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Statics and Dynamics of a Diffusion-Limited Reaction: Anomalous Kinetics, Nonequilibrium Self-Ordering, and a Dynamic Transition

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We solve exactly the one-dimensional diffusion-limited single-species coagulation process ($A + A \to A$) with back reactions ($A \to A + A$) and/or a steady input of particles ($B \to A$). The exact solution yields not only the steady-state concentration of particles, but also the exact time-dependent concentration as well as the time-dependent probability distribution for the distance between neighboring particles, i.e., the interparticle distribution function (IPDF). The concentration for this diffusion-limited reaction process does not obey the classical "mean-field" rate equation. Rather, the kinetics is described by a finite set of ordinary differential equations only in particular cases, with no such description holding in general. The reaction kinetics is linked to the spatial distribution of particles as reflected in the IPDFs. The spatial distribution of particles is totally random, i.e., the maximum entropy distribution, only in the steady state of the strictly reversible process $A + A \leftrightarrow A$, a true equilibrium state with detailed balance. Away from this equilibrium state the particles display a static or dynamic self-organization imposed by the nonequilibrium reactions. The strictly reversible process also exhibits a sharp transition in its relaxation dynamics when switching between equilibria of different values of the system parameters. When the system parameters are suddenly changed so that the new equilibrium concentration is greater than exactly twice the old equilibrium concentration, the exponential relaxation time depends on the initial concentration.

KEY WORDS: Diffusion-reaction systems; reaction kinetics; nonequilibrium phase transitions.

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1. INTRODUCTION

Diffusion-reaction systems are those in which the reactants are transported by diffusion.[1,2] Two fundamental time scales characterize these systems: the diffusion time, which is the time that elapses between collisions of reacting particles, and the reaction time, the time that particles take to react when in proximity. If the reaction time is much larger than the diffusion time, the process is *reaction limited.* In this case the law of mass action holds and the kinetics of such systems is described by classical rate equations. In recent years there has been an increasing interest in the less tractable *diffusion-limited* processes, where the reaction time scale is negligible compared to the diffusion time.[3–8] Applications of diffusion-limited reactions include ionic recombination, electron–hole recombination in a variety of physical systems, and kinetics of processes occurring in atmospheric dust, colloids, micellar systems, and polymers in solution, to name just a few. In practice, any diffusion-reaction system may exhibit diffusion-limited behavior: as the concentration of the reactants decreases, the time between collisions of the reactants increases, and at very low concentrations, the diffusion time is larger than the characteristic reaction time, dominating the process in the absence of convective (or stirring) transport.

For diffusion-limited processes the effect of self-stirring is negligible, the law of mass action does not hold, and a naive application of classical rate equations fails to describe the dynamics. Indeed, the usual derivation of classical rate equations either completely neglects the spatial distribution of reactants or only takes them into account through some kind of *mean-field* approximation. The kinetics of diffusion-limited reactions is often dominated by fluctuations, most notably spatial fluctuations in the concentrations of the reactants[7–10] and fluctuations in the number of particles involved, arising because of their individuality (fluctuations in number space).[11] In general, the starting point for analysis of such systems is a master equation for the state probability. Apart from very special cases, such master equations pose a formidable mathematical problem and some approximation techniques are needed. For example, fluctuations in number space may be approached with the help of Van Kampen's $1/\Omega$ expansion.[3,11] Scaling has proved useful in dealing with spatial inhomogeneities (see refs. 7 for reviews). Effective rate equations with nonclassical reaction terms have been put forward as a possible approximation (see refs. 12 for reviews). Needless to say, with such immense theoretical difficulties, numerical studies are of great importance and diffusion-limited systems are often modeled as cellular automata, where the diffusive transport is provided by a stochastic update rule.[13,14]

Most research to date in the area of diffusion-limited reactions has focused on the simplest reaction schemes, such as one-species coagulation, $A + A \to A$, one-species annihilation, $A + A \to$ *inert*, two-species annihilation, $A + B \to$ *inert*, and similar processes. (Refs. 7 reviews some of those. More complicated diffusion-reaction systems are modeled by cellular automata in ref. 14.) While some exact results exist, these are few in number. In particular, very little is known about the microscopic spatial structure of these systems, and this scarcity of exact solutions makes it difficult to evaluate the usefulness of various general approximations or approaches.

In this paper we present the exact solution of a diffusion-limited coagulation process in one spatial dimension. These exact results clearly reveal the crucial role played by the spatial degrees of freedom in nonequilibrium processes. The model includes forward and back reactions, $A + A \to A$, and $A \to A + A$, respectively, and the possibility of a stochastic input of particles at a constant rate ($B \to A$ with B in excess). It is rich in its range of kinetic behavior, displaying in one case a dynamic "phase" transition. Moreover, the mathematical analysis of these nontrivial interacting particle systems is surprisingly simple—we reduce the problem to a *linear* partial differential equation—so that this example should serve as a basic model for the study of various phenomena in diffusion-reaction systems. This system should additionally prove useful both as a benchmark for Monte Carlo simulations and as a testing ground for various approximation and perturbation techniques currently in use.

The simplest case of irreversible coagulation, $A + A \to A$, is a nonequilibrium process with a trivial steady state (zero concentration of A-species particles). When input is included, one obtains a nontrivial steady state, albeit a *nonequilibrium* one. On the other hand, the reversible reaction $A + A \leftrightarrow A$ without input has an *equilibrium* stationary state. Our exact solution provides the concentration of particles as a function of time, including the approach to the various stationary states. The concentration always relaxes exponentially to the nonequilibrium steady state. For the reversible process we find a sharp transition in the dynamics of the approach to equilibrium, depending on the initial conditions, resulting from far-from-equilibrium spatial correlation effects. Additionally, the reversible reaction process can display a purely algebraic relaxation to the equilibrium state, as slowly as desired, depending explicitly on the spatial distribution of the particles. We also derive the exact probability density function for the distance between nearest particles. This gives us useful information on the microscopic spatial ordering of the system in various nonequilibrium situations. Based on these exact solutions, we discuss the applicability of effective rate equations for this system.

The rest of this paper is organized as follows. In Section 2, we intro-

duce the diffusion-limited coagulation process in detail. For clarity, and to connect with cellular automata and numerical simulations, the process is described on a spatial lattice (but in continuous time). The concepts of interparticle distribution functions (IPDFs) and of other related statistical functions are presented, and a kinetic equation for the evolution of the system is derived. The spatial continuum limit is described at the end of Section 2. In Section 3 we present the general solution for the kinetic equation derived previously. We specialize this solution to specific cases of interest in the following sections: the completely irreversible reaction $A + A \to A$ in Section 4; the same irreversible reaction, but with a steady input of particles in Section 5; and the reversible reaction $A + A \leftrightarrow A$ in Section 6.

In Section 7 we discuss the question of rate equations for the kinetics of the various limiting cases of the system. We find that rate equations apply only under very restricted conditions and that, in general, a different approach is needed. Our analysis is based on our knowledge of the microscopic ordering as reflected in the exact IDPFs. We include a discussion of some other diffusion-limited processes, the one-species annihilation process, and the point-particle coagulation model of particles with different "masses" in Section 8. Our discussion there is largely on a heuristic level supported by numerical simulations, as there are fewer exact results than for the coagulation process studied in this paper. We summarize and discuss our results, as well as some future directions for research, in Section 9.

2. THE DIFFUSION-LIMITED COAGULATION PROCESS

Our model is a reversible one-dimensional coagulation process of point particles together with a steady input of particles.[15–17] The system is most easily defined on a lattice with lattice spacing Δx, with the continuum limit taken at a later stage. There are four different processes taking place, as described below.

Diffusion. Particles move randomly to the nearest lattice site with a hopping rate $2D/(\Delta x)^2$. The diffusion is symmetric, with rate $D/(\Delta x)^2$ to the right and $D/(\Delta x)^2$ to the left. On long length and time scales this yields normal diffusion with diffusion coefficient D.

Birth. A particle gives birth to another at an adjacent site, at rate $v/\Delta x$. This means rate $v/2\Delta x$ for birth on each side of the original particle. Notice that while v is a constant (with units of velocity), the rate $v/\Delta x$ diverges in the continuum limit of $\Delta x \to 0$. This is necessary because of the possible recombination of the newborn and the original particle, which also

takes place at an infinite rate when $\Delta x \to 0$. Symbolically, the birth process is $A \to A + A$.

Input. Any empty site spontaneously becomes occupied at probability rate $R\Delta x$. Here R is the average number of particles input per unit length, per unit time.

Coagulation. When a particle lands on another through diffusion or bith, then it disappears. Symbolically, the coagulation process is $A + A \to A$.

Each of these processes—except coagulation—takes place independently of the others. The various processes are illustrated in Fig. 1.

To solve the system, it is useful to define $E_n(t)$, the probability that a randomly chosen segment of n consecutive sites is empty, i.e., contains no particles.[16,17] The probability that a site is occupied is thus $1 - E_1$ and the density, or concentration, of particles is expressed as

$$c(t) = (1 - E_1)/\Delta x \tag{2.1}$$

Notice that the coagulation process is realized by permitting at most one particle at any given site.

E_n gives the probability that, say, sites 1 through n are empty, while E_{n+1} gives the probability that 1 through $n+1$ are empty. The event that 1 through n are empty contains the event that 1 through $n+1$ are empty. Thus, the probability that a segment of n sites is empty, but that there *is* a particle at the adjacent site $n+1$, is $E_n - E_{n+1}$.

We construct a closed kinetic equation for the evolultion of the E_n. Consider the changes in E_n due to the different processes during a small time interval Δt:

Diffusion. We may have an empty segment of n sites and site $n+1$ occupied, with the particle at site $n+1$ moving into site n of the segment

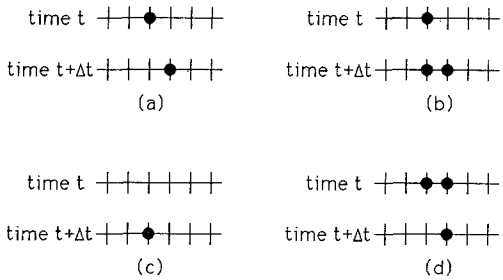

Fig. 1. (a) Diffusion, (b) birth, (c) input, and (d) coagulation processes which take place in our reaction-diffusion system.

in a short time interval Δt. This will decrease E_n by an amount $D/(\Delta x)^2(E_n - E_{n+1})\,\Delta t$. Likewise, we may have an empty segment of $n-1$ sites with a particle on the nth site. The end particle can move out to site $n+1$, increasing E_n by an amount $D/(\Delta x)^2(E_{n-1} - E_n)\,\Delta t$. Putting these processes together, we get a rate of change of E_n due to diffusion

$$(\partial_t E_n)_{\text{diffusion}} = 2\frac{D}{(\Delta x)^2}(E_{n+1} - 2E_n + E_{n-1}) \tag{2.2}$$

The additional factor of 2 results from the fact that both processes can occur at either of the two ends of the segment independently.

Input. The input of particles decreases the probability E_n of having an empty interval of length n. Particles are input at a rate $R\Delta x$ *per lattice site*, so the rate of change due to input is

$$(\partial_t E_n)_{\text{input}} = -Rn\,\Delta x\,E_n \tag{2.3}$$

The factor of n results from the fact that the rate of input to *each* of the n sites is independently $R\Delta x$.

Birth. Particles *adjacent* to the end of an empty segment may give birth to a particle *into* the end site of the segment, decreasing E_n by $(v/2\Delta x)(E_n - E_{n+1})\,\Delta t$. Since this can occur at either end of an empty interval, this process contributes

$$(\partial_t E_n)_{\text{birth}} = -\frac{v}{\Delta x}(E_n - E_{n+1}) \tag{2.4}$$

Coagulation. The coagulation reaction fixes the boundary conditions for E_n. To see this, consider changes in the *number* of particles in the system due to coagulation. The concentration decreases when two adjacent sites (say, 1 and 2) are both occupied and either of the two particles hops onto the other, thereby disappearing. The probability of having two adjacent sites occupied is $1 - 2E_1 + E_2$, as illustrated in Fig. 2. Then, using the hopping probability and Eq. (2.1),

$$-\partial_t c\Delta x = \partial_t E_1 = 2\frac{D}{\Delta x^2}(1 - 2E_1 + E_2) \tag{2.5}$$

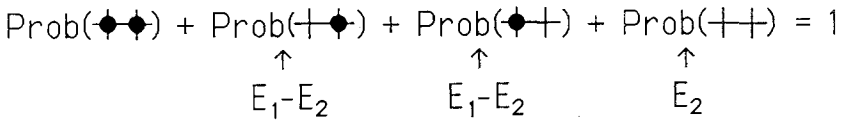

Fig. 2. Probability of having two adjacent sites occupied by particles. This is a necessary stage preceding coagulation and is used to determine the boundary condition (2.6).

To make this consistent with Eq. (2.2) for the case $n=1$, we impose the boundary condition

$$E_0 = 1 \tag{2.6}$$

to account for coagulation.

Combining all the different contributions to changes in E_n, we get

$$\partial_t E_n = 2\frac{D}{\Delta x^2}(E_{n+1} - 2E_n + E_{n-1}) - \frac{v}{\Delta x}(E_n - E_{n+1}) - Rn\,\Delta x\,E_n \tag{2.7}$$

with the boundary condition (2.6). An additional boundary condition is $E_\infty(t) = 0$ for a nonzero population of particles. We may also consider the initial condition $E_n(0) = 1$ describing an empty system. (Note that E_n is a nonincreasing function of n.)

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 $E(x, t)$. Letting $\Delta x \to 0$, we have Eq. (2.7) replaced by

$$\frac{\partial E(x,t)}{\partial t} = 2D\frac{\partial^2 E}{\partial x^2} + v\frac{\partial E}{\partial x} - RxE \tag{2.8}$$

with boundary conditions $E(0, t) = 1$ and $E(\infty, t) = 0$. Once $E(x, t)$ is obtained, the concentration of particles is derived using Eq. (2.1), which in the continuum limit becomes

$$c(t) = -\left.\frac{\partial E(x,t)}{\partial x}\right|_{x=0} \tag{2.9}$$

From $E(x, t)$ we may also derive $p(x, t)$, the probability density function for finding the nearest particle a distance x on one side of a given particle. We refer to this density as the interparticle distribution function (IPDF).[15–17] The relation between p and E is derived from the discrete representation, and we take the continuum limit at the very end. Let p_n be the probability that the nearest neighbor to (say, the right of) a given particle is n lattice spacings away. Thus, p_1 is the probability that the nearest neighbor lies in the site next to the particle, p_2 is the probability that the nearest neighbor is two sites away, etc. The p_n are normalized, $\sum p_n = 1$, and the average distance between adjacent particles is the reciprocal of the concentration

$$\langle n\Delta x\rangle = \sum_{n=1}^{\infty} np_n\,\Delta\chi = \frac{1}{c} \tag{2.10}$$

Choose a lattice site at random. The probability that the next n sites are empty E_n, may be expressed in terms of p_n. The probability that the chosen point lies within a gap of length m is proportional to mp_m, which can be normalized with the help of Eq. (2.10), yielding the probability distribution $c\,\Delta x\, mp_m$. The probability that there are k lattice spacings until the next particle, given that the point is in the gap of length m, is $1/m$ if $1 \leqslant k \leqslant m$, and 0 otherwise. Thus, the (unconditional) probability that there are exactly k lattice spacings to the next particle is

$$\sum_{m=k}^{\infty} \frac{1}{m} c\,\Delta x\, mp_m = c\,\Delta x \sum_{m=k}^{\infty} p_m \tag{2.11}$$

Finally, the probability that the next n sites are empty, i.e., E_n, is the probability that $k > n$:

$$E_n = c\,\Delta x \sum_{k=n+1}^{\infty} \sum_{m=k}^{\infty} p_m \tag{2.12a}$$

This can be inverted to yield

$$c\,\Delta x\, p_n = E_{n+1} - 2E_n + E_{n-1} \tag{2.12b}$$

In the continuum limit these relations become

$$E(x, t) = c(t) \int_x^{\infty} dx' \int_{x'}^{\infty} dx''\, p(x'', t) \tag{2.13a}$$

and

$$c(t)\, p(x, t) = \frac{\partial^2 E(x, t)}{\partial x^2} \tag{2.13b}$$

3. GENERAL SOLUTION

We now present with the general solution of Eq. (2.8). Expand $E(x, t)$ in eigenfunctions of

$$-\lambda E_\lambda(x) = 2D \frac{\partial^2 E_\lambda(x)}{\partial x^2} + -v \frac{\partial E_\lambda(x)}{\partial x} - RxE_\lambda(x) \tag{3.1}$$

Then $E(x, t)$ is expressed as a linear combination of the eigenfunctions as $E(x, t) = \sum a_\lambda E_\lambda(x) e^{-\lambda t}$. Let

$$E_\lambda(x) = F_\lambda(x) e^{-vx/4D} \tag{3.2}$$

From Eq. (3.1) we obtain

$$2D\frac{\partial^2 F_\lambda(x)}{\partial x^2} = [Rx + (v^2/8D - \lambda)]F_\lambda(x) \tag{3.3}$$

This is Airy's equation, with the solution

$$F_\lambda(x) = \mathrm{Ai}\{(R/2D)^{1/3}x + (v^2/8D - \lambda)/(2DR^2)^{1/3}\} \tag{3.4}$$

$\mathrm{Ai}(z)$ is Airy's function, satisfying $\mathrm{Ai}''(z) = Z\,\mathrm{Ai}(z)$. [The linearly independent solution $\mathrm{Bi}(z)$ is excluded because it grows faster than $e^{vx/4D}$ as $x \to \infty$, violating the boundary condition $E \to 0$ as $x \to \infty$.]

The steady-state solution is obtained from Eq. (3.4) by setting $\lambda = 0$ and using the boundary condition $E(0, t) = 1$, which translates to $F_0(0) = 1$. We find

$$E_0(x) = e^{-vx/4D}\frac{\mathrm{Ai}\{(R/2D)^{1/3}x + (v^2/8D)(2DR^2)^{-1/3}\}}{\mathrm{Ai}\{(v^2/8D)(2DR^2)^{-1/3}\}} \tag{3.5}$$

From this we obtain the steady-state concentration using Eq. (2.9):

$$c_s = \frac{v}{4D} - \left(\frac{R}{2D}\right)^{1/3}\frac{\mathrm{Ai}'\{(v^2/8D)(2DR^2)^{-1/3}\}}{\mathrm{Ai}\{(v^2/8D)(2DR^2)^{-1/3}\}} \tag{3.6}$$

In the above, $\mathrm{Ai}'(z)$ denotes the derivative of $\mathrm{Ai}(z)$. The steady-state interparticle distribution function $p_s(x) = p(x, \infty)$ may also be computed using c_s and Eq. (2.13b).

The transient solutions correspond to $\lambda > 0$. In this case the boundary condition $E(0, t) = 1$, combined with $F_0(0) = 1$, implies $F_\lambda(0) = 0$ for $\lambda > 0$. Applying this to Eq. (3.4), we find a discrete relaxation spectrum for nonvanishing R and D:

$$\lambda_n = v^2/8D + (2DR^2)^{1/3}|a_n| \tag{3.7}$$

where a_n is the nth zero of the Airy function $\mathrm{Ai}(z)$. These zeros are all negative, and are tabulated in the literature.[18] For example, $a_1 = -2.3381...$, $a_2 = -4.0879...$, etc. The spectrum of eigenvalues is illustrated in Fig. 3.

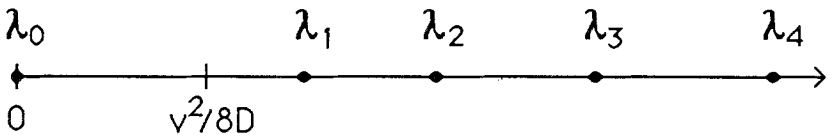

Fig. 3. Spectrum of eigenvalues λ_n for Eq. (3.1). The limit $R \to 0$ is *not* trivial, because spectrum appears in the gap $(0, v^2/8D)$ (see Section 6).

In the next three sections we study some specific limits of the process: the irreversible process $A+A \to A$ ($R=v=0$), the irreversible process $A+A \to A$ with input ($v=0$), and the reversible reaction $A+A \leftrightarrow A$ ($R=0$).

4. IRREVERSIBLE COAGULATION $A+A \to A$

The simplest case for the process is when there is no input ($R=0$), and when there are no back reactions ($v=0$).[15,19,20] In this case one has the irreversible coagulation process $A+A \to A$ alone, as illustrated in Fig. 4. This process has a trivial steady state with zero concentration of particles, so only the kinetic behavior will be studied.

For $R=v=0$, Eq. (2.8) reduces to

$$\frac{\partial E(x,t)}{\partial t} = 2D\frac{\partial^2 E}{\partial x^2} \tag{4.1}$$

with the boundary conditions of $E(0,t)=1$ and $E(\infty,t)=0$. The time-dependent solution to this diffusion equation is complicated by the unusual boundary condition of $E(0,t)=1$, and it is simpler[15] to consider the second derivative of Eq. (4.1) with respect to x, yielding

$$\frac{\partial \rho(x,t)}{\partial t} = 2D\frac{\partial^2 \rho}{\partial x^2} \tag{4.2}$$

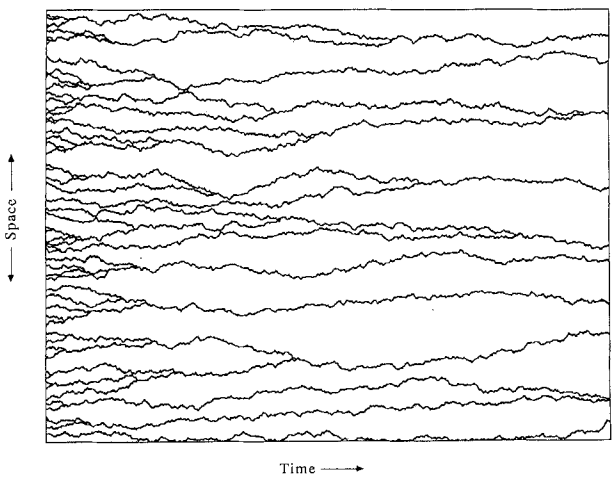

Fig. 4. Space-time evolution of the process $A+A \to A$. The concentration of particles decays to zero at long times.

where $\rho(x, t) = c(t)\, p(x, t)$, from Eq. (2.13b). For $\rho(x, t)$ we have the boundary conditions $\rho(0, t) = \rho(\infty, t) = 0$. The Green function for Eq. (4.2) is

$$G(x, x', t) = \frac{1}{(8\pi Dt)^{1/2}} \left\{ \exp\left[-\frac{(x-x')^2}{8Dt} \right] - \exp\left[-\frac{(x+x')^2}{8Dt} \right] \right\} \tag{4.3}$$

so that

$$\rho(x, t) = \int_0^\infty dx'\, G(x, x', t)\, \rho(x', 0) \tag{4.4}$$

Given an initial IPDF $p(x, 0)$, using Eqs. (4.3) and (4.4) and the relation $c(t) = \int_0^\infty dx\, \rho(x, t)$, one obtains a full solution for the time-dependent concentration $c(t)$ and the IPDF $p(x, t)$.

The long-time asymptotic limit ($t \to \infty$) is easily computed from

$$G(x, x', t) \to \frac{2x'}{(8\pi Dt)^{1/2}} \frac{2x}{8Dt} \exp\left(-\frac{x^2}{8Dt} \right) \tag{4.5}$$

Substituting in Eq. (4.4) and using the expression $c(t)^{-1} = \int_0^\infty dx\, xp(x, t)$, we obtain

$$c(t) \to \frac{1}{(2\pi Dt)^{1/2}} \qquad \text{as} \quad t \to \infty \tag{4.6}$$

and

$$p(x, t) \to \frac{x}{4Dt} \exp\left(-\frac{x^2}{8Dt} \right) \qquad \text{as} \quad t \to \infty \tag{4.7}$$

independent of the initial conditions. The dimensionless, or *scaling*, interparticle distance $z = c(t)x$ approaches the *stationary* distribution

$$p(z, t) \to \frac{\pi}{2} z \exp\left(-\frac{\pi}{2} \frac{z^2}{2} \right) \qquad \text{as} \quad t \to \infty \tag{4.8}$$

The transient behavior depends strongly on the initial distribution $p(x, 0)$. For example, starting with a completely *random* distribution, where $p^{\text{ran}}(x, 0) = c_0 \exp(-c_0 x)$, the transient behavior is

$$\frac{c^{\text{ran}}(t)}{c_0} \cong 1 - \left(\frac{8c_0^2 Dt}{\pi} \right)^{1/2} + O(c_0^2 Dt) \tag{4.9}$$

with an infinite initial reaction rate: $dc^{\text{ran}}/dt|_{t=0} = \infty$. This happens because the random initial configuration places many particles very close together. In contrast, for an ordered, *periodic* initial distribution where $p^{\text{per}}(x, 0) = \delta(x - c_0^{-1})$, the reaction proceeds at a transcendentally small rate until $t = O[(c_0^2 D)^{-1}]$:

$$\frac{c^{\text{per}}(t)}{c_0} \cong 1 - \left(\frac{8c_0^2 Dt}{\pi}\right)^{1/2} \exp\left(-\frac{1}{8c_0^2 Dt}\right)[1 + O(c_0^2 Dt)] \tag{4.10}$$

and $dc^{\text{per}}/dt|_{t=0} = 0$.

A very interesting initial configuration is the *scaling* distribution of Eq. (4.8), i.e., $p^{\text{sc}}(x, 0) = (\pi/2)c_0^2 x \exp[-(\pi/2)c_0^2 x^2/2]$. This distribution falls between the two extremes of initial order (the periodic distribution) and disorder (the random distribution). In this case, the integral in Eq. (4.4) is easily evaluated in closed form, yielding

$$\frac{c^{\text{sc}}(t)}{c_0} = \frac{1}{(1 + 2\pi c_0^2 Dt)^{1/2}} \tag{4.11}$$

For this initial condition the interparticle distribution *remains* in its scaling form:

$$p^{\text{sc}}(x, t) = \frac{\pi}{2} c(t)^2 x \exp\left[-\frac{\pi}{2}\frac{c(t)^2 x^2}{2}\right] \tag{4.12}$$

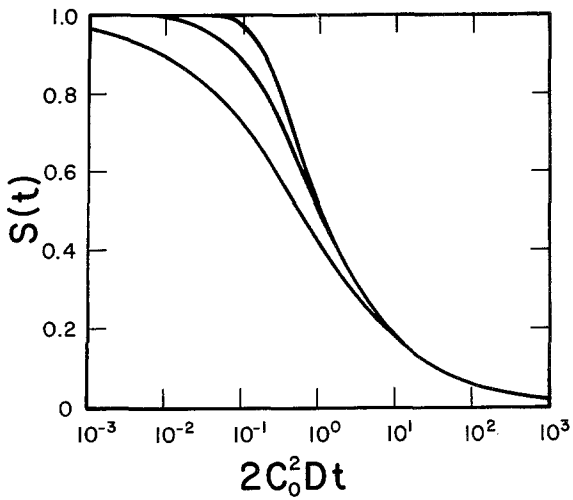

Fig. 5. Survival probability $[S(t) = C(t)/C_0]$ vs. dimensionless time for the single-species coagulation model. The initial conditions for the various curves are (top) periodically spaced particles, (middle) invariant scaling distribution, and (bottom) totally random distribution.

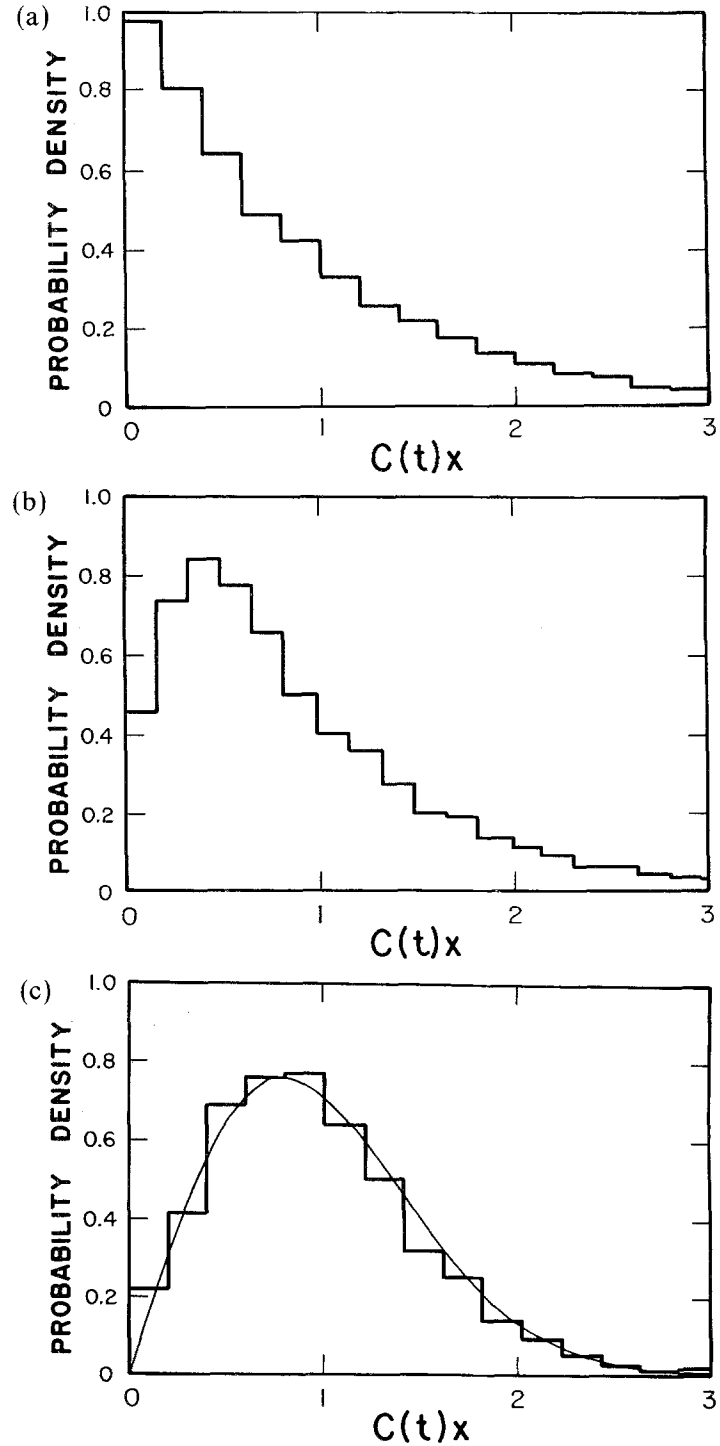

Fig. 6. Time-dependent interparticle distributions for particles initially distributed totally at random: (a) initial density at $t=0$, (b) density at an early time, $2C_0^2Dt=0.066$, and (c) density at a late time, $2C_0^2Dt=4.2$. The histograms represent data from numerical simulations and the smooth curve is the analytic result shown for comparison.

It is clear why the concentration falls between the two extremes in this case. There is little probability of particles starting off close to each other (the density vanishes as $x \to 0$), so the reaction rate is less than that in the case of totally random initial conditions. On the other hand, there *is* a nonvanishing probability of particles being initially found arbitrarily close, so the rate is greater than for the periodically ordered initial configuration.

In Fig. 5 we show the time evolution of the concentration for the random, periodic, and scaling distributions discussed above. In Fig. 6 we plot the evolution of $p(z, t)$ as a function of time, starting from a totally random initial configuration and up to the asymptotic long-time stationary distribution of Eq. (4.8). For both figures the computation is carried out using Eq. (4.4).

The IPDF of Eq. (4.12) displays an interesting microscopic structure for this nonequilibrium state. In thermal equilibrium one expects the maximum entropy distribution of particles, characterized by an exponential IPDF, $p(x) = ce^{-cx}$. (In fact, this is just what we find in Section 6 below for the *equilibrium* stationary state of the reversible reaction $A + A \leftrightarrow A$.) In the coagulation process the scaling form of the IPDF vanishes near $x = 0$, indicating an effective repulsion of the particles. The probability of large gaps decays much faster than exponential [proportional to a power of $\exp(-x^2)$]. This simple interacting model thus serves as an example of *dynamic self-ordering* in a far-from-equilibrium system.

5. A + A → A WITH INPUT

We now turn to the case of coagulation $A + A \to A$ with input ($R > 0$), but with no back reactions ($v = 0$),[16,21,22] as shown in Fig. 7. The solution is obtained by a straightforward substitution of $v = 0$ in the results for the general case of Section 3. In contrast to the trivial long-time asymptotic limit of the pure coagulation process of the previous section, when there is a constant input, the system reaches a nontrivial stationary steady state with a nonvanishing concentration c_s. Note, however, that this is a *nonequilibrium* steady state, as the processes involved are strictly irreversible, so there is no detailed balance.

Substituting $v = 0$ in Eq. (3.6), we find the steady-state concentration

$$c_s(R, D) = \frac{|\mathrm{Ai}'(0)|}{\mathrm{Ai}(0)} \left(\frac{R}{2D}\right)^{1/3} = (0.72901\ldots)\left(\frac{R}{2D}\right)^{1/3} \tag{5.1}$$

[where $\mathrm{Ai}(0) = 0.35502\ldots$ and $\mathrm{Ai}'(0) = -0.25881\ldots$]. The fact that c_s is proportional to $(R/D)^{1/3}$ can be deduced from a scaling argument (really just dimensional analysis): Assume that the initial concentration plays no

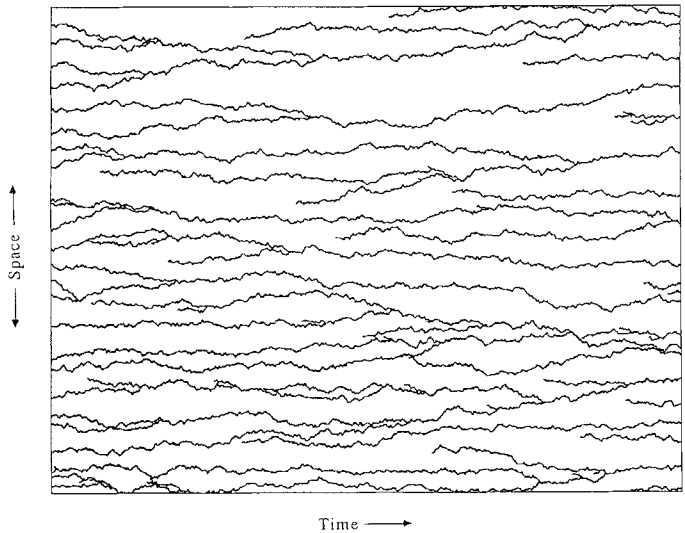

Fig. 7. Space-time diagram for the evolution of $A + A \rightarrow A$ with input.

role in the steady state. Then the only physical parameters influencing the process are the diffusion constant D, with dimensions of $(\text{length})^2/(\text{time})$, and the input rate R, with dimensions of $(\text{length} \times \text{time})^{-1}$. To obtain the correct dimension of c_s, $(\text{length})^{-1}$, one must combine them as $(R/D)^{1/3}$. In contrast, notice that for the reaction-limited process, a classical rate equation would predict $c_s \sim R^{1/2}$. We will discuss classical rate equations and their applicability to diffusion-limited processes in Section 7.

The stationary IPDF as computed from Eq. (3.5) with $v = 0$ is

$$p_s(x) = \frac{1}{c_s(R, D)} \frac{\partial^2 E_0(x)}{\partial x^2} = \left(\frac{R}{2D}\right)^{1/3} \frac{\text{Ai}''((R/2D)^{1/3}x)}{|\text{Ai}'(0)|} \tag{5.2}$$

This stationary distribution is plotted in Fig. 8. It is interesting to notice that the probability for large gaps between particles falls off as $\exp(-x^{3/2})$, which is *slower* than $\exp(-x^2)$ of the IPDF for the pure coagulation process. This can be understood in view of the random input of A particles, which is an effective disordering agent. Notice, however, that the random input does not manage to induce complete disorder, and the stationary IPDF displays a *greater* ordering than a totally random distribution of particles (a purely exponential IPDF). Moreover, the vanishing of the steady state IPDF at $x = 0$ indicates an effective repulsion of particles in this nonequilibrium situation. The steady state of the coagulation process with input thus serves as an example of *static self-ordering* in a far-from-equilibrium system.

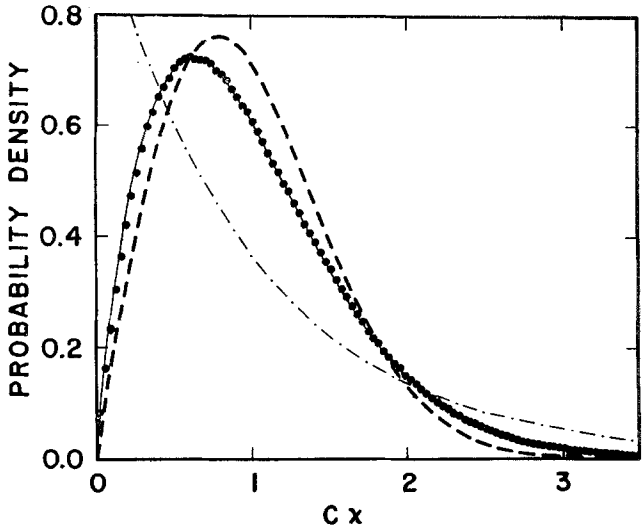

Fig. 8. Monte Carlo (points) and theoretical (solid line) steady-state IPDF for the coagulation model with input. The broken line is the dynamic scaling IPDF for $R=0$ (Section 4), while the dash-dotted line is the exponential IPDF for equilibrium. Results are scaled by the average distance between particles.

The transient behavior of the system is represented by the eigenfunctions of Eq. (3.2) corresponding to eigenvalues $\lambda > 0$. From Eq. (3.7), we see that for $v=0$ the eigenvalues still form a discrete spectrum, $\lambda_n = (2DR^2)^{1/3}|a_n|$. Hence, at long times the transient behavior is dominated by the eigenfunction E_1, and there is an exponential approach to steady state with decay rate $\lambda_1 = (2DR^2)^{1/3}|a_1| = (2.3381...)(2DR^2)^{1/3}$.

6. REVERSIBLE REACTION $A + A \leftrightarrow A$

We now consider the reversible coagulation process, $A + A \leftrightarrow A$.[17] That is, the birth process is included ($v > 0$), but we do *not* allow for input of particles ($R=0$). In this case there is again a nontrivial steady state, but this is an *equilibrium* steady state, as the process is fully reversible, so that detailed balance holds in the steady state. This process is shown in Fig. 9. Notice that the process does not conserve mass and therefore, strictly speaking, should not be termed "reversible." We use this terminology to avoid the more cumbersome alternative "forward and back-reaction...."

To obtain the solution for this model, one could formally take the limit $R \to 0$ in the results for the general process of Section 3. However, this turns out to be a very singular limit of the dynamic equation: note that the spectrum in Eq. (3.7) becomes continuous when $R \to 0$.

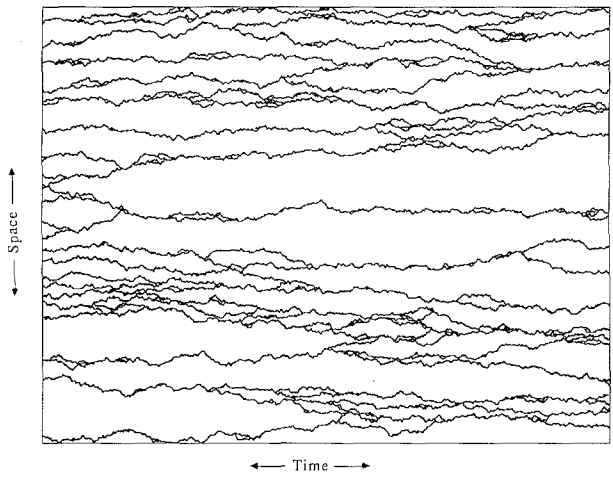

Fig. 9. Space-time diagram for coagulation $A + A \rightarrow A$, with the back reaction $A \rightarrow A + A$. Notice the ambiguity in the direction of time in the stationary state, a hallmark of equilibrium with detailed balance.

The easiest approach is to start from the eigenvalue equation (3.3) and set $R = 0$. We have, recalling $E_\lambda(x) = F_\lambda(x)e^{-vx/4D}$,

$$0 = 2D\frac{\partial^2 F_\lambda(x)}{\partial x^2} - \left(\frac{v^2}{8D} - \lambda\right)F_\lambda(x) \tag{6.1}$$

The stationary solution is obtained by setting $\lambda = 0$. The boundary condition at $x = 0$ implies $E_0(0) = F_0(0) = 1$, and we find

$$E_0(x) = e^{-vx/2D} \tag{6.2}$$

Using Eqs. (2.9) and (2.13b), we derive

$$c_s = \frac{v}{2D} \tag{6.3}$$

and

$$p_s(x) = \frac{v}{2D}e^{-vx/2D} = c_s e^{-c_s x} \tag{6.4}$$

Thus, the stationary IPDF is exponential, corresponding to maximum entropy as in the case of thermal equilibrium. This result is expected because of the reversible nature of the process—the steady state has the property of detailed balance. The statistical time-reversible invariance of

this equilibrium steady state can be seen in Fig. 9, where the direction of time is ambiguous (compare with Figs. 4 and Fig. 7). In fact, the stationary state of this process is *exactly* a totally random (Poisson) distribution of particles on the line, obviously the maximum entropy state. This result can be derived from the N-body level of description.[23]

For the transient behavior we want to solve for the eigenvalues $\lambda > 0$. If one were to take a naive $R \to 0$ limit of the spectrum in Eq. (3.7), one would have guessed that we would still have a gap between the stationary eigenvalue $\lambda = 0$ and the first decaying solution $\lambda = v^2/8D$. It so happens that this is *not* the case, and there *is* spectrum in the interval $(0, v^2/8D)$.

For $\lambda > 0$, $F_\lambda(x)$ need *not* necessarily vanish as $x \to \infty$, because $E_\lambda = e^{-vx/4D} F_\lambda$, and the boundary conditions require only that $E_\lambda \to 0$ as $x \to \infty$. Suppose first that $\lambda > v^2/8D$. Then $F_\lambda(0) = 0$ [see discussion preceding Eq. (3.7)], and the solution of (6.1) is

$$F_\lambda(x) = \sin\left[\left(\frac{\lambda}{2D} - \frac{v^2}{16D^2}\right)^{1/2} x\right], \qquad \lambda > \frac{v^2}{8D} \tag{6.5a}$$

For $\lambda = v^2/8D$, we have

$$F_\lambda(x) = x, \qquad \lambda = \frac{v^2}{8D} \tag{6.5b}$$

while for $\lambda < v^2/8D$ (but still $\lambda > 0$),

$$F_\lambda(x) = \sinh\left[\left(\frac{v^2}{16D^2} - \frac{\lambda}{2D}\right)^{1/2} x\right], \qquad \lambda < \frac{v^2}{8D} \tag{6.5c}$$

Notice that F_λ in this last case diverges slower than $e^{vx/4D}$, so that E_λ vanishes as $x \to \infty$, as required. The eigenfunctions for $\lambda > 0$ are thus

$$E_\lambda(x) = e^{-vx/4D} \sin\left[\left(\frac{\lambda}{2D} - \frac{v^2}{16D^2}\right)^{1/2} x\right], \qquad \lambda > \frac{v^2}{8D} \tag{6.6a}$$

$$E_\lambda(x) = x e^{-vx/4D}, \qquad \lambda = \frac{v^2}{8D} \tag{6.6b}$$

$$E_\lambda(x) = e^{-vx/4D} \sinh\left[\left(\frac{v^2}{16D^2} - \frac{\lambda}{2D}\right)^{1/2} x\right], \qquad 0 < \lambda < \frac{v^2}{8D} \tag{6.6c}$$

From the above one can infer the approach to equilibrium for various initial conditions. If the initial IPDF falls off as $\exp(-c_0 x)$ as $x \to \infty$, with $c_0 > v/4D = c_s/2$, then the time-dependent solution cannot contain any modes with $\lambda < v^2/8D$, as in (6.6c), because these modes decay slower than

$\exp(-c_s x/2)$. In this case the slowest decaying component corresponds to $\lambda = v^2/8D = Dc_s^2/2$ and $c(t) - c_s \sim \exp(-Dtc_s^2/2)$ as $t \to \infty$. If the initial IPDF falls off as $\exp(-c_0 x)$ as $x \to \infty$, with $c_0 < v/4D = c_s/2$, then it must contain a mode of the form of (6.6c), with $\lambda = c_0 v - 2c_0^2 D = 2Dc_0(c_s - c_0)$. This would be the slowest decaying mode, so that $c(t) - c_s \sim \exp[-2Dtc_0(c_s - c_0)]$ as $t \to \infty$. Thus, there is a sharp transition in the dynamics of the approach to equilibrium, i.e., in the exponential relaxation time

$$\tau = -\lim_{t \to \infty} t^{-1} \ln |c(t) - c_s| \tag{6.7}$$

governed by the spatial decay of the initial IPDF. This transition is depicted graphically in Fig. 10.

In fact, given a specific initial IPDE, one can obtain an explicit solution for the transient dynamics. In ref. 17 we carried out such a calculation for the particular case when the initial distribution is exponential, $p(x, 0) = c_0 \exp(-c_0 x)$, corresponding to an equilibrium state with concentration c_0. These initial states are natural in the sense that they correspond to the system's equilibrium steady state at some fixed value of the parameters D and v. The long-time behavior, computed from the exact expression valid for all times, is

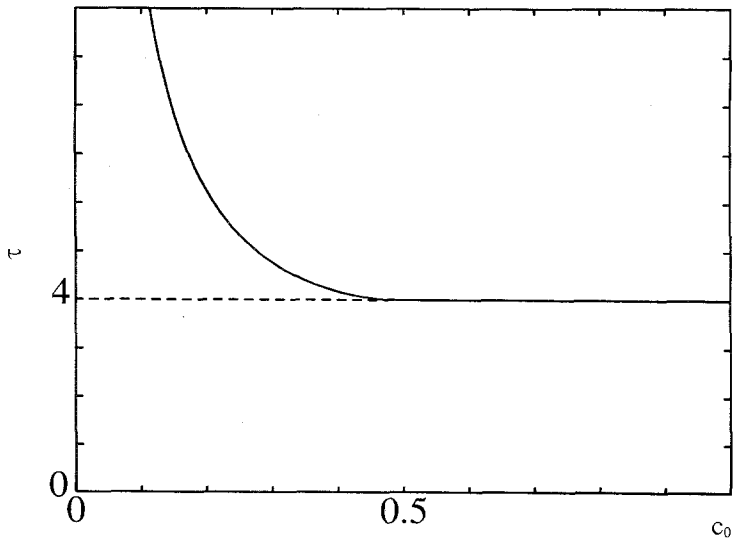

Fig. 10. The exponential relaxation time τ as a function of the initial concentration c_0. The units are $\frac{1}{2}D^{-1}c_{eq}^{-2}$ and c_{eq}, respectively.

$$c(t) \sim c_s - (c_s - 2c_0)\exp[-2Dtc_0(c_s - c_0)], \qquad c_0 < \frac{c_s}{2} \tag{6.8a}$$

$$v(t) \sim c_s - \frac{1}{(2\pi Dt)^{1/2}} \exp\left(-\frac{2Dtc_s^2}{2}\right) \qquad c_0 = \frac{c_s}{2} \tag{6.8b}$$

$$c(t) \sim c_s + \frac{2}{\sqrt{\pi}}[c_s^{-2} - (c_s - 2c_0)^{-2}] \frac{1}{(2Dt)^{3/2}} \exp\left(-\frac{Dtc_s^2}{2}\right), \qquad c_0 > \frac{c_s}{2} \tag{6.8c}$$

in agreement with our foregoing discussion for general initial conditions. In Fig. 11 we show the excellent agreement obtained between the exact solution and computer simulations of the process with an initial exponential IPDF.

Moreover, the approach to equilibrium for the coagulation process with back reactions can be made as slow as desired. Under appropriate initial conditions the approach to equilibrium may even be *algebraic* in time. Indeed, an exact analysis of Eq. (6.1) shows that if the initial condition decays as $E(x, 0) \sim x^{-\varepsilon}$ as $x \to \infty$, *for any* $\varepsilon > 0$, then $c(t) \sim c_s + O(t^{-\varepsilon})$. Such a decay in $E(x, 0)$ corresponds to a well-defined *fractal* distribution of particles on the line.

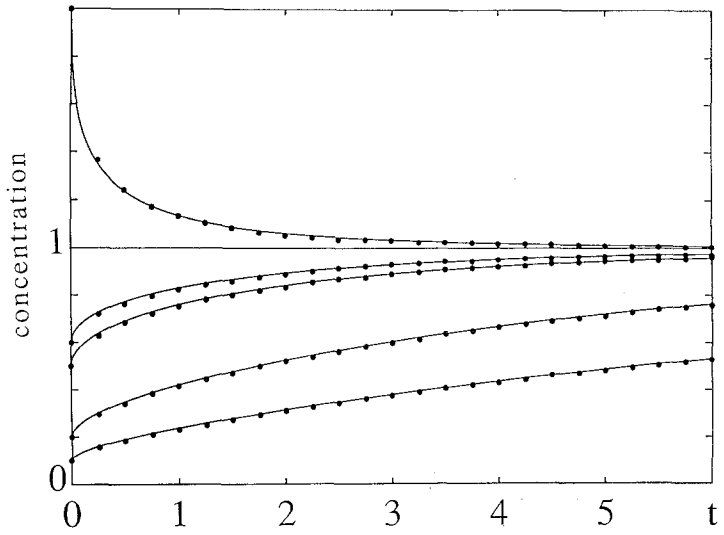

Fig. 11. The approach of the concentration $c(t)$ to its equilibrium value c_{eq} for various initial concentrations: $c_0/c_{eq} = 0.1$, 0.2, 0.5, 0.6, and 2.0. The Monte Carlo results (dots) are plotted together with the exact results. The units are c_{eq} and $\frac{1}{2}D^{-1}c_{eq}^{-2}$, respectively.

Spatial correlations in the microscopic distribution of particles provide the physical mechanism for the slow relaxation "phase." When there are large gaps between neighboring particles, as occurs in a low-concentration Poisson distribution of particles, then the relaxation is dominated by the time taken to fill these gaps. These large empty regions can only be filled in from the sides, and a simple argument provides the correct decay time: concentration fronts drift into empty regions at speed v, and a typical initial interparticle distance is c_0^{-1}; thus, the time taken for the typical gap to be filled is $\tau = (c_0 v)^{-1} = (2Dc_s c_0)^{-1}$, the correct value [Eq. (6.8a)] of the exponential relaxation time as $c_0 \to 0$. This argument is clearly invalid for concentration perturbations above the equilibrium concentration, and a relaxation time uniform in initial conditions is not surprising. What is (perhaps) surprising is that the mechanism described above exerts its influence at a specific critical initial concentration, $c_0 = c_s/2$, well below c_s.

7. RATE EQUATIONS AND IPDFs

We now investigate the existence and the usefulness of rate equations in describing diffusion-limited nonequilibrium processes.[15–17] On the hydrodynamic level our system is usually described by a diffusion-reaction equation of the form

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2} - k_1 c(x, t)^2 + k_2 c(x, t) + R \tag{7.1}$$

where $c(x, t)$ is the local concentration of particles, and k_1 and k_2 denote, respectively, the forward- and back-reaction rate constants. This level of description results, for example, from a cluster expansion, i.e., an expansion in increasing orders of the strength of the interaction.[24] Such an expansion takes the form of a hierarchy of kinetic equations for the multiple-point correlation functions which may be truncated if the correlations between particle positions is small. This is the case for an equilibrium system with no interparticle forces and reversible reactions (where the equilibrium state is a state of maximum entropy), and for a nonequilibrium system if the reaction probability for colliding particles is small. The correlations are also small for some systems during the transient regime following a special initial condition with small or no correlations.[24]

The general conditions under which such a truncation is justified are not known quantitatively, but it is clear from the preceding sections that there are generally strong particle–particle correlations away from equilibrium in diffusion-limited systems. Hence, it is not surprising that the usual diffusion-reaction equation—or its spatially homogeneous "mean-

field" rate equation—breaks down. What is not clear *a priori* is whether such a mean-field description is valid close to the equilibrium state of the purely reversible reaction $A + A \leftrightarrow A$, where correlations are small, but interactions are strong, or whether some other "effective" rate equation holds far from equilibrium.

Let us analyze the predictions of the usual hydrodynamic description, Eq. (7.1). Consider first the simplest case of the irreversible coagulation process ($k_2 = 0$) with no input ($R = 0$) as in Section 4. Then Eq. (7.1) reduces to

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2} - k_1 c^2(x, t) \tag{7.2}$$

For a spatially homogeneous system on the macroscopic scale, $c(x, t) = c(t)$, so Eq. (7.2) becomes an ordinary differential equation. The predicted decay of concentration is then $c(t) \sim 1/k_1 t$, in contradiction to the true ($t^{-1/2}$) decay, as shown in Section 4. Neglect of the microscopic spatial variations in this case leads to a breakdown of the usual hydrodynamic equation. One possibility is that by taking some spatial inhomogeneities into account, as is done by allowing a variation of the density c with space, the anomalous kinetics of the diffusion-limited process could be predicted. This kind of calculation does give the correct behavior of the diffusion-limited two-species annihilation process $A + B \to inert$. *Macroscopic* segregation occurs for the two-species annihilation process, and the hydrodynamic equation is apparently able to account for the effect of *long-range* spatial inhomogeneities on the reaction rate. This is not the case for the single-species reaction, where the nonequilibrium spatial structure remains on a microscopic level. To see the failure of Eq. (7.2), suppose the system is enclosed within a volume L. Define a spatial-average global concentration by

$$c(t) = L^{-1} \int_0^L dx\, c(x, t) \tag{7.3}$$

Performing this spatial average on Eq. (7.2), we obtain

$$\frac{dc(t)}{dt} = -k_1 L^{-1} \int_0^L dx\, c^2(x, t) \leqslant -k_1 \left\{ L^{-1} \int_0^L dx\, c(x, t) \right\}^2 = -k_1 c^2(t) \tag{7.4}$$

where the diffusion term vanishes assuming zero flux at the boundaries, and we have used the Cauchy–Schwartz inequality. It follows that the mean-field decay, $c(t) \sim 1/k_1 t$, is an *upper bound* on the decay of the

spatially averaged concentration as given by the nonlinear partial differential equation (7.2). This is, however, in clear contradiction with the exact solution, which is *slower* than $1/t$. The attempt to separate the effect of diffusion from that of reaction, as in done in diffusion-reaction rate equations, leads to wrong results.

Some researchers have proposed effective reaction terms in classical-like rate equations to describe diffusion-limited reactions. The effective reaction term is supposed to account for the effects of the diffusion mechanism, the spatial inhomogeneities and correlations, and the reaction combined. For example, it has been suggested that for the irreversible diffusion-limited coagulation process in one dimension, the reaction term is proportional to the cube of the concentration.[12,22] This is in agreement with the exact results in Section 4. Indeed, the long-time behavior, $c(t) \to (2\pi Dt)^{-1/2}$, is consistent with the rate equation

$$\frac{dc(t)}{dt} = -\pi D c(t)^3 \qquad \text{as} \quad t \to \infty \tag{7.5}$$

Moreover, if the gaps between nearest particles are initially distributed according to the scaling distribution $p^{sc}(x, 0) = (\pi/2)c_0^2 x \exp[-(\pi/2)c_0^2 x^2/2]$, Eq. (7.5) is exact for *all* times, since it yields $c(t) = c_0/(1+\pi c_0^2 Dt)^{1/2}$, i.e., the exact result for this IPDF in Eq. (4.11). If the initial IPDF is other then p^{sc}, Eq. (7.5) is valid only in the long-time asymptotic limit. Thus, there *can* be an autonomous polynomial rate equation for the irreversible coagulation process in one dimension, valid for *all* times, but its existence depends on the *microscopic* initial conditions.

Consider now the irreversible coagulation process with input (Section 5). As discussed above, in the absence of input ($R=0$) the concentration (eventually) obeys $dc/dt = -\pi Dc^3$. On the other hand, if the diffusion is turned off ($D=0$), the concentration obeys $dc/dt = R$. It is sensible to hypothesize an effective autonomous polynomial rate equation for the combined process, as the combination of the reaction and diffusion separately, of the form $dc/dt = -\pi Dc^3 + R$. However, this is incompatible with the correct stationary concentration given in Eq. (5.1). (Notice, though, that it predicts the correct—and nonclassical—scaling of c_s with D and R.)

Near the nonempty stationary states an approximate rate equation can be derived on the basis of the exact concentration and the relaxation spectrum (see the end of Section 5). The asymptotic approach to a nonempty stationary state is given by $c(t) = c_s + \delta c\, e^{-\lambda_1 t}$, with $c_s = [|\mathrm{Ai}'(0)|/\mathrm{Ai}(0)](R/2D)^{1/3}$, and $\lambda_1 = |a_1|(2DR^2)^{1/3}$. Hence, the simplest

autonomous, first-order equation which correctly captures *both* the nontrivial concentration and its relaxation is

$$\frac{dc(t)}{dt} = -\alpha D c^3 + \beta R \tag{7.6a}$$

where

$$\alpha = \frac{2|a_1|\ \mathrm{Ai}(0)^2}{3\ \mathrm{Ai}'(0)^2}, \qquad \beta = \frac{|a_1| \cdot |\mathrm{Ai}'(0)|}{3\ \mathrm{Ai}(0)} \tag{7.6b}$$

The difference in the reaction kinetics in the presence of *both* diffusion-reaction and input can be traced to the spatial structure of the nonequilibrium states. The IPDFs, different for the reaction with or without input, determine the rate at with particles interact; hence, it is not surprising that the reactions proceed at different rates with different microscopic configurations even if the macroscopic concentrations coincide.

We may combine our knowledge of the system's behavior in the limits $D/R \to 0$ and ∞, as well as the stationary case, to construct the necessary form of a rate equation for this process reproducing all the correct dynamics. Any such first-order equation must be of the form

$$dc(t)/dt = (-\alpha D c^3 + \beta R)\, F(c/c_s) \tag{7.7a}$$

where $c_s = c_s(R, D)$, the exact stationary concentration given in Eq. (5.1), and the "scaling" function $F(z)$ satisfies

$$F(0) = \frac{1}{\beta}, \qquad F(1) = 1, \qquad F(\infty) = \frac{\pi}{\alpha} \tag{7.7b}$$

The claim is that this *nonpolynomial* rate equation [no polynomial satisfies Eq. (7.7b)] describes the time-dependent concentration after initial transients have died away. Perhaps such a rate equation is valid even for some restricted class of time-dependent problems; for example, if R was modulated periodically. (We will return to this question in the discussion in Section 9.)

Most importantly, our exact results also show that *no* autonomous first-order rate equation can possibly describe the dynamics for *arbitrarily fast* input rate changes in the one-dimensional single-species coagulation process. Here is a counterexample: Consider an experiment in which $R = 0$ from some large, negative time until $t = 0$, so that the interparticle distances are distributed according to Eq. (4.12) with $c_0 = c(0) \neq 0$. At time $t = 0$, R is suddenly switched to the value R^* so that the stationary concentration for input rate R^* is exactly $c(0)$, i.e., $c_s(R^*, D) = c(0)$. If the concentration

obeyed a first-order equation, then $c(t) = c(0)$ for all $t \geqslant 0$. However, dc/dt at $t = 0^+$ is easily evaluated from Eqs. (3.1) and (2.9) (with $v = 0$), and it is nonvanishing. In fact, the concentration *increases* past $t = 0$ before relaxing back to $c(0)$ as $t \to \infty$. Thus, in general, at least a *second-order* macroscopic rate equation is required, depending also on dR/dt.

For the completely reversible process $A + A \leftrightarrow A$ (i.e., $R = 0$) we cannot construct a rate equation *of any finite order*. The typical decay to equilibrium, as given in Eq. (6.8c), is *not* purely exponential or purely algebraic as would be predicted by any finite-dimensional dynamical system description of the process, *even arbitrarily close to equilibrium*. Moreover, the purely exponential approach to equilibrium in Eq. (6.8a) depends on the initial condition. This behavior can obviously never be accounted for by a finite system of ordinary equations with coefficients independent of the initial conditions. Below the transition point, $c_0 < c_s/2$, where the *initial* state is far enough from equilibrium, spatial correlations among the particle positions persist forever.

8. OTHER REACTIONS

In this section we discuss some reactions which are closely related to the single-species coagulation process. The single-species *annihilation* process

$$A + A \to \textit{inert} \tag{8.1}$$

is similar to the coagulation process except that when particles react they annihilate (or combine to yield an inert species irrelevant to the kinetics of the process, as in the irreversible reaction $A + A \to B$). Another related reaction is the *aggregation* process,

$$A_i + A_j \to A_{i+j} \qquad (i, j = 1, 2, 3, \ldots) \tag{8.2}$$

in which a cluster of i particles aggregates to a cluster of j particles, resulting in a larger cluster of $i + j$ particles. It is assumed that all clusters diffuse with the same diffusion coefficient D, and clusters are treated as point particles, independent of the cluster size. While there exist exact results for the macroscopic concentration of particles for both models,[15,19,20,25–27] there are only partial, nonrigorous results concerning the microscopic ordering of particles. We discuss these models for the sake of completeness. We first consider the totally irreversible versions of these reactions, without any input of any kind.

The aggregation process is an abstract generalization of coagulation and annihilation, containing both processes, as noted by Spouge.[20]

Indeed, if one focuses on the reaction between clusters, disregarding their size, the process degenerates to the one-species *coagulation* process. For example, the concentration of A particles in the coagulation process is given by

$$c^{\text{coag}}(t) = \sum_{i=1}^{\infty} c_i(t) \tag{8.3}$$

where $c_i(t)$ is the concentration of i-clusters in the aggregation process. If, on the other hand, one focuses only on clusters with an *odd* number of particles, disregarding the *even* clusters, the result is a one-species *annihilation* process, because the aggregation of odd clusters to each other converts them into even clusters, while aggregation of even clusters to *any* other clusters leaves the number of odd clusters unchanged:

$$A_{\text{odd}} + A_{\text{odd}} \to A_{\text{even}}; \qquad A_{\text{odd}} + A_{\text{even}} \to A_{\text{odd}}; \qquad A_{\text{even}} + A_{\text{even}} \to A_{\text{even}} \tag{8.4}$$

The concentration of A particles in the annihilation process is the sum of the concentrations of odd clusters alone:

$$c^{\text{ann}}(t) = \sum_{j=0}^{\infty} c_{2j+1}(t) \tag{8.5}$$

The IPDF for the annihilation process is given by the distribution of gaps between adjacent odd clusters (ignoring all even clusters that may occur in between).

The analogy between the aggregation, coagulation, and annihilation processes can be exploited to draw conclusions from one process and apply them to another. Consider, for example, the distribution of i-clusters as a function of i in the aggregation model. This can be linked to the IPDF of the coagulation model as follows. Suppose that at time $t=0$ we start the aggregation process, with initially only one-particle "clusters" (monomers). Denote the initial locations of these monomers by $x_k(0)$, i.e., particle number k is initially at $x_k(0)$ (see Fig. 12a). After the system has evolved for some long time t, we find an i_1-cluster at $x_{i1}(t)$, followed by an i_2 cluster at $x_{i2}(t)$, etc... (Fig. 12b). This situation means that particles 2,..., i_1 have all aggregated to particle 1 by time t, and in the meanwhile particle 1, now an i_1-cluster, has changed its location from $x_1(0)$ to $x_{i1}(t)$. Likewise, particles i_1+2, i_1+3,..., i_1+i_2 have all aggregated to particle i_1+1 and the resulting i_2-cluster is now at $x_{i2}(t)$, etc. But, on the average, $x_{ij}(t) = x_{ij}(0)$, because the i_jth particle has merely performed a symmetric random walk during this time. Let the average distance between particles, when the process

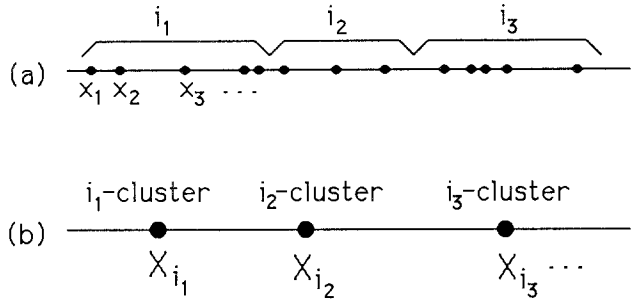

Fig. 12. Relation between interparticle distances and the distribution of k-clusters in the coagulation model. (a) The system at some initial state. (b) The clustering of particles at some later time. The distance between the clusters is roughly proportional to their masses.

started, be $1/c_0$. It follows that, at time t, the distance between a k-cluster and its nearest neighbor cluster is $x = k/c_0$, on the average. Thus, $p(x)\,dx$, the distribution of gaps x between nearest particles (the IPDF) in the coagulation process, is related to $q(k)\,dk$, the distribution of clusters of size k in the aggregation process. In fact,

$$q(k) = \frac{1}{c_0} p\left(\frac{k}{c_0}\right) = \frac{k}{4Dc_0^2 t} \exp\left(\frac{-k^2}{8Dc_0^2 t}\right) \quad \text{as} \quad t \to \infty \tag{8.6}$$

where we have made use of Eq. (4.7). We may also use Eq. (4.8) to obtain a dynamic scaling distribution for the cluster sizes,

$$q\left(\frac{k}{k^*}\right) = \frac{\pi}{2} \frac{k}{k^*} \exp\left[-\frac{\pi}{2} \frac{(k/k^*)^2}{2}\right] \quad \text{as} \quad t \to \infty \tag{8.7}$$

where $k^* \sim c_0(2\pi Dt)^{1/2}$ is the long-time asymptotic average cluster size.

Another interesting conclusion is that for the annihilation process the asymptotic long-time concentration of particles is exactly half that of the coagulation process: $c^{\text{ann}}(t) = (1/2)c^{\text{coag}}(t)$ as $t \to \infty$. This follows from Eqs. (8.3) and (8.5) and the fact that the distribution of cluster sizes is smooth and vanishes fast enough (faster than algebraically) as $k \to \infty$, Eq. (8.6). In fact, the concentration of particles for the annihilation model can be exactly solved[19,26–28] and the above observation is confirmed by the exact solution.

A slight modification of the aggregation model allows us to discuss both coagulation and annihilation with *input*. Consider the aggregation model with a random input of monomers at a rate R (concentration per unit time). Again, focusing on either all clusters, or just the odd-sized ones, we can select between the two cases of annihilation and coagulation. On

the other hand, the back-reaction process $A \to A + A$ has no obvious analog in the annihilation model and we shall not discuss it here. The stationary concentration for annihilation with input has been obtained exactly.[28] One would be tempted to guess that, similar to the processes without input, $c_s^{\text{ann}} = (1/2)c_s^{\text{coag}}$. This is *not* the case. The exact result is $c_s^{\text{ann}} = 2^{-2/3}c_s^{\text{coag}}$. This can be traced to the fact that for annihilation with input, $q(k)$ falls off only algebraically (with a cutoff) as $k^{-4/3}$ for large k.[21]

No exact results exist for the stationary IPDF of the annihilation process. The asymptotic $x \to \infty$ limit has been studied. It is has been proved that $p(x) \sim e^{-x}$ [rather than as $\exp(-x^{3/2})$] as in the coagulation process).[19] This can be understood by the following heuristic argument.[6] The IPDF of the annihilation process is given by the distribution of gaps between nearest *odd* clusters in the aggregation process. Between two nearest odd clusters any number of even clusters can occur. Assuming that there is little (i.e., short-range) correlation between the parity of subsequent clusters, the probability of having n even clusters in between two nearest odd clusters is a power of e^{-n}. Assigning a typical length to the distance between clusters, one arrives at the conclusion $p(x) \sim e^{-x}$.

A final point of interest concerning the annihilation process with input is the existence of rate equations for the macroscopic concentration in the vein of the discussion in Section 7. Recall that the stationary concentration of the annihilation process with input is related to that of the coagulation process with input by $c_s^{\text{ann}} = 2^{-2/3}c_s^{\text{coag}}$. Similarly, the exact solution shows that the approach to stationarity is exponential with rate

$$\lambda_1^{\text{ann}} = 2^{2/3}|a_1|(2DR^2)^{1/3} = 2^{2/3}\lambda_1^{\text{coag}}$$

Thus, by the same arguments as in Section 7, a first-order rate equation must be of the form

$$\frac{dc^{\text{ann}}}{dt} = [-\alpha D(2^{2/3}c^{\text{ann}})^3 + \beta R]G\left(\frac{2^{2/3}c^{\text{ann}}}{c_s^{\text{coag}}}\right) \tag{8.8}$$

where the dimensionless constants α and β are the *same* as in Section 7, and the scaling function $G(z)$ satisfies the *same* constraints as $F(z)$ of Section 7, i.e., $G(z) = F(z)$ for $z = 0, 1$, and ∞. This result suggests the interesting possibility that if they exist in some sense, then $G(z) = F(z)$ for *all* z.

We have studied the annihilation process with and without input, numerically. Our data are in agreement with the results of this section. Of

[6] We thank F. Leyvraz for pointing this out to us.

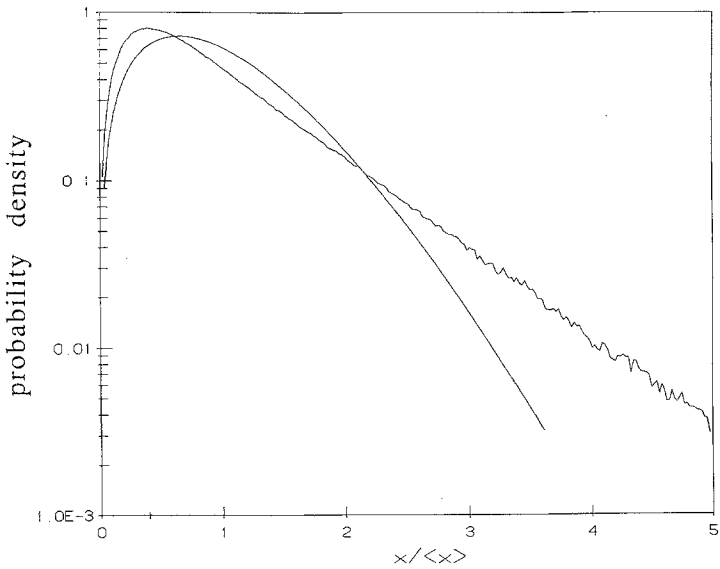

Fig. 13. The logarithm of the IPDF for the annihilation model with input is plotted against the reduced distance $x/\langle x \rangle$. The exponential decay of the tail of the IPDF is evident from this plot. This is contrasted with the $\exp(-x^{3/2})$ decay of the tail for the coagulation model with input.

most interest are the IPDFs for which complete exact results do not exist. Our Monte Carlo data for the annihilation process with input are compared to the analytic IPDF of the coagulation process in Fig. 13. The data for the annihilation process with input show the asymptotic exponential tail discussed above.

9. SUMMARY AND DISCUSSION

To summarize, the diffusion-reaction system studied in this paper provides an exactly soluble example of a nontrivial interacting-particle model. The model yields the macroscopic particle density and its kinetics in a variety of nonequilibrium situations with a remarkably simple and straightforward analysis. The failure of naive mean-field theory, i.e., the law of mass action, is clearly displayed in these diffusion-limited reactions. The role of microscopic correlations in the reactant positions in determining the system kinetics—an example of nonequilibrium self-ordering—is explicitly illustrated.

Apart from quantitative disagreement with the law of mass action, the reversible coagulation process $A + A \leftrightarrow A$ exhibits a sharp, second-order-

like "phase" transition in its relaxation dynamics. To the best of our knowledge, this is the first discovery of such a transition in the dynamics of an interacting-particle system. The transition depends explicitly on long-lived microscopic fluctuations, or spatial correlations, and is a striking example of the failure of any kind of macroscopic rate equation description of the dynamics.

Several natural questions come to mind concerning the results of these investigations. First of all, our restriction to one spatial dimension certainly limits the applicability of the model, and it is approporiate to ask wether our analysis, or any of our results, can be extended to higher dimensions. The simplicity of our solution of this model stems from its formulation in terms of the probability $E(x, t)$ of finding an interval of length x void of particles. This is in distinction to the usual formulation of diffusion-reaction systems on a microscopic level in terms of a hierarchy of evolution equations for, say, the joint probability distributions of the particle positions. Although straightforward generalizations of $E(x, t)$ can be formulated in higher spatial dimensions, e.g., the probability of finding a d-dimensional box or sphere empty, we cannot construct a *closed* equation for its evolution. The problem is that particles outside an empty region can have correlations in their positions along the boundary in higher dimensions. As has been discovered throughout the history of statistical mechanics, the simple topology of one spatial dimension allows for great simplifications in the solution of certain problems.

Any attempt to formulate other reaction process in terms of $E(x, t)$, even in one dimension, faces similar closure problems. The single-species annihilation process $A + A \to inert$ and the two-species annihilation process $A + B \to inert$ fall into this category. In both cases $E(x, t)$ does not satisfy a closed kinetic equation. This can be seen by simply noting that with annihilation processes occurring, occupied intervals can become empty due to reactions taking place *inside* the interval, and not just due to processes occurring at its endpoints. Even the natural extension of the coagulation process allowing for the spontaneous disappearance of particles (equivalent to the back reaction of the input process) suffers from this closure problem. Nonetheless, our solution of the coagulation process—including information on the spatial correlations away from equilibrium—is of interest in its own right, and will prove useful in investigations of other more general problems.

Consider, for example, Monte Carlo simulations for diffusion-limited reactions. Computer simulations are an important tool in the study of diffusion-reaction systems, and it is of unquestionably great value to have a simple, yet nontrivial benchmark to check the quality of such numerical experiments. In more analytical investigations, chemical reaction processes

are often studied via truncation of a hierarchy of multiple-point distribution functions. Such truncations can take the form of an expansion in some small parameter, or they can be accomplished by some more intuitive closure schemes. The advantage of a systematic expansion is that, at least qualitatively, the region of validity of the approximation can be determined. On the other hand, unsystematic mean-field-like truncations can prove themselves remarkably good *a posteriori*. One valuable use of an exact solution, like the one provided in this study, is to serve as a check on the quality of such approximations. We refer the reader to a recent application of our solution to just this question.[29] In another direction, the exact solution in the diffusion-limited case contrasts nicely with the solution of the *reaction-limited* case, where the law of mass action, and low-order corrections to this limit, is recovered.[30] Having control of the process in two opposing limits with very different static and dynamic behavior in the two extremes calls for an investigation of the nature of the crossover regime.

An open problem that remains for the reversible coagulation process is the question of the existence of the transition in its relaxation dynamics in higher spatial dimensions, or if the strict diffusion-controlled limit is relaxed. As noted above, our exact solution does not have anything to say about this question. It seems reasonable, however, to guess that the mechanism for the transition is valid in higher-dimensional spaces and for low concentrations slightly away from the diffusion-limited extreme; the reversible coagulation process should still be sensitive to the existence of large, empty regions, as there is no other agency for the equilibration of these voids other than diffusion in from the edges. The questions are these: What is the upper critical dimension d_c for the kinetic transition? If $d_c < \infty$, how do the critical exponents vary with dimension? Does the usual law of mass action take over in high enough dimension, even for initial conditions *very far* from equilibrium? How far away from the diffusion-limited regime does the transition survive?

An interesting point about the model studied in this paper, which we have not previously mentioned, is that the problem can be solved just as easily in a finite volume as in infinite volume. All we need to do is retain translation invariance by imposing periodic boundary conditions. Then the kinetic equation for $E(x, t)$ in Eq. (2.8) [or Eq. (2.7) on a lattice] remains valid, as does as the boundary condition $E(0, t) = 1$. The only change is that, for the system on a line of length L, the other boundary condition becomes $E(L, t) = 0$ as long as at least one particle is present. The study of finite-system-size effects are most interesting in relation to the transition in the purely reversible process. Not unexpectedly, restriction to finite volume destroys the transition in a strict sense because the relaxation spectrum

develops a gap which depends on the volume. The gap in the spectrum does not, however, vanish continuously as $L \to \infty$. Rather, the gap is always bounded from below by $v^2/8D$ for any $L < \infty$, similar to the situation noted in Section 6 in our discussion of the spectrum perturbed by a constant input of particles. The system in infinite volume is a surprisingly singular limit of the finite-volume problem. In distinction to the conventional wisdom concerning 1D finite-volume effects from transfer matrix studies, we find the emergence of an *unbounded* characteristic finite-size time scale near the location of the infinite-volume transition. We refer the interested reader to a recent paper discussing this phenomenon in detail.[31]

Several other aspects of the reaction with input deserve some more comment. In Section 7 we mentioned the possibility, albeit heuristically, of a finite-dimensional dynamical system description of the macroscopic behavior of the process subject to a *time-dependent* input rate R. Chemical reactions play an important role as realizations of concepts in nonlinear dynamical systems theory, and it would be interesting to see if this single-species reaction process can be rigorously formulated as a finite set of ordinary differential equations (ODEs). Clearly it is in realilty an infinite-dimensional dynamical system described by the partial differential equation (PDE) in Eq. (2.8), even in the spatially homogeneous case. However, driven by a periodic input rate $R(t)$, say, one would expect a low-dimensional attractor to emerge in the system's phase space. Recent research[32] in dissipative PDEs has investigated this idea, mostly for the time-asymptotic behavior of autonomous systems, and perhaps these techniques can be extended to this model. Such an analysis would provide a nice example of the reduction of a nonequilibrium model from microscopic stochastic dynamics, to a PDE, to ODEs. In particular, we raise the following question: given an arbitrary input function $R(t)$ for $t \geqslant 0$, is there a finite set of ODEs for the concentration and some auxiliary dynamical variables?

Finally, the simplicity of solution of our model suggests that it may also be useful for the investigation of the effect of *external noise* on a diffusion-reaction system.[33] The linearity of Eq. (2.8) holds promise that the system might even be solved for a *stochastic* macroscopic input, where $R(t)$ is a random process. The question of the influence of external noise in spatially distributed nonlinear systems is a topic of current interest (see, e.g., ref. 34), and this model may serve to illuminate some phenomena that are lost with the neglect of spatial degrees of freedom.

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