Diffusion-Limited Coagulation in the Presence of Particle Input: Exact Results in One Dimension

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We solve the diffusion-limited single-species coagulation process $(A+A\rightarrow A)$ with random particle input in one spatial dimension. We derive the exact time-dependent concentration, the spectrum of relaxation rates, and the distribution of interparticle distances in the nonequilibrium steady state. These results imply an interesting microscopic spatial structure induced by the nonequilibrium constraints. The validity of rate-equation descriptions of the macroscopic statics and kinetics is investigated, and we compare our results to the closely related single-species annihilation process $(A+A\rightarrow \text{inert})$ in the presence of input.

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The role of fluctuations in irreversible diffusion-reaction processes has attracted much attention in recent years.[1-4] "Diffusion-limited" reactions take place on a time scale much shorter than the typical time between reactant encounters. Spatial fluctuations in diffusion-limited reactions can dominate the kinetics of these processes, invalidating the standard "mean-field" rate-equation approach to the macroscopic dynamics.[5-9] In the presence of uniform particle input, where one expects a stationary state to be achieved, some processes display spontaneous spatial inhomogeneities,[10,11] or even no steady state at all.[12] In this Letter we study what is perhaps the simplest model of a diffusion-limited reaction, the one-dimensional single-species coagulation process, in the presence of particle sources.[13-16] We derive the exact time-dependent concentration and the steady-state distribution of distances between adjacent particles. These are the first analytic results for the microscopic spatial structure of such a nonequilibrium stationary state.

The diffusion-limited single-species coagulation process, $A+A\rightarrow A$, is a collection of particles executing independent Brownian motions suffering a "fusion" interaction when two particles meet (so this process is the same as the irreversible chemical reaction scheme $A+A\rightarrow A+B$, $B\rightarrow$ inert). In one spatial dimension we may consider point particles, and in the *absence* of sources the exact time-dependent concentration of A-species particles, $C(t)$, has been previously derived.[13-15] The concentration does not obey the usual mean-field rate equation $dC/dt=-kC^2$ (for a review, see Ref. 17). Rather, at late times it obeys the rate equation $dC/dt=-\pi DC^3$, where D is the diffusion coefficient. In fact, this asymptotic rate equation is valid for all times if and only if the initial distribution of particles on the line has a probability density of interparticle distances x given by

$$p_0(x)=(\pi/2)C_0^2x\exp\{-(\pi/2)C_0^2x^2/2\}\,, \qquad (1)$$

where C_0 is the initial concentration. This result, and a previous study of the relation between interparticle distribution functions (IPDF's) and rate equations, appears in Ref. 15.

To study the process in the presence of particle input, we assume that the diffusion-reaction process described above is taking place with particles appearing randomly at rate R particles per unit time, per unit length. (Thus, if the reaction or diffusion were "turned off" the concentration would obey $dC/dt=R$.) The key to the exact solution is the fact that the problem can be reduced to a soluble one body-problem[13-15] for the evolution of the probability distribution of the interval between adjacent particles, i.e., the IPDF. To formulate the evolution equation for the IPDF it is convenient to consider a derived quantity—the time-dependent probability of finding that an arbitrary interval of given length is void of particles.[18]

Let $p(x,t)$ be the time-dependent IPDF so that $p(x'',t)dx''$ is the probability that the nearest neighbor (on one side) to a randomly chosen *particle* lies at a distance between x'' and $x''+dx''$. Choose a *point* at random and consider this point to be an end of a randomly located interval of length x. Then the probability that this point falls in an interparticle gap whose length is between x'' and $x''+dx''$ is

$$x''p(x'',t)dx''\Big/\int_0^\infty yp(y,t)dy=C(t)x''p(x'',t)dx''\,, \qquad (2)$$

where we use the fact that the concentration $C(t)$ is the inverse of the average distance between adjacent particles. If this randomly chosen point falls in a gap of length x'', then the probability that the next particle on one side lies at a distance between x' and $x'+dx'$ from the point is the uniform distribution in the interval of length x'', i.e., $\theta(x''-x')dx'/x''$. Thus, the probability that the nearest particle (on one side) to a randomly chosen point lies at a distance between x' and $x'+dx'$ is

$$\int_0^\infty \{C(t)x''p(x'',t)dx''\}\{\theta(x''-x')dx'/x''\}=\left\{\int_{x'}^\infty C(t)p(x'',t)dx''\right\}dx'\,. \qquad (3)$$

Finally, the probability $E(x,t)$, that an interval of length x is *empty*, is the probability that the nearest particle (on one side) to the randomly chosen point lies at a distance *greater* than x. Thus,

$$E(x,t)=\int_{x}^{\infty}\left\{\int_{x'}^{\infty}C(t)p(x'',t)\,dx''\right\}dx'. \tag{4}$$

Knowledge of $E(x,t)$ allows for an easy recovery of both the time-dependent concentration and the IPDF:

$$C(t)=-\partial E(x,t)/\partial x\,|_{x=0}, \tag{5}$$

$$p(x,t)=C(t)^{-1}\partial^2 E(x,t)/\partial x^2. \tag{6}$$

To derive an evolution equation for $E(x,t)$ we consider the possible processes which contribute to its time evolution. The probability will *increase* in a small time interval Δt only if an interval of length x contains just one particle, located at an end point of the interval, and this particle diffuses *out* of the interval. Using Eq. (3), this contribution to the change in probability is

$$\Delta E_1=2(D\Delta t/\Delta x^2)\{-\partial E(x,t)/\partial x\}\Delta x. \tag{7}$$

The factor of 2 above results from the fact that this process can occur at either of the two ends of the interval. The probability will *decrease* due to two processes. First, a particle just *outside* the interval can diffuse into the interval (at either end):

$$\Delta E_2=2(D\Delta t/\Delta x^2)\{\partial E(x+\Delta x,t)/\partial x\}\Delta x. \tag{8}$$

Second, the input at rate R particles per unit length per unit time leads to the loss term

$$\Delta E_3=-Rx\Delta t E(x,t). \tag{9}$$

Combining these terms leads to the master equation

$$\partial E/\partial t=2D\,\partial^2 E/\partial x^2-RxE, \tag{10a}$$

with the boundary conditions

$$E(0,t)=1 \tag{10b}$$

(because we are considering point particles), and

$$E(\infty,t)=0 \tag{10c}$$

(for nonvanishing concentration). In the derivation above we have made no mention of the coagulation process. The reaction $A+A\rightarrow A$ is imposed by the requirement (used above) that only *one* particle may be at a single point in space.

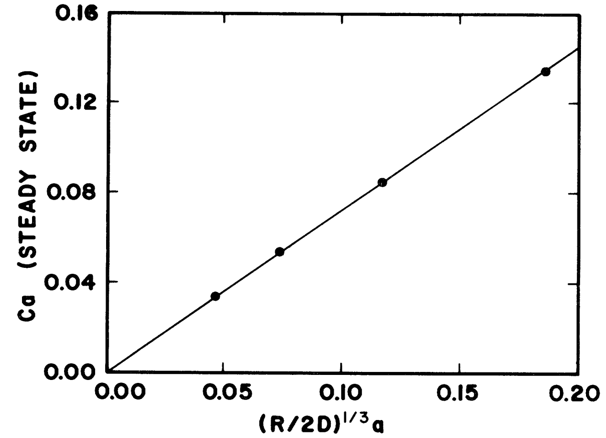

FIG. 1. Monte Carlo (points) and theoretical (line) steady-state concentration vs particle input rate. These dimensionless quantities are expressed in units of the simulation's lattice spacing a.

The general solution of Eq. (10) may be expressed as a sum of terms of the form $e^{-\lambda t}E_\lambda(x)$, with the eigenfunctions $E_\lambda(x)$ satisfying

$$-\lambda E_\lambda(x)=2D\,\partial^2 E_\lambda/\partial x^2-RxE_\lambda. \tag{11}$$

This eigenvalue problem is solved by inspection—this is just Airy's equation.[19] The properly normalized stationary ($\lambda=0$) solution is

$$E_0(x)=\mathrm{Ai}[(R/2D)^{1/3}x]/\mathrm{Ai}[0], \tag{12}$$

where Ai[z] is Airy's function,[19] satisfying $\mathrm{Ai}''[z]=z\mathrm{Ai}[z]$, and, in particular, $\mathrm{Ai}[0]=0.35502\ldots$. The rest of the spectrum is

$$\lambda_n=|a_n|(2DR^2)^{1/3},\quad n=1,2,\ldots, \tag{13}$$

with a_n the nth zero of Airy's function. For example, $-a_1=2.3381\ldots$, $-a_2=4.0879\ldots$, etc.[19] The higher eigenfunctions, now labeled by n, are

$$E_n(x)=\mathrm{Ai}[(R/2D)^{1/3}x+a_n]. \tag{14}$$

The stationary concentration $C_s(R,D)$ of the single-species coagulation process with random particle input is, from Eq. (5),

$$\begin{aligned}C_s(R,D)&=(|\mathrm{Ai}'[0]|/\mathrm{Ai}[0])(R/2D)^{1/3}\\&=(0.72901\ldots)(R/2D)^{1/3},\end{aligned} \tag{15}$$

with $\mathrm{Ai}'[0]=-0.25881\ldots$. The stationary IPDF computed from Eqs. (6) and (12) is

$$p_s(x)=(R/2D)^{1/3}\mathrm{Ai}''[(R/2D)^{1/3}x]/|\mathrm{Ai}'[0]|. \tag{16}$$

We have performed Monte Carlo simulations to confirm these results, and in Fig. 1 we show the theoretical and measured stationary (time-averaged) concentrations as a function of $(R/2D)^{1/3}$. The simulations were performed on a lattice of 10^5 sites, by the "direct" simulation method.[20] The interparticle probability density was also measured in the simulations, and the results are compared with theory [Eq. (16)] in Fig. 2. In both cases the agreement is excellent. When $R=0$ the spatial structure of the particles achieves a *dynamic-scaling* form[15] characterized by the IPDF in Eq. (1) with C_0 replaced by $C(t)$. For $D=0$ no reactions take place and

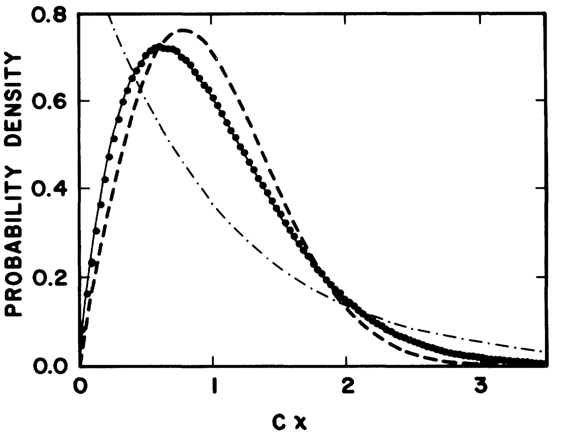

FIG. 2. Monte Carlo (points) and theoretical (solid line) steady-state IPDF, scaled by the average distance between particles. The broken line is the dynamic-scaling IPDF for $R=0$, while the dash-dotted line is the exponential IPDF for equilibrium or $D=0$.

the concentration approaches $C(t)=Rt$, while the IPDF approaches $p(x,t)=Rte^{-Rtx}$.

The IPDF's in Eqs. (1) and (16) display an interesting microscopic structure for these nonequilibrium states. In thermal equilibrium one expects the maximum-entropy distribution of particles characterized by an exponential IPDF, $p(x)=Ce^{-Cx}$. In the nonequilibrium steady state the IPDF vanishes near $x=0$ indicating an effective repulsion of particles, and the probability of large gaps between particles decays much faster than exponential (proportional to a power of $\exp\{-x^{3/2}\}$). These facts indicate a far more regular spatial arrangement of particles. The probability of large gaps decays even faster in the dynamic-scaling state (proportional to a power of $\exp\{-x^2\}$), indicating even *more* order. This simple interacting-particle model thus serves as an example of static and dynamic self-ordering in far-from-equilibrium systems.

Our results have some implications for the validity of a rate-equation description of this system's macroscopic kinetics. In the absence of input, $R=0$, the concentration (eventually) obeys $dC(t)/dt=-\pi DC^3$. On the other hand, if the diffusion is turned off, $D=0$, the concentration obeys $dC(t)/dt=R$. It is not unreasonable to hypothesize an autonomous polynomial rate equation for the combined process of the form $dC(t)/dt=-\pi DC^3+R$. However, this is incompatible with the correct stationary concentration given in Eq. (15).

Near the nonempty stationary states an approximate rate equation can be derived on the basis of the exact concentration and the relaxation spectrum Eq. (13). The asymptotic approach to a nonempty stationary state is described by $C(t)=C_s+\delta Ce^{-\lambda_1 t}$, with $\lambda_1=|a_1|\times(2DR^2)^{1/3}$. Hence, the simplest first-order equation which correctly captures *both* the nontrivial concentration and its relaxation is

$$dC(t)/dt=-\alpha DC^3+\beta R\,, \tag{17a}$$

where

$$\alpha=2|a_1|\,\mathrm{Ai}[0]^2/3\mathrm{Ai}'[0]^2\,,$$
$$\beta=|a_1|\,|\mathrm{Ai}'[0]|/3\mathrm{Ai}[0]\,. \tag{17b}$$

The difference in the reaction kinetics in the presence of *both* reaction and diffusion and/or input can be traced in part to the spatial structure of the nonequilibrium states. The IPDF's influence the rate at which particles interact, so it is not surprising that the reactions proceed at different rates in different situations 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 a rate equation for this process reproducing all the correct dynamics. Such a first-order equation must be of the form

$$dC(t)/dt=\{-\alpha DC^3+\beta R\}F(C/C_s)\,, \tag{18a}$$

where $C_s=C_s(R,D)$ is given in Eq. (15), and the "scaling" function $F(z)$ satisfies

$$F(0)=1/\beta,\quad F(1)=1,\quad F(\infty)=\pi/\alpha\,. \tag{18b}$$

The claim is that this *nonpolynomial* rate equation would describe the time-dependent concentration after initial transients have died away. This rate equation may even be valid for some time-dependent problems, for example, if R was modulated periodically.

These considerations apply as well to the single-species annihilation process $A+A\to$ inert subject to random input at rate R. We have investigated the IPDF's in this process via Monte Carlo simulations,[15,21] observing the scaling behavior without input, and a stationary IPDF with input. (The functional forms of the IPDF's are *not* the same as in the coagulation process. For example, the *steady-state* probability of large gaps decays proportional to a power of e^{-x}.) The concentration[14,22] eventually obeys $dC'/dt=-4\pi DC'^3$ for $R=0$, and Rácz[23] has found the stationary concentration and relaxation rate when $R\neq 0$. Amazingly, they are also closely related to those of the coagulation process with input:

$$C_s'=2^{-2/3}(|\mathrm{Ai}'[0]|/\mathrm{Ai}[0])(R/2D)^{1/3}=2^{-2/3}C_s$$

and $\lambda_1'=2^{2/3}|a_1|(2DR^2)^{1/3}=2^{2/3}\lambda_1$. Thus, a first-order rate equation must be of the form

$$dC'(t)/dt=\{-\alpha D(2^{2/3}C')^3+\beta R\}G((2^{2/3}C')/C_s)\,, \tag{19}$$

where $C_s(R,D)$ is given before in Eq. (15), α and β are the same as in Eq. (17b), and the scaling function $G(z)$ satisfies the *same* constraints as $F(z)$, i.e., $G(z)=F(z)$ for $z=0$, 1, and ∞. This result suggests the interesting possibility that, if they exist, $G(z)=F(z)$ for all z. Further investigation of this problem is left to a future study.

Finally, and most importantly, our exact results also show that *no* autonomous first-order rate equation can possibly exist 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 then distributed according to the IPDF in Eq. (1) [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 $t\geq 0$. However, dC/dt at $t=0^+$ may be evaluated from Eq. (10a). 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 for the concentration, depending also on dR/dt.

To summarize, we have solved the irreversible single-species diffusion-limited coagulation process $A+A\to A$, with steady input, in one spatial dimension. Our results illustrate a microscopic self-ordering in the nonequilibrium stationary state, and show that no first-order polynomial rate equation applies to the system's macroscopic behavior. We hope to generalize our analytical approach, in terms of the dynamics of empty spaces, to several other processes: the *reversible* process $A+A\rightleftharpoons A$, and the coagulation process in higher spatial dimensions.

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