

Fluctuations and Correlations in a Diffusion-Reaction System: Exact Hydrodynamics

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We present an exact closed formulation of the reversible diffusion-limited coagulation-growth reactions $2A \leftrightarrow A$ with irreversible input $B \rightarrow A$ in one spatial dimension. The treatment here accommodates spatial as well as temporal variations in the particle density with a complete account of microscopic fluctuations and correlations. Moreover, spatial and/or temporal variations in the transport and reaction coefficients can be included in the model. A general solution to the reversible process is presented, and we explore the phenomenon of wavefront propagation.

KEY WORDS: Diffusion-reaction system; reaction kinetics; nonlinear waves.

1. INTRODUCTION

Reaction-diffusion systems have often been used to model spatiotemporal pattern formation in chemistry,⁽¹⁾ biology,⁽²⁾ geology,⁽³⁾ and physics.⁽⁴⁾ Usually a macroscopic level of description is adopted. The state of the system is characterized by mean-field quantities, viz. the densities of the reacting species, which are assumed to obey the law of mass action and Fick's law. On this level of description the temporal evolution of the system is governed by a reaction-diffusion equation. Such a treatment neglects fluctuations and correlations that occur on microscopic length scales. This assumption is legitimate for most situations of solution chemistry. However, recent studies have shown that microscopic fluctuations can alter

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the macroscopic dynamics for diffusion-limited reactions in systems of low spatial dimensionality (see, e.g., ref. 5). Such situations are encountered, for instance, in zeolite catalysis.⁽⁶⁾ Reactions here are often diffusion-limited, and mordenite and other zeolites have a one-dimensional system of channels with diameters on molecular length scales.

In this paper we consider a specific model system, namely the reversible coagulation-growth process $2A \leftrightarrow A$ with irreversible input $B \rightarrow A$, which has the advantage of being amenable to analysis at the microscopic level of description. We consider the coagulation reaction $2A \rightarrow A$ in the diffusion-controlled limit, where the transport of particles constitutes the rate-limiting step. Thus we model the reaction as taking place instantaneously upon contact of two of the A species particles.^(7,8) The usual mean-field reaction-diffusion equation is generally valid only in the reaction-controlled limit for small perturbations from states with no interparticle correlations.⁽⁹⁾ However, strong particle-particle correlations can develop in unstirred diffusion-limited processes away from equilibrium, and these can greatly modify the macroscopic dynamics. The spatially homogeneous mean-field version of the reversible process ($2A \leftrightarrow A$) is the well-studied Verhulst rate equation (see, e.g., ref. 10)

$$\frac{d\rho}{dt} = k_1\rho - k_2\rho^2 \quad (1.1)$$

where k_1 and k_2 are, respectively, the rate coefficients for the $A \rightarrow 2A$ and $2A \rightarrow A$ reactions. Inhomogeneities on the hydrodynamic level, in the mean-field description, are described by the Fisher reaction-diffusion equation (see, e.g., ref. 11)

$$\frac{\partial\rho}{\partial t} = D\Delta\rho + k_1\rho - k_2\rho^2 \quad (1.2)$$

with macroscopic diffusion coefficient D , which has propagating wavefront solutions.

These particular reactions, in one spatial dimension, allow for an exact and closed microscopic formulation of the problem in terms of a single *linear* partial differential equation, from which we may extract the space-time-dependent concentration, or density, of particles. We will therefore be able to directly confront the mean-field results with exact solutions from a microscopic treatment. In this way we can demonstrate explicitly how microscopic fluctuations affect the macroscopic behavior of diffusion-limited reactions in low-dimensional systems. It will also allow us to assess the validity of the reaction-diffusion equation, in particular its prediction of a propagating wavefront.

The concentration we derive is an ensemble average—a hydrodynamic quantity—and does not itself fluctuate, but it fully takes into account all the microscopic fluctuations in the system and any correlations which may develop. The model can also take into account, in an exact way, spatial and/or temporal variations in the diffusion and reaction coefficients. The results presented here are the generalization to the spatially inhomogeneous case of the homogeneous model developed in ref. 7, and reviewed in ref. 8. In this paper, the first of a series, we concentrate on the general formulation of the problem and study the evolution of spatial inhomogeneities resulting from inhomogeneous initial conditions. The outline of the rest of this paper is as follows. In Section 2 we define the model by specifying the microscopic reaction and diffusion processes in a spatially discrete formulation of the problem. The kinetic equation is derived here, and we take the continuum limit to reduce the problem to a partial differential equation. Our attention is restricted to the strictly reversible process in Section 3, where we write down a closed-form expression for the space- and time-dependent concentration in terms of an initial (spatially-dependent) concentration, assuming no correlations in the particle positions in the initial state. As a specific application, we consider the initial condition of half the line in the equilibrium state and half the line empty, the usual setting for the study of front propagation. In the final Section 4 we indicate more precisely some other directions for exploration which will form the contents of other papers in this series.

2. DEFINITION OF THE MODEL AND DERIVATION OF THE KINETIC EQUATION

We initially formulate our model on a one-dimensional lattice, of lattice spacing Δx , each of whose sites is either occupied or empty. We refer to the objects which can occupy the sites as “particles.” The microscopic kinetic processes which make up the system are illustrated in Fig. 1. They are:

Diffusion. A particle at site x hops to a neighboring site $x \pm \Delta x$, as shown in Fig. 1a, at probability rate $D(x, t)/\Delta x^2$. It hops to either side at this rate, so it evacuates the site x at rate $2D(x, t)/\Delta x^2$. This corresponds to macroscopic diffusion with diffusion coefficient $D(x, t)$ which may be space and time dependent.

Birth. The reaction $A \rightarrow 2A$ is modeled as shown in Fig. 1b. A particle at site x “gives birth” to another particle at a neighboring site $x \pm \Delta x$ at probability rate $v/(2\Delta x)$, independent of all other processes. Again, this is the rate to give birth on either side, so the birth rate of an isolated particle is $v/\Delta x$.

Coalescence. The reverse reaction, $2A \rightarrow A$, is illustrated in Fig. 1c. If a particle either jumps or is born into an occupied site, then it instantly coalesces with the previous occupant to become a single particle. We impose this reaction on the lattice by restricting the occupation numbers to either 0 or 1.

Input. A spontaneous generation of particles, denoted schematically as $B \rightarrow A$, is shown in Fig. 1d. An empty site at x spontaneously becomes occupied at probability rate $R(x, t) \Delta x$, independent of all other processes. We refer to this process as “input,” and note that $R(x, t)$ is the (possibly space- and time-dependent) local rate of input of particles per unit length per unit time.

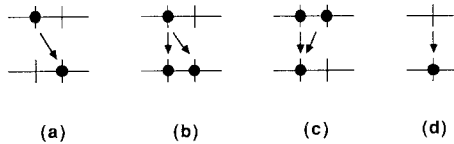


Fig. 1. The microscopic processes defining the diffusion-reaction system. Occupied sites on the lattice are indicated by the presence of particle. (a) Diffusive hopping occurs at rate $D/\Delta x^2$ to the right and $D/\Delta x^2$ to the left. (b) The reaction $A \rightarrow 2A$ occurs at rate $v/\Delta x$, half this rate to the right and half this rate to the left. (c) Coagulation occurs when one particle hops onto another. (d) Input to an empty site occurs at rate $R \Delta x$.

A typical approach to such a many-body problem in statistical physics is to construct the kinetic equations for a hierarchy of joint probability density functions.⁽¹²⁾ The usual closure problems arise at this stage because the evolution of the one-particle density, or concentration, depends on some two-particle correlations, which in turn depend on higher-particle-number correlations, and so on. The key to formulating a closed evolution equation for this process, from which we may recover the particle concentration, is to consider an auxiliary quantity. We have discovered that there is a certain quantity, peculiar to the reaction processes outlined above, which satisfies a closed kinetic equation without reference to any other probabilities. This quantity, denoted $E(x, y, t)$ and defined for all $x \leq y$, is

$$E(x, y, t) = \text{Prob}\{\text{the sites between } x \text{ and } y \text{ (inclusive) are empty at time } t\} \tag{2.1}$$

We will refer to this quantity as the “empty interval probability,” and we illustrate its meaning schematically in Fig. 2.

$$E(x,y) = \text{Prob}\{ \text{---} \overset{x}{|} \text{---} \text{---} \text{---} \text{---} \underset{y}{|} \text{---} \}$$

Fig. 2. Schematic definition of the empty interval probability.

This empty interval probability determines the ensemble-averaged particle concentration. The density of particles at site x at time t , denoted $\rho(x, t)$, is the probability per unit length that the site at x occupied. That is,

$$\begin{aligned} \rho(x, t) \Delta x &= \text{Prob}\{\text{site } x \text{ is occupied at time } t\} \\ &= 1 - \text{Prob}\{\text{site } x \text{ is empty at time } t\} \\ &= 1 - E(x, x, t) \end{aligned} \tag{2.2}$$

Thus, we may recover the local concentration from a knowledge of $E(x, y, t)$.

To derive a kinetic equation for $E(x, y, t)$, we combine all of the processes which can contribute to the evolution of this probability. These processes are illustrated schematically in Fig. 3. Consider a short time interval Δt , so short that we may neglect the simultaneous occurrence of two hops, births, and/or inputs. Then the interval between x and y can be vacated in this short time interval, *increasing* $E(x, y, t)$, only if the interval is empty except at endpoint x and the particle there hops to the left [with conditional probability $D(x, t)\Delta t/\Delta x^2$], or if it is empty except at endpoint y , where the particle hops to the right [with conditional probability $D(y, t)\Delta t/\Delta x^2$]. These are the first two terms on the right-hand side of the equality in Fig. 3. Similarly, an empty interval can become occupied if it

$$\begin{aligned} \Delta E(x,y) &= \\ &= \frac{D(x,t)\Delta t}{\Delta x^2} \text{Prob}\left\{ \begin{array}{c} \bullet \\ | \\ x \end{array} \text{---} \text{---} \text{---} \text{---} \begin{array}{c} | \\ y \end{array} \right\} \\ &+ \frac{D(y,t)\Delta t}{\Delta x^2} \text{Prob}\left\{ \begin{array}{c} | \\ x \end{array} \text{---} \text{---} \text{---} \text{---} \begin{array}{c} \bullet \\ | \\ y \end{array} \right\} \\ &- \frac{D(x-\Delta x,t)\Delta t}{\Delta x^2} \text{Prob}\left\{ \begin{array}{c} \bullet \\ | \\ x-\Delta x \end{array} \text{---} \text{---} \text{---} \text{---} \begin{array}{c} | \\ y \end{array} \right\} \\ &- \frac{D(y+\Delta x,t)\Delta t}{\Delta x^2} \text{Prob}\left\{ \begin{array}{c} | \\ x \end{array} \text{---} \text{---} \text{---} \text{---} \begin{array}{c} \bullet \\ | \\ y+\Delta x \end{array} \right\} \\ &- \frac{v(x-\Delta x,t)\Delta t}{\Delta x} \text{Prob}\left\{ \begin{array}{c} \bullet \\ | \\ x-\Delta x \end{array} \text{---} \text{---} \text{---} \text{---} \begin{array}{c} | \\ y \end{array} \right\} \\ &- \frac{v(y+\Delta x,t)\Delta t}{\Delta x} \text{Prob}\left\{ \begin{array}{c} | \\ x \end{array} \text{---} \text{---} \text{---} \text{---} \begin{array}{c} \bullet \\ | \\ y+\Delta x \end{array} \right\} \\ &- [R(x,t)+\dots+R(y,t)]\Delta t\Delta x \text{Prob}\left\{ \begin{array}{c} | \\ x \end{array} \text{---} \text{---} \text{---} \text{---} \begin{array}{c} | \\ y \end{array} \right\} \end{aligned}$$

Fig. 3. Schematic description of the change ΔE in the empty interval probability over a short time interval Δt .

was empty, *decreasing* $E(x, y, t)$, if there was a particle at $x - \Delta x$ which hops to the right [with conditional probability $D(x - \Delta x, t)\Delta t/\Delta x^2$] or a particle at $y + \Delta x$ which hops to the left [with conditional probability $D(y + \Delta x, t)\Delta t/\Delta x^2$]. These are the second pair of terms in Fig. 3. The birth of particles into otherwise empty intervals also decreases $E(x, y, t)$, due to a particle at $x - \Delta x$ giving birth into site x [with conditional probability $v(x - \Delta x, t)\Delta t/(2\Delta x)$] or one at $y + \Delta x$ giving birth into site y [with conditional probability $v(y + \Delta x, t)\Delta t/(2\Delta x)$]. These constitute the third pair of terms in Fig. 3. Finally, input of particles decreases the probability that each site z between x and y (inclusive) is empty at rate $R(z, t)\Delta x$, for a total rate

$$\sum_{z=x}^y R(z, t) \Delta x \tag{2.3}$$

This contributes the final term in Fig. 3.

The key to the closure of the kinetic equation for the empty interval probability is illustrated in Fig. 4. For example, the event that the interval from $x + \Delta x$ to y is empty is the disjoint union of two alternative events: that $x + \Delta x$ to y is empty and so is x , and that $x + \Delta x$ to y is empty, but x is not. Because the probability of the union of two disjoint alternatives is just the sum of the probabilities of the alternatives, we can express the

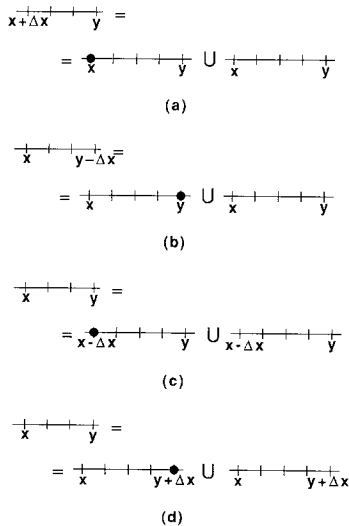


Fig. 4. Disjoint unions of events involving the empty interval and related events.

probability that $x + \Delta x$ to y is empty but x is occupied in terms of the empty interval probabilities. That is,

$$\text{Prob}\{\text{the interval from } x + \Delta x \text{ to } y \text{ is empty but site } x \text{ is occupied at time } t\} \\ = E(x + \Delta x, y, t) - E(x, y, t) \tag{2.4}$$

This fact is expressed schematically in Fig. 5, along with the other variations relevant to closing the kinetic equation in Fig. 3. These allow us to express the evolution of the empty interval probabilities wholly in terms of other empty interval probabilities.

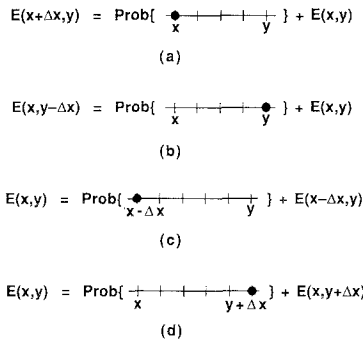


Fig. 5. Schematic illustration of the probabilities of the events in Fig. 4.

Combining the terms in Fig. 5 with those in Fig. 3, we arrive at the closed kinetic equation

$$\frac{dE(x, y, t)}{dt} = \frac{D(x, t)}{\Delta x^2} \{E(x + \Delta x, y, t) - E(x, y, t)\} \\ + \frac{D(y, t)}{\Delta x^2} \{E(x, y - \Delta x, t) - E(x, y, t)\} \\ - \frac{D(x - \Delta x, t)}{\Delta x^2} \{E(x, y, t) - E(x - \Delta x, y, t)\} \\ - \frac{D(y + \Delta x, t)}{\Delta x^2} \{E(x, y, t) - E(x, y + \Delta x, t)\} \\ - \frac{v(x - \Delta x)}{2\Delta x} \{E(x, y, t) - E(x - \Delta x, y, t)\} \\ - \frac{v(y + \Delta x)}{2\Delta x} \{E(x, y, t) - E(x, y + \Delta x, t)\} \\ - \sum_{z=x}^y R(z, t) \Delta x E(x, y, t) \tag{2.5}$$

This equation is valid for all discrete variables $y > x$. We must also supply the kinetic equation for $E(x, y, t)$ when $y = x$, and this follows from considerations like those above, with one exception. The probability that the site x is not empty at time t is just $1 - E(x, x, t)$, so that analogs of the first and third closure equations in Fig. 5 for the case $y = x$ are obtained by replacing, respectively, $E(x + \Delta x, y, t)$ by 1 and $E(x, y - \Delta t, t)$ by 1. Thus, we may assert that Eq. (2.5) is valid even for $y = x$ with the understanding that the previously undefined quantities $E(x + \Delta x, x, t)$ and $E(x, x - \Delta x, t)$ are given by the *boundary conditions*

$$E(x + \Delta x, x, t) = 1 \quad \text{and} \quad E(x, x - \Delta x, t) = 1 \quad (2.6)$$

The empty interval probability contains information about the microscopic spatial structure of the system, although not in the form of the familiar correlation functions. Rather, from $E(x, y, t)$ we can deduce a nearest neighbor joint probability distribution for particles in the system. To see this, consider the event that the interval from $x + \Delta x$ to $y - \Delta x$ is empty at time t . As illustrated in Fig. 6, this event is the disjoint union of the four alternatives that (i) there are particles at x and y with the intervening sites empty, (ii) there is one particle at x , none at y , and none in between, (iii) there is no particle at x , and none until site y , which is occupied, and (iv) there are no particles between x and y inclusive. Again, the probability of this disjoint union is the sum of the probabilities of the alternatives, so, using the previously derived relationship illustrated in Fig. 5, we can express the probability that there are particles at x and y with none in between in terms of the empty interval probabilities. We have the relation

$$\begin{aligned} & \text{Prob}\{x \text{ and } y \text{ are occupied with no particles in between at time } t\} \\ &= E(x, y, t) + E(x + \Delta x, y - \Delta x, t) - E(x + \Delta x, y, t) - E(x, y - \Delta x, t) \end{aligned} \quad (2.7)$$

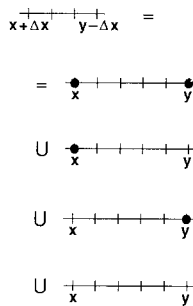


Fig. 6. Disjoint union of events involving the empty interval and related events.

This quantity provides information on local, microscopic spatial correlations in the system. In spatially homogeneous systems this quantity (when divided by the particle density) is the interparticle distribution function as introduced in ref. 7.

Now we will take the spatial continuum limit of the system and its kinetic equation. As the lattice spacing $\Delta x \rightarrow 0$, the empty interval probability goes over to a function $E(x, y, t)$ of x, y , and t . Its physical interpretation remains the same: it is the probability that the interval from x to y is empty at time t . Assuming that all quantities vary slowly on the scale of the vanishing lattice spacing, we expand all the terms in the kinetic equation (2.5) in a Taylor series about x and y , noting that the coefficient in the last expression is in the form of a Riemann integral. Then, taking the continuum limit $\Delta x \rightarrow 0$, we find the partial differential equation

$$\frac{\partial E(x, y, t)}{\partial t} = \frac{\partial}{\partial x} D(x, t) \frac{\partial E}{\partial x} + \frac{\partial}{\partial y} D(y, t) \frac{\partial E}{\partial y} - \frac{1}{2} v(x, t) \frac{\partial E}{\partial x} + \frac{1}{2} v(y, t) \frac{\partial E}{\partial y} - \left\{ \int_x^y R(z, t) dz \right\} E(x, y, t) \quad (2.8)$$

This *linear* partial differential equation, defined in the region $y > x$ of the $x - y$ plane, is to be supplemented with an initial condition $E_0(x, y)$ and two boundary conditions. From Eq. (2.6) we see that at coincidence points we have the boundary condition

$$\lim_{y \downarrow x \text{ or } x \uparrow y} E(x, y, t) = 1 \quad (2.9)$$

The other boundary conditions imposed as either $y \rightarrow +\infty$ or $x \rightarrow -\infty$ depend on the specific conditions at hand. For example, if there are no particles to the right of a point x_0 at some instant of time t , then for all $x, y > x_0$ we have $E(x, y, t) = 1$. Such a condition may be fleeting, though. Even if there is no particle input for $x > x_0$, and the initial conditions start with no particles in that region, then particles will certainly diffuse into the "vacuum." However, the transport will proceed at a finite rate—this is just the setup for the wave propagation problem—so that far enough to the right the system is eventually empty. Then we would have

$$\lim_{y > x \rightarrow \infty} E(x, y, t) = 1 \quad (2.10)$$

On the other hand, if we consider a more homogeneous system where the particle concentration is nonvanishing everywhere to the right of x_0 , then

$$\lim_{y \rightarrow \infty} E(x, y, t) = 0 \quad (2.11)$$

Rather than listing all the possibilities here, we just observe that the appropriate boundary conditions can be deduced in all reasonable physical circumstances.

The continuous-space version of the particle density is, from Eqs. (2.2) and (2.6) with the boundary condition in Eq. (2.9),

$$\begin{aligned} \rho(x, t) &= \lim_{\Delta x \downarrow 0} \frac{1}{\Delta x} [1 - E(x, x, t)] \\ &= \lim_{\Delta x \downarrow 0} \frac{1}{\Delta x} [E(x, x - \Delta x, t) - E(x, x, t)] \\ &= - \left. \frac{\partial E(x, y, t)}{\partial y} \right|_{y=x} \end{aligned} \quad (2.12)$$

And finally, the conditional joint probability *density* that there are particles at x and y but none in between is, from Eq. (2.7),

$$\begin{aligned} p(x, y, t) &= \lim_{\Delta x \downarrow 0} \frac{1}{\Delta x^2} \text{Prob}\{x \text{ and } y \text{ are occupied with no particles in between}\} \\ &= - \frac{\partial^2 E(x, y, t)}{\partial x \partial y} \end{aligned} \quad (2.13)$$

3. SOME GENERAL SOLUTIONS AND SPECIFIC EXAMPLES

The time-stationary and spatially-homogeneous version of this problem, where both the system coefficients (D , v , and R) and the initial conditions are translation invariant, has been solved in refs. 7 and 8. In this section, and for the remainder of this paper, we will focus on the case of constant (in space and time) coefficients, but with inhomogeneous initial conditions. Thus, we will study the relaxation to the statistically homogeneous steady state from an initially inhomogeneous configuration. Furthermore, we will restrict the analysis to the reversible model $2A \leftrightarrow A$, i.e., $R(x, t) \equiv 0$. First we will derive the general solution for the space- and time-dependent density $\rho(x, t)$ in terms of an initially specified density $\rho_0(x)$ under the assumption that there are no correlations in the particle positions in the initial configuration. Then we will consider a specific initial condition where the half-space $x < 0$ is in the equilibrium state while the half-space $x > 0$ is void of particles. This will allow us to study the front-propagation problem for this diffusion-reaction system.

Taking the diffusion coefficient D and the birth rate v to be constant, the partial differential equation for the empty interval probability becomes

$$\frac{\partial E(x, y, t)}{\partial t} = D \frac{\partial^2 E}{\partial x^2} + D \frac{\partial^2 E}{\partial y^2} - \frac{v}{2} \frac{\partial E}{\partial x} + \frac{v}{2} \frac{\partial E}{\partial y} \quad (3.1)$$

on the half-space $y > x$, with the boundary condition

$$\lim_{y \downarrow x \text{ or } x \uparrow y} E(x, y, t) = 1 \quad (3.2)$$

As noted in the last section, the other boundary condition depends on the details of the situation under consideration. Spatial inhomogeneities in the initial configuration of the system are specified by the initial condition $E_0(x, y)$.

Note that there is a unique stationary, spatially homogeneous solution to Eqs. (3.1) and (3.2) which describes the equilibrium state:

$$E_{\text{eq}}(x, y) = e^{-v(y-x)/2D} \quad (3.3)$$

The concentration is spatially uniform in the equilibrium state:

$$\rho_{\text{eq}} = - \left. \frac{\partial E_{\text{eq}}(x, y)}{\partial y} \right|_{y=x} = \frac{v}{2D} \quad (3.4)$$

We see that the equilibrium concentration is proportional to the birth rate v and inversely proportional to the diffusion coefficient which controls the (equilibrium) rate of the coalescence reaction.

The kinetic equation (3.1) is of the form of a convection-diffusion equation, and combined with the simplicity of the boundary conditions, it is not surprising that it can be completely solved in closed form. To derive the general solution, we first change independent variables to dimensionless sum and difference variables

$$\xi = \frac{v}{2D} (y + x) \quad \text{and} \quad \zeta = \frac{v}{2D} (y - x) \quad (3.5)$$

It is convenient to rescale the time as well, so we introduce the dimensionless time variable

$$\tau = \frac{v^2}{2D} t \quad (3.6)$$

Then Eqs. (3.1) and (3.2) become

$$\frac{\partial E(\xi, \zeta, \tau)}{\partial \tau} = \frac{\partial^2 E}{\partial \xi^2} + \frac{\partial^2 E}{\partial \zeta^2} + \frac{\partial E}{\partial \zeta} \quad (3.7)$$

on the half-space $-\infty < \xi < \infty, 0 < \zeta < \infty$, with boundary condition

$$\lim_{\zeta \downarrow 0} E(\xi, \zeta, \tau) = 1 \tag{3.8}$$

The initial condition may similarly be expressed in terms of the dimensionless variables as $E_0(\xi, \zeta)$. The equilibrium solution in the dimensionless units is simply

$$E_{eq}(\xi, \zeta) = e^{-\xi} \tag{3.9}$$

We may reduce the problem further, to an elementary heat equation in the upper half $\xi-\zeta$ plane, by changing the dependent variable to the function

$$F(\xi, \zeta, \tau) = e^{\tau/4 + \zeta/2} (E(\xi, \zeta, \tau) - e^{-\xi}) \tag{3.10}$$

which obeys the diffusion equation

$$\frac{\partial F(\xi, \zeta, \tau)}{\partial \tau} = \frac{\partial^2 F}{\partial \xi^2} + \frac{\partial^2 F}{\partial \zeta^2} \tag{3.11}$$

and the boundary condition

$$\lim_{\zeta \downarrow 0} F(\xi, \zeta, \tau) = 0 \tag{3.12}$$

The initial condition for F is

$$F_0(\xi, \zeta) = e^{\zeta/2} (E_0(\xi, \zeta) - e^{-\xi}) \tag{3.13}$$

The equation for F is solved by introducing the Green function for the heat equation on the half-space $\zeta > 0$ with Dirichlet boundary conditions along the line $\zeta = 0$. That is,

$$F(\xi, \zeta, \tau) = \int_{-\infty}^{\infty} d\xi' \int_0^{\infty} d\zeta' G(\xi, \xi', \zeta, \zeta', \tau) F_0(\xi', \zeta') \tag{3.14}$$

where

$$G(\xi, \xi', \zeta, \zeta', \tau) = \frac{1}{4\pi\tau} e^{-(\xi - \xi')^2/4\tau} [e^{-(\zeta - \zeta')^2/4\tau} - e^{-(\zeta + \zeta')^2/4\tau}] \tag{3.15}$$

Reexpressing the solution in terms of the empty interval probability, we find the general solution

$$\begin{aligned} E(\xi, \zeta, \tau) &= e^{-\xi} + e^{-\tau/4 - \zeta/2} \int_{-\infty}^{\infty} d\xi' \int_0^{\infty} d\zeta' G(\xi, \xi', \zeta, \zeta', \tau) e^{\zeta'/2} [E_0(\xi', \zeta') - e^{-\xi'}] \end{aligned} \tag{3.16}$$

The concentration is derived from this solution as

$$\rho(x, t) = -\frac{v}{2D} \left. \frac{\partial E(\xi, \zeta, \tau)}{\partial \zeta} \right|_{\zeta=0} \tag{3.17}$$

Before we explicitly evaluate the space- and time-dependent particle density, let us restrict our attention to initial conditions which possess no correlations between particle positions. In this situation we determine the empty interval probability from the initial concentration $\rho_0(x)$ as

$$E_0(x, y) = \exp \left[- \int_x^y \rho_0(z) dz \right] \tag{3.18}$$

In terms of the dimensionless variables ξ and ζ this gives

$$E_0(\xi, \zeta) = \exp \left[- \frac{2D}{v} \int_{\xi/2 - \zeta/2}^{\xi/2 + \zeta/2} \rho_0 \left(\frac{2D\sigma}{v} \right) d\sigma \right] \tag{3.19}$$

Inserting Eq. (3.19) into Eq. (3.16), and evaluating the density as in Eq. (3.17), we have, after some algebra, the general solution

$$\begin{aligned} \rho(x, t) = & \frac{v}{2D} \left[1 + \int_{-\infty}^{\infty} \frac{d\xi'}{(4\pi\tau)^{1/2}} e^{-\xi'^2/4\tau} \int_0^{\infty} \frac{d\zeta'}{(4\pi\tau)^{1/2}} \frac{\zeta'}{\tau} e^{-(\zeta' - \tau)^2/4\tau} \right. \\ & \left. \times \left\{ e^{-\zeta'} - \exp \left[- \frac{2D}{v} \int_{\xi/2 + \xi'/2 - \zeta'/2}^{\xi/2 + \xi'/2 + \zeta'/2} \rho_0 \left(\frac{2D\sigma}{v} \right) d\sigma \right] \right\} \right] \tag{3.20} \end{aligned}$$

In the above, $\xi = vx/D$ on the right-hand side of the equation.

Focusing now on a specific initial condition, we consider the case of an equilibrium configuration on the left half-line and no particles on the right half-line. The initial concentration is then

$$\rho_0(x) = \frac{v}{2D} [1 - \theta(x)] = \begin{cases} v/2D, & x < 0 \\ 0, & x > 0 \end{cases} \tag{3.21}$$

where $\theta(\cdot)$ is the usual step function. Inserting Eq. (3.21) into (3.20), we find the “propagating front” solution

$$\rho(x, t) = \frac{v}{4D} \operatorname{erfc} \left[\frac{(x - vt/2)}{(4Dt)^{1/2}} \right] \tag{3.22}$$

where $\operatorname{erfc}(\cdot)$ is the complementary error function.⁽¹³⁾ Several snapshots of the front are plotted in Fig. 7. The front propagates at speed $v/2$, while the

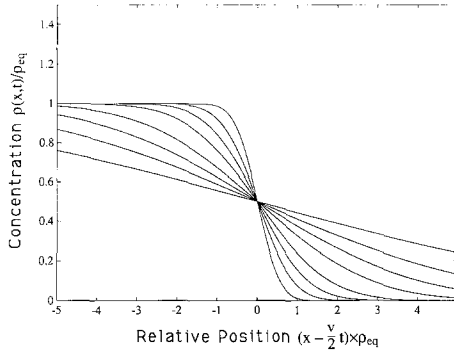


Fig. 7. Snapshots of the concentration profile evolving from the initial condition of the equilibrium state on the half-line $x < 0$, and no particles on the half-line $x > 0$. The times are $t = 0.2, 0.5, 1, 2, 5, 10, 20$, and 50 , in units of $2D/v^2$.

width of the front spreads proportional to \sqrt{t} . The location of the half-density point, where $\rho(x, t) = v/4D = \rho_{eq}/2$, is exactly $x = vt/2$.

An interesting variation on this problem is the initial condition, like that above, of the left half-line in equilibrium and the right half-line empty, but with a particle definitely at the interface location $x = 0$. That is,

$$\rho_0(x) = \frac{v}{2D} [1 - \theta(x)] + \delta(x) \tag{3.23}$$

Inserting this into the general solution and performing the integrations, we find

$$\rho(x, t) = \frac{v}{4D} \operatorname{erfc} \left[\frac{(x - vt/2)}{(4Dt)^{1/2}} \right] + \left(\frac{D}{\pi v^2 t} \right)^{1/2} \exp \left[- \frac{(x - vt/2)^2}{4Dt} \right] \tag{3.24}$$

Several snapshots of this solution are plotted in Fig. 8, and we can compare these with the previous example. As before, the front eventually propagates at speed $v/2$ and the width of the front spreads proportional to \sqrt{t} . After the transient decays, however, the location of the half-density point is shifted to the right, as compared to the previous example, by a distance equal to $\rho_{eq}^{-1} = 2D/v$ (this is just the typical interparticle spacing in the equilibrium state). It is interesting to note in both of these examples that, contrary to the predictions of the nonlinear mean-field reaction-diffusion equation, there is no “real” front solutions where the shape becomes time-independent in the comoving reference frame.

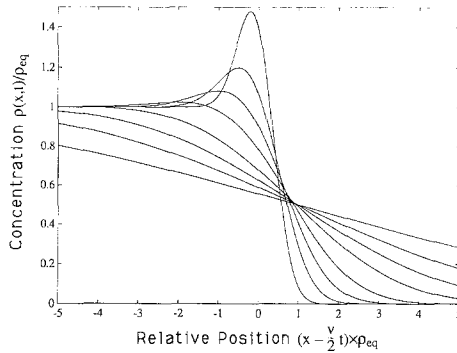


Fig. 8. Snapshots of the concentration profile evolving from the initial condition on equilibrium on the half-line $x < 0$, no particles on the half-line $x > 0$, but with a particle definitely at $x = 0$. The times are the same as in Fig. 7: $t = 0.2, 0.5, 1, 2, 5, 10, 20$, and 50 , in units of $2D/v^2$.

4. DISCUSSION

We have presented a simple model of a diffusion-reaction process in one spatial dimension which is amenable to a detailed analysis without resort to the usual truncations or approximations. Fluctuations and correlations are accounted for exactly, and we have found discrepancies with the predictions of the usual mean-field reaction-diffusion equations. The central new result of this paper is the generalization of the exact solution to spatially varying systems. There are a variety of directions for future research suggested by the results reported here, several of which we will discuss in this section.

The exact formulation of the process in terms of the empty interval probability, as given in Eq. (2.8), allows for the consideration of complex space- and time-dependent coefficients D , v , and R . In fact, there is no reason why the coefficients themselves cannot be random variables. Then the evolution equation becomes a stochastic partial differential equation which may be used to explore a variety of situations. The effect of externally imposed spatial and/or temporal randomness in many-body and nonlinear systems is a topic of current interest and activity,^(14,15) and a number of specific possibilities come to mind here. For example, the coefficients may be constant in time, but random in space. Such "frozen-in" randomness may be relevant to the study of the effect of variations in the strength of sorption and active sites in zeolites, for instance. Granted, analytical progress in the solution of this stochastic system may be slow,

but the ability to reduce such a complex system to a relatively simple description must be regarded as a useful step.

We may also consider the situation of spatially constant, but temporally random coefficients. Our model offers the opportunity for a study of the interplay of internal and external fluctuations in a way that has not been possible before. The effect of external noise on the mean-field rate equation, the Verhulst equation, has previously been studied in great detail in ref. 14. In those studies, however, it was necessary to neglect spatial variations on both microscopic and hydrodynamic length scales. Our treatment here allows us to handle these variations in several ways. First, we may consider Eq. (2.8) with temporally random coefficients where the statistics of the coefficient stochastic processes are independently specified. This provides a stochastic partial differential equation as the starting point for the analysis.

On the other hand, we may exploit the fact that Eq. (2.8) is the evolution equation for a *probability* to formulate a “grand” master equation for the joint empty interval and coefficient probability simultaneously. To be precise, let us consider the case where the birth rate coefficient jumps between two values v_{\pm} in the manner of a Markov process. Then we may write down the exact evolution equation for the quantities

$$E_{\pm}(x, y, t) = \text{Prob}\{\text{interval from } x \text{ to } y \text{ is empty and } v = v_{\pm} \text{ at time } t\} \quad (4.1)$$

If the process $v(t)$ jumps from v_{+} to v_{-} at rate α , and back from v_{-} to v_{+} at rate β , then the probabilities E_{\pm} obey

$$\frac{\partial}{\partial t} \begin{pmatrix} E_{+} \\ E_{-} \end{pmatrix} = \begin{pmatrix} L_{+} - \alpha & \beta \\ \alpha & L_{-} - \beta \end{pmatrix} \begin{pmatrix} E_{+} \\ E_{-} \end{pmatrix} \quad (4.2)$$

where the operators L_{\pm} are

$$L_{\pm} = D \frac{\partial^2}{\partial x^2} + D \frac{\partial^2}{\partial y^2} - v_{\pm} \frac{\partial}{\partial x} + v_{\pm} \frac{\partial}{\partial y} \quad (4.3)$$

This is an exact formulation of an interacting, many-body, spatially distributed system under the influence of external noise in terms of two coupled *linear* partial differential equations. Further development of this topic will be left to a future work.

In a different direction for further research, we remark that the techniques introduced in this paper—specifically the use of empty interval probabilities—can be used to investigate the microscopic spatial structure

of these diffusion-limited reactions through the pair correlation function. We had earlier noted in Eq. (2.13) that the mixed second derivative of the empty interval probability yields the conditional probability density of finding two particles with none in between. To compute the more familiar unconditional two-point joint density function, we may expand the notion of the empty interval probability to that of the probability of finding two disjoint intervals empty. A closed evolution equation for this quantity may be formulated along the same logical lines that we have presented here, i.e., by considering the various processes occurring within and at the boundaries of a pair of disjoint intervals. The evolution of this two-interval probability couples to the single-interval probability through the boundary conditions, but it does not couple to any higher-interval probabilities. The complete development and solution of this problem is left for the future.

Finally, we have shown in this paper that there are *no* true wavefronts for the diffusion-limited reaction $2A \leftrightarrow A$ in one spatial dimension, contrary to the prediction of the mean-field reaction-diffusion equation, Fisher's equation. Fluctuations in the local density cause an ever-broadening transition region, so a stationary situation is never achieved in any frame of reference. This brings up the question of whether the predictions of the mean-field equations are *ever* qualitatively valid for the diffusion-limited process. (It also raises the question of the development and significance of corrections to this process if we relax the strict diffusion-controlled limit.⁽¹⁶⁾) There is typically a crossover from fluctuation-dominated kinetics to mean-field kinetics in diffusion-limited reactions above a certain "critical" spatial dimension. In general the critical dimension depends on the specific reaction scheme, and whether one consider irreversible decay or relaxation to equilibrium or nonequilibrium steady states. Such phenomena have been studied in great detail for statistically homogeneous systems (see refs. 5, 7, and 8), but have remained largely unexplored in spatially inhomogeneous problems. Hence we close with the following question: Is there a critical dimension above which the diffusion-limited reaction $2A \leftrightarrow A$ supports wavefronts that are (asymptotically) time independent in the comoving reference frame?

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REFERENCES

1. G. Nicolis and I. Prigogine, *Self Organization in Nonequilibrium Systems* (Wiley, New York, 1977); H. Haken, *Synergetics: An Introduction* (Springer, Berlin, 1978).
2. A. M. Turing, *Phil. Trans. R. Soc. Lond. B* **237**:37 (1952); H. Meinhardt, *Models of Biological Pattern Formation* (Academic Press, London, 1982); J. D. Murray, *Mathematical Biology* (Springer, Berlin, 1989).
3. P. Ortoleva, G. Auchmuty, J. Chadam, J. Hettner, E. Merino, C. H. Moore, and E. Ripley, *Physica D* **19**:334 (1988); T. Dewers and P. Ortoleva, *J. Phys. Chem.* **93**:2842 (1989).
4. B. Röhrich, J. Parisi, J. Peinke, and O. E. Rössler, *Z. Phys. B* **65**:259 (1986); H.-G. Purwins, C. Radehaus, and J. Berkemeier, *Z. Naturforsch* **43a**:17 (1988).
5. K. Kang and S. Redner, *Phys. Rev. A* **32**:435 (1985); R. Kopelman, *Science* **241**:1620 (1988).
6. R. Szostak, *Molecular Sieves—Principles of Synthesis and Identification* (Van Nostrand Reinhold, New York, 1989); R. M. Barrer, in *Inclusion Compounds I*, J. L. Atwood, J. E. D. Davies, and D. D. MacNicol (Academic Press, London, 1984); A. Dyer, *An Introduction to Zeolite Molecular Sieves* (Wiley, New York, 1988).
7. C. R. Doering and D. ben-Avraham, *Phys. Rev. A* **38**:3035 (1988); C. R. Doering and D. ben-Avraham, *Phys. Rev. Lett.* **62**:2563 (1989); M. A. Burschka, C. R. Doering, and D. ben-Avraham, *Phys. Rev. Lett.* **63**:700 (1989); C. R. Doering and M. A. Burschka, *Phys. Rev. Lett.* **64**:245 (1990).
8. D. ben-Avraham, M. A. Burschka, and C. R. Doering, *J. Stat. Phys.* **60**:695 (1990).
9. M. A. Burschka, *J. Stat. Phys.* **45**:715 (1986).
10. C. E. Smith and H. C. Tuckwell, in *Lecture Notes in Biomathematics*, Vol. 2, S. Levin, ed. (Springer, Berlin, 1974); F. Schlögl, *Z. Physik.* **253**:147 (1972).
11. P. C. Fife, *Mathematical Aspects of Reacting and Diffusing Systems* (Springer, Berlin, 1979); J. J. Tyson, *The Belousov-Zhabotinskii Reaction* (Springer, Berlin, 1976); P. Kaliappan, *Physica D* **11**:368 (1984).
12. N. G. van Kampen, *Int. J. Quantum Chem. Quantum Chem. Symp.* **16**:101 (1982); J. C. Lin, C. R. Doering, and ben-Avraham, *Chem. Phys.* **146**:355 (1990).
13. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
14. W. Horsthemke and R. Lefever, *Noise Induced Transitions* (Springer, Berlin, 1984).
15. C. R. Doering, H. R. Brand, and R. E. Ecke, eds., Proceedings of the workshop on external noise and its interaction with spatial degrees of freedom in nonlinear dissipative systems, *J. Stat. Phys.* **54**(5/6) (1989).
16. M. A. Burschka, Exact solution of the N -body initial value problem for the diffusion-limited logistic diffusion-reaction system, preprint (1991).