ARTICLES

Front propagation in the one-dimensional autocatalytic $A+B \rightarrow 2A$ reaction with decay

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We consider front propagation in the autocatalytic scheme $A+B \rightarrow 2A$, where we also allow the A particles to decay, $A \rightarrow 0$, with a constant decay rate β. In a one dimensional, discrete, situation the A domain moves as a pulse, and its dynamics differs from what is found in higher dimensions. Thus the velocity of the pulse tends to a finite value when β approaches from below the critical value β_c, at which pulses die out. On the other hand, when approaching β_c from above, the mean lifetime of the pulse grows as $T \propto (\beta-\beta_c)^{-2}$. [S1063-651X(99)13103-9]

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I. INTRODUCTION

Reaction kinetics in low dimensions were extensively investigated in the last two decades, since they differ significantly from the situation in high-dimensional spaces, and often violate strongly the classical (mean-field) kinetical schemes based on the mass-action law [1–4]; this happens in particular for $d=1$ and 2, where the reaction terms show a strong dependence on high-order particle correlation-functions [5–8].

Recently much attention was attracted to autocatalytic reaction schemes for which traveling wave front forms and velocities were investigated [9–15]. An important feature of such reaction schemes is the fact that the reactants are particles, and hence obey discrete spatial distributions; this leads to qualitative deviations from the predictions of classical, mean-field-like theories, as stated in Refs. [16–20]. Following our investigations of Refs. [18,19], here we extend the autocatalytic $A+B \rightarrow 2A$ study by also including the possibility that the A species decays (or, in chemical language, gets inactivated). Formally the problem is described by the chemical expressions

$$A+B \rightarrow 2A \tag{1}$$

and

$$A \rightarrow 0. \tag{2}$$

To fix the ideas we start from a planar front and have to its right, in the whole half-space, only B particles whose mean concentration is $C_B(\infty)=C_0$. We initiate the reaction by adding a thin layer of A particles to the left of the front. The autocatalytic character of the reaction [Eq. (1)] leads to the creation of a new A particle whenever one A particle present comes into contact with a B particle. This leads to the propagation of the reaction front to the right, into the B-filled domain. On the other hand, since the A particles have only a finite mean lifetime τ_0 (corresponding to a decay rate $\beta=\tau_0^{-1}$) as time passes, the probability of finding A particles far to the left of the reaction front decreases. Thus the A particles are to be found only within a bounded region of space; this region may be viewed as an A pulse, which propagates to the right. Here one is interested in knowing under which conditions such a pulse propagates, and what its velocity v is. Now stable pulse propagation is only possible when the decay rate is not too high. Otherwise the number of A particles created per unit time (at any velocity of stable propagation) becomes smaller than the number of particles which decay; eventually then all A particles die out and the process stops.

Let us first recall the situation in three dimensions, and in a continuous picture [21], in which a flat front is moving to the right. Let D be the diffusion coefficient of both species ($D_A=D_B=D$) and let the first, autocatalytic, stage be described by an effective reaction rate coefficient k. The analysis of the stability of the traveling wave solutions [21] shows that stable front propagation is possible if the front's velocity exceeds the value $v_c \geqslant v_{\min}=2\sqrt{kC_0D[1-(\beta/kC_0)^2]}$. Moreover, since under the marginal stability principle one expects that the system chooses a minimum velocity at the propagation, it follows that stable front propagation is impossible for $\beta \geqslant \beta_c = kC_0$. When β approaches β_c from below, v_{min} decreases as

$$v \propto \sqrt{\beta_c-\beta}, \tag{3}$$

thus showing a critical behavior of mean-field type.

In what follows we consider the same problem in one dimension, but in a discrete picture. Here the B particles are initially randomly distributed, say at the right of the origin, and the reaction is initiated by adding A particles to the left of the origin. This leads to the formation of a pulse of finite length, which then propagates into the B region. We find that the situation in this one-dimensional (1D) case differs strongly from the one reported above. First the 1D situation is special in that (possibly after an initial stage) the number of particles in the pulse is always finite. This means that due to fluctuations there always exists a nonzero probability for the pulse to die out; hence for purely statistical reasons the lifetime of any such pulse is always finite. However, as we proceed to show, for low β values the number of A particles in each pulse is large enough to render purely statistical extinction times extremely long. On the other hand, parallel to the findings in high dimensions, when β is large enough the A pulse does not succeed in getting enough new material through the reaction [Eq. (1)], and dies out. Hence pulse extinctions for small and large β occur on vastly different time scales. The two β domains are separated by a critical value β_c. As we show in the following, in one dimension, when β_c is approached from below, v tends to a constant, nonzero value, a fact clearly at variance with Eq. (3). Furthermore when approaching β_c from above the mean lifetime of the pulse grows as $T \propto (\beta - \beta_c)^{-2}$.

II. SIMULATIONS

In the simulation we use 1D systems of length $L=10^4$ and $L=2\times 10^4$ and perform (as a rule) 10^3 independent runs for each average. A lattice site can only be occupied by one particle, and we use reflective boundary conditions for the particles at both ends. At the beginning of the simulation we start at the left border with an A pulse consisting of ten particles which occupy ten adjacent sites. The rest of the lattice is randomly filled with B particles of concentration C_0 (the values $C_0=0.1$ and $C_0=0.2$ are used). We stop the simulation before the pulse has a chance to reach the right border. We study two different cases: (i) the case of immobile B particles with $D_B=0$ and $D_A=1$, and (ii) the case of equally mobile particles, $D_A=D_B=D=\frac{1}{2}$. In the simulation all mobile particles perform random walks on the lattice, and the particle to move next is chosen at random. The step is accepted if the corresponding neighboring site is empty, otherwise the chosen particle keeps its old position. Whenever an A-B pair is found in a nearest neighbor position, the reaction occurs instantaneously, and the B particle is relabeled A. Finally, if the trial particle is an A we remove it from the system with probability q. We consider that one Monte Carlo step (MCS) elapsed when on the average each particle with $D\neq 0$ was picked once. 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 $a=1$). The value of the decay rate β is connected with q through $\beta = q/\Delta t$. The length of the lattice L and the maximal simulation time t_{max} are chosen such that $\beta t_{max} \gg 1$ and $L \gg v t_{max}$ hold. The first condition is very restrictive since, as we proceed to show, the interesting values of β are extremely small; thus, for example, in the case $D_A=1$, $D_B=0$, and $C_0=0.2$, β_c has to be of the order of 10^{-4}.

First we consider the case of immobile B particles ($D_A=1$, $D_B=0$), and take $C_0=0.2$. Now, as discussed above pulse extinction (the disappearance of all A's) may always occur, but its occurrence probability depends strongly on β. For $\beta < 4\times 10^{-4}$ we observe no pulse extinction during simulation times of 10^4. On the other hand, for β around 10^{-3}, pulse extinction occurs frequently. In Fig. 1(a) we present (for values of β ranging from 0 to 10^{-3}) the average position of the front $\langle X_A \rangle$. The position $X_A(t)$ is that of the rightmost A particle, and the average $\langle\ \rangle$ is taken over those runs (out of 10^3 realizations) in which the pulses survive up to time t.

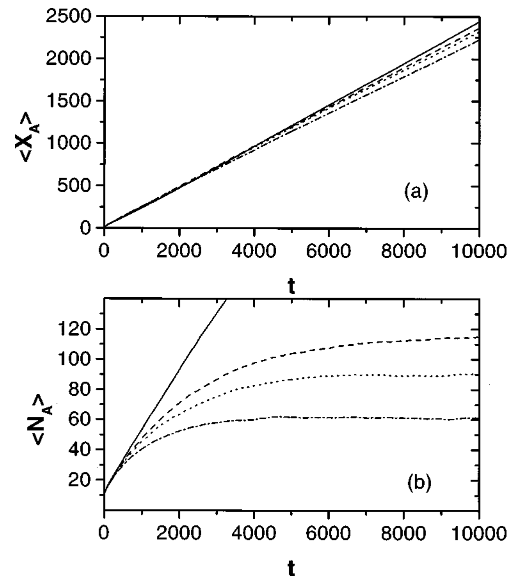

FIG. 1. The temporal evolution of a pulse for different values of the decay rate β. The lines correpond $\beta=0$ (solid line), $\beta=10^{-4}$ (dashed line), $\beta=4\times 10^{-4}$ (dotted line), and $\beta=10^{-3}$ (dash-dotted line). The time t is given in Monte Carlo steps (MCS); see text for details. (a) The time dependence of the average front position $\langle X_A\rangle$ of a propagating pulse. (b) The mean number $\langle N_A\rangle$ of A particles in the pulses still alive at time t.

In Fig. 1(b) we show $\langle N_A\rangle$, the averaged number N_A of A particles; here the average is performed over the same set of realizations as for $\langle X_A\rangle$. For $\beta\neq 0$ we infer from the figure that $N_A(t)$ reaches a limiting value $N_A(\beta)$, which depends markedly on β: $N_A(\beta)$ decreases with increasing β.

For larger β the survival probability of the pulse $W(t)$ (defined as the relative number of pulses still alive at time t) turns out to be closely exponential, i.e., it is $W(t) \propto \exp(-t/T)$, with T being the average extinction time. In Fig. 2 we plot $T^{-1/2}$ as a function of β for $\beta \in [8\times 10^{-4}, 20\times 10^{-4}]$. It is clear by inspection that the $T^{-1/2}$ vs

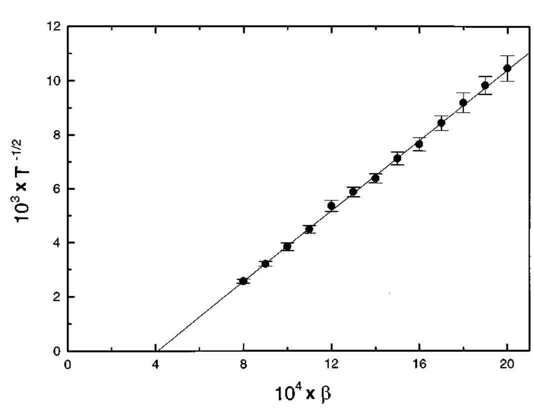

FIG. 2. Mean pulse lifetimes T as a function of β for $\beta > \beta_c$. Plotted is $T^{-1/2}$ vs β. Note the linear dependence which allows one to determine β_c.

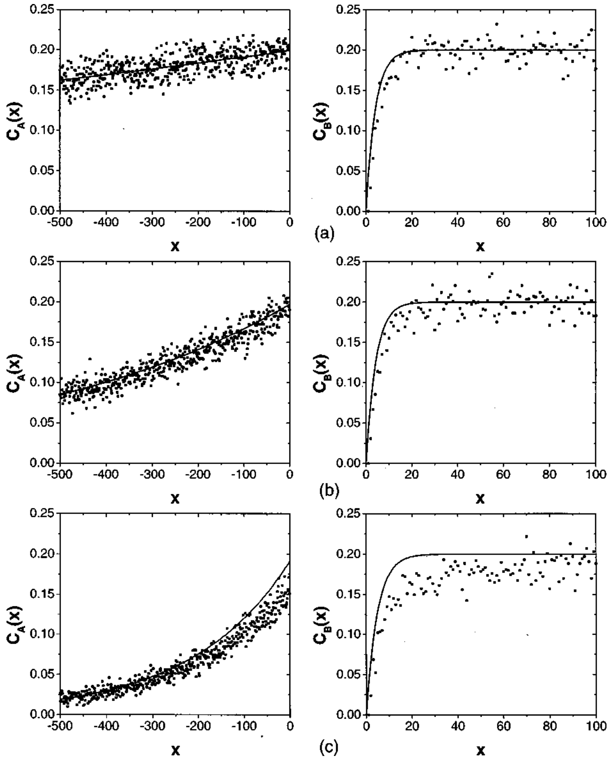

FIG. 3. The average density distributions under pulse propagation. Left column: $C_A(x)$ left from the front. Right column: $C_B(x)$ right from the front. Note the differences in the x scales in the left and right columns. The values of β correspond to (a) $\beta=10^{-4}$; (b) $\beta=4\times10^{-4}$, and (c) $\beta=10^{-3}$.

β dependence is well described by a linear law, i.e., $T^{-1/2}=s(\beta-\beta_c)$, or equivalently $T=s^{-2}(\beta-\beta_c)^{-2}$. A least-square analysis of the data fixes the values of the constants to $\beta_c=4.1\times10^{-4}$ and $s=6.54$.

Let us focus on the velocity of the pulses, $v(\beta)$, defined through $d\langle X_A\rangle/dt$. Now $v(\beta)$ behaves near β_c differently than the mean-field predictions of Eq. (3). Equation (3) suggests that the velocity of the pulse vanishes when $\beta\to\beta_c$. In our case, for β slightly larger than β_c, the pulses still alive at time t propagate with a well-defined, nonzero velocity. As typical numerical values for $v(\beta)$, we thus find $v(0)=0.275$ and $v(\beta_c)=0.234$.

Simulations in the case in which both kinds of particles are mobile ($D_A=D_B=\frac{1}{2}$ and $C_0=0.1$) show results which are qualitatively similar to those for immobile B particles. Also here, for fixed $\beta,\beta\in[0,10^{-3}]$, the pulses move with constant average velocities $v(\beta)$. Remarkably here, β_c turns out to be near 5×10^{-5}, i.e., it is almost an order of magnitude smaller than in the $D_A=1,\ D_B=0$ case.

Now we turn to the distribution of A particles in the pulse, and of B particles next to it. We fix the origin of the coordinate system on the rightmost A (the front particle). In Fig. 3 we display the density distribution of the A particles to the left of the front, and also that of B particles to the right. As parameters we take $D_A=1,\ D_B=0$, and $C_0=0.2$ (i.e., immobile B particles). The three rows of Fig. 3 correspond to the cases $\beta<\beta_c$, $\beta\sim\beta_c$, and $\beta>\beta_c$. The density of A particles as a function of the distance x from the front decays nearly exponentially with x, a feature which is to be expected for an almost constant front velocity. The characteristic decay length is much larger than the interparticle distance. The distribution of B-particles shows a narrow depletion zone in the immediate vicinity of the front and tends to C_0 for larger values of x.

Our numerical findings can be explained within a framework based on the Smoluchowski picture, as we proceed to show. This approach led for $\beta=0$ to qualitatively correct results in the 1D case, as we demonstrated in Ref. [19]. This is also here the case, as can be inferred from Fig. 3, in which the solid lines are the theoretical curves calculated using the procedure which follows.

III. SMOLUCHOWSKI APPROACH

In what follows we explain theoretically our numerical findings. We consider $\beta<\beta_c$, and assume that the pulse propagates stably, with velocity v. Starting points for us are the equations for the densities of the A and the B particles, written in the frame which moves with the pulse. Setting as in Ref. [19], $\bar{D}_A=2D_A$ and $\bar{D}_B=D_A+D_B$, for the A particles we have for $x<0$,

$$\frac{\partial C_A}{\partial t}-v\frac{\partial C_A}{\partial x}=\bar{D}_A\frac{\partial^2 C_A}{\partial x^2}-\beta C_A, \tag{4}$$

and for the B particles, for $x>0$,

$$\frac{\partial C_B}{\partial t}-v\frac{\partial C_B}{\partial x}=\bar{D}_B\frac{\partial^2 C_B}{\partial x^2}. \tag{5}$$

In the same moving frame the stationary solutions (if they exist) correspond to

$$\bar{D}_A\frac{\partial^2 C_A(x)}{\partial x^2}-\beta C_A(x)+v\frac{\partial C_A(x)}{\partial x}=0 \tag{6}$$

for $x<0$, and to

$$\bar{D}_B\frac{\partial^2 C_B(x)}{\partial x^2}+v\frac{\partial C_B(x)}{\partial x}=0 \tag{7}$$

for $x>0$. As boundary conditions on C_A and C_B we have $C_A(x)\to0$ for $x\to-\infty$ and $C_B(\infty)\to C_0$ for $x\to\infty$, together with $C_B(0)=0$.

The solution of Eq. (6), which stays finite for $x\to-\infty$, is

$$C_A(x)=a\exp\left(\frac{px}{\bar{D}_A}\right), \tag{8}$$

where a is a constant, and

$$p=\frac{\sqrt{v^2+4\bar{D}_A\beta}-v}{2}>0. \tag{9}$$

The solution of Eq. (7) is

$$C_B(x)=C_0\left[1-\exp\left(-\frac{vx}{\bar{D}_B}\right)\right]. \tag{10}$$

We can now fix the value of a by requiring that the particle flux through the front (i.e., at the origin) is conserved. This condition is

$$j_A(0^-)=j_B(0^+). \tag{11}$$

Now the particle flux $j_\lambda(x)$ for both species ($\lambda=A$ or $\lambda=B$) is

$$j_\lambda(x)=vC_\lambda(x)+\overline{D}_\lambda\frac{\partial C_\lambda(x)}{\partial x}. \tag{12}$$

This, together with Eqs. (8) and (10), leads to

$$a(v+p)=j_A(0^-)=j_B(0^+)=C_0v, \tag{13}$$

so that

$$a=C_0\frac{2}{\sqrt{1+4\overline{D}_A\beta/v^2}+1}. \tag{14}$$

It follows (parallel to the findings of Ref. [19] for $\beta=0$) that also for $\beta\neq 0$ the Smoluchowski approach is able to deduce the front forms for a given v, but that it is unable to determine the value of v.

The forms of the A and B distributions given by Eqs. (8), (10), and (14) are shown by solid lines in Fig. 3. Here we used the values of the velocities $v(\beta)$ which follow from the simulations; we performed a least-square fit to the values of $\langle X_A\rangle$ of Fig. 1. For $\beta=0.0001$, 0.0004, and 0.001, we find $v=0.244$, 0.234, and 0.206, respectively. One readily sees by inspection that the theoretical forms and the simulation results agree very well for $\beta\leqslant\beta_c$. Note that even for $\beta>\beta_c$ the theoretical forms describe the numerical findings reasonably well, although this case lays outside the validity domain of our theoretical picture, which assumes a stable propagation of the front.

In order to fix v we must (as in Ref. [19]) take the discrete nature of the reactants into consideration. Under stable propagation the front's form does not change with time, so that in the front region neither particle accumulation nor depletion occur. Let us turn to a theoretical estimate of v, and consider the situation immediately after the reaction: Two A particles now occupy neighboring places on the lattice. This newly formed AA pair separates on average by the distance $L_{AA}\propto\sqrt{\overline{D}_A\tau}$, before the next reaction occurs; here τ is the average time needed by the next B particle to encounter the rightmost A, i.e., the front position. Thus, using Eq. (12),

$$\tau=j_B^{-1}(0^+)=1/vC_0, \tag{15}$$

so that a *typical* distance between the two A particles in a propagating pulse is

$$L_{AA}\propto\sqrt{\overline{D}_A/vC_0}. \tag{16}$$

On the other hand, L_{AA} can be also derived starting from the stationary concentration of the A particles close to the front, as described in Ref. [19]. In a simple approximation, when β is small and hence the number N_A of particles in the pulse is large ($N_A\gg 1$), one has, from Eq. (8) very close to the front,

$$L_{AA}\approx c_A^{-1}(0^-)=1/a. \tag{17}$$

From Eqs. (16) and (17), we now obtain the following expression:

$$\frac{\sqrt{1+4\overline{D}_A\beta/v^2}+1}{2C_0}=K\sqrt{\frac{\overline{D}_A}{C_0v}}. \tag{18}$$

Here K is some numerical constant of the order of unity, whose value can be estimated based on simulations. One should note that Eq. (18) then allows one to determine v.

Let us investigate the behavior of Eq. (18) in more detail. Introducing the dimensionless units V and b for the velocity and the decay rate, respectively, so that

$$v=C_0\overline{D}_AV \quad\text{and}\quad \beta=C_0^2\overline{D}_Ab, \tag{19}$$

we obtain

$$\frac{\sqrt{V^2+4b}+V}{2V}=K\sqrt{\frac{1}{V}}. \tag{20}$$

We can now discuss the existence of solutions of Eq. (20). For this we consider the behavior of b as a function of V. Solving for b in Eq. (20) we obtain

$$b=KV(K-\sqrt{V}). \tag{21}$$

The function $b(V)$ shows a simple maximum, $b_c=(4/27)K^4$, which corresponds to $V_c=(4/9)K^2$.

For $b\to b_c$ one has

$$V(b)=V_c+\frac{2}{3}\sqrt{b_c-b}. \tag{22}$$

For $b<b_c$ the mean number N_A of A particles in a stationary pulse stays finite. This can be inferred from the balance equation

$$0=dN_A/dt=j_B(0^+)-\beta N_A=vC_0-\beta N_A, \tag{23}$$

from which $N_A=vC_0/\beta$ follows. At b_c the number of particles in the pulse is $N_A^c=V_c/b_c=3K^{-2}$.

For $b>b_c$, Eq. (20) has no solutions, which we interpret as the existence of a critical decay rate $b=b_c$ (or equivalently $\beta=\beta_c$). Note that the behavior of $V(b)$ differs strongly from a continuous mean-field-type transition, as predicted by classical kinetics: For $b\to b_c$ the value of $V(b)$ does not go to zero as in Eq. (3) but reaches a constant, nonzero, value V_c. Above b_c the pulse ceases to propagate not because its propagation velocity tends to zero, but because the pulse itself disappears, and no other stationary solution apart from the trivial one (only B's present) exists.

We remark that the qualitative predictions of our theoretical approach describe the numerical findings very closely: the transition to a nonpropagating regime takes place discontinuously, both in what the propagation velocity and also in what the number of particles in the pulse are concerned. The corresponding values of β_c are rather small. On the other hand, the dependence on K of the numerical values predicted is too strong to obtain a quantitative agreement. Thus estimates for $\beta=0$ based on the data of Ref. [19] lead to $v \approx 0.5\overline{D}_A C_0$, and give $K \approx 0.7$.

Reverting to natural units we obtain $V_c \approx 2C_0\overline{D}_A/9$ and $\beta_c \approx C_0^2\overline{D}_A/27$. For the values of $C_0=0.2$ and $\overline{D}_A=2$ used in simulations, we obtain $V_c=4/9V(0)\approx 0.09$ and $\beta_c \approx 0.003$. At β_c, for the number N_A of particles in a pulse we obtain $N_A \approx 6$. Thus taking $K \approx 0.7$ overestimates the value of β_c by a factor of 8, and underestimates N_A at β_c by the same factor. On the other hand, we attain these values by simply assuming K to be smaller by a factor of 1.7, which clearly is not bad given the very simple approximation, Eq. (18).

IV. CONCLUSIONS

In this work we numerically analyzed the autocatalytic reaction $A+B \rightarrow 2A$ in one dimension under A-particle decay. This reaction, initiated by adding A particles to a half-line filled by B's, leads to a propagating A pulse. For β larger than a critical value β_c, stationary pulse propagation is impossible, since all A particles die out quite rapidly. Contrary to the predictions of the classical, mean-field scheme, which suggests that the velocity of the pulse vanishes when approaching $\beta \rightarrow \beta_c$, we find that at β_c the transition to a nonpropagating situation takes place discontinuously, so that the value of the pulse's velocity does not vanish for $\beta \rightarrow \beta_c$. At $\beta=\beta_c$ the mean number N_A of A particles in a typical pulse also stays finite. We can explain these findings in the framework of a Smoluchowski-type approach, which also allows us to describe the distribution of the A and B densities around the propagating front.

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