

Fluctuation-dominated kinetics in diffusion-controlled reactions

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The kinetics of a number of prototypical diffusion-controlled reactions are studied, primarily through the application of scaling approaches. Our goal is to investigate the effects of spatial inhomogeneities in the particle densities on the reaction kinetics. In general, we find that there exists an upper critical dimension below which the kinetics cannot be described by a rate-equation analysis, an approach which gives the kinetic laws of a mean-field approximation. Below the upper critical dimension, spatial inhomogeneities in the particle densities give rise to new fluctuation-dominated kinetics. For irreversible reactions, with bimolecular decay $A + B \rightarrow \text{inert}$ being a simple generic example, universal kinetic laws are obtained which are a function only of the spatial dimension, the number of particles needed to initiate a reaction, and the nature of the particle-conservation laws for the system. We also consider the generalization of bimolecular decay to a multistate process where particles of variable "heights" and traps of variable "depths" react. This phenomenologically rich example serves as an illustrative testing ground for scaling ideas. The introduction of a small reaction probability on bimolecular decay provides an example of a dramatic crossover from an initial mean-field decay to the fluctuation-dominated decay law at large times. When the possibility of a reverse reaction is allowed in bimolecular decay, the available evidence suggests that there is a power-law approach to the equilibrium state, rather than an exponential approach predicted by the rate equation. Many of our new theoretical predictions are tested by extensive numerical simulations.

I. INTRODUCTION

The understanding of the kinetics of diffusion-controlled reactions is an important basic science problem with a wide variety of applications.¹⁻³ It has become increasingly appreciated, especially very recently,⁴⁻¹¹ that the effects of spatial inhomogeneities in the densities of the reacting particles can have rather dramatic effects on the kinetics. The primary aim of this paper is to elucidate the role of these inhomogeneities, or spatial fluctuations, in determining the kinetics of various simple model diffusion-controlled reactions.

The traditional approach for studying reaction kinetics is the rate equation. It is to be emphasized that this approach gives results which are analogous to mean-field predictions in the theory of critical phenomena. The rate-equation approach implicitly assumes that the reactant densities are everywhere spatially uniform, i.e., the local and global densities coincide. This uniformity can be thought of as arising from either an infinite mobility of the reactants, or from a vanishingly small probability that a chemical reaction actually takes place when reactive species meet. Both of these mechanisms ensure that each particle has the same probability of reacting with any other particle in the system. However, if the particle mobility becomes sufficiently small, or equivalently, if the microscopic chemical-reaction probability becomes large enough, there is a crossover to a new regime where a given

particle is more likely to react with local neighbors rather than with distant particles. This behavior defines the regime of the diffusion-controlled reaction, where spatial fluctuations can develop and ultimately determine the kinetic behavior.

One example of a diffusion-controlled reaction where fluctuations modify the kinetic behavior is the unimolecular trapping reaction, which may be written as $A + B \rightarrow (1-\epsilon)A + B$ ($0 < \epsilon \leq 1$). Here A particles are absorbed when they meet a B particle, either partially ($\epsilon < 1$) or perfectly ($\epsilon = 1$), while the B 's are unaffected by the reaction. If the A particles diffuse and the B 's are static and randomly distributed, then it has been established that the density of the A 's, $\rho_A(t)$, decays as $\exp(-k\rho_B^{2/(d+2)}t^{d/(d+2)})$, where k is a constant, ρ_B is the concentration of B 's (traps), and d is the spatial dimension.¹²⁻²⁰ This unusual decay law stems from the predominant role played by large trap-free regions, events which occur with an exponentially small probability. In a trap-free region of linear dimension l , the decay is exponential, but with a decay time proportional to l^2 . Averaging over all such trap-free regions then leads to a shift in the decay law from purely exponential, as would be predicted by a rate-equation approach, to the slower quasiexponential decay mentioned above.

While spatial inhomogeneities in the trap density ultimately govern the asymptotic decay, this example is somewhat pathological as the long-time decay depends

crucially on the presence of extremely rare events which happen to be present in a fixed initial distribution of disorder. As a result, the anomalous long-time decay in the trapping reaction may not be experimentally observable.²⁰ However, if both the A and B species undergo a reaction upon meeting, then both particle distributions will be changing as a function of time. Thus fluctuation effects—if present—may be generated by the kinetics of the reaction itself. This should provide a more experimentally realizable situation with which one can investigate the effects of spatial inhomogeneities.

A simple, but extremely useful, testing ground for investigating these fluctuation effects is provided by the irreversible bimolecular reaction $A + B \rightarrow \text{inert}$. An initial breakthrough in understanding the influence of fluctuations in this reaction was made by Toussaint and Wilczek.⁹ For equal initial densities of the A and B particles, they showed that $\rho_A(t)$ decays as $t^{-d/4}$ for $d < 4$. They also performed a striking simulation which demonstrates that a homogeneous but random initial particle distribution evolves into an alternating array of A -rich and B -rich domains. Recombination takes place only along the domain boundaries, with smaller domains eventually being annihilated by larger ones. This domain-annihilation process ultimately gives rise to a decay which is slower than the $1/t$ law predicted by the rate equation.

Very recently we have developed a scaling theory to investigate the fluctuation-dominated kinetics of the bimolecular reaction.¹⁰ This simple approach correctly predicts the asymptotic decay laws for the cases of equal and unequal initial densities of A 's and B 's, as well as for different forms of particle transport. We will extend this theoretical approach to a broader range of diffusion-controlled reactions, with the goal of describing very general aspects of fluctuation-dominated kinetics.

In Sec. II we first explain the scaling approach for the simple recombination processes $A + B \rightarrow \text{inert}$ and $A + A \rightarrow \text{inert}$. A simple intuitive domain picture is developed from which the kinetics can be derived easily. The decay laws for the case of biased diffusion, appropriate for describing the motion of charged particles in a uniform external electric field, are also derived. In addition, the scaling approach is generalized to describe the multiparticle reaction processes $A_1 + A_2 + \dots + A_N \rightarrow \text{inert}$ and $NA \rightarrow \text{inert}$. A more general reaction involving interactions between particles of variable "heights" and antiparticles of variable "depths" is introduced and studied in Sec. III. This reaction may serve as a description of soliton-antisoliton annihilation or of multistate recombination processes. An unusual dependence of the decay laws on the heights and depths of the reactants is derived and verified numerically. In Sec. IV we investigate the effects of introducing a small reaction probability, defined as the probability that interacting particles actually undergo a reaction when they meet, on the kinetics of bimolecular decay. The asymptotic independence of the decay on the reaction probability is interpreted in terms of the scaling approach and the domain picture mentioned above. In Sec. V we describe the anomalously slow approach to equilibrium in the reversible bimolecular reaction $A + B \leftrightarrow C$ and discuss the role played by spatial fluctua-

tions. Finally, we conclude in Sec. VI.

II. SCALING APPROACH FOR IRREVERSIBLE BIMOLECULAR REACTIONS

A. Two-species reaction $A + B \rightarrow \text{inert}$

This reaction may be used to describe electron-hole recombination in condensed-matter systems, or ionic recombination in plasmas in the limiting situation where the Debye screening length is small so that interparticle interactions can be neglected. We describe these reactions in terms of an idealized model in which an inert particle species is formed instantly and irreversibly when an A and a B particle meet. This inert species is assumed to play no further role as long as the reaction is strictly irreversible. In addition, no reaction between particles of the same species is allowed. As we shall see, the most interesting situation occurs when the initial spatial distributions of the two particle species are homogeneous but random.

The standard approach to describe the kinetics of this reaction is the following rate equation:²¹

$$\frac{d\rho_A(t)}{dt} = -k\rho_A(t)\rho_B(t), \quad (1)$$

where $\rho_A(t)$ and $\rho_B(t)$ are the densities of species A and B at time t , respectively, and k is the rate coefficient. The right-hand side represents the probability that an A and a B particle will meet, thus contributing to the time dependence of the particle density. Without loss of generality, we may assume that $\rho_B(0) \geq \rho_A(0)$ in the ensuing discussion. Under this assumption, the solution to Eq. (1) is

$$\rho_A(t) = \begin{cases} C/[1 + C/\rho_A(0)]e^{Ckt} - 1, & C > 0 \\ \rho_A(0)/[1 + k\rho_A(0)t], & C = 0 \end{cases} \quad (2a)$$

$$(2b)$$

where the constant C is the conserved initial particle-density difference, $\rho_B(0) - \rho_A(0)$. In the situation where $C \ll \rho_A(0)$, Eq. (2a) yields two important asymptotic limits:

$$\rho_A(t) \cong \begin{cases} 1/kt, & \tau_0 \ll t \ll \tau \\ \exp\{-k[\rho_B(0) - \rho_A(0)]t\}, & t \gg \tau \end{cases} \quad (3a)$$

$$(3b)$$

where $\tau_0 = [k\rho_B(0)]^{-1}$ is the time required before any reaction is initiated, and the crossover time τ is given by $\tau = \{k[\rho_B(0) - \rho_A(0)]\}^{-1}$. The physical meaning of Eqs. (3) is that as long as the density of the minority species (A) is much larger than the particle-density difference, then the system cannot distinguish which of the particle species is in the majority. Therefore the decay coincides with the $1/t$ decay of a system with equal initial densities. In particular, when the initial density difference equals zero, the $1/t$ decay persists asymptotically. However, if the initial densities of A and B are unequal, a situation is eventually reached where $\rho_A(t) \ll \rho_B(0) - \rho_A(0)$. It is then likely that each A particle will be isolated within a large region which is (sparsely) populated only by B particles. In this case, subsequent decay of the A 's will not be

affected by whether or not the corresponding annihilation of the B 's continues to occur. In this limit, therefore, the decay crosses over to that of the trapping reaction, i.e., exponential decay.

As mentioned in the Introduction, Eqs. (2) and (3) represent the mean-field limits of the decay laws since spatial fluctuations in the particle density have been neglected. That is, the rate equation is written in terms of the global density $\rho_A(t)$ which has been taken to coincide with the local density. The rate-equation approximation breaks down, however, if the initial distribution of reactants is homogeneous but random. To account for the effects of spatial fluctuations in this case, we note that if $\rho_B(0) > \rho_A(0)$, then the number of A and B particles in a finite volume V will satisfy the *same* inequality, $N_B > N_A$, only for V sufficiently large. For smaller volumes, local \sqrt{N} -type fluctuations may reverse the sense of the inequality in the particle numbers. Consequently, the nature of the decay at short and large length scales will be qualitatively different. Since the diffusing particles explore larger spatial scales as time increases, we can therefore expect a crossover in the decay law as a function of time.

To develop this idea quantitatively,¹⁰ consider a spatial region of linear dimension l and volume l^d . The number of A particles in this volume at $t=0$ is

$$N_A = \rho_A(0)l^d \pm \sqrt{\rho_A(0)l^d} \quad (4)$$

and similarly for N_B . Here the second term represents the local fluctuations inherent in the random distribution of particles. The particle-number difference in this volume is, therefore,

$$N_B - N_A = [\rho_B(0) - \rho_A(0)]l^d \pm [\sqrt{\rho_B(0)} \pm \sqrt{\rho_A(0)}]l^{d/2}. \quad (5)$$

Due to fluctuations, embodied by the second term in Eq. (5), it is possible to have $N_B < N_A$ in a sufficiently small volume even if $\rho_B(0) > \rho_A(0)$. For a fixed initial density difference, the size of the largest volume in which the minority species can predominate may be estimated by considering the maximum positive fluctuation in the minority species (A), and the maximum negative fluctuation in the majority species (B), and setting $N_A = N_B$. This yields a characteristic length scale for the maximal volume,

$$\xi \sim [\sqrt{\rho_B(0)} - \sqrt{\rho_A(0)}]^{-2/d}. \quad (6)$$

This length is equivalent to a characteristic time scale $t_\xi \sim \xi^2/D$, where D is the diffusion coefficient. This is the time required for a diffusing particle to traverse a volume of radius ξ .

In terms of this time scale, we now make the following scaling ansatz for the particle density, in analogy with the crossover phenomenon displayed by the rate equation,

$$\rho_A(t) \sim C_A t^{-\alpha} f_A(t/t_\xi) \quad (7)$$

and similarly for $\rho_B(t)$. Here $f_A(x)$ and $f_B(x)$ are scaling functions of the dimensionless variable $x \equiv t/t_\xi$, and C_A and C_B are constants which depend on the initial conditions. We expect that the scaling functions will approach

constants for $x \ll 1$ and that they will decay faster than power laws for $x \gg 1$. To fix the unknowns in Eq. (7), we first use the conservation of particle-density difference $\rho_A(t) - \rho_B(t) = \rho_A(0) - \rho_B(0)$ and then use Eq. (6) to rewrite the initial particle-density difference in terms of t . This gives

$$C_B f_B(t/t_\xi) - C_A f_A(t/t_\xi) = [\sqrt{\rho_B(0)} + \sqrt{\rho_A(0)}] t_\xi^{-d/4} t^{-\alpha}. \quad (8)$$

Since f_A and f_B are functions only of the scaling variable t/t_ξ , it follows that the right-hand side of Eq. (8) must be expressible in terms of this variable only. This fact, together with the condition $C_A = C_B$ when $\rho_A(0) = \rho_B(0)$ then yields

$$\alpha = d/4, \quad C_A = C_B \cong [\sqrt{\rho_A(0)} + \sqrt{\rho_B(0)}]. \quad (9)$$

In the limit $\rho_A(0) \rightarrow \rho_B(0)$, the above result agrees with the decay law first predicted by Toussaint and Wilczek,⁹ for the special case of equal initial particle densities. The result (9) should hold for spatial dimensions $d < 4$, where the decay due to the fluctuation mechanism is slower than the rate-equation decay. At $d=4$, these two decays coincide, thus identifying $d=4$ as the upper critical dimension. Above this dimension, the mean-field decay law of $1/t$ holds since it is the slower decay of the two processes.

The prediction (9) for the decay law is in excellent agreement with our simulations, and representative results are shown in Fig. 1. Since the relevant transport parameter is the relative diffusion coefficient of the A 's and B 's, we have, for reasons of technical convenience only, taken one of the species to be at rest in our simulations. The numerical results of this system are essentially identical to the results obtained when both particle species move.^{9,22} From our numerical results, one can also confirm the scaling theory by verifying that data collapsing occurs.¹⁰

It is possible to give a simple pictorial derivation of the decay for equal initial particle densities, which makes use of the observed segregation of the particles into distinct domains of opposite species.⁹ In Fig. 2 we illustrate the evolution of a system of randomly distributed A and B particles due to the reaction. Initially, in a region of volume $V = l^d$ the number of A particles is $N_A = \rho_A(0)l^d \pm \sqrt{\rho_A(0)l^d}$. After a time $t \sim l^2/D$ the particles will have time to completely "mix" within the volume V and annihilate in pairs leaving only the residual fluctuations. These residual particles define a domain in which the number of particles is simply $\sqrt{\rho_A(0)l^d}$, or equivalently a particle density of $\sqrt{\rho_A(0)}/l^{d/2}$, as illustrated in Fig. 2(b). Since the system is a homogeneous collection of alternating A -rich and B -rich domains, each of size $l \sim (Dt)^{1/2}$, the global density is approximately one-half the density within a single domain. We therefore conclude that $\rho_A(t) \sim \sqrt{\rho_A(0)}(Dt)^{-d/4}$.

It is also instructive to give an alternative argument for the $t^{1/2}$ dependence of the domain size to illustrate the domain-growth mechanism more clearly. Since the system can be viewed as a homogeneous collection of domains of approximately the same linear dimension (up to \sqrt{N} -type fluctuations), the primary growth mechanism is the annihilation of smaller domains by the coalescence

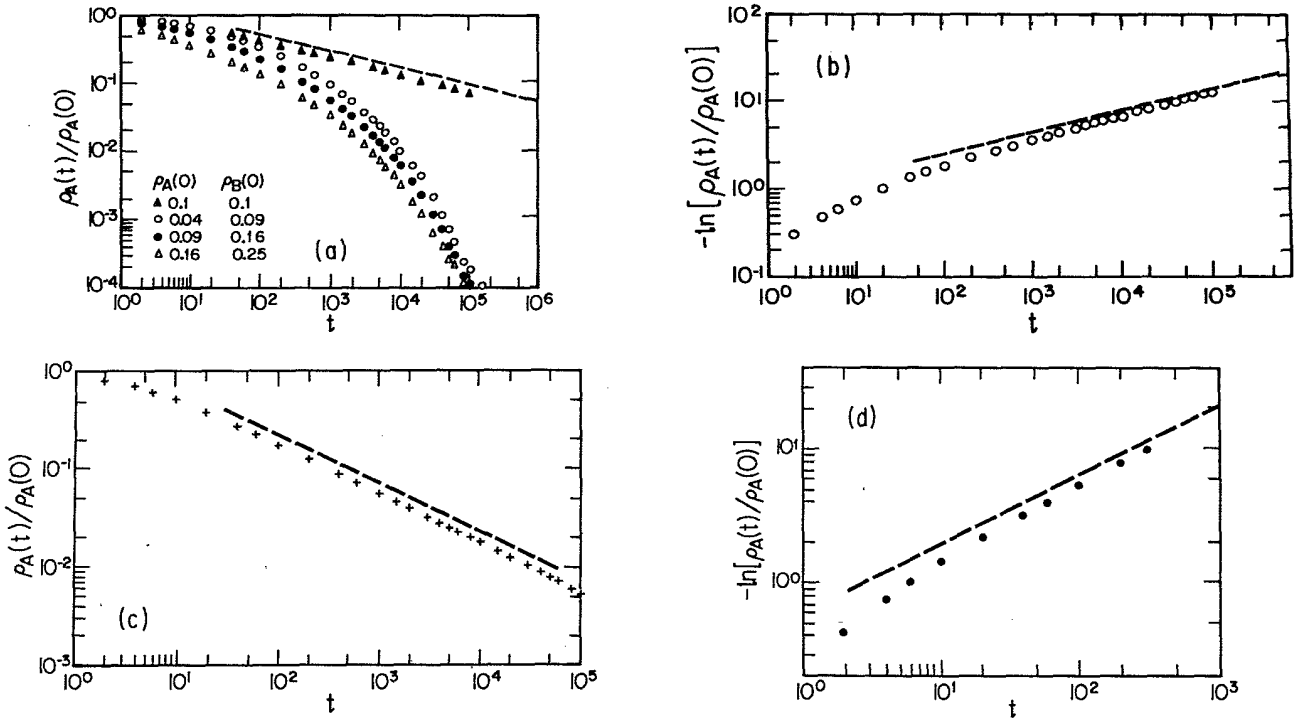


FIG. 1. Representative data for bimolecular decay in one dimension. (a) Plot of the surviving fraction $\rho_A(t)/\rho_A(0)$ vs time on a double logarithmic scale for a single configuration of isotropically diffusing A particles on a lattice of 10^6 sites, for various initial densities. The dashed line has slope $-\frac{1}{4}$. (b) Results from 10 configurations on a lattice of 2.5×10^6 sites shown for an initial state where $\rho_A(0)=0.1$ and $\rho_B(0)=0.2$. Plotted is the negative of the logarithm of the surviving fraction vs time on a double logarithmic scale to illustrate the $\exp(-t^{1/4})$ dependence of the density. Here the dashed line has slope $+\frac{1}{4}$. (c) Results for the decay of drifting particles for 20 configurations on a chain of 10^6 sites for $\rho_A(0)=\rho_B(0)=0.1$. In these simulations we considered the extreme case where the mobile A particles move in only one direction. The dashed line has slope $-\frac{1}{2}$. (d) Logarithm of the density for drifting particles for 50 configurations on a chain of 2.0×10^6 sites with $\rho_A(0)=0.1$ and $\rho_B(0)=0.2$. The dashed line has slope $+\frac{1}{2}$.

of larger surrounding domains as indicated in Fig. 2(c). When this happens the larger domains have grown in linear dimension by an amount of the order of l . The coalescence occurs when all the particles in the smaller domain have had time to diffuse to the domain boundary where they are annihilated, i.e., in a time $t \sim l^2/D$. This leads immediately to a domain size which grows as $t^{1/2}$, and ultimately to the $t^{-d/4}$ decay law.

To obtain the long-time decay when $\rho_A(0) < \rho_B(0)$ we employ the following heuristic argument. The rate equation (1) can be modified to give the correct $t^{-d/4}$ decay law for the equal initial density case by allowing the rate coefficient to acquire the time dependence $k(t) \sim t^{d/4-1}$. This may be viewed as an attempt to represent phenomenologically the decrease of the meeting probability of an A and a B particle due to domain formation.²³ For unequal initial particle densities, we assume that the rate equation with this new time-dependent rate coefficient will continue to hold. This, together with the assumption of a scaling form for $\rho_A(t)$, then gives

$$\rho_A(t) \approx \exp\{-[\sqrt{\rho_B(0)} - \sqrt{\rho_A(0)}]t^{d/4}\}. \quad (10)$$

This decay law is in good agreement with numerical simulations in $d=1$ and $d=2$ [Fig. 1(b)]. However, there is an apparent contradiction for $2 < d \leq 4$. In this case, Eq.

(10) predicts a decay which is faster than that of the unimolecular trapping reaction. Since one can view the bimolecular decay as a trapping reaction in which the traps disappear together with the particles, it seems that the asymptotic decay in the bimolecular reaction must be slower than in the trapping reaction. We believe that the apparent difficulty stems from the fact that our simple-

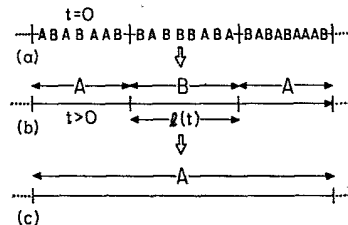


FIG. 2. Schematic illustration of the domain-growth process (drawn in one dimension for simplicity). In the first line we sketch an initial random configuration of A 's and B 's. At an intermediate time, shown on the second line, particles have time to mix locally within a length scale $l(t) \sim \sqrt{Dt}$, leaving behind only residual fluctuations which form domains. These domains are continuously growing by coalescence of larger domains as illustrated in the third line.

mind approach is not sensitive to the very rare but large trap-free regions whose consideration will be required to account correctly for the asymptotic decay in the unequal density case.

The arguments given above can be easily extended to the situation where there is a relative drift velocity between the A and B particles in addition to the diffusive motion. This may be relevant for understanding the recombination of charged particles in a uniform external electric field. In this case, there are two different length scales which characterize the spatial volume explored by a mobile particle. Along the bias particles will drift a distance $l_{\parallel} \sim t$, while in the $d-1$ perpendicular directions particles will diffuse a distance $l_{\perp} \sim t^{1/2}$. Thus the volume explored by a drifting, diffusing particle will be proportional to $l_{\parallel} l_{\perp}^{d-1}$, and this volume grows with time as $t^{(d+1)/2}$. By considering the local fluctuations of the particle-number difference in this volume, and following the same arguments that led to the decay laws for the case of isotropic diffusion, we obtain the asymptotic decays

$$\rho_A(t) \approx \begin{cases} \sqrt{\rho_A(0)} t^{-(d+1)/4}, & t \ll t_{\xi} \\ \exp\{-[\sqrt{\rho_B(0)} - \sqrt{\rho_A(0)}] t^{(d+1)/4}\}, & t \gg t_{\xi} \end{cases} \quad (11a)$$

(11b)

where the crossover time t_{ξ} is now given by $[\sqrt{\rho_B(0)} - \sqrt{\rho_A(0)}]^{-4/(d+1)}$. These decays should be valid below an upper critical dimension of 3. The decay laws quoted in Eqs. (8), (10), and (11) are in good agreement with our numerical simulation as illustrated in Figs. 1(c) and 1(d).

B. Single-species reaction $A + A \rightarrow \text{inert}$

A simpler scaling approach can be developed to study the single-species reaction $A + A \rightarrow \text{inert}$.^{9,10,22,24} We anticipate that this decay process should be in a different universality class than the two-species reaction since there is no conservation law analogous to the invariance of the particle-density difference. In order to write a scaling form for the particle density, we note the existence of a fundamental time scale $\tau \sim \rho_A(0)^{-2/d}$, which is the time required for a particle to diffuse a distance of the order of the initial interparticle spacing. For $t < \tau$, there should be essentially no decay, while for $t > \tau$, the asymptotic decay law should set in. This crossover may be described by the scaling form

$$\rho_A(t) \sim \rho_A(0) f(t/\tau), \quad (12)$$

where the scaling function $f(x) \rightarrow \text{const}$ for $x \ll 1$ and $f(x) \sim x^p$ for $x \gg 1$. To fix the exponent p in the limiting form of $f(x)$ we use the observed fact that the asymptotic decay for single-species decay is independent of the initial density.^{10,22,24} This fixes $f(x)$ to vary as $x^{-d/2}$ when x is large, so that the dependence on $\rho_A(0)$ in Eq. (12) will be canceled in the asymptotic limit. This leads to the asymptotic decay law of $t^{-d/2}$ for the particle density. From comparing Eq. (12) with the rate-equation solution, we expect an upper critical dimension of 2.

It is also worth mentioning that both the two-species

and single-species decays can be investigated on fractal sets.^{10,22,25} Roughly speaking, the decay laws can be obtained by simply replacing the spatial dimension d , in the results given in Eqs. (9)–(12), by the fraction dimension of the fractal set on which the reaction is taking place. This result follows directly by replacing the diffusion exponent of 2 appropriate for a Euclidean space with the corresponding exponent on a fractal and by replacing the spatial dimension d with the fractal dimension of the set under consideration.

C. Multiparticle reactions

The kinetics of the multiparticle reactions $A_1 + A_2 + \dots + A_N \rightarrow \text{inert}$ and $NA \rightarrow \text{inert}$ can be also studied by extending the scaling approaches for $A + B \rightarrow \text{inert}$ and $A + A \rightarrow \text{inert}$.²⁶ Such multiparticle processes can be constructed in practice through a sequence of bimolecular processes if the intermediate steps take place very quickly and the products of the intermediate steps can be eliminated adiabatically.²⁷

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

$$\dot{\rho}_i(t) = -k \rho_1(t) \rho_2(t) \dots \rho_N(t). \quad (13)$$

Here $\rho_i(t)$ is the density of the i th species at time t and k is the rate coefficient. For simplicity we consider the case $N=3$ and also assume that the initial densities obey the inequalities $\rho_1(0) < \rho_2(0) < \rho_3(0)$. In this case the exact solution to Eq. (13) is

$$\left[\frac{\rho_1(t)}{\rho_1(0)} \right] \left[\frac{\rho_2(0)}{\rho_2(t)} \right]^{(C_1+C_2)/C_2} \left[\frac{\rho_3(t)}{\rho_3(0)} \right]^{C_1/C_2} = \exp[-C_1(C_1+C_2)kt] \quad (14)$$

with $C_1 = \rho_2(0) - \rho_1(0)$ and $C_2 = \rho_3(0) - \rho_2(0)$.

From this relatively complicated solution several limiting behaviors can be extracted which depend on the relative concentrations of the various species, in analogy with the discussion following Eq. (3) for the two-body case. The generalization to the N -body reaction follows by straightforward extension. At short times, but beyond the time required for any reaction to begin, none of the species is established as the majority except in very microscopic regions. Therefore the decay is the same as a system with equal initial densities of the reactants, i.e., a power-law decay of

$$\rho_A(t) \approx (kt)^{-1/2}, \quad \tau_0 \ll t \ll \tau \quad (15a)$$

where τ_0 is again the time needed before the reaction starts and τ is the shortest of the various crossover times to an intermediate regime, which will be defined below. For an arbitrary value of N the appropriate decay would be $(kt)^{-1/(N-1)}$, i.e., a progressively slower decay law as the number of reactants required to initiate the reaction is increased. This decay law also describes the asymptotic particle density in the single-species reaction $NA \rightarrow \text{inert}$.

Then there follows an intermediate-time regime where

two distinct possibilities can occur, as indicated schematically in Fig. 3. One generic case is obtained by choosing the initial condition $\rho_1(0) \lesssim \rho_2(0) \ll \rho_3(0)$. For this initial state, species 1 and 2 are established as being in the minority with respect to species 3 in the intermediate time regime, but the system cannot determine between 1 and 2 as the absolute minority. The rate-equation kinetics in this regime thus coincides with the asymptotic behavior of a system with the initial density conditions $\rho_1(0) = \rho_2(0) < \rho_3(0)$. The latter system displays a power-law decay for $\rho_i(t)$ equal to $[(C_1 + C_2)kt]^{-1}$. The other generic possibility is that the initial density condition is $\rho_1(0) \ll \rho_2(0) \lesssim \rho_3(0)$. In the intermediate-time regime, species 1 is established as the absolute minority, while the absolute-majority species remains undetermined. Within the rate-equation approximation, the kinetics now coincides with that of a system with the initial conditions $\rho_1(0) < \rho_2(0) = \rho_3(0)$. That is, $\rho_1(t)$ decays as $\exp(-C_1^2 kt)$. Finally there is the asymptotic regime where the system establishes the global inequality in the densities of all three species, and the asymptotic decay is

$$\rho_i(t) \sim \exp[C_1(C_1 + C_2)kt] \text{ as } t \rightarrow \infty. \quad (15b)$$

To include the effects of spatial fluctuations we again treat the three-body reaction $A_1 + A_2 + A_3 \rightarrow \text{inert}$ in detail, and the generalization to the N -body case is immediate. The number of particles of the i th species in a volume l^d is

$$N_i = \rho_i(0)l^d \pm \sqrt{\rho_i(0)l^d} \quad (i=1,2,3). \quad (16)$$

Therefore the particle-number difference between the j th and k th species in this volume will be

$$N_j - N_k \sim [\rho_j(0) - \rho_k(0)]l^d \pm [\sqrt{\rho_j(0)} \pm \sqrt{\rho_k(0)}]l^{d/2}. \quad (17)$$

In analogy with the two-body reaction, we may then estimate a characteristic length scale where local fluctuations between the j th and k th species are important:

$$\xi_{jk} \sim [\sqrt{\rho_k(0)} - \sqrt{\rho_j(0)}]^{-2/d} [\rho_j(0) < \rho_k(0)]. \quad (18)$$

Equivalently, there is a characteristic time scale t_{jk} pro-

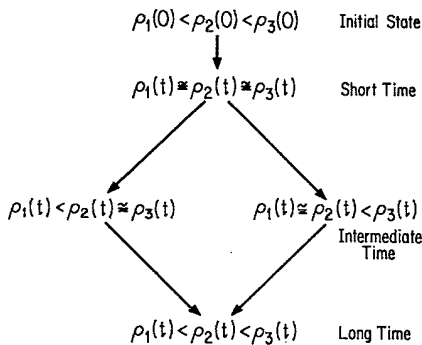


FIG. 3. The two possible generic evolutions of the relative particle densities for a three-species system of unequal initial densities due to annihilation of particles through three-body recombination.

portional to ξ_{jk}^2 . With this time scale we now write a scaling form for $\rho_i(t)$ by assuming that the decay will be a power law for t less than the smallest time scale from the set $\{t_{jk}\}$,

$$\rho_i(t) \sim C_i t^{-\alpha} f_i(\{x_{jk}\}), \quad (19)$$

where $f_i(\{x_{jk}\})$ is a scaling function of the set of dimensionless variables $x_{jk} \equiv t/t_{jk}$, and C_i is a constant which depends on the initial conditions.

To fix the exponent α it is 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 (19) can now be written more simply as

$$\rho_i(t) \sim C_i t^{-\alpha} \tilde{f}_i(t/\tau), \quad (20)$$

where $\tilde{f}_i(t/\tau) = f_i(0, t/t_{13}, t/t_{12})$. From the conservation of particle-density difference, $\rho_1(t) - \rho_2(t) = \rho_1(0) - \rho_2(0)$ and from Eq. (20), we have

$$[\rho_1(0) - \rho_2(0)]t^\alpha = C_1 \tilde{f}_1(t/\tau) - C_2 \tilde{f}_2(t/\tau). \quad (21)$$

By using the fact that $\tilde{f}_i(x)$ is a function only of the scaling variable x and by rewriting the density difference in terms of t_{jk} according to Eq. (18) we find

$$\alpha = d/4, \quad C_1 = C_2 \equiv [\sqrt{\rho_1(0)} + \sqrt{\rho_2(0)}]. \quad (22)$$

In the limit $\rho_1(0) \rightarrow \rho_2(0)$, the purely $t^{-\alpha}$ power-law decay will be recovered in Eq. (20). We therefore predict

$$\rho_i(t) \sim \sqrt{\rho_i(0)} t^{-d/4} \quad (23)$$

for the case of equal initial densities of three reactants.

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

To generalize to the N -body reaction for equal initial densities of the reactants, we choose the initial conditions $\rho_1(0) < \rho_2(0) = \rho_3(0) = \dots = \rho_N(0)$ and follow the same steps as outlined above. This gives $\rho_i(t) \sim \sqrt{\rho_i(0)} t^{-d/4}$ below $d_c = 4/(N-1)$, while for $d \geq d_c$, the decay law obeys the rate-equation form of $t^{-1/(N-1)}$. The universal N -independent kinetics predicted for $d < d_c$ stems from the fact that local fluctuations in density difference decay only by diffusion and not by the reaction process. Hence the decay should be independent of the number of reactants needed to initiate the reaction.

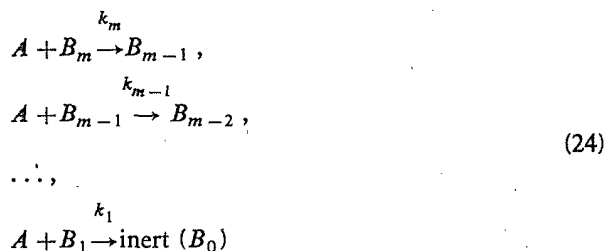
We can also extend scaling to the single-species reaction $NA \rightarrow \text{inert}$. This reaction is simpler than the multispecies reaction as there is only one time scale, $\tau \sim \rho_A(0)^{-2/d}$, the time required for a particle to diffuse a distance of the order of the initial interparticle separation. We can write a scaling form for the particle density which is analogous to the one postulated in Eq. (12) for the bimolecular single-species reaction. In addition, we continue to make the assumption that $\rho_A(t)$ will be independent of the initial density as $t \rightarrow \infty$. From these considerations we find $\rho_A(t) \sim t^{-d/2}$ for $d < d_c = 2/(N-1)$, while the mean-field decay of $t^{-1/(N-1)}$ holds for $d \geq d_c$.

III. REACTION WITH PARTICLES OF FINITE "HEIGHT" AND TRAPS OF VARIABLE "DEPTH"

In this section we use scaling ideas to investigate the kinetics of a more general bimolecular reaction in which there are a number of intermediate states along the reaction path which ultimately converts active reactants to a final inert state. The model that we introduce for this multistate process is illustrated schematically in Fig. 4. This generalization is very simple to visualize, yet it displays a rich phenomenology and it also serves as a non-trivial testing ground for the scaling approach. Moreover, this multistate reaction may be relevant for describing soliton-antisoliton decay in a Sine-Gordon chain after a sudden quench from high temperatures^{28,29} and also for describing the smoothing out of a rough surface during an annealing process.

The model that we consider involves *A*-type particles of an arbitrary "height" a_i reacting with *B*-type particles of an arbitrary "depth" b_i . These two species move diffusively, and when an *A*- and *B*-type particle meet, they instantaneously and irreversibly undergo the following reaction: For an *A* particle of height a_i and a *B* of depth b_i , the reaction product will be either an *A* particle of height $a_i - b_i$, if $a_i > b_i$, or a *B* particle of depth $b_i - a_i$, if $b_i > a_i$ (Fig. 4). By varying the initial distribution of heights and depths of the reactants, and also by varying the dependence of the rate coefficient on these heights and depths, a very wide range of kinetic behavior can be probed, ranging from the universality class of the trapping reaction (when $b_i/a_i \rightarrow \infty$) to the universality class of simple bimolecular decay (when $b_i/a_i \rightarrow 1$).

We begin our analysis by considering first the special case where the *A* particles all have height unity. Thus when an *A* meets a *B* particle of depth i (denoted by B_i), the trap is partially "filled in," leaving a B_{i-1} particle of depth $i - 1$ in analogy with the process illustrated in Fig. 4. The reaction scheme for this system is



where k_i is the rate coefficient characterizing the reactivity of an *A* with a B_i , and it will prove to be convenient to

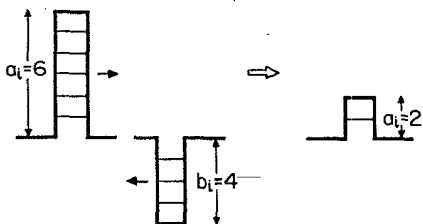


FIG. 4. Schematic illustration of reaction process for a particle of height a_i and a trap of depth b_i . Simple bimolecular decay corresponds to the case where $a_i = b_i = 1$ for all reactants.

regard the inert species as a trap of depth zero. The rate equations for these reactions are

$$\begin{aligned}
 \frac{d}{dt}\rho_A(t) &= -k_m\rho_A(t)\rho_{B_m}(t) - k_{m-1}\rho_A(t)\rho_{B_{m-1}}(t) \\
 &\quad - \dots - k_1\rho_A(t)\rho_{B_1}(t), \\
 \frac{d}{dt}\rho_{B_m}(t) &= -k_m\rho_A(t)\rho_{B_m}(t), \\
 \frac{d}{dt}\rho_{B_{m-1}}(t) &= -k_{m-1}\rho_A(t)\rho_{B_{m-1}}(t) + k_m\rho_A(t)\rho_{B_m}(t), \\
 &\quad \dots, \\
 \frac{d}{dt}\rho_{B_1}(t) &= -k_1\rho_A(t)\rho_{B_1}(t) + k_2\rho_A(t)\rho_{B_2}(t), \\
 \frac{d}{dt}\rho_{B_0}(t) &= +k_1\rho_A(t)\rho_{B_1}(t).
 \end{aligned}
 \tag{25}$$

For concreteness and simplicity we consider only the situation where all the rate coefficients are equal to a common value k . In addition, we first treat the case where initially traps of depth m only are present. Accompanying this initial trap-depth distribution are two generic initial conditions for the densities of the *A*'s, in close analogy with bimolecular recombination. These initial conditions follow naturally from a conservation law of the system, that the difference $\Delta \equiv \rho_A(t) - \sum_{k=1}^m k\rho_{B_k}(t)$ equals its initial value $\rho_A(0) - m\rho_{B_m}(0)$. Here $\sum_{k=1}^m k\rho_{B_k}(t)$ is the total trap depth, and the conserved quantity is simply the difference between the total particle height and the total trap depth. The two generic initial conditions are then $\Delta = 0$ and $\Delta < 0$. In the former case, which we term the "zero-sum" initial condition, the total trap depth is just sufficient to accommodate all the particles, and the final state consists of only inert particles. In the latter case, there is an excess of trap depth, leading to a final state where some or all of the traps are not completely filled in. Based on the correspondence between Δ in the multistate reaction and the particle-density difference in the two-species recombination process, we anticipate that the mean-field, or rate-equation, prediction for the kinetics will be a power-law decay of $\rho_A(t)$ for $\Delta = 0$ and an exponential-type decay for $\Delta < 0$.

The general solution of the rate equations is rather involved; however, it is possible to obtain a very simple asymptotic solution valid for $t \rightarrow \infty$. Notice that by summing the rate equations for the traps [all but the first equation in (25)], we can immediately conclude that the total trap density, including traps of depth zero, is conserved. Moreover in the zero-sum initial condition, this constant simply equals $\rho_A(0)/m$. Using this in the first line of Eq. (25), we obtain a simple rate equation for the *A* particles

$$\dot{\rho}_A(t) = -k\rho_A(t)[\rho_A(0)/m - \rho_{B_0}(t)].
 \tag{26}$$

In the zero-sum initial condition we now assume that at long times the system arrives at a situation where there are only *A*, B_0 , and B_1 particles. This assertion is based

on a mean-field picture in which the traps are all filled in at essentially the same rate. Under this assumption we may write

$$\begin{aligned} \rho_{B_0}(t) &\sim \rho_{B_m}(0) - \rho_A(t) \quad \text{as } t \rightarrow \infty \\ &= \rho_A(0)/m - \rho_A(t). \end{aligned} \quad (27)$$

Using this in the rate equation for the A 's then gives

$$\dot{\rho}_A(t) = -k[\rho_A(t)]^2. \quad (28)$$

This is identical to the rate equation for simple bimolecular decay, when the initial densities of the A 's and B 's are equal. Thus we find, for the zero-sum initial condition, a mean-field decay proportional to $1/t$ and *independent* of m . The latter result embodies the intuitively plausible fact that in mean-field theory, N traps of depth 1 have the same global reactivity as N/m traps of depth m . Similar considerations applied to the initial condition $\Delta < 0$ indicate that the density of A 's decays exponentially within mean-field theory.

With the insights gained in Sec. II from the application of the scaling approach to bimolecular decay, we are now led to examine the effects of spatial fluctuations in Δ on the multistate reaction. First we shall treat the situation considered in the rate-equation approach, that is, traps of depth m only present initially. Suppose there is an initial excess of trap depth, i.e., the conserved quantity $\Delta < 0$. Due to fluctuations, there will be local regions where Δ may be positive. We can estimate the maximum size of a volume where these fluctuations may occur by first calculating the initial number of A particles and B particles of depth m in a volume $V = l^d$:

$$N_A = \rho_A(0)l^d \pm \sqrt{\rho_A(0)l^d}, \quad (29)$$

$$N_{B_m} = \rho_{B_m}(0)l^d \pm \sqrt{\rho_{B_m}(0)l^d}.$$

Then, as in Sec. II, we choose the maximum positive fluctuation in N_A , the maximum negative fluctuation in N_{B_m} , and set $N_A = mN_{B_m}$. This determines a characteristic length scale, where local fluctuations in Δ are important, given by

$$\xi \sim \left[\frac{m \sqrt{\rho_{B_m}(0)} + \sqrt{\rho_A(0)}}{m \rho_{B_m}(0) - \rho_A(0)} \right]^{2/d}. \quad (30)$$

That is, in a volume of linear dimension $l < \xi$, the number of A particles can be greater than the local total trap depth, even though the reverse inequality holds globally. Now writing a scaling ansatz for $\rho_A(t)$ and $\rho_{B_k}(t)$ as in Sec. II, and following the approach developed there, we find for the zero-sum initial condition,

$$\rho_A(t) = \sum_{k=1}^m \rho_{B_k}(t) \simeq (\sqrt{m} + 1) \sqrt{\rho_A(0)} t^{-d/4}. \quad (31)$$

By comparing this decay with that predicted by the rate equation we deduce that the upper critical dimension is equal to 4, above which the rate-equation prediction will be valid.

In addition to the temporal dependence of the decay, we obtain an interesting dependence on the initial trap depth m . Due to the dispersion of trap depths generated during the course of the reaction, the overall absorption rate of N/m randomly distributed traps of depth m is *weaker* than the absorption rate of N randomly distributed traps of depth unity.

To test the above predictions we have performed numerical simulations in one and two dimensions, and typical results for one dimension are shown in Fig. 5. In Fig. 5(a) we investigate the dependence of $\rho_A(t)$ at fixed t on the initial trap depth m . The linearity of the displayed plot of $\rho_A(t=10000)$ versus $\sqrt{m} + 1$ confirms the m dependence given in Eq. (31). In Fig. 5(b) we show the time dependence of $\rho_A(t)$ and $\rho_{B_k}(t)$ for the case $m = 10$.

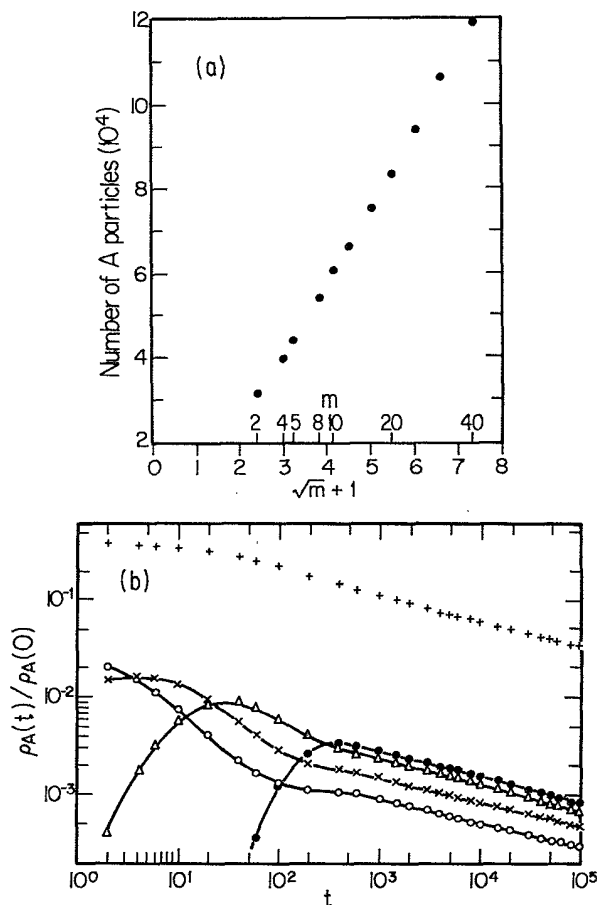


FIG. 5. Simulation data in one dimension for particles of height unity and traps of initial depth m . Results from a single configuration of 10^5 time steps on a chain of 10^6 sites are shown for a number of values of the depth m . The initial density $\rho_A(0)$ is chosen to be 0.4, and consequently $\rho_{B_m}(0) = 0.4/m$. (a) The number of A particles at a fixed time of 10000 steps is plotted vs $\sqrt{m} + 1$ for a range of m values between 2 and 40 to confirm the m dependence given in Eq. (31). (b) Temporal dependence of the particle density and various trap densities for an initial trap depth $m = 10$. Plotted are $\rho_A(t)$ (+), $\rho_{B_k}(t)$ with $k = 10$ (O), $k = 9$ (X), $k = 7$ (Δ), and $k = 1$ (\bullet) vs time on a double logarithmic scale. The thin lines are intended to serve as guides for the eye. Asymptotically the data lie on straight lines of slope $-\frac{1}{4}$ as predicted in Eq. (31).

Both $\rho_A(t)$ and each of the $\rho_{B_k}(t)$ decay asymptotically at the same rate of $t^{-1/4}$, but notice that a nonmonotonicity, or population inversion, develops in the distribution of $\rho_{B_k}(t)$ versus k at fixed time. Finally, notice that at short times the density of the deepest traps decays relatively quickly since there are relatively many more particles than deep traps.

The above scaling approach can be extended to more general initial configurations of particle heights and trap depths straightforwardly. Consider the situation where the initial distribution of trap depths is arbitrary, with the exception of a relatively weak constraint to be stated below. Now the zero-sum initial condition generalizes to $\rho_A(0) = \sum_{k=1}^m k \rho_{B_k}(0)$. In close analogy with the derivation given above for the case where only a unique trap depth m is present initially, we find a characteristic length scale

$$\xi \sim \left[\frac{\sum_{k=1}^m k \sqrt{\rho_{B_k}(0) + \sqrt{\rho_A(0)}}}{\sum_{k=1}^m k \rho_{B_k}(0) - \rho_A(0)} \right]^{2/d} \quad (32)$$

From this length we then determine the decay law to be

$$\rho_A(t) = \sum_{k=1}^m k \rho_{B_k}(t) \simeq \left[\sqrt{\rho_A(0)} + \sum_{k=1}^m k \sqrt{\rho_{B_k}(0)} \right] t^{-d/4} \quad (33)$$

We expect that this decay will remain valid even as $m \rightarrow \infty$, as long as $\sum_{k=1}^m k \sqrt{\rho_{B_k}(0)}$ is finite.

A final generalization is the case where the A -type particles may also have a distribution of arbitrary heights. Again following the scaling approach, we find that for the zero-sum initial condition $\sum_{j=1}^n j \rho_{A_j}(0) = \sum_{k=1}^m k \rho_{B_k}(0)$, the density decays as

$$\sum_{j=1}^n j \rho_{A_j}(t) = \sum_{k=1}^m k \rho_{B_k}(t) \simeq \left[\sum_{j=1}^n j \sqrt{\rho_{A_j}(0)} + \sum_{k=1}^m k \sqrt{\rho_{B_k}(0)} \right] t^{-d/4} \quad (34)$$

The $t^{-d/4}$ dependence of the various particle species in the zero-sum initial condition is expected to hold asymptotically for finite values m and n . For either m or $n \rightarrow \infty$, the same decay laws will continue to be valid as long as the various moments over the particle-height (or trap-depth) distribution used in the scaling approach converge.

IV. "IMPERFECT" RECOMBINATION

Thus far we have been considering reactions where the microscopic chemical-reaction time is instantaneous, i.e., much less than a typical interparticle diffusion time. Thus the slower diffusion time ultimately controls the re-

action rate, and this regime of behavior is the diffusion-controlled limit. On the other hand, if a system is mixed sufficiently strongly, the interparticle transport time may become so short that many molecular collisions can occur before the intrinsic chemical rates allow a reaction to take place. Consequently, the system has time to homogenize between reactions, and the microscopic reaction time controls the reaction rate. This extreme case^{30,31} may be thought of as the mean-field limit discussed in the Introduction, since the system is homogeneous. To describe the crossover between these two regimes, we introduce a reaction probability p , with $0 < p < 1$, into bimolecular decay. The meaning of this parameter is that when an A and a B particle meet, they react with probability p , while with probability $1-p$ the two particles continue to execute independent diffusive motions. This is an attempt to account empirically for the effects of rapid mixing, or other experimentally relevant homogenizing effects, which can induce a crossover to the mean-field limit.

In the framework of the rate-equation approach, the parameter p can be identified with the rate coefficient in Eq. (1). Therefore in the mean-field limit we expect that the amplitude of the decay will vary continuously with p , while the essential temporal behavior is the same as the case $p=1$. However, when fluctuation effects are included, a different result may be anticipated. Local fluctuations in the density difference decay *only* by diffusion, independent of any reaction details. This observation suggests the surprising result that the asymptotic decay will be *independent* of the reaction probability, when the system is below the upper critical dimension.

To see how this striking result might arise, let us compare the kinetics of bimolecular decay for the two cases of $p=1$ and $p \ll 1$. For simplicity we consider the case of equal initial densities of A 's and B 's in this section. In the case of perfect reaction, $p=1$, there is a crossover between a short-time regime of *no* decay, when particles have not had enough time to diffuse a distance of the order of the interparticle spacing, to the asymptotic $t^{-d/4}$ decay as indicated in Fig. 6. The characteristic time for this crossover to occur is given by $T_1 = \rho_A(0)^{-2/d}$.

When $p \ll 1$, the short-time regime of no decay now persists until a time $T'_1 = T_1/p$, since, on average, $1/p$

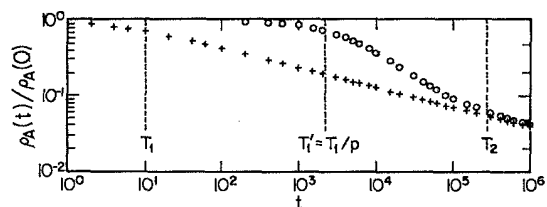


FIG. 6. Double logarithmic plot of the surviving fraction vs time for "imperfect" recombination in one dimension for the cases $p=1$ (+) and $p=0.002$ (o). In the former case, the decay exhibits a crossover from a short-time regime of no decay to the asymptotic $t^{-1/4}$ decay at a crossover time T_1 . In the latter case, there are now three time regimes. At $T'_1 = T_1/p$ there is a crossover to a new intermediate-time regime where the decay rate is much *faster* than the asymptotic decay rate of the $p=1$ case. Finally, at T_2 the decay coincides with that of the $p=1$ case.

particle collisions are required to initiate a reaction. Once the decay begins, each particle survives for a sufficiently long time that the system has time to become homogenized between reactions. Thus in this (intermediate) time regime we expect a mean-field decay proportional to $1/pt$. If we extrapolate this decay to $t \rightarrow \infty$, a problem arises which is analogous to the Kauzmann paradox³² in the theory of glasses. Eventually the density in the decay process where $p \ll 1$ would become less than the density for the reaction where $p = 1$, a clearly nonsensical result.

To resolve this paradox we appeal to the domain-growth picture. Since the decay of fluctuations is insensitive to the details of the reaction, we are led to a modified picture in which domains are attempting to grow, but their growth is retarded by particles of one species being able to penetrate through and persist in a domain of the opposite species. Eventually, however, the domains become sufficiently large that particles of one species will always be annihilated once they enter a domain of the opposite particle species. In this long-time regime, the kinetic behavior must therefore be *independent* of p , thus coinciding with the decay of the $p = 1$ case.

A characteristic time T_2 , giving the crossover between the intermediate mean-field-type decay of $1/pt$ and the asymptotic $\sqrt{\rho_A(0)t^{-d/4}}$ decay can now be found by matching these two kinetic laws. We thus find a second crossover time

$$T_2 \approx [p^4 \rho_A(0)^2]^{1/(d-4)}. \quad (35)$$

Notice that T_2 diverges as d approaches 4 from below, indicating that in the mean-field limit, the intermediate-time p -dependent decay extends to $t \rightarrow \infty$.

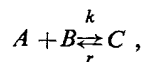
Alternatively, this crossover time can be obtained directly from the domain picture. If a B particle enters an A -rich domain and is annihilated with certainty, then the system is in the long-time regime. If, on the other hand, the B particle can pass through the A -rich domain, then the system is in the intermediate regime. The transition between these two behaviors determines the crossover time T_2 . Let us therefore estimate the minimum size of a domain which is "opaque" to particles of the opposite species. For a domain of linear dimension l , the number of steps required for a particle to get across a domain is proportional to l^2 . The condition that ensures that a B particle just fails to pass through an A -rich domain is that the expected number of reactions during the average residence of a B particle in the domain is unity. That is, $p l^2 \rho_A(t) = 1$, where $\rho_A(t)$ is the density of A (or B) particles within the domain. Now using the facts that $\rho_A(t) \sim \sqrt{\rho_A(0)/l^d}$, and $l \sim \sqrt{t}$, we may solve to obtain the crossover time T_2 introduced above.

In conclusion, the results of this section suggest that if mixing or other homogenizing effects can be represented in terms of a variable-reaction probability, then the asymptotic behavior is ultimately independent of these mixing effects and is actually governed by the diffusion-controlled limit. The ramifications of this fact should be of great relevance for experimental studies of reaction kinetics. As long as one waits long enough for the crossover to the diffusion-controlled limit to occur, fluctuation-dominated kinetics should be observable. For shorter

times, nonuniversal power-law decays are to be expected which are indicative of an intermediate-time regime rather than of an asymptotic behavior.

V. REVERSIBLE BIMOLECULAR REACTION

In this section we study the approach to equilibrium^{33,34} for the reversible bimolecular reaction



where the reaction product resulting from the recombination of an A and a B particle is now denoted by C . These C particles may spontaneously split into an A and a B particle at a rate governed by a reverse-reaction coefficient. The variable reversibility may be regarded as arising from introducing a variable temperaturelike parameter which controls the nature of the equilibrium state.

As in previous sections, we first study the rate equation for this reaction in order to serve as a starting point for further developments. For simplicity we shall again only consider the case where the densities of A 's and B 's are equal. Furthermore, we will study only the situation where the reverse reaction is "turned on" at $t = 0$. One could envision the more general situation where the reverse reaction is not turned on until a given time delay has passed. However, numerical studies indicate that the approach to equilibrium is insensitive to the starting time for the reverse reaction, and we therefore consider the simplest case where the reverse reaction is present initially.

The rate equation may be rewritten as

$$\dot{\rho}_A(t) = -k\rho_A(t)^2 + r\rho_C(t), \quad (36)$$

where k is the rate coefficient for the forward reaction and r is the reverse rate coefficient. By using the conservation law $\rho_C(t) = \rho_A(0) - \rho_A(t)$, the rate equation may be written in terms of ρ_A only, to read

$$\dot{\rho}_A(t) = -k\rho_A(t)^2 + r\rho_A(0) - r\rho_A(t). \quad (37)$$

If we write the polynomial on the rhs of (37) as $[\rho_A(t) - \rho_+][\rho_A(t) - \rho_-]$, with

$$\rho_{\pm} = \{-r \pm [r^2 + 4kr\rho_A(0)]^{1/2}\} / 2k,$$

we find the solution for $\rho_A(t)$ to be

$$\begin{aligned} & \{[\rho_A(t) - \rho_+][\rho_A(0) - \rho_-]\} / \{[\rho_A(0) - \rho_+][\rho_A(t) - \rho_-]\} \\ & = \exp[-k(\rho_+ - \rho_-)t]. \quad (38) \end{aligned}$$

From this equation one concludes that the density decays to an equilibrium value, $\rho_A(\infty)$, which is equal to ρ_+ . The rate of approach is purely exponential with a characteristic decay time

$$\tau_{\text{eq}} \sim k^{-1}(\rho_+ - \rho_-)^{-1} = [r^2 + 4kr\rho_A(0)]^{-1/2}.$$

Furthermore, once equilibrium is reached, the rate-equation predicts that there will be no fluctuations in density about the equilibrium value.

We now present a simple-minded approach which suggests that density fluctuations will result in a power-law approach to equilibrium, rather than an exponential ap-

proach. It is based on modifying the rate equation to account for the influence of residual long-range fluctuations on the uniform background equilibrium configuration which is in the process of forming. At finite times these residual fluctuations in density difference serve to reduce the meeting probability between opposite species, thus modifying the approach to equilibrium predicted by the rate equation.

To account for this effect consider a macroscopic region Ω whose size coincides with that of a typical size-density fluctuation. Roughly speaking, the density of either the A 's or B 's in this region is uniform, but these local densities may not coincide with the global density. In such a region the maximum density of A 's attainable though statistical fluctuations is $\rho_A(t) + \sqrt{\rho_A(0)t^{-d/4}}$ and the minimum density of B 's is $\rho_B(t) - \sqrt{\rho_B(0)t^{-d/4}}$, where $\rho_A(t)$ and $\rho_B(t)$ are the global densities of A and B , and the second terms represent fluctuations. Under these conditions the meeting probability between A and B species in Ω will be the product of the two particle densities

$$k[\rho_A(t) + \sqrt{\rho_A(0)t^{-d/4}}][\rho_B(t) - \sqrt{\rho_B(0)t^{-d/4}}] \cong k[\rho_A(t)\rho_B(t) - \rho_A(0)t^{-d/2}], \quad (39)$$

where the cross term cancels, since we have assumed that $\rho_A(t) = \rho_B(t)$. This line of reasoning suggests how the rate equation might be modified by the effects of residual fluctuations. According to (39), the rate equation, Eq. (37), becomes

$$\dot{\rho}_A(t) = -k[\rho_A(t)]^2 + r[\rho_A(0) - \rho_A(t)] + k\rho_A(0)t^{-d/2}. \quad (40)$$

The asymptotic behavior of this equation can be investigated by dividing $\rho_A(t)$ into two terms,

$$\rho_A(t) = \rho_A(\infty) + \delta\rho_A(t), \quad (41)$$

where $\rho_A(\infty)$ is the equilibrium solution of Eq. (40) and $\delta\rho_A(t)$ is the deviation in density from the equilibrium value. Now substituting this expression for $\rho_A(t)$ into Eq. (40) and keeping terms of only linear order in $\delta\rho_A(t)$, we find

$$\delta\dot{\rho}_A(t) \cong -[2k\rho_A(\infty) + r]\delta\rho_A(t) + k\rho_A(0)t^{-d/2}. \quad (42)$$

To lowest order in $\delta\rho_A(t)$, we find

$$\delta\rho_A(t) \sim Ct^{-d/2}, \quad (43)$$

where $C = k\rho_A(0)/[2k\rho_A(\infty) + r]$. Thus we predict that the approach to equilibrium follows a power law, rather than the exponential law predicted by the rate equation. This result is rather surprising in that fluctuations are predicted to modify even the qualitative features of the mean-field kinetics. In all the previous examples discussed in this paper, the effect of fluctuations was to change the exponent of the time in a mean-field kinetic law, rather than modify the actual functional form of the law.

To test this theory, we turn to a simulation study of reversible recombination. To incorporate the reverse reaction in the simulation procedure, each of the existing C

particles is allowed to decay into an A - B pair with probability r in the course of a single time step. For reasons of technical simplicity only, we have also introduced an excluded-volume interaction for the C 's. Ostensibly, we have taken the forward rate coefficient k to be equal to unity in our simulations. However, due to the slight modification caused by the introduction of the excluded-volume interaction, the correspondence between k in the rate equation and the forward rate coefficient in our simulations is not exact. Therefore the equilibrium value of the density obtained numerically may not necessarily coincide with the equilibrium value predicted by the corresponding rate equation.

We chose to focus our attention on a one-dimensional chain of 50 000 sites in which the initial densities are $\rho_A(0) = \rho_B(0) = 0.2$, $\rho_C(0) = 0.0$, and the reverse rate r was chosen to be 0.1. The rate equation then predicts an equilibrium density of $\rho_A(\infty) = \rho_B(\infty) = 0.1$, with the characteristic time of the exponential decay being of the order of 10 time steps. These predictions were checked by first performing a simulation in which mobile A particles could move equiprobably to any lattice site in a single time step. This infinite mobility law should correspond exactly to the mean-field limit. We found that equilibrium was reached very rapidly, requiring approximately 10 time steps, and that the approach to equilibrium is consistent with a purely exponential decay. However, we obtain an equilibrium value for the density which is slightly lower than the rate equation prediction of 0.1. The difference is significant, and we attribute this difference to the presence of the excluded-volume interaction for the C 's.

When the mobile particles undergo nearest-neighbor diffusive motion, the kinetic behavior is much more interesting. The approach to equilibrium is extremely slow, and to effectively monitor this temporal behavior it is useful to consider the cumulative average density defined by

$$\rho_{\text{cum}}(t) = \frac{1}{t - t_0} \int_{t_0}^t \rho_A(t) dt. \quad (44)$$

This average will have the same time dependence as the raw density, if the latter quantity has a power-law behavior. The lower cutoff t_0 may be chosen arbitrarily,

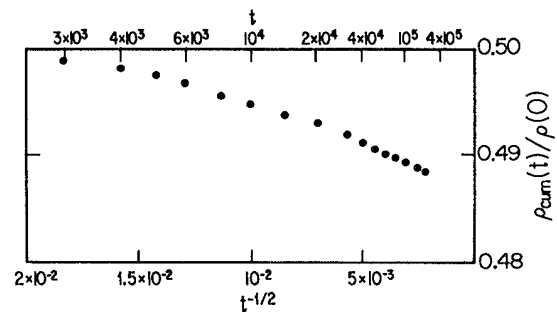


FIG. 7. Representative results for the approach to equilibrium in the reversible bimolecular reaction. Shown are the results from a single configuration on a chain of 50 000 sites with a reverse reaction rate $r = 0.1$. Shown is the cumulative density, as defined in the text, plotted vs $t^{-1/2}$ when the time delay t_0 was chosen to be 1000.

and typically we have used values for t_0 in the range 200–2000. This cumulative density drastically smooths out local temporal fluctuations in the instantaneous density, so that systematic effects can be more readily discerned. In Fig. 7 we plot $\rho_{\text{cum}}(t)$ as a function of $1/\sqrt{t}$ as suggested by Eq. (43). Asymptotically the data appear to lie on a straight line which extrapolates to the equilibrium value of the density. This data strongly suggests that the approach to equilibrium in the reaction $A + B \leftrightarrow C$ follows a power-law, rather than the exponential approach predicted by the rate equation.

VI. SUMMARY AND CONCLUSIONS

In this article we have investigated how spatial inhomogeneities in the particle density can dramatically affect the kinetics of a general class of diffusion-controlled reactions. Starting with an initial random distribution of particles, density fluctuations on all length scales occur, and during the evolution of a reacting particle system, these fluctuations can become more pronounced in both appearance and effect. For example, in the irreversible bimolecular decay $A + B \rightarrow \text{inert}$, the density difference is globally conserved so that fluctuations in density difference evolve *only* by diffusion. However, the decay by the reaction process is faster than the decay of fluctuations by diffusion (for $d \leq 4$), so that the diffusional spread of fluctuations actually appears as a growth of domains. This effect is dramatically apparent in numerical simulations and gives rise to the very slow observed decay laws.

We have first developed a scaling approach to study the kinetics of a number of simple irreversible reactions, including bimolecular and N -body recombination for both purely diffusing particles and for drifting particles. Furthermore, a domain-growth picture was developed which shows simply how the fluctuations in particle density evolve.

A very general model of a multistate recombination process was also introduced. In this model particles of variable heights can react with traps of variable depths to produce a reaction product whose height (or depth) is the vector sum of the height and depth of the incident particles. This system is readily amenable to our scaling approach, and we have explored some of the simplest, but rather interesting, aspects of this model. We can determine simply how fluctuations in both the reactant densities and the reactant heights and depths influence the asymptotic kinetics. The wide range of useful results obtained from this simple model suggest that it will be very worthwhile to explore the multistate recombination model in all its generality.

It is also worth noting that there is another closely related version of multistate recombination which is of great utility. Consider a model in which there exist particles of only one "sign," i.e., particles of variable heights only. When two such particles meet, they are defined to coalesce and form a single particle with a height which is equal to the sum of the heights of the two incident particles. In the most general case, one can envision a model in which the dependence of the reactivity, or reaction kernel, on the heights of the two incident particles is arbi-

trary. If this height is interpreted as a particle mass, a quantity which is conserved by the reaction process, then the coalescence reaction can be viewed as a model for irreversible coagulation.³⁵ Our model reaction of particle coalescence mimics the essential kinetic aspects of coagulation, but ignores the geometrical effects introduced by the actual growth of aggregating clusters.^{36,37} Due to the former feature of our model, it is possible to make a direct connection between particle coalescence and the Smoluchowski kinetic equation for coagulation.^{38,39} As a result of the latter feature, we can determine exactly and also adjust arbitrarily the form of the reaction kernel in our model. Because of these desirable features, we have determined the value of the upper critical dimension as well as predicted the kinetic laws below the upper critical dimension for the simplest case of a constant reaction kernel.³⁵ Many interesting unanswered questions remain regarding physically relevant generalizations of the coalescence model. In particular, attributes such as a mass-dependent diffusivity or mass-dependent reactivity have been described mathematically by more general forms of the interaction kernel.^{40–44} The feature of a reactivity increasing as a power law of mass is particularly interesting because it can lead to the possibility of a gelation transition in a finite time.^{42–44} We anticipate that fluctuation effects will strongly modify many of the rate-equation predictions for such general forms of the reaction kernel.

We have also considered generalizations of bimolecular recombination to situations which may be of direct experimental relevance. These include allowing for the possibilities of either imperfect reactivity or reversibility. The former effect was introduced in order to account empirically for the influence of various mixing effects. Typically such effects make it possible for many particle collisions to occur before a microscopic chemical reaction takes place. Consequently the system may be expected to exhibit mean-field kinetics, as there is time for particles to effectively mix between reactions.

In studying imperfect recombination with a reaction probability $p \ll 1$, rather dramatic results are obtained. An intermediate-time regime now exists where the system follows the relatively rapid mean-field decay. This mean-field-like regime occurs because the particle density is reasonably uniform throughout the system. However, this rapid decay can persist only as long as the particle density remains greater than the decay of the $p = 1$ case. Due to this constraint, the asymptotic decay *must* be independent of the reaction probability, a result which follows naturally from the domain-growth picture. In this picture the domains are attempting to grow, but their growth is slowed by particles of one species being able to penetrate a domain of the opposite species. Eventually, however, the domains become large enough that this can no longer occur. The crossover from the intermediate-time to the asymptotic decay corresponds exactly to this transition from transparent to opaque domains.

The reversibility feature is considered in order to study whether fluctuation effects, which play a predominant role in irreversible reactions, will continue to have an influence on the approach to an equilibrium state. We have argued that the effect of fluctuations is to slow the ap-

proach to equilibrium, from the exponential decay of the rate equation, to a power-law decay. This prediction can be justified heuristically by a modification of the rate equation in which fluctuation effects are included in a simple-minded manner. Such a result is rather surprising, as the effect of fluctuations in the examples of irreversible diffusion-controlled reactions is merely to modify the exponent of time in a power-law or quasiexponential decay.

Many of the new predictions presented here are readily visualized and quantitatively verified by numerical simulations. It would therefore be of great interest to subject our predictions to experimental tests.

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