Diffusion-Limited Three-Body Reactions in One Dimension

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We study the diffusion-limited reactions $3A \rightarrow 2A$ and $3A \rightarrow A$ in one dimension. The analytic method of interparticle distribution functions is extended to the case where lattice sites can be occupied by more than one particle. The exact leading time behavior of the concentration decay, and the distribution of distances between nearest particles in the long time asymptotic limit are computed. Results of extensive numerical simulations are also presented. From the numerical data, we observe the previously postulated logarithmic corrections to the concentration power-law decay.

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Diffusion-limited reactions in low dimensions have attracted much interest in recent years [1-8]. Most research has focused on the bimolecular reaction $A+B \rightarrow C$ [1], and on one-component coalescence, $A+A \rightarrow A$ [2-4], and annihilation, $A+A \rightarrow 0$ [5,6]. The last two reactions were solved exactly in one dimension, where it was shown that the concentration of particles, c, decays as $c \sim 1/\sqrt{t}$, in disagreement with the prediction of classical rate equations. A less well studied problem are the one-dimensional n-body reactions $nA \rightarrow mA$ $(m<n)$, when $n>2$. For $n>3$, the mean-field rate equation $dc/dt=-kc^n$ (k is a constant) yields an accurate description of the long time asymptotic limit, $c \sim 1/t^{1/(n-1)}$. The case of $n=3$ is marginal. The reaction rate, k, is expected to vanish as $1/\ln t$ [7] but the resulting logarithmic corrections, $c \sim \sqrt{\ln t/t}$, were never observed.

In this Letter, we study the reactions $3A \rightarrow 2A$ and $3A \rightarrow A$ using both simulations and an analytic approach. The analytic approach is an extension of the method of interparticle distribution functions (IPDF's) [4] to the case where lattice sites are multiply occupied. We compute the IPDF, i.e., the distribution of distances between nearest particles, and the rate constants k. The agreement of the IPDF and the decay rates to simulations is excellent. The adaptation of the IPDF method to the present problem is proper only in the long time asymptotic limit. For this reason, it fails to predict the logarithmic corrections. Nevertheless, these are clearly observed and measured from the numerical simulations data.

Our model is defined on a one-dimensional lattice with lattice spacing Δx. Each site can be either empty, or occupied with one or two particles. The particles move randomly to a nearest neighbor site with a hopping rate $D/(\Delta x)^2$ (to each side). On long length and time scales this yields normal diffusion with diffusion coefficient D. When a particle hops onto a doubly occupied site, an *immediate* reaction takes place: the new site becomes singly occupied, if the process $3A \rightarrow A$ is being modeled (case I), or it simply remains doubly occupied, in the case of $3A \rightarrow 2A$ (case II).

To solve the system, we follow the IPDF method previously used for the solution of $A+A \rightarrow A$ in one dimension [4]. We define, as usual, $E_n(t)$, the probability that a randomly chosen segment of n consecutive sites is empty, i.e., contains no particles. The probability that a site is occupied by either one or two particles is thus $1-E_1$. We introduce now the variable $q(t)$, the conditional probability that an occupied site is *doubly* occupied. (The site would be singly occupied with probability $1-q$.) Thus the density, or concentration, of particles is expressed as

$$c(t)=[1+q(t)][1-E_1(t)]/\Delta x\,. \tag{1}$$

From the E_n one can also obtain p_n, the probability that two nearest occupied sites lie n sites apart [4],

$$c\Delta x p_n = E_{n+1}-2E_n+E_{n-1}\,. \tag{2}$$

The p_n constitute an "interparticle distribution function" and the method derives its name from this fact.

One can readily write down an evolution equation for $E_n(t)$,

$$\partial_t E_n = \frac{2D}{(\Delta x)^2}[(1-q)(E_{n-1}-E_n) - (1+q)(E_n-E_{n+1})]\,. \tag{3}$$

$E_n - E_{n+1}$ is the probability that n consecutive sites are empty but the $(n+1)$th site is occupied. Thus, the first term on the right-hand side (rhs) of Eq. (3) describes the creation of an empty n-sites interval through the hopping of a (single) particle at the inner edge, out of the interval. Similarly, the second term describes annihilation through the hopping of a particle at the outer edge into the empty interval. Equation (3) is valid for $n>1$. To make it valid also for $n=1$ we require the boundary condition

$$E_0(t)=1\,. \tag{4}$$

Notice that Eqs. (3) and (4) are independent of the reaction process and apply for both cases I and II.

An additional equation comes from the consideration of reaction events. The probability that two adjacent sites are occupied is *exactly* given by $1-2E_1+E_2$. To compute the reaction rate we need the probability that one of these sites, the target site, is doubly occupied (only then will there be a reaction). We make the approxima-

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tion that the actual number of particles in each of the two sites is uncorrelated. Thus, for example, the probability that the two adjacent sites are both doubly occupied is $q^2(1-2E_1+E_2)$. In the long time asymptotic limit, when $q \to 0$, this decoupling approximation yields the correct dependence in powers of q. For this reason, we expect it to be a good approximation, though it fails to predict the logarithmic corrections observed in simulations (see below). The change in the concentration due to reactions is

$$\partial_t[(1+q)(1-E_1)] = -(3-m)\frac{2D}{(\Delta x)^2}q(1+q)(1-2E_1+E_2)\,, \tag{5}$$

where $m=1$ ($m=2$) corresponds to case I (case II). Combining Eqs. (3)-(5) we get

$$\partial_t q = \frac{2D}{(\Delta x)^2}(1+q)\left([1-(2-m)q]\frac{1-2E_1+E_2}{1-E_1} - 2q\right). \tag{6}$$

We now pass to the continuum limit by defining the spatial coordinate $x = n\Delta x$. The probabilities $E_n(t)$ are replaced by the function $E(x,t)$. For a completely random distribution, one has $q = c\Delta x$. This motivates the scaling assumption $q = \omega(t)\Delta x$. Letting $\Delta x \to 0$, Eqs. (3) and (6) are replaced by

$$\partial_t E = 2D\partial_x^2 E + 4D\omega\partial_x E\,, \tag{7}$$

$$\omega(t) = -[\partial_x^2 E(x,t)|_{x=0}]/[2\partial_x E(x,t)|_{x=0}]\,, \tag{8}$$

and the boundary condition of Eq. (4) becomes

$$E(0,t) = 1\,. \tag{9}$$

In the continuum limit the difference between the two reaction cases is retained only in Eq. (5), which becomes

$$\partial_t(\partial_x E|_{x=0}) = 2(3-m)D\omega\partial_x^2 E|_{x=0}\,. \tag{10}$$

Equations (3) and (6), with the boundary condition of Eq. (4) can be iterated numerically for arbitrary initial conditions. The long time asymptotic behavior obtained from this procedure shows a clean power-law decay of the concentration, $c \sim 1/\sqrt{t}$, with no logarithmic corrections. The limiting behavior can also be obtained from the continuous Eqs. (7)-(10) using the following ansatz. Assume that in this limit $E(x,t) = E(x/\sqrt{Dt})$. Then, in terms of the dimensionless variable $z \equiv x/\sqrt{Dt}$, Eq. (8) yields $\omega = [-E''(0)/2E'(0)]/\sqrt{Dt} \equiv \Omega_m/\sqrt{Dt}$, where the prime denotes differentiation with respect to z, and Ω_m is a dimensionless constant whose value depends on the reaction process. Substitution into Eq. (7) yields

$$2E''(z) + (4\Omega_m + \tfrac{1}{2}z)E'(z) = 0\,. \tag{11}$$

This, together with the boundary conditions $E(z=0)=1$ [Eq. (9)] and $E(z\to\infty)=0$ [9], yields

$$E(z) = \mathrm{erfc}[(8\Omega_m+z)/\sqrt{8}]/\mathrm{erfc}(\sqrt{8}\Omega_m)\,, \tag{12}$$

where $\mathrm{erfc}(u) \equiv 1-\mathrm{erf}(u)$ is the complimentary error function [10]. Finally, the value of Ω_m is determined from Eq. (10); $\Omega_1 = 1/4$, and $\Omega_2 = 1/\sqrt{8}$.

The long time asymptotic decay of the concentration can now be determined. Since $c = -\partial_x E|_{x=0}$ [Eq. (1)], we get $c(t) = \gamma_m/\sqrt{Dt}$, where $\gamma_m = \exp(-8\Omega_m^2)/\sqrt{2\pi} \times \mathrm{erfc}(\sqrt{8}\Omega_m)$. For $3A \to A$, $\gamma_1 \approx 0.762568$, and for $3A \to 2A$, $\gamma_2 \approx 0.933016$. The reaction can then be described by the classical rate equation $dc/dt = -kc^3$, with $k = D/2\gamma_m^2$. Similarly, the interparticle distribution function is derived from Eq. (2); $c(t)p(x,t) = \partial_x^2 E(x,t)$. When p is expressed as a function of the dimensionless, or *scaling* interparticle distance z, it approaches the *stationary* distribution

$$p(z) = \tfrac{1}{4}(8\Omega_m + z)\exp(-2\Omega_m z - \tfrac{1}{8}z^2)\,, \tag{13}$$

where p has been normalized with respect to z. The results are in excellent agreement with the numerical integration of the discrete equations.

We now turn to simulation results. Simulations for the $3A \to mA$ process with both $m=1$ and $m=2$ were carried out on a cluster of RISC/6000 workstations. The simulations followed common, efficient algorithms, where only occupied sites are treated at each Monte Carlo step (this is achieved by keeping separate lists of singly and doubly occupied sites) [8,11]. Typical lattices consisted of 100000 sites with periodic boundary conditions. Several initial configurations were tested, including: (a) initial density $c(0)=2$ (each site is doubly occupied—the maximal possible density), (b) initial random distribution with $c(0)=0.2$, and (c) an initial configuration where every fifth site is singly occupied [$c(0)=0.2$, but the distribution is sharply peaked, not random]. The various cases differ in their initial transient stage, but after a short relaxation time they all converge to the same results. Data was recorded for the concentration as a func-

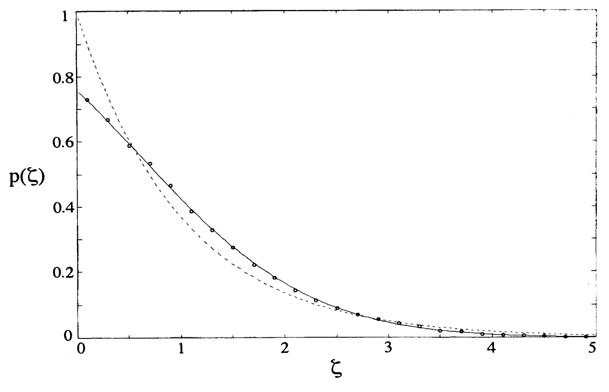

FIG. 1. The IPDF $p(\zeta)$ as a function of $\zeta \equiv cx$ as computed from Eq. (13) (solid line) and compared to the simulations data (o). The IPDF of a completely random distribution $p(\zeta) = \exp(-\zeta)$ is shown for comparison (broken line).

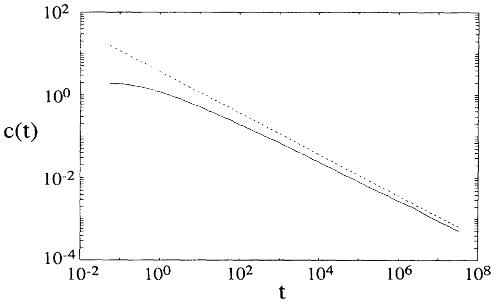

FIG. 2. Concentration decay as a function of time for the process $3A \rightarrow 2A$. Comparison with the broken line of slope $\frac{1}{2}$ shows that the decay is not purely algebraic.

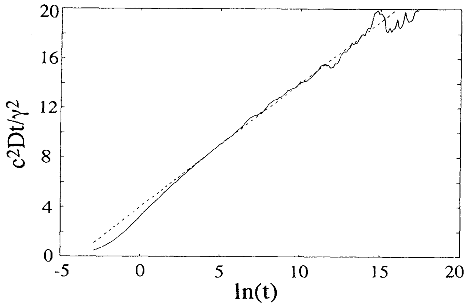

FIG. 3. Logarithmic corrections. Shown is $[c/(\gamma_2/\sqrt{Dt})]^2$ vs $\ln(t)$. The broken line of slope 1 is shown for comparison. The data also confirm the computed numerical value of γ_2.

tion of time, and for the IPDF when $c=0.02$ (at this stage convergence to the long time asymptotic limit has taken place, but enough particles remain for good statistics).

For brevity, we present results only for case II, $3A \rightarrow 2A$. In Fig. 1, we plot the IPDF as measured numerically and as computed from Eq. (13). For comparison with simulations it is convenient to use the scaling variable $\zeta \equiv c(t)x = \gamma_2 z$. We emphasize that no fitting parameters were used in producing this figure. Also shown in Fig. 1 is the IPDF for a completely random distribution, $p(\zeta) = \exp(-\zeta)$, which is expected in the reaction-limited case where classical rate equations are valid.

In Fig. 2, we plot $c(t)$ as a function of time. It is evident that even after long times the concentration decay is not given by a clean power law. In Fig. 3, we plot $[c/(\gamma_2/\sqrt{Dt})]^2$ vs $\ln(t)$. The resulting curve of slope 1 shows that the corrections are logarithmic, $c \sim \gamma_2\sqrt{\ln(t)/Dt}$, and confirms the correctness of the numerical value of γ_2. Similar results are observed for case I, $3A \rightarrow A$.

In conclusion, we have presented an analytical approach for the reactions $3A \rightarrow mA$ ($m=1,2$) in one dimension, based on the method of interparticle distribution functions. This approach predicts accurately the leading time behavior and the IPDF's in the long time asymptotic limit. These predictions were confirmed by extensive numerical simulations. From the simulation data, we were able to observe the previously postulated logarithmic corrections to the concentration time decay.

There remain several interesting open problems. The IPDF method cannot deal with complete annihilation, $3A \rightarrow 0$. It will be interesting to compare this case to the reactions studied here. We have solved our equations only in the long time asymptotic limit. The transient behavior, however, is quite rich (with a pronounced dependence on the initial IPDF's). Finally, our analytic approach has yielded only the leading time behavior; the logarithmic corrections were demonstrated numerically. Can this method be perfected, or perhaps a more powerful approach be found, that will predict the logarithmic corrections analytically?

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