Front form and velocity in a one-dimensional autocatalytic $A+B\rightarrow 2A$ reaction

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We consider the general irreversible $A+B\rightarrow 2A$ autocatalytic reaction in one dimension, for which the corresponding diffusion constants D_A and D_B may differ. Contrary to mean-field-type predictions, the Monte Carlo simulations show that, as long as $D_A>0$, only a unique, stable front propagates with constant velocity. When $D_A=0$ the behavior changes drastically: both the front's position and its characteristic width grow with $t^{1/2}$. These findings are adequately described within a Smoluchowski-type approach.
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I. INTROUCTION

Reaction kinetics in low dimensions were extensively investigated in the past two decades, since they differ significantly from the situation in high-dimensional spaces, and thus violate strongly the classical kinetics schemes based on the mass-action law [1,2]. Remarkably, such violations did not find much attention in the society of scientists dealing with front propagation in autocatalytic reactions. The autocatalytic $A+B\leftrightarrow 2A$ conversion (where both the direct and the back reaction follow the bimolecular scheme) can be described in the mean-field limit by the quadratic Fisher equation [Eq. (11.31) of Ref. [3]], whose solution fronts may propagate with different velocities v; here the initial conditions determine whether a certain velocity is attained [3]. We note that a mean-field-type description is not appropriate in low dimensions ($d=1$ and 2) where the reaction term depends strongly on particle correlations [4–7]. The reaction $A+B\leftrightarrow 2A$ was investigated analytically and via Monte Carlo simulations in Refs. [8, 9], where, based on ensemble-averaged quantities, in one and two dimensions strong deviations from the mean-field-type behavior were detected. A detailed study of the *irreversible* autocatalytic reaction $A+B\rightarrow 2A$ in one dimension was provided in Ref. [10] for equal diffusion constants $D_A=D_B$. This reaction is the simplest model for infection spreading, by which (irreversibly infected) A particles infect at first encounter healthy B particles. Here we analyze the situation for general D_A and D_B.

In fact, the question of the front structure falls into the class of spontaneous local ordering phenomena, which have found much attention in connection with the $A+A\rightarrow 0$, $A+A\rightarrow A$, and $A+B\rightarrow 0$ reactions [11–22]. Especially the last reaction shows (due to fluctuations effects) nontrivial large-scale spatial structures (clusters); these findings lay outside the classical kinetics scheme, and for their understanding need much more elaborated theories and extensive numerical studies. Note that a microscopic description of the front structure requires a knowledge of the local ordering of the A and the B particles near the front.

In Ref. [10] only the case $D_A=D_B$ was considered. Then the particles are mathematically equivalent, and the whole reaction consists solely in the renaming of B particles to A on encounter. This introduces an additional, rather unrealistic symmetry into the problem; here we consider the general situation of *physically different* particles, and let the diffusion coefficients of the A and the B particles differ. We show that as long as $D_A>0$ we recover the previously found result, namely, that there exists only one stable velocity of propagation; furthermore, the velocity is proportional to D_A, and the front form is universal (independent of D_A).

In our simulations we start from a one-dimensional lattice of length $L=10^4$ (with lattice constant $a=1$), which is initially randomly filled with B particles whose concentration is c_0. We take excluded-volume interactions into account: any lattice site can be occupied by only one particle. The excluded-volume condition is not important for B particles at low concentrations, but it is crucial when the diffusion coefficient of the A particles tends to zero. At the left end of the system we place an A particle. All particles perform random walks on the lattice, and the particle to move next is chosen at random. Whenever an A particle meets a B particle sitting on a neighboring site, the reaction takes place immediately, and the B particle is relabeled A. In this way the front propagates.

The random motion of the particles is characterized by the diffusion coefficients D_A and D_B of single, free A and B particles (in the absence of excluded-volume interactions). To reduce the number of free parameters we set $D_A+D_B=1$. The simulation procedure is as follows: One first draws at random a particle which will attempt the next move. In our simulations we also distinguish whether $D_A\geqslant D_B$ or $D_A<D_B$ holds. For the sake of simplicity we discuss the $D_A\geqslant D_B$ case only. Then, if an A particle is drawn, it attempts to step to the left or to the right with probability $\frac{1}{2}$. The step is accepted if the corresponding neighboring site is empty, otherwise the A particle keeps its position. If a B particle is drawn, it makes an attempt to step to the left (or to the right) with probability $D_B/2D_A$ (again, this step is accepted if the corresponding neighboring site is empty) or does not attempt

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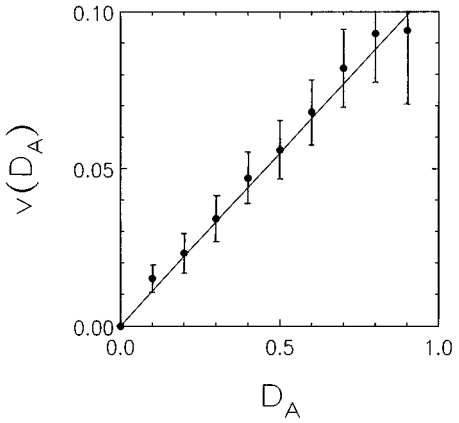

FIG. 1. The front's velocity v as a function of the diffusion coefficient D_A for $c_0=0.1$. The circles give the results of the simulations, and the error bars are the standard deviation. The slope of the full line is 0.11, corresponding to $\alpha=1.1$ in Eq. (6).

to make a step, with probability $1-D_B/D_A$. One Monte Carlo step (MCS) is completed when N drawings of particles (corresponding to their total number) take place. Normally, the time associated with one MCS is $\Delta t = a^2[2\max(D_A,D_B)]^{-1}$ in natural units, with a being the lattice spacing (we have $a^2=1$).

During the simulations we monitor the position of the front (i.e., the position of the rightmost A particle) and the distributions p_{AA} and p_{AB} of the distances from the A at the front to its left and right nearest neighbors. The results were averaged over 1000 realizations of the process. The initial concentration of particles is chosen to be $c_0=0.1$. For this value of c_0 we checked for $D_A=D_B$ that under excluded-volume conditions the front's velocity and form do not differ (within the error bars of our simulations, see Fig. 1) from the free case (without excluded-volume conditions) reported in Ref. [10].

In the standard Fisher approximation for $A+B\rightarrow 2A$, the evolution of the particles' concentrations is based on reaction-diffusion equations. For example, for $D_A=D_B=D$, one has, for the B particles,

$$\frac{\partial}{\partial t}\,c_B = D\Delta c_B - kc_Ac_B = D\Delta c_B - kc_B(c-c_B). \qquad (1)$$

Here we used $c_A+c_B=c=\text{const}$, which also implies $\partial c_A/\partial t = -\partial c_B/\partial t$. Equation (1) leads to a stable front propagation, as long as the front's velocity exceeds the value $v_c = 2\sqrt{kD}$. However, irreversible reactions on contact require, in one dimension, strict segregation of the A and B particles, which cannot result from Eq. (1) except in the physically not meaningful limit $k\rightarrow\infty$. In the Fisher picture this would mean that no stable propagation is possible, clearly in contradiction to our numerical findings.

The classical kinetic scheme is a preaveraged approach which neglects ordering on length scales comparable to the interparticle distance and (as stated above) does not apply in one dimension, where the structure of the depletion zones near the fronts is of great importance. Therefore the overall assumption of a time-independent reaction rate k does not hold in low dimensions; see Ref. [1]. Therefore we consider another mean-field approximation; that, however, accounts for the formation of a depletion zone in one dimension. The procedure follows Smoluchowski's approach to classical kinetics [23,24], which is based on a two-particle approximation, and which leads in low-dimensional space- to time-dependent reaction coefficients $k(t)$.

Note first that with excluded-volume interactions in one dimension the front moves due to the reaction of the leftmost B particle with the rightmost A, whose actual position we denote by x_f. Let $D_B=D_A+D_B$ be the relative diffusion coefficient of the A-B pair, and y their mutual distance. Let us fix the coordinate system at the rightmost A. In an uncoupled scheme the density $c_B(y,t)$ of the B particles obeys

$$\frac{\partial c_B}{\partial t} = \overline{D}_B\,\frac{\partial^2 c_B}{\partial y^2} \qquad (2)$$

and the boundary condition is $c_B(0,t)=0$. Now the front's motion between two reaction corresponds to the diffusive displacement of the rightmost A particle (say, the nth one). After a reaction act, the number of A's increases by one, and the front moves from the nth to the $(n+1)st$ A. In a mean-field approximation the displacement of the front can be viewed in the laboratory frame as an overall drift with average velocity v superimposed on the random, diffusive motion considered. In the coordinate system moving together with the front, we hence have $y=x-vt$ and

$$\frac{\partial c_B}{\partial t} - v\,\frac{\partial c_B}{\partial x} = \overline{D}_B\,\frac{\partial^2 c_B}{\partial x^2}. \qquad (3a)$$

We note that a similar equation governs the density of A particles left of the front:

$$\frac{\partial c_A}{\partial t} - v\,\frac{\partial c_A}{\partial x} = \overline{D}_A\,\frac{\partial^2 c_A}{\partial x^2}, \qquad (3b)$$

where now the effective diffusion coefficient is given by $\overline{D}_A=2D_A$. We now turn to two distinct cases, namely, $D_A>0$ and $D_A=0$.

II. CASE OF MOBILE *A* PARTICLES

In this case there exist stationary (time independent) solutions of Eqs. (3a) and (3b). These solutions of Eqs. (3) satisfy the equation

$$\frac{d^2}{dx^2}\,c_{A,B}(x) = -\frac{v}{\overline{D}_{A,B}}\,\frac{d}{dx}\,c_{A,B}(x) \qquad (4)$$

to the left (right) of the boundary. The solution for $c_B(x)$ which satisfies $c_B(0)=0$ and $c_B(+\infty)=c_0$ is given by

$$c_B(x) = c_0(1-e^{vx/\overline{D}_B}). \qquad (5)$$

On the other hand one has $c_A=\text{const}$, which is the only solution satisfying $c_A(-\infty)<\infty$.

Now we invoke the equality of the particle fluxes to the left ($j_-=vc_A$) and to the right [$j_+=D_B(\partial/\partial x)c_B(+0)$] of the boundary. This requirement is fulfilled only if $c_A=c_0$, but it does not fix v, the front's propagation velocity. This

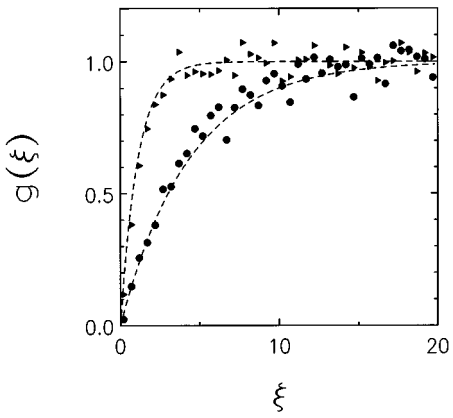

FIG. 2. Front forms $g(\xi)$ for $D_A=0.2$ (triangles) and $D_A=0.8$ (circles); the dashed lines represent the theoretical expression $g(\xi)=1-\exp(-v\xi/c_0D_B)$, where $D_B=1$ and v is taken from the simulations.

parallels our findings in the special case $D_A=D_B$ [10]. As in this special case, the continuous-medium picture does not fix the value of the front's velocity v: in order to determine v one has to take the discrete aspect of the problem (the presence of particles) into account.

Next we include discreteness arguments into the analytical model. As we proceed to show, this then determines v unambiguously. Let us consider the situation immediately after the reaction: Two A particles are now occupying neighboring places on the lattice. The numerical results show that the front's form is stable, and that no shock-wave-type structure is formed (leading to a higher concentration of A's on the front than far to its left). Thus we are justified in assuming that the newly formed A-A pair separates on average at least by the distance $l\sim c^{-1}$ during the time τ required by the next B particle to reach the front. Hence τ equals j_+^{-1}, where $j_+\propto D_B[\partial c_B(0)/\partial x]$ is the flux of B particles toward the A (within the Smoluchowski approximation). This consideration leads to $c^{-1}\propto\sqrt{D_A\tau}\propto\sqrt{2D_A/cv}$, from which it follows that

$$v\cong\alpha c_0 D_A, \tag{6}$$

where α is some, until now unspecified, constant. Note that in this approximation the velocity is linear in D_A, so that it vanishes for $D_A=0$.

We turn now to the results of the simulations, and display in Fig. 1 the velocity of the front as a function of D_A. The plot confirms clearly that the linear dependence of v on D_A, Eq. (6), is obeyed. Moreover, the numerical results lead to a prefactor α very close to unity, so that $v\cong c_0D_A$.

In Fig. 2 we plot the front forms $g(\xi)=c_B(x)/c_0$, as a function of the dimensionless distance $\xi=c_0x$, for two values of D_A, namely, 0.2 and 0.8. The dots are the results from the simulations, whereas the dashed lines correspond to the theoretical form $g(\xi)=1-\exp(-\xi/\lambda)$, which follows from Eq. (5); here we set $\lambda=c_0D_B/v$, and used for v the numerically obtained values from Fig. 1. The findings displayed in Fig. 2 prove that the overall front form is reproduced quite well by the mean-field approximation, Eq. (5).

In order to have a further, more stringent test for the validity of the independent pair approximation used in the derivation of Eqs. (3), we now evaluate analytically the mean AB distance at the front's position (which, *a priori*, depends on interparticle correlations) and we compare it to the results of simulations.

A simple mean-field expression for the AB distance at the front can be obtained by taking the B particles to be independent of each other. Let $c(x)$ describe the probability to find a B particle at x. Dividing the x axis from the rightmost A particle into partitions of length Δx, one has $c(x_i)\Delta x$ as the probability to find a B particle within the ith partition, where x_i denotes the center of the partition. The probability to find the leftmost B inside the kth partition is given by $p(x_k)=c(x_k)\Delta x\Pi_{i=0}^{k-1}[1-c(x_i)\Delta x]$, which corresponds to the probability to find a B particle within the kth partition and not to find any B-particles in each of previous partitions. Using the fact that $\Pi_{i=0}^{k=1}[1-c(x_i)\Delta x]=\exp[\Sigma_{i=0}^{k-1}\ln(1-c(x_i)\Delta x)]\approx\exp[-\Sigma_{i=0}^{k-1}c(x_i)\Delta x]$, and changing from a sum to an integral in the exponent, one obtains the probability density to find the leftmost B at the distance y measured from the rightmost A:

$$p(y)=c(y)\exp\left(-\int_0^y c(x')dx'\right), \tag{7}$$

which is an extension of Hertz's formula [25,26] valid in one dimension for an x-dependent concentration. This gives, e.g., for the mean AB distance

$$L_{AB}=\int_0^\infty xp(x)dx=\int_0^\infty dx\ xc(x)\exp\left(-\int_0^x c(x')dx'\right). \tag{8}$$

Partial integration leads to

$$L_{AB}=\int_0^\infty dx\ \exp\left(-\int_0^x c(x')dx'\right). \tag{9}$$

Using Eq. (5) we obtain

$$L_{AB}=c_0^{-1}\int_0^\infty d\xi\ \exp\{-\xi-\lambda[1-\exp(-\xi/\lambda)]\}, \tag{10}$$

where ξ is the dimensionless distance introduced above. Changing the integration variable to $\zeta=\lambda^{-1}[1-\exp(-\lambda\xi)]$, we have

$$L_{AB}=c_0^{-1}\lambda^{\lambda-1}e^\lambda\int_0^\lambda\zeta^{\lambda-1}e^{-\zeta}d\zeta=c_0^{-1}\lambda^{1-\lambda}e^\lambda\gamma(\lambda,\lambda), \tag{11}$$

where $\gamma(\alpha,x)$ is the incomplete γ function. In Table I we display the theoretical values of L_{AB} [given by Eq. (11)], and confront them with the results from the simulations. The good agreement between the numerically determined values (obtained as an average taken for each Monte Carlo step) and the calculated values shows that interparticle correlations are of minor importance.

TABLE I. Mean AB distance L_{AB} determined theoretically [Eq. (11)], and through simulations.

D_A	L_{AB}, simulations	L_{AB}, theory
0.2	32.8±1.7	31.9
0.5	23.0±1.5	22.0
0.8	20.4±1.3	18.5

III. CASE OF IMMOBILE *A* PARTICLES

For $D_A=0$ we again start from Eq. (3a) and have now $D_B=D_B$. Note that the velocity v given by Eq. (6) vanishes for $D_A=0$. This is due to the fact that for $D_A=0$ no stationary solution of Eq. (3a) for $c_B(x)$ exists. On the other hand, for $D_A=0$ it is clear that the velocity of the front is governed by the flow of B particles toward the A boundary, and that the A cluster left from the boundary has a density equal to unity. The A cluster hence grows by the accretion of colliding B particles, and the front moves with a *time-dependent* velocity

$$v(t)=-D_B\left.\frac{\partial c_B(x,t)}{\partial x}\right|_{x_f=0}. \tag{12}$$

This result suggests to extending Eq. (3a) to the form

$$\frac{\partial c_B}{\partial t}-v(t)\,\frac{\partial c_B}{\partial x}=D_B\,\frac{\partial^2 c_B}{\partial x^2}. \tag{13}$$

Furthermore, Eqs. (12) and (13) are closely related to trapping by a single sink, Ref. [1], and to the target problem [1,27], whose solutions in one dimension scale with $x/\sqrt{D_Bt}$. We hence also assume that

$$c_B(x,t)=c_0 g\left(\frac{x}{\sqrt{D_Bt}}\right), \tag{14}$$

which automatically leads to a time dependence of the velocity of the form $v(t)=A/\sqrt{D_Bt}$, so that the front's position x_f goes as $x_f\propto t^{1/2}$. In Fig. 3 we plot the numerically found $x_f(t)$ vs t on double logarithmic scales. The figure indicates

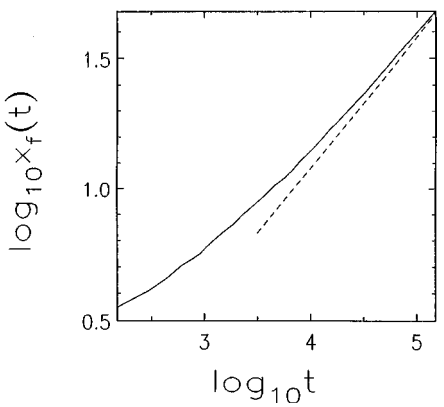

FIG. 3. Front's position $x_f(t)$ for $D_A=0$. Note the double-logarithmic scales. The dashed line has a slope of 1/2.

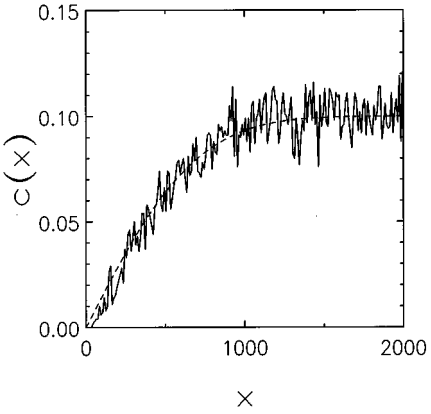

FIG. 4. Front form $c_B(x)$ for $D_A=0$ at $t=10\,000$. The dashed line is the theoretical approximation (18).

that $x_f(t)\propto t^{1/2}$ may hold in the long-time asymptotic regime, although this convergence is slow.

Now, Eq. (13) for the dimensionless variable $\xi=x/\sqrt{D_Bt}$ takes the form

$$g''(\xi)+\left(\frac{\xi}{2}+A\right)g'(\xi)=0, \tag{15}$$

with the following solution, which satisfies the boundary conditions $g(0)=0$ and $g(+\infty)=c_0$:

$$g(\xi)=\frac{\mathrm{erf}(\xi/2-A)-\mathrm{erf}(A)}{1-\mathrm{erf}(A)}. \tag{16}$$

Here erf(z) is the error function; see Eq. (7.1.1) of Ref. [28]. Note that Eq. (12) implies that $A=c_0g'(0)$, from which a closed equation for A follows:

$$A=\frac{c_0}{\sqrt{\pi}e^{A^2}(1-\mathrm{erf}\,A)}. \tag{17}$$

For small concentrations one has, from Eq. (17), $A\approx c_0/\sqrt{\pi}$, and therefore Eq. (16) gives, for the dimensionless density profile,

$$g(\xi)\approx\mathrm{erf}(\xi/2)=\mathrm{erf}\left(\frac{x}{2\sqrt{D_At}}\right), \tag{18}$$

which approximation is still very good for the value $c_0=0.1$ used in simulations; see Fig. 4.

IV. CONCLUSIONS

We conclude by summarizing our findings: We analyzed numerically and analytically the irreversible $A+B\to 2A$ autocatalytic reaction in one dimension for the general case, in which $D_A=D_B$ does not necessary hold. The simulations show that for $D_A>0$ the front propagates with a stable velocity v, which is proportional to D_A. Analytically, the

continuous-medium approximation does not fix the value of v; on the other hand, v can be found from simulations and is related to the discrete nature (particles) of the problem. Furthermore, for $D_A \neq 0$, the continuous-medium approximation reproduces quite well several properties of the model (for example, the form of the front and the mean AB distance at the front's position), *provided* that v is known. In the case $D_A = 0$ both the front's position and the front's width grow with $t^{1/2}$; in this case the position and form of the front are well reproduced by the continuous-medium picture.

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