Transition in the Relaxation Dynamics of a Reversible Diffusion-Limited Reaction

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The reversible one-species diffusion-limited reaction $X+X\rightleftharpoons X$ is solved exactly in one dimension. We find that the asymptotic approach to equilibrium exhibits a sharp (second-order-type) transition depending on the initial density ρ_0. The exponential relaxation time becomes infinitely long as $\rho_0 \rightarrow 0$.

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We consider the reversible one-species coagulation process $X+X\rightleftharpoons X$ in one dimension. On the hydrodynamic level such a system is commonly described by a diffusion-reaction equation for the local density, $\rho(x,t)$, of the form

$$\frac{\partial}{\partial t}\rho(x,t)=D\frac{\partial^2}{\partial x^2}\rho(x,t)-k_1\rho^2(x,t)+k_2\rho(x,t)\,. \quad (1)$$

One validating argument for this level of description depends on a cluster expansion, i.e., an expansion in increasing orders of the strength of the interaction.[1] This expansion takes the form of a hierarchy of kinetic equations for multiple-point correlation functions which can be truncated if the correlations between particle positions are small. This is the case for an equilibrium system with no interparticle forces and reversible reactions, where the equilibrium state is a state of maximal entropy, and for a nonequilibrium steady-state 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.[1]

The general conditions under which this truncation is justified are not known quantitatively. In particular, it is not clear whether the truncation can be used for a system that is close to its equilibrium state so that the correlations are small, but where the interactions are strong. This case occurs in reversible diffusion-limited reactions, where the interaction between colliding particles is so strong that they react immediately.[2,3] Although there are now several exact results[4-9] for the microscopic dynamics of some diffusion-limited reaction models, none of these applies to this question, mostly because they include irreversible reactions.[10] Such systems approach either an equilibrium state with zero density, or a nonequilibrium steady state with strong correlations.[9]

This Letter presents the first exact results for a *reversible* diffusion-limited system in continuous space which achieves a true equilibrium state with detailed balance, a nonzero density, and no correlations between particle positions. We study the relaxation dynamics by considering the time-dependent density starting from an initial state with no correlations between particle positions, but with arbitrary density. Our exact solution shows that the system does not obey any hydrodynamic equation, but that its asymptotic dynamics at long times [Eq. (15)] generally depends upon the initial conditions. In particular, if the initial density is less than exactly half of the equilibrium density, then the asymptotic dynamics is dominated by large gaps between particles, corresponding to large correlations between many particle positions.[11] These large correlations develop even if all particle positions are initially uncorrelated.

We now proceed to the analysis. Starting with a spatially discrete system we first explain the equilibrium distribution for the general process. We then focus on the diffusion-limited regime to derive the kinetic equation, and take the continuum limit to obtain the solution.

The kinetic behavior of the system $X+X\rightleftharpoons X$ is characterized by three simultaneous processes. (1) The particles perform random walks with jump rate $2Dl^{-2}$ on a lattice with lattice constant l. This appears macroscopically as diffusion with diffusion coefficient D. (2) Every particle can generate another one at the same site with a probability rate b. In the mean-field approximation b would be identified with the rate constant of the reaction $X\rightarrow X+X$. (3) When the number of particles N at a site exceeds one, there is a probability rate $al^{-1}N(N-1)$ that two of them react and merge into a single particle. In the mean-field approximation a would be identified with the rate constant for the reaction $X+X\rightarrow X$.

In equilibrium this system is simultaneously in equilibrium with respect to both the reaction and the diffusion processes. Equilibrium with respect to reaction means that the probability distribution P_N of occupation numbers N at any particular site is a superposition of the two equilibrium states with respect to the reaction process: the *vacant* state $P_N^{\text{vac}}=\delta_{N,0}$ and the *occupied* state

$$P_N^{\text{occ}}=(1-\delta_{N,0})\left[\exp\left(\frac{bl}{a}\right)-1\right]^{-1}\frac{1}{N!}\left(\frac{bl}{a}\right)^N .$$

(These equilibrium distributions are the stationary solutions of the single-site master equation in number space.) The relative weight of these two states in the equilibrium distribution of the spatially distributed system is determined by the condition that there is also equilibrium with respect to the different process, because the transition between *occupied* and *vacant* states occur by diffusive jumps of particles to and from the adjacent sites. Equilibrium with respect to diffusion means that the system is statistically homogeneous and there are no correlations between occupancies of different sites. In particular, the rate at which occupied sites are vacated (hop rate times P_1^{eq}) equals the rate at which vacant sites become occupied:

$$2Dl^2 P_1^{\mathrm{eq}} = 2Dl^2 P_0^{\mathrm{eq}} \sum_{N=1}^{\infty} N P_N^{\mathrm{eq}} . \tag{2}$$

The right-hand term above is composed of the probability that the site is empty (P_0^{eq}), times the hop rate into the empty site of any of the N particles in the two neighboring sites ($2Dl^2 N P_N^{\mathrm{eq}}$), summed over N. This defines the equilibrium distribution uniquely as a Poisson distribution with the average value bl/a:

$$P_N^{\mathrm{eq}} = e^{-\rho_{\mathrm{eq}} l} \frac{1}{N!} (\rho_{\mathrm{eq}} l)^N , \tag{3}$$

where $\rho_{\mathrm{eq}} \equiv b/a$ is the equilibrium density.

The diffusion-limited regime is $D\rho_{\mathrm{eq}}^2 \ll b$. Then the interaction between particles at the same site is so strong that any two particles at different sites have zero probability of exchanging their positions without reacting. That is, the partial equilibrium with respect to the reaction processes at each site is reached instantaneously. Formally, the diffusion-controlled limit is $a \to \infty$, $b \to \infty$, keeping $\rho_{\mathrm{eq}} \equiv b/a = \mathrm{const}$.

Our method of solution for the dynamic problem takes advantage of the fact that in the diffusion-limited regime the change in the distribution of *intervals between occupied sites* does not depend upon any correlations between adjacent intervals. The time-dependent probability $E_n(t)$ of finding n adjacent sites *empty* obeys a closed kinetic equation. We have derived this kinetic equation from the N-body level of description,[11] but it also follows directly from the following reasoning.

The probability of finding sites $1, \dots, n$ empty, $E_n(t)$, changes in time because of the following gain and loss rates: (1) Sites $1, \dots, n-1$ may be empty, site n singly occupied,[12] and the particle at site n may jump to the site $n+1$, increasing E_n at a rate

$$[E_{n-1}(t) - E_n(t)] \frac{\rho_{\mathrm{eq}} l e^{-\rho_{\mathrm{eq}} l}}{1 - e^{-\rho_{\mathrm{eq}} l}} D l^{-2} . \tag{4}$$

In this expression the first factor is the probability of finding sites $1, \dots, n-1$, but not *all* sites $1, \dots, n$, empty. The second factor is the probability that site n is singly occupied given that it is not empty, and the third factor is the jump rate from site n to $n+1$. (2) Sites $1, \dots, n$ may be empty, and site $n+1$ occupied by exactly m particles, any one of which may jump to site n, decreasing E_n at a rate

$$-[E_n(t) - E_{n+1}(t)] \frac{(1/m!)(\rho_{\mathrm{eq}} l)^m e^{-\rho_{\mathrm{eq}} l}}{1 - e^{-\rho_{\mathrm{eq}} l}} m D l^{-2} . \tag{5}$$

The first factor above is the probability of finding sites $1, \dots, n$ but not *all* sites $1, \dots, n+1$, empty. The second factor is the probability that site n is occupied by exactly m particles given that it is not vacant, the factor m counting the particles that can jump. The factor Dl^{-2} is the jump rate from site $n+1$ to site n. The sum of these rates over all $m > 0$ is

$$-[E_n(t) - E_{n+1}(t)] \frac{\rho_{\mathrm{eq}} l}{1 - e^{-\rho_{\mathrm{eq}} l}} D l^{-2} . \tag{6}$$

Each of the above rates is doubled because the same contributions arise from corresponding independent processes at the other end of the empty stretch $1, \dots, n$.

The resulting master equation is

$$\frac{\partial E_n(t)}{\partial t} = 2Dl^{-2} \frac{\rho_{\mathrm{eq}} l}{1 - e^{-\rho_{\mathrm{eq}} l}} [E_{n-1}(t) - 2E_n(t) + E_{n+1}(t)] + 2D\rho_{\mathrm{eq}} l^{-1} [E_n(t) - E_{n-1}(t)] . \tag{7}$$

For the continuum limit, $l \to 0$, we define the probability $E(x,t)$ of finding a given interval of length x empty by $E(nl,t) \equiv E_n(t)$. This probability obeys the master equation

$$\frac{\partial}{\partial t} E(x,t) = 2D \frac{\partial^2}{\partial x^2} E(x,t) + 2D\rho_{\mathrm{eq}} \frac{\partial}{\partial x} E(x,t) . \tag{8}$$

The boundary condtions are $E(0,t) = 1$, because the point particles occupy a set of measure zero, and $E(\infty,t) = 0$ as long as the concentration is nonvanishing. The density $\rho(t)$ is the probability that a segment of infinitesimal length dx is not empty, divided by the length dx:

$$\rho(t) \equiv \lim_{dx \to 0} \frac{1 - E(dx,t)}{dx} = -\frac{\partial}{\partial x} E(x,t) \bigg|_{x=0} .$$

We now consider the time-dependent approach to equilibrium. From this point we adopt the dimensionless variables $\bar{x}$, $\bar{t}$, and c, defined by

$$\begin{gathered} \bar{x} = \rho_{\mathrm{eq}} x, \quad \bar{t} = 2\rho_{\mathrm{eq}}^2 D t , \\ \bar{E}(\bar{x},\bar{t}) = E(x,t), \quad c(\bar{t}) = \rho(t)/\rho_{\mathrm{eq}} . \end{gathered} \tag{9}$$

Dropping the overbars, Eq. (8) becomes

$$\frac{\partial}{\partial t} E(x,t) = \frac{\partial^2}{\partial x^2} E(x,t) + \frac{\partial}{\partial x} E(x,t) . \tag{10}$$

This equation has the stationary solution $E_0(x) = e^{-x}$, and there are two classes of time-dependent elementary solutions. (1) Solutions that oscillate in space and decay relative *fast* for large values of x:

$$E_q^f(x,t) = e^{-x/2} \sin(qx) e^{-(1/4+q^2)t} , \tag{11}$$

labeled by the dimensionless wave number $q \geq 0$. (2) Nonoscillatory solutions that decay relatively slowly in space and in time:

$$E_q^s(x,t) = e^{-x/2}\sinh(qx)e^{-(1/4-q^2)t}, \qquad (12)$$

for $0 < q < \frac{1}{2}$.

The slowly decaying elementary solutions E_q^s appear in the solution only if the asymptotic decay of the initial condition, $E(x,0)$, is *slower* than $e^{-x/2}$ for large x. This condition does not generally involve the initial density $c_0 = c(0)$. However, we now focus on initial conditions that can be prepared "experimentally" in the form of ***equilibrium states*** of the system at ***different*** values of the microscopic parameters. That is, we consider initial conditions consisting of a random distribution of particles, with no correlations, and a dimensionless density c_0 differing from unity. The initial condition is then $E(x,0) = e^{-c_0 x}$.

The slowly decaying elementary solutions $E_q^s(x,t)$ appear in the solution *only* if the initial density is less than *half* the equilibrium density, as the exact solution of this initial-value problem shows:

$$\begin{aligned} E(x,t) = {} & e^{-x} + 2\Theta(\tfrac{1}{2} - c_0)e^{-x/2}\sinh[(\tfrac{1}{2} - c_0)x]e^{-c_0(1-c_0)t} \\ & + \tfrac{1}{2}e^{-x/2}[+e^{x/2}\operatorname{erfc}(\tfrac{1}{2}t^{1/2} + \tfrac{1}{2}xt^{-1/2}) - e^{-x/2}\operatorname{erfc}(\tfrac{1}{2}t^{1/2} - \tfrac{1}{2}xt^{-1/2}) \\ & \qquad - e^{|1/2-c_0|x - c_0(1-c_0)t}\operatorname{erfc}(|\tfrac{1}{2} - c_0|t^{1/2} + \tfrac{1}{2}xt^{-1/2}) \\ & \qquad + e^{-|1/2-c_0|x - c_0(1-c_0)t}\operatorname{erfc}(|\tfrac{1}{2} - c_0|t^{1/2} - \tfrac{1}{2}xt^{-1/2})], \end{aligned} \qquad (13)$$

where $\Theta(x)$ denotes the Heaviside step function, and $\operatorname{erfc}(x)$ is the complementary error function.[13]

The time-dependent density is

$$c(t) = -\frac{\partial}{\partial x}E(x,t)\bigg|_{x=0} = 1 - \tfrac{1}{2}\operatorname{erfc}(\tfrac{1}{2}t^{1/2}) + |\tfrac{1}{2} - c_0|e^{-c_0(1-c_0)t}[\operatorname{erfc}(|\tfrac{1}{2} - c_0|t^{1/2}) - 2\Theta(\tfrac{1}{2} - c_0)]. \qquad (14)$$

The asymptotic approach to the equilibrium density is

$$c(t) \sim \begin{cases} 1 - (1-2c_0)e^{-c_0(1-c_0)t} & \text{for } 0 < c_0 < \frac{1}{2}, \\ 1 - \pi^{-1/2}t^{-1/2}e^{-t/4} & \text{for } c_0 = \frac{1}{2}, \\ 1 + 2\pi^{-1/2}[1 - (1-2c_0)^{-2}]t^{-3/2}e^{-t/4} & \text{for } c_0 > \frac{1}{2}. \end{cases} \qquad (15)$$

The exponential relaxation time τ for this approach, as a function of the initial density, is shown in Fig. 1. The constant value for initial densities $c_0 > \frac{1}{2}$ is $\tau = 2 \times (D\rho_{\text{eq}}^2)^{-1}$. For smaller initial densities τ increases and eventually diverges for $c_0 \rightarrow 0$. At the transition point, $c_0 = \frac{1}{2}$, the first derivative of τ with respect to c_0 is continuous and is zero, but the second derivative is discontinuous.

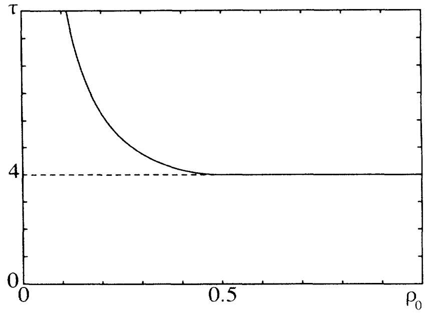

FIG. 1. The exponential relaxation time τ as a function of the initial density ρ_0. The units are $\frac{1}{2}D^{-1}\rho_{\text{eq}}^{-2}$ and ρ_{eq}, respectively.

We have checked our analysis with Monte Carlo simulations of a system of 10^5 sites and an equilibrium density of 1 particle per 10 sites for various initial densities ρ_0. The results are plotted together with the predictions for an infinite continuum system in Fig. 2.

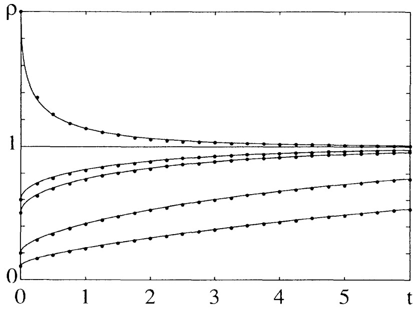

FIG. 2. The approach of the density $\rho(t)$ to its equilibrium value ρ_{eq} for various initial densities: $\rho_0/\rho_{\text{eq}} = 0.1$, 0.2, 0.5, 0.6, and 2.0. The Monte Carlo results (dots) are plotted together with the exact results. The units are ρ_{eq} and $\frac{1}{2}D^{-1}\rho_{\text{eq}}^{-2}$, respectively.

The transition in the exponential relaxation time reflects the domination of the dynamics by large gaps between particles, which occur due to large fluctuations in the spatial distribution of particles at low initial densities. The length of these gaps can decrease only by diffusion of the bounding particles at their ends. We have checked that this dominance of fluctuations *disappears* if we extend our model system to allow for spontaneous particle generation with any positive rate constant.[9,14] This irreversible reaction mechanism "breaks up" the large gaps.

Our solution illustrates several points about diffusion-reaction systems in general. First, the time-dependent density in a diffusion-reaction system does not necessarily obey a rate equation, i.e., an autonomous ordinary differential equation with coefficients that are independent of the initial conditions. Second, the choice of an initial condition with no correlations between particle positions does *not* ensure that there is a transient regime where one can truncate a cluster expansion to obtain a rate equation. Finally, spatial fluctuations can dominate the dynamic behavior arbitrarily close to an equilibrium state. The absence of correlations in the equilibrium state, which follows from the absence of an interaction potential in our case, does not help in this respect. The asymptotic approach to equilibrium can *still* be dominated by correlations on the *microscopic* level.

Our method of solution is closely related to the method of *interparticle distribution functions* (IPDF) used earlier for the exact solution of the irreversible diffusion-reaction system $X+X\rightarrow X$ with[9] and without[4,9] spontaneous single particle creation $Y\rightarrow X$. In fact, the IPDF is proportional to the second derivative of $E(x,t)$ with respect to x.[9] This allows for the investigation of spatial correlations. It would be desirable to develop this method into a general systematic technique which could be applied to other interesting reaction schemes with transitions,[15] and to higher dimensions, where the reported transition may or may not be present.

Finally, we note that it is evident from our derivative of Eq. (8) from the microscopic level that the diffusion-controlled regime is a low-density limit of this system. We are currently exploring systematic corrections to the diffusion-controlled limit for higher densities.

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[1] N. G. van Kampen, Int. J. Quantum Chem. Quantum Chem. Symp. **16**, 101–115 (1982).

[2] R. Kopelman, J. Stat. Phys. **48**, 315 (1986); Science **241**, 1620 (1988).

[3] K. Kang and S. Redner, Phys. Rev. A **32**, 435 (1985).

[4] M. Bramson and D. Griffeath, Z. Wahrsch. Gebiete **53**, 183 (1980); Ann. Probab. **8**, 183 (1980).

[5] D. C. Torney and H. M. McConnel, Proc. Roy. Soc. London A **387**, 147 (1983).

[6] Z. Rácz, Phys. Rev. Lett. **55**, 1707 (1985).

[7] A. A. Lushnikov, Phys. Lett. A **120**, 135 (1987).

[8] J. L. Spouge, Phys. Rev. Lett. **60**, 871 (1988).

[9] C. R. Doering and D. ben-Avraham, Phys. Rev. A **38**, 3035 (1988); Phys. Rev. Lett. **62**, 2563 (1989).

[10] Model II of Ref. 6 can in fact be viewed as a reversible diffusion-limited reaction $X+X\rightleftharpoons Y$ in the limit where the diffusion constant of the Y particles is infinite. It does not apply to the question of validity of a spatially continuous local description.

[11] D. ben-Avraham, M. A. Burschka, and C. R. Doering (to be published).

[12] We do not need to consider the multiple occupancy of site n because the contribution from this configuration involves simultaneous jumps of several particles, for which the probability rate is zero.

[13] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).

[14] The exact solution for that more general case will be published in Ref. 11.

[15] R. Dickman, Phys. Rev. B (to be published).