LETTER TO THE EDITOR

Universal behaviour of N-body decay processes

K Kang†, P Meakin‡, J H Oh§, and S Redner†

† Center for Polymer Studies|| and Department of Physics, Boston University, Boston MA 02215, USA
‡ E I DuPont de Nemours and Company Inc. Experimental Station Central Research and Development Department, Wilmington DE 19898, USA
§ Department of Physics, Korea Advanced Institute of Science and Technology, Seoul, Korea

Abstract. We present a scaling approach to investigate the kinetics of the diffusion-controlled multiparticle reactions $A_1 + A_2 + \ldots + A_N \to inert$, and $NA \to inert$, for a random initial distribution of particles. For the first reaction, if the initial densities of all the particle species are equal, the particle density decays with time t as $t^{-\alpha}$, where $\alpha = \frac{1}{4}d$, and d is the spatial dimension. This exponent value is *independent* of N below an upper critical dimension of $d_c = 4/(N-1)$, while for $d \geq d_c$, α assumes the mean-field value of $1/(N-1)$. For the decay $NA \to inert$, $\alpha = \frac{1}{2}d$, again independent of N, for $d < d_c = 2/(N-1)$. These universal decays stem from the reaction kinetics being governed by the decay of spatial fluctuations, an effect which is insensitive to the details of the reaction. Our predictions are tested by extensive computer simulations. We also examine in detail the reaction $A_1 + A_2 + A_3 \to inert$ for arbitrary initial densities of the three reactants and elucidate a number of interesting asymptotic properties.

Recently, it has been recognised that irreversible diffusive recombination processes exhibit anomalous decay laws for a random initial distribution of particles. The reaction is defined by allowing particles to move by diffusion, and when reactive species meet, an inert particle is irreversibly created. Due to the initial randomness, spatial fluctuations in density exist on all length scales, and these play a fundamental role in governing the reaction kinetics.

For the two-body reaction $A + B \to inert$, the particle density is found to decay with time t as $t^{-d/4}$ for equal initial densities of A and B, and as $\exp(-t^{d/4})$ for unequal initial densities (see e.g., Toussaint and Wilszek 1983, Kang and Redner 1984, Meakin and Stanley 1984). On the other hand, the rate equation predicts a decay of $1/(kt)$ or $\exp(-kt)$, respectively, for these two initial conditions (see e.g., Blumen *et al* 1983, Calef and Deutch 1983). The apparent shortcoming of the rate equation stems from the neglect of spatial fluctuations in the initial random distribution of the particles. The rate equation is valid only if the particle distribution is spatially homogeneous at all times, a situation which would occur if the mobilities of the reactants were infinite. This may be viewed as the mean-field limit of the decay law.

The inadequacy of the rate equation for two-body reactions motivates us to consider its validity for more general diffusion-controlled reactions. In this letter, we apply scaling to study the kinetics of the N-body reactions $A_1 + A_2 + \ldots + A_N \to inert$, and

$NA \rightarrow inert$, and computer simulations are employed to test our predictions. Our primary interest is the relatively simple situation where the initial densities of all the reactants are equal; however, we also give a brief analysis of the decay for arbitrary initial densities. It should be noted that Fisher (1984) has given an exact analysis of N-body decays in one dimension when the initial number of particles is specified; this is complementary to the ensemble that we consider in which the initial density is specified.

To begin our discussion, we first consider the rate equation appropriate to describe the reaction $A_1 + A_2 + \ldots + A_N \rightarrow inert$

$$\partial \rho_i(t)/\partial t = -k\rho_1(t)\rho_2(t) \ldots \rho_N(t) \tag{1}$$

Here $\rho_i(t)$ is the density of the ith species at time t, and k is a rate constant. When the initial densities of all the reactants are equal, the asymptotic form of $\rho_i(t)$ is

$$\rho_i(t) \sim (kt)^{-1/(N-1)}. \tag{2}$$

That is, a progressively slower decay law is predicted as the number of reactants needed to initiate the reaction is increased. This decay also describes the asymptotic particle density in the reaction $NA \rightarrow inert$.

In analogy with the recent insights gained from studies of the two-body decay, we expect, however, that the rate equation predictions will be drastically modified by spatial fluctuations. To account for their influence, we estimate the fluctuations in particle number in a spatial region of linear dimension l and volume l^d. The initial number of the ith species in this volume is

$$N_i \approx \rho_i(0)l^d \pm \sqrt{\rho_i(0)l^d} \tag{3}$$

where the second term indicates the statistical fluctuations. Accordingly, the difference $\Delta_{ij} \equiv N_i - N_j$ is given by

$$(\rho_i(0) - \rho_j(0))l^d \pm (\sqrt{\rho_i(0)} \pm \sqrt{\rho_j(0)})l^{d/2}. \tag{4}$$

In the absence of fluctuations, Δ_{ij} (with $i < j$) will always be less than zero for any size volume when $\rho_i(0) < \rho_j(0)$ ($i < j$). However, the second term in equation (4) makes it possible to have small regions where some of the Δ_{ij} ($i < j$) are positive. The size of such a region can be estimated by considering the maximum positive fluctuation of the minority species (A_i), and the maximum negative fluctuation of the majority species (A_j), and then setting $N_i = N_j$. This condition determines the maximum length scale where fluctuations in N_i and N_j are sufficiently large that either of the two species may be in the local majority. We thus find the length scale

$$\xi_{ij} \sim (\sqrt{\rho_j(0)} - \sqrt{\rho_i(0)})^{-d/2}. \tag{5}$$

Equivalently, there is a characteristic time scale t_{ij} proportional to ξ_{ij}^2, which is the time required for a particle to diffuse across a region of linear dimension ξ_{ij}. For $t < t_{ij}$, the reaction has not yet had enough time to eliminate relative local fluctuations between species A_i and A_j in a volume $V < \xi_{ij}^d$, while for longer times, $N_j > N_i$ with overwhelming probability in the volume V. This defines a crossover from fluctuation-dominated behaviour at short times, to fluctuation-free behaviour at long times.

We now use the time scale defined above to the derive the decay law when the initial densities of the reactants equal. For simplicity, we treat the three-body reaction, but the generalisation to the N-body case is immediate. In analogy with the two-body reaction (Kang and Redner 1984), we write a scaling form for $\rho_i(t)$ by assuming that

the decay will be a power law for t less than the shortest time scale (t_{13} for the three-body reaction),

$$\rho_i(t) \simeq C_i t^{-\alpha} f_i(x_{23}, x_{13}, x_{12}) \tag{6}$$

where $f_i(x_{23}, x_{13}, x_{12})$ is a scaling function of the dimensionless variables $x_{ij} = t/t_{ij}$, and C_i is a constant which depends on the initial conditions.

To fix the exponent α, it is now useful to consider the particular initial condition $\rho_1(0) < \rho_2(0) = \rho_3(0)$, so that t_{23} diverges, while $t_{13} = t_{12} \equiv \tau$. Equation (6) can then be written more simply as

$$\rho_i(t) \simeq C_i t^{-\alpha} \tilde{f}_i(t/\tau) \tag{7}$$

where $\tilde{f}_i(t/\tau) = f_i(0, t/t_{13}, t/t_{12})$, and α is assumed to be independent of the initial conditions.

From the conservation of the particle density difference, $\rho_1(t) - \rho_2(t) = \rho_1(0) - \rho_2(0)$, and from equation (7), we have

$$(\rho_1(0) - \rho_2(0)) t^\alpha = C_1 \tilde{f}_1(t/\tau) - C_2 \tilde{f}_2(t/\tau) \tag{8}$$

Since $\tilde{f}_i(x)$ is a function *only* of the scaling variable x, it follows that the left-hand side of (8) must also depend only on x. However $\rho_1(0) - \rho_2(0)$ can be rewritten as $(\sqrt{\rho_1(0)} + \sqrt{\rho_2(0)})\tau^{-d/4}$ (Kang and Redner 1984), from which we can immediately determine α and C_i to be

$$\alpha = \tfrac{1}{4}d, \qquad C_1 = C_2 \simeq (\sqrt{\rho_1(0)} + \sqrt{\rho_2(0)}). \tag{9}$$

In the limit $\rho_1(0) \to \rho_2(0)$, the $t^{-\alpha}$ decay law will be recovered in equation (7). We therefore find,

$$\rho_i(t) \simeq \sqrt{\rho_i(0)}\, t^{-d/4} \tag{10}$$

for the case of equal initial densities of three reactants.

In two dimensions, this decay law is the same as the rate equation prediction for $N = 3$; this defines the upper critical dimension d_c to be equal to 2. We therefore expect a $t^{-d/4}$ decay law below two dimensions, and a $t^{-1/2}$ decay for $d \geq 2$.

To generalise to the N-body decay for equal initial densities of the reactants, we choose the initial condition $\rho_1(0) < \rho_2(0) = \rho_3(0) = \ldots = \rho_N(0)$, and follow the same steps of equations (7)–(10). This gives $\rho_i(t) \simeq \sqrt{\rho_i(0)}t^{-d/4}$ below $d_c = 4/(N-1)$, while for $d \geq d_c$, the decay law has the rate equation form of $t^{-1/(N-1)}$. The universal N-independent decay predicted for $d < d_c$ stems from the fact that local fluctuations decay *only* by diffusion, and *not* due to the reaction (Toussaint and Wilszek 1983). Since these reaction-independent fluctuations govern the decay, we therefore expect that the decay rate will also be indepenent of the number of reactants needed to initiate the reaction.

We can also apply scaling to the single-species reaction $NA \to inert$. This reaction is simpler than the decay with different species as there is only one time scale, $\tau \simeq \rho_A(0)^{-2/d}$, the time required for a particle to diffuse a distance of the order of the initial particle separation. The scaling form of the particle density may be written as

$$\rho_A(t) \simeq \rho_A(0)f(t/\tau). \tag{11}$$

In analogy with the two-body reaction (Toussaint and Wilszek 1983, Torney and McConnell 1983a, b), we postulate that $\rho_A(t)$ will be independent of the initial density

as $t \to \infty$. This condition immediately fixes the decay law to be $\rho_A(t) \sim t^{-d/2}$ for $d < d_c = 2/(N-1)$, while the mean-field decay of $t^{-1/(N-1)}$ should hold for $d \geq d_c$.

We may generalise further to treat the M-body reaction $n_1 A_1 + n_2 A_2 + \ldots + n_N A_N \to$ *inert*, with $\Sigma_{i=1}^{N} n_i = M$. A natural initial condition to consider is $\rho_1(0)/n_1 = \rho_2(0)/n_2 = \ldots = \rho_N(0)/n_N$; this yields a final state of no particles. A direct generalisation of the approach given in equations (6)–(8) predicts the decay law

$$\rho_i(t) = \sqrt{\rho_i(0)} \, t^{-d/4} \tag{12}$$

below $d_c = 4/(M-1)$, while for $d \geq d_c$, the mean-field decay

$$\rho_i(t) \sim t^{-1/(M-1)} \tag{13}$$

holds. Finally, one may consider N-body decays on self-similar structures, such as regular fractals or a percolation cluster at the threshold (Kang and Redner 1984, Meakin and Stanley 1984, Kopelman *et al* 1984). We predict that the asymptotic decay can be obtained by replacing the Euclidean dimension appearing in the decay laws, with the fracton dimension of the self-similar structure (Alexander and Orbach 1982), when the fractal dimension of the structure is less than the upper critical dimension for the reaction. A summary of the decay laws is given in table 1.

Table 1. The exponent for N-particle decay processes: (a) the reaction $A_1 + A_2 + \ldots + A_N \to$ *inert*, (b) the reaction $NA \to$ *inert*, and (c) the reaction $NA + B \to$ *inert*.

$N \backslash d$	1	2	3	4	∞
(a) 2	1/4	1/2	3/4	1	1
3	1/4	1/2	1/2	1/2	1/2
4	1/4	1/3	1/3	1/3	1/3
5	1/4	1/4	1/4	1/4	1/4
(b) 2	1/2	1	1	1	1
3	1/2	1/2	1/2	1/2	1/2
4	1/3	1/3	1/3	1/3	1/3
(c) 2	1/4	1/2	1/2	1/2	1/2
3	1/4	1/3	1/3	1/3	1/3
4	1/4	1/4	1/4	1/4	1/4

To test our predictions, we have first simulated the reaction $A_1 + A_2 + A_3 \to$ *inert* for equal initial densities of all reactants. The simulation data are in good agreement with the prediction of a $t^{-1/4}$ decay for $d = 1$, and a decay of $t^{-1/2}$ for $d \geq 2$ (figure 1). Unfortunately, it is not possible to obtain information on higher-body decays due to prohibitive computer time requirements. We have also simulated the reaction $NA \to$ *inert* in one dimension. For the case $N = 2$, d_c is greater than one, and the $t^{-1/2}$ decay predicted by scaling has been observed (Toussaint and Wilszek 1983, Torney and McConnell 1983a, b, Meakin and Stanley 1984). For $N = 3$, $d_c = 1$, and one should therefore observe a $t^{-1/2}$ decay, possibly modified by a logarithmic correction (Meakin and Stanley 1984). However for $N = 4$, the upper critical dimension now equals $\frac{2}{3}$, and the decay in one dimension should now follow the rate equation result of $t^{-1/3}$. This general picture is in excellent agreement with the results presented in figure 2.
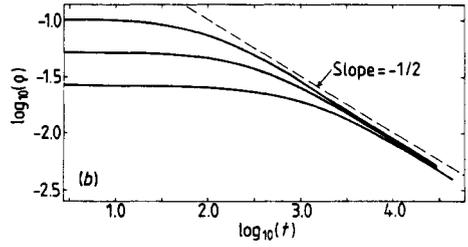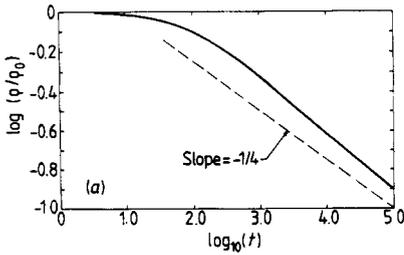
Figure 1. Plot of the survival probability against time for the reaction $A + B + C \to inert$ in (a) one and (b) two dimensions. The initial densities of the reactants are equal, and the slope of the lines are $-\frac{1}{4}$ and $-\frac{1}{2}$ respectively, indicating a $t^{-1/4}$ and a $t^{-1/2}$ decay at long times.
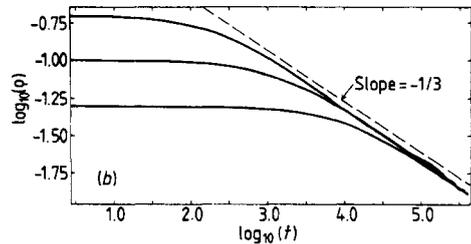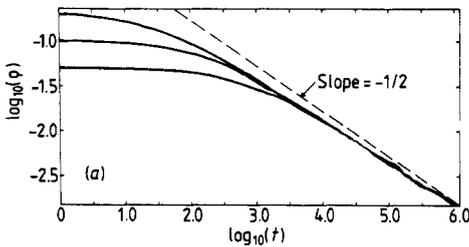
Figure 2. Plot of the survival probability against time for the reaction $NA \to inert$ in one dimension for the case (a) $N = 3$, and (b) $N = 4$. The data appear to follow a $t^{-1/2}$ decay and a $t^{-1/3}$ decay respectively.

We now turn to a discussion of the decay laws for arbitrary initial densities of the reactants. As before, we explicitly treat the three-body decay, and the generalisation to higher-body decays is straightforward. The decay begins with a short-time regime defined by t much less than any of the t_{ij}. In this short-time regime, relative fluctuations in particle number predominate. In analogy with the two-body reaction (Kang and Redner 1984), the decay should be the same as the case of equal initial densities of all three species. At longer times, the differences in the densities of the various species manifest themselves, and there are several possible asymptotic decays.

To enumerate the possibilities, we first introduce a simple generalisation of the rate equation which appears to incorporate fluctuation effects (de Gennes 1982, Kang and Redner 1984). For equal initial densities of the reactants, the original rate equation, (1), can be modified to give the correct asymptotic decay found by scaling by introducing a time-*dependent* rate coefficient, $k(t)$. Such a modification is employed to account for the fact that the probability of reactive species meeting is not constant, but rather is decreasing with time due to the growth of large-scale inhomogeneities (see e.g., Toussaint and Wilszek 1983 for the two-body case). For the three-body reaction, we recover the decay law given in equations (7) and (9) by taking $k(t)$ in the rate equation to be proportional to $t^{d/2-1}$.

Based on solving this time-dependent rate equation, there are three distinct asymptotic behaviours which originate from the following generic initial conditions: (a) one species in the minority, and the densities of the other two species otherwise arbitrary, (b) two species with equal density less than the density of the third species, and (c) equal densities. As already mentioned, all three initial conditions give rise to

a decay of $t^{-a/4}$ at short times. However, at longer times there is a crossover to an asymptotic decay of $\exp(-t^{d/2})$ for case (a), and an asymptotic decay of $t^{-d/2}$ for case (b). This general picture appears to be in agreement with our preliminary data.

In summary, we have studied the kinetics of N-body irreversible diffusion-controlled reactions $A_1 + A_2 + \ldots + A_N \rightarrow inert$, and $NA \rightarrow inert$. From a scaling approach, we find that the asymptotic decay should be universal, independent of the details of the reaction, when the system is below the upper critical dimension. This results because the decay is determined by the decay of local fluctuations, an effect which is independent of any reaction details. We have also introduced a time-dependent rate equation to treat the multi-species reaction for unequal initial densities of reactants. A variety of asymptotic decays are predicted, determined by the number of distinct particle species which are in the minority.

References

Alexander S and Orbach R 1982 *J. Physique* **43** L625
Blumen A, Klafter J and Zumhofen G 1983 *Phys. Rev.* B **27** 3429
Calef D F and Deutch J M 1983 *Ann. Rev. Phys. Chem.* **34** 493
de Gennes P G 1982 *J. Chem. Phys.* **76** 3316
Fisher M E 1984 *J. Stat. Phys.* **34** 667
Kang K and Redner S 1984 *Phys. Rev. Lett.* **52** 955
Kopelman R, Klymko P W, Newhouse J S and Anacker L W 1984 *Phys. Rev.* B **29** 3747
Meakin P and Stanley 1984 *J. Phys. A: Math. Gen.* **17** L173
Torney D C and McConnell H M 1983a *J. Phys. Chem.* **87** 1441
—— 1983b *Proc. R. Soc.* A **387** 147
Toussaint D and Wilszek F 1983 *J. Chem. Phys.* **78** 2642