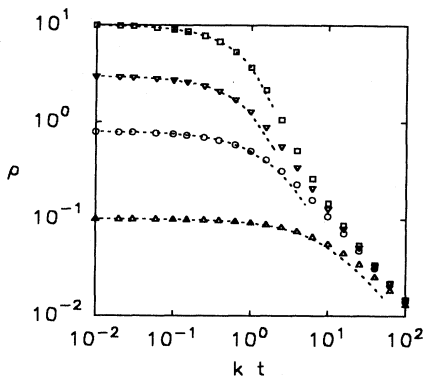

FIG. 5. Particle density vs kt in the early time regime. We display the Monte Carlo results (symbols) and analytic results from Eq. (4.3) (dashed line) for different initial densities. Here $\rho_0 = 10$ (□), 3 (▽), 0.8 (○), 0.1 (△).

we can recover Eq. (3.4). The Monte Carlo simulation results (see Fig. 4) shows that Eq. (3.4) is satisfied for all time. Notice that in the hard-core model $n_j \to s_j$ and Γ_n is simply the pairs density of the nearest-neighbors occupied sites [7].

IV. TIME EVOLUTION OF PARTICLE DENSITY

At the initial time we start with a random sites distribution. The site occupation number s_j is independent of the neighbors particles number (n_{j+1}, n_{j-1}). Then Eq. (3.4) becomes

$$\Gamma_n(\rho) = \sigma\rho\,, \tag{4.1}$$

where

$$\sigma(t) = \frac{1}{L}\sum_{j=1}^{L} s_j(t)$$

is the occupied sites density. In the early time regime, the particles merely diffuse with a finite reaction rate and there is a negligible change in the initial density (see Fig. 4, dashed line a). The early time evolution equation for $\rho(\tau)$ near to ρ_0 ($\tau = kt$) is

$$\frac{d\rho}{d\tau} = -\sigma\rho\,, \tag{4.2}$$

with initial condition $\rho(0) = \rho_0$. Expanding $\sigma = 1 - e^{-\rho}$ in Eq. (4.2) around ρ_0 up to first order the solution is

$$\rho(\tau) = \frac{\alpha\rho_0}{(\alpha+\beta)\,e^{\alpha\tau} - \beta}, \tag{4.3}$$

where $\alpha = 1 - e^{-\rho_0} - \rho_0\, e^{-\rho_0}$ and $\beta = \rho_0\, e^{-\rho_0}$. The good agreement between the Monte Carlo simulation results and Eq. (4.3) at the early time regime is displayed in Fig. 5. Let us explain the meaning of α and β: from Eq. (2.1) the probability to find any site with two or more particles is $P(J \geq 2) = \alpha$, the probability to find any site with exactly one particle is $P(J = 1) = \beta$, and the probability to find any site with one or more particles is $P(J \geq 1) = \alpha + \beta = \sigma$.

In the limit $\rho_0 \ll 1$ we obtain $\rho(\tau)/\rho_0 \approx 1/(1 + \rho_0\tau)$. This mean field solution describes the second-order reactions ($d\rho/d\tau = -\rho^2$) characteristic of the hard-core coagulation models in their initial regime. The crossover time between the early and intermediate regime is approximately $t_1 = (k\rho_0)^{-1}$ [6]. The mean field approximation holds in our model because the probability to find any empty site is $P(J = 0) = 1 - O(\rho_0)$ and the probability to find any site with j particles is $P(J = j) = O(\rho_0^j)$. The low density regime is satisfied when $\sigma_0 \to \rho_0$. In this case the average distance between particles goes to $1/\rho_0$.

In the other limit, $\rho(\tau)/\rho_0 \to e^{-\tau}$ when $\rho_0 \to +\infty$. This solution satisfies the differential equation $d\rho/d\tau = -\rho$ of a first-order reaction. In our case this equation is strictly valid for the early regime ($\tau \leq 1$). So, $t_1 = k^{-1}$ is appproximately the crossover time between the initial regime and the intermediate regime. The height

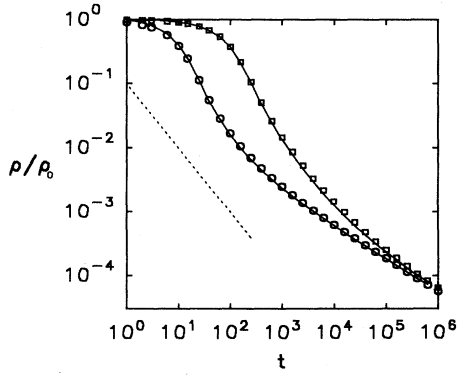

FIG. 6. Relative particle density vs time. Monte Carlo results for $k = 0.1$ (○), 0.01 (□), and $\rho_0 = 10$ are shown. The solid line shows the numerical integration results of Eq. (4.5). The dashed line has a slope of -1.

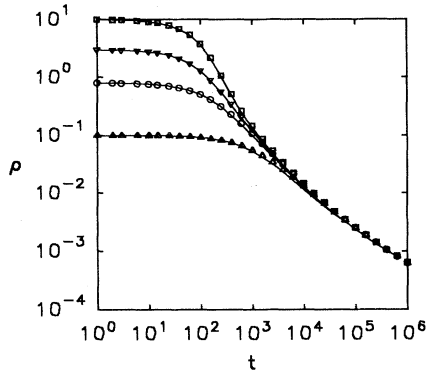

FIG. 7. Particle density vs time. Simulation results for $\rho_0 = 10$ (□), 3 (▽), 0.8 (○), 0.1 (△), and $k = 0.01$ are shown. Shown also are the numerical integration results of Eq. (4.5) (solid line).

density limit is satisfied when $\sigma_0 \to 1$. This mean that the average distance between particles, $1/\sigma_0 \to 1$. This is why the reaction time goes faster than in the low density regime.

In the long time regime ($\rho \to 0$) the mean distance of interoccupied sites is very large. Then, the diffusion time is larger than the reaction time. The evolution equation [1] is

$$\frac{d\rho}{dt} = -\frac{\pi}{2}\rho^3 , \tag{4.4}$$

which is independent of k. Figure 4 (dashed line b) shows how $\Gamma_n \to -\pi\rho^3/(2k)$ when $t \to +\infty$. This regime is characterized by a diffusion-limited decay ($\rho \sim t^{-1/2}$).

From Fig. 4, we see that the intermediate regime can be explained as an interpolation between the initial decay and the diffusion-limited decay. We describe the intermediate regime matching the long time asymptotic regime [Eq. (4.4)] and early time regime [Eq. (4.2)]. The evolution equation is

$$-\frac{2}{\pi}\frac{\dot{\rho}}{\rho^2} = \rho + \frac{1}{k}\frac{\dot{\rho}}{\sigma} . \tag{4.5}$$

Notice that at low initial particle density $\sigma \to \rho$ for all time and Eq. (4.5) becomes the hard-core evolution equation with $k \ll 1$ [6]. In Figs. 6 and 7 we plot the particle density decay results from the numerical integration of Eq. (4.5) and from the Monte Carlo simulations. The agreement between both results is excellent for all time. For high initial particle densities Fig. 6 shows an intermediate regime with two behaviors: first the particle density decays faster than the classical limit ($\rho \sim t^{-1}$) and later it decays faster than the diffusion-limited regime ($\rho \sim t^{-1/2}$), but not quite as fast as the classical limit. In the early and intermediate regimes the nucleation effects enhance the reaction.

V. CONCLUSIONS

We have introduced a diffusion-limited coalescence model $A + A \to A$ with nucleation and finite reaction rates for the particle density decay by means of the Monte Carlo simulation and the analytic modeling. Summarizing, the principal features of the model are (a) the particles can be crowded in the same site, (b) the nucleated particles cannot react between them, and (c) the reaction is allowed between particles of adjacent sites. One consequence of the model is that the particle number in any site has Poisson distribution in the early time regime and holds approximately for all time when $k \ll 1$. The time evolution of the particle density in the early and intermediate regime shows a characteristic behavior because the nucleation effects enhance the reaction. We have derived the master equation (3.1) for the local particle number and the rate equation (3.3) for the particle density. The early time regime has been characterized by an analytic approach and compared with Monte Carlo simulation results.

Our model shows that the early time regime is strongly dependent of the initial particle density. The particle density decays faster than the classical limit [$\rho \sim t^{-1}$] and lower than the exponential limit [$\rho \sim \exp(-kt)$]. At very high particle densities the first-order reaction behavior in the early time regime is the consequence of the nucleation effect. This is the largest difference between our model at high densities and the hard-core model. At very low densities we recover the same results of hard core, i.e., a second-order-type reaction at short time. In the long time regime the diffusion-limited decay is recovered. We show that the intermediate regime is merely an interpolation between the initial decay and the diffusion limit. The results show two behaviors in the intermediate regime for the high initial particle density: first the density decays faster than the classical limit, and later it decays faster than the diffusion-limited regime, but not quite as fast as the classical limit. The agreement between the simulation and numerical integration of Eq. (4.5) is excellent for all time.

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