Nucleation model for multiparticle reactions with finite reaction rates in one dimension

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We study one-dimensional reactions $\mu A \rightarrow \nu A$ $(\mu > \nu)$ with nucleation and finite reaction rate $(k \ll 1)$ in one dimension for the particle density decay by means of a Monte Carlo simulation and analytic modeling. The anomalous case $\mu = 2$ was studied in our previous work. The marginal case $\mu = 3$ is described without logaritmic corrections in the mean field approach. The case $\mu > 3$ is well described by classical rate equations. The rate equation for the particle density is derived for all μ. We present a mean field approach for the early time regime (reaction-controlled limit) for any initial density. Also, the mean field aproximation is derived in a simple way from the rate equation for any time at low densities. [S1063-651X(96)08012-9]

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I. INTRODUCTION

The reaction-diffusion systems in low dimensions have been investigated widely in recent years [1–6,8]. Most 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 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 [8,9]. 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 finite rate.

When the particles do not bounce off the model is known as the nucleation model [7]. In this model, for the one-dimensional coalescence with finite reaction rate, the early time regimen 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 low densities we recover the same results of the hard-core model. The long time regime (anomalous diffusion) where $\rho \sim t^{-1/2}$ is recovered. One consequence of this model is that the particle number in any site has a Poisson distribution in the early time regime and holds approximately for all time when the probability of reaction $k \ll 1$.

A less studied problem is the one-dimensional μ-body hard-core reactions $\mu A \rightarrow \nu A$ $(\mu > \nu)$, when $\mu > 2$. For $\mu > 3$ the asymptotic large-time behavior is mean field, while $\mu = 3$ is marginal. Study of multiparticle reactions has been emphasized due to the relevance to certain deposition processes [10]. The $\mu A \rightarrow 0$ reaction kinetics is asympototically equivalent to the dynamics of empty sites in deposition processes with diffusional relaxations. For the μ-body hard-core reactions the short-time regime has not, to our knowledge, been studied so far.

In this paper we study the one-dimensional multiple-body reactions with nucleation and finite reaction rate. The physical model assumes that one or more particles in a finite space region act as a nucleus for the particles that diffuse into a region without reacting. 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 [7]. We use the nucleation model for the particle density decay by means of the Monte Carlo simulation and the analytic model.

The paper is organized as follows. In Sec. II we present our model and the Monte Carlo simulation. The rate equation for the particle density is obtained. Also, we develop an analytic approach for the time evolution of particle density. The early time regime and diffusion-controlled regime are described, when the diffusion rate is much greater than that of the reaction rate $(k \ll 1)$. In both regimes we applied the mean field approximation for $\mu > 2$. Finally, we conclude with a discussion in Sec. III.

II. THEORETICAL APPROACH AND MONTE CARLO SIMULATION

In this model the particles perform a random walk between nearest-neighbor sites in a one-dimensional lattice of length L with periodic boundary conditions. The particles are allowed to nucleate in the same position.

At the initial time, we start with a fix density of particles ρ_0. The lattice sites are chosen at random to be occupied with 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 Poisson distribution is appropiate to model the random variable J that denotes the number of particles in any site.

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 occupied by less than $(\mu - 1)$ particles the picked particle diffuses. If the chosen

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site is occupied less by $(\mu-1)$ particles, $(\mu-\nu)$ particles react with probability k. If the reaction takes place these particles are removed from the system and the number of particles decreases $[N(t)\to N(t)-(\mu-\nu)]$. Otherwise, the selected particle stays in the chosen site with probability $(1-k)$. At each Monte Carlo step the time is increased by $\delta t=1/N(t)$.

For $k=0$ the particles merely diffuse, so the Poisson distribution holds for all time. When k is very small but finite, there has been seen little deviation from the Poisson distribution [7]. 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.

In one Monte Carlo step $\delta t=1/N(t)$, if the reaction is successful then $\delta\rho=-(\mu-\nu)/L$. 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 $\Theta(n_{j+1}-\mu-2)n_j/(2N)$. Here $\Theta(x)$ is the Heaviside function [$\Theta(x)=1$ for $x>0$ and is equal to 0 otherwise]. Similarly, the probability to select one of the n_{j+1}'s to diffuse to the jth site and react is $\Theta(n_j-\mu-2)n_{j+1}/(2N)$. The probability that the number of particles in the system decreases in $(\mu-\nu)$ is

$$W[N\to N-(\mu-\nu)] = k\sum_{j=1}^{L}\frac{\Theta(n_{j+1}-\mu-2)n_j+\Theta(n_j-\mu-2)n_{j+1}}{2N},$$

for all ν, and taking into account that

$$\frac{d\rho}{dt}=\frac{\delta\rho}{\delta t}W[N\to N-(\mu-\nu)],$$

the rate equation for the particle density $[\rho(t)=1/L\,\Sigma_{j=1}^{L}n_j(t)]$ is

$$\frac{d\rho}{dt}=-k(\mu-\nu)\Gamma_n(\mu), \tag{2.1}$$

where

$$\Gamma_n(\mu)=\frac{1}{L}\sum_{j=1}^{L}\Theta(n_j-\mu-2)\left(\frac{n_{j-1}+n_{j+1}}{2}\right).$$

Otherwise, Eq. (2.1) can be derived from a master equation [7]. Notice that when $\mu=2$ the Heaviside function is the jth site occupation number. We recover the rate equation [7] for the coalescence model $(\nu=1)$.

For $\mu>3$ the mean field behavior became more pronounced as k decreased. The marginal case $\mu=3$ also has mean field behavior with logarithmic corrections. The mean field approximation for Eq. (2.1) is

$$\frac{d\rho}{dt}=-k(\mu-\nu)P[J\geqslant\mu-1]\rho, \tag{2.2}$$

where $P[J\geqslant\mu-1]$ is the probability to find more than $(\mu-1)$ particles at any site.

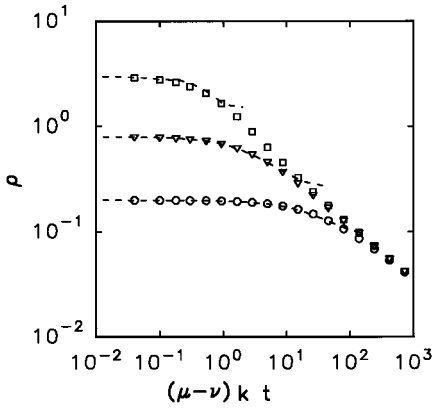

FIG. 1. Particle density vs $(\mu-\nu)kt$ in the early time regime. We display the Monte Carlo results (symbols) and analytic results from Eq. (2.4) (dashed line) for different initial densities. Here $\mu=3$, $\nu=1$, $k=0.01$ and $\rho_0=3$ (□), 0.8 (▽), 0.2 (○).

At the initial time we start with a random site distribution. Then in Eq. (2.2) the probability has a Poisson distribution

$$P[J\geqslant\mu-1]=\sum_{j\geqslant\mu-1}\frac{\rho^j e^{-\rho}}{j!}. \tag{2.3}$$

In the early time regime, the particles merely diffuse with a finite reaction rate and there is a negligible change in the initial density. Expanding the probability in Eq. (2.2) around ρ_0 up to first order, the solution [with initial condition $\rho(0)=\rho_0$] is

$$\rho(\tau)=\frac{\alpha\rho_0}{(\alpha+\beta)e^{\alpha\tau}-\beta}, \tag{2.4}$$

where $\tau=k(\mu-\nu)t$, $\beta=\rho_0 P_0[J=\mu-2]$, and $\alpha=P_0[J\geqslant\mu-1]-\beta$ (P_0 is the probability evaluated at ρ_0). The good agreement between the Monte Carlo simulation results and Eq. (2.4) at the early time regime is displayed in Fig. 1.

In the long time regime for $k\ll 1$ mean field holds, so

$$\rho(\tau)=\left[\frac{1}{\rho_0^{\mu-1}}+\frac{\tau}{(\mu-2)!}\right]^{-1/(\mu-1)}, \tag{2.5}$$

as $t\to\infty$. Notice that for $\mu=2$ the kinetics is anomalous (disagrees with the classical prediction).

When $k\ll 1$, Eq. (2.3) holds approximately. So, when $\rho\ll 1$, we keep the first order term in Eq. (2.3) and we recover Eq. (2.5) from Eq. (2.2) in a simple way. Clearly, within this approximation we cannot reproduce the logarithmic corrections of the marginal case $3A\to\nu A$ $(\nu=0,1,2)$ (see the deviation in Fig. 2). It is easy to see that for $\rho_0\ll 1$ and $k\ll 1$, this equation also holds in the early time regime. However, we observed that above a certain initial density Eq. (2.5) fails in the early time regime (see Figs. 2,3).

III. CONCLUSIONS

We have introduced a diffusion limited $\mu A\to\nu A$ $(\mu>\nu)$ with nucleation and finite reaction rate in one dimen-

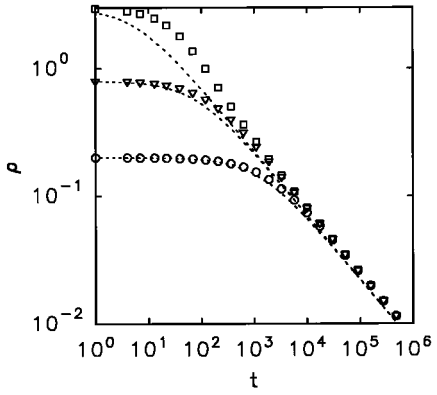

FIG. 2. Particle density vs time. Monte Carlo results for $k=0.01$ and $\rho_0=3$ (□), 0.8 (▽), 0.2 (○). The dashed lines shows the mean field approximation. Here $\mu=3$ and $\nu=1$.

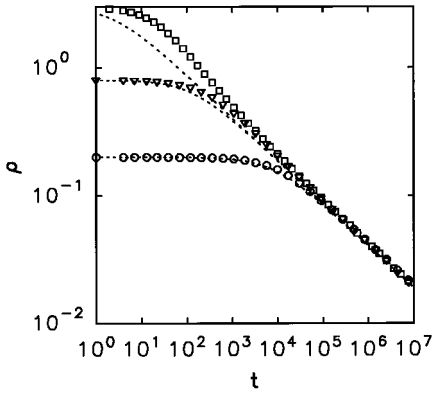

FIG. 3. Same as Fig. 2 but with $\mu=4$ and $\nu=1$.

sion for the particle density decay by means of the Monte Carlo simulation and the analytic modeling. Summarizing, the principal features of the model are the following: (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 the 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 $k \ll 1$. We have derived the rate equation (2.1) for the particle density. The early time regime has been characterized by an analytic approach and compared with Monte Carlo simulation results. In spite of the fact that we cannot reproduce logaritmic correction of the marginal case, the most important feature of this model is that the Poisson distribution allows us to obtain, in an easy way, the mean field solution. This solution holds for all time for $\rho_0 \ll 1$ and in the asympotic regime for $\rho_0 \gg 1$.

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