Front Propagation and Local Ordering in One-Dimensional Irreversible Autocatalytic Reactions

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We consider the irreversible $A + B \rightarrow 2A$ autocatalytic reaction via Monte Carlo simulations in 1D. Contrary to mean-field-type predictions, the simulations show that only a unique, stable front propagates. Its structure is time independent and the spatial correlations turn out to be universal functions of the dimensionless interparticle distances. These findings are due to the discrete character (particles) of the model and to the 1D topological constraints. The temporal changes of the averaged front form stem from velocity fluctuations and are not a sign of unstable propagation. [S0031-9007(96)01642-0]

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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 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 problems of front propagation in autocatalytic reactions.

The autocatalytic $A + B \leftrightarrow 2A$ conversion (where both direct and back reactions follow the bimolecular scheme) can be described in the mean-field limit by the quadratic Fisher equation [(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 shows a strong dependence on correlation functions up to high orders [4,5]. The reaction $A + B \leftrightarrow 2A$ was investigated analytically and via Monte Carlo simulations in Refs. [6,7], where based on ensemble-averaged quantities, in 1D and 2D strong deviations from mean-field-type behavior were detected.

On the other hand, an ensemble-averaged approach tells only part of the story since it disregards the local ordering of the particles, an aspect which is of great importance in low dimensions. Such local ordering aspects were investigated in detail for the reactions $A + A \rightarrow 0$, $A + A \rightarrow A$, and $A + B \rightarrow 0$ [8–20]. Especially the last reaction shows nontrivial large-scale spatial structures (clusters) due to fluctuation effects [13–20]; these findings lay outside the classical kinetics scheme and need for their understanding much more elaborated theories and extensive numerical studies. Note that the microscopic description of the front structure requires the knowledge of the local ordering of the A and B particles near the front. On the other hand, the distribution of the front positions under ensemble averaging provides a macroscopic picture. These two points of view correspond to significantly different experimental situations and are known to lead to strongly different results in the case of $A + B \rightarrow 0$ reactions in 1D; see Refs. [19,20]. In general an ensemble-averaged approach is not suitable for distinguishing between instabilities and statistical fluctuations.

In Ref. [6] the $A \leftrightarrow 2A$ scheme was used to model the reversible $A + B \leftrightarrow 2A$ reaction. This scheme veils the role of the B particles, since (in contrast to their discrete nature) it implies that their distribution is uniform at all times. Here, however, we focus on the *irreversible* autocatalytic reaction $A + B \rightarrow 2A$ in 1D. This reaction is the simplest model for infection spreading, by which (irreversibly infected) A particles infect at first encounter the healthy B particles. As we show, this reaction gives rise to a universal, parameter-free behavior, determined by the discrete nature of the particles. Contrary to the mean-field predictions, the reaction front retains its microscopic form under propagation and its velocity is only slightly fluctuating. We present here the results of extensive Monte Carlo simulations of the system and compare them with the mean-field predictions.

In our simulations we start from a one-dimensional lattice of length $L = 10^4$ which is initially randomly filled with B particles whose concentration is c. 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 encounters a B particle the reaction takes place immediately and the B particle is relabeled A. In this way the front propagates. 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. We view as one Monte Carlo step (MCS) the time during which each particle has performed on the average one move. The overall simulation time was chosen to be $t_{\max} = 3 \times 10^4$ MCS; the results were averaged over 1000 realizations of the process.

The only parameters of our one-dimensional problem are the particle concentration c (which provides a scale for the mean interparticle distance $\lambda = c^{-1}$) and the diffusion coefficient D, which together with λ defines the characteristic time scale of the problem, $\tau = \lambda^2/D = 1/c^2 D$. The lack of further parameters in this simple

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1D $A + B \rightarrow 2A$ model renders dimensional analysis a very useful tool. Consider as an example the front velocity: The average time necessary for the rightmost A particle (say, the nth particle, whose position x is roughly $x = n\lambda$) to react with the leftmost B is given by the characteristic time $\tau = \lambda^2/D$ needed to diffuse through the mean interparticle distance. On reaction the mean front position moves to $x \cong (n + 1)\lambda$. Thus the front's velocity ν behaves as $\nu \propto D/\lambda = cD$. The dimensionless combination

$$\alpha = \frac{\nu}{cD} \tag{1}$$

is thus the most important dimensionless parameter of the system.

The front velocity is inevitably fluctuating. We have determined numerically the positions $x(t)$ of the front, from which we obtained $\nu(t)$ as well as $w(t)$, the dispersion of the front's position. We find that ν is constant and that w^2 grows as t (cf. Ref. [6]). In Fig. 1 we present for $t = 5000$ and $c = 0.1$ the cumulative normalized distribution function of the front positions, $F(\zeta) = N(x_f < \zeta w + \nu t)/N$, where $N(x_f < x)$ is the number of realizations (out of N simulations) for which the actual front position x_f is less than x. This form obtained by simulations is compared in Fig. 1 to the cumulative normal Gaussian. As is evident by inspection, the agreement is excellent.

The parameter dependency of the front width can be visualized as follows: The squared dispersion $w^2(t)$ of the front positions at time t is of the order of $\sigma^2 n(t)$, where σ is the dispersion of the front displacement per step and n is the mean number of steps within t. Now $n(t) \propto t/\tau = c^2 Dt$ and σ, being a length, scales with $\lambda = c^{-1}$; hence $w^2(t) \propto Dt$, independent of concentration. The dimensionless combination

$$\beta = \frac{cw^2(t)}{\nu t} \propto cD/\nu \tag{2}$$

is then time independent.

The results of our numerical simulations for $c = 0.025$, $c = 0.05$, and $c = 0.1$ support these assertions and lead to $\alpha = 1.05$ and $\beta = 3.57$; the uncertainties correspond to the last decimal digit. Note that taking λ as unit length and τ as unit time we have a parameter-free, universal situation; this is an extremely interesting feature of the $A + B \rightarrow 2A$ reaction in 1D considered here.

Since the β value is bounded (the velocity fluctuations are finite) ν is sharply defined. Moreover, on a microscopic scale the front (being localized at the rightmost A) is sharp and of limited width (some 2λ). We stress that the increase of the front width under ensemble averaging is due the *velocity* fluctuations and is not connected to any instability of propagation (cf. Refs. [6,7]).

The structure of the front region is characterized by the distance distributions p_{AB} (between the leftmost B and the rightmost A) and p_{AA} (between the rightmost A and its next A neighbor to the left). We find numerically that the distribution of distances between all other particles is indistinguishable from an exponential (the Hertz distribution in 1D), which is of no surprise when remembering that the reaction consists in a pure renaming of particles. Thus the non-Markovian aspects are felt in the *a posteriori* p_{AA} and p_{AB}; the distributions of the B-B distances are *a priori*, while the A-A distances other than the one of p_{AA} "forget" the reaction (renaming) stage quickly.

The probability distributions p_{AB} and p_{AA} for different values of concentrations ($c = 0.025$, 0.05, and 0.1) are shown in Figs. 2 and 3. Figure 2 presents the dependency of the value $\rho(\xi) = c^{-1} p_{AB}(x)$ on the scaled distance $\xi = cx$; Fig. 3 presents the same for the function $\theta(\xi) = c^{-1} p_{AA}(x)$. The results fall on master curves, a fact which stresses the scaling and parameter-free nature of the model.

We continue by analyzing continuous-medium descriptions of the reaction. In the standard Fisher approximation [3] the evolution of the particles' concentrations is based on reaction-diffusion equations. For example one has for the B particles

$$\frac{\partial}{\partial t} c_B = D\Delta c_B - k c_A c_B = D\Delta c_B - k c_B (c - c_B) . \tag{3}$$

Here we used that $c_A + c_B = c = \text{const}$, which also implies $\partial c_A/\partial t = -\partial c_B/\partial t$. Equation (3) leads to a stable front propagation [3], as long as the front's velocity exceeds the value $\nu_c = 2\sqrt{kD}$. For irreversible reactions on contact we have to require that $k \rightarrow \infty$ in order to forbid the occurrence of B particles on the left side of the front. The front structure given by Eq. (3) is then abrupt. Moreover, $k \rightarrow \infty$ implies $\nu_c \rightarrow \infty$; in the Fisher picture this would mean that no stable propagation is possible, clearly a contradiction to our numerical findings.

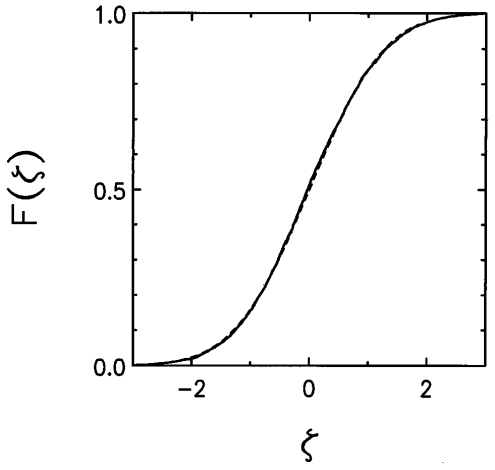

FIG. 1. The cumulative distribution function of the front positions $F(\zeta)$ shown as a function of $\zeta = (x_f - \nu t)/\sigma(t)$. The values are obtained at $t = 5000$ MCS in $N = 5000$ realizations of a system with $c = 0.1$. The dashed line corresponds to the cumulative distribution function of the Gaussian distribution, $F(\zeta) = [1 + \text{erf}(\zeta)]/2$.

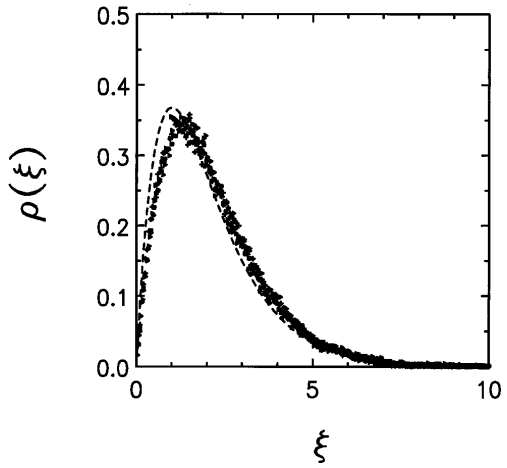

FIG. 2. $\rho(\xi)$, the distribution of distances between the rightmost A and the leftmost B particles. The concentration c is given through crosses (0.025), triangles (0.05), and squares (0.1). The dashed line is the result of the mean-field theory, Eq. (10).

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 1D, where the structure of the depletion zones near the reactants is of great importance. We hence consider another mean-field approximation which can account for the formation of a depletion zone; it follows Smoluchowski's approach to classical kinetics [21,22].

In the Smoluchowski picture the irreversible reaction takes place due to the diffusive flux of B particles towards the rightmost A. This flux is described by a diffusion equation for the correlation function $g(x,t)$, which is the probability density to find a B particle (not necessarily the next-neighbor one) at the distance x from the rightmost A:

$$\frac{\partial}{\partial t} g = D\Delta g\,. \tag{4}$$

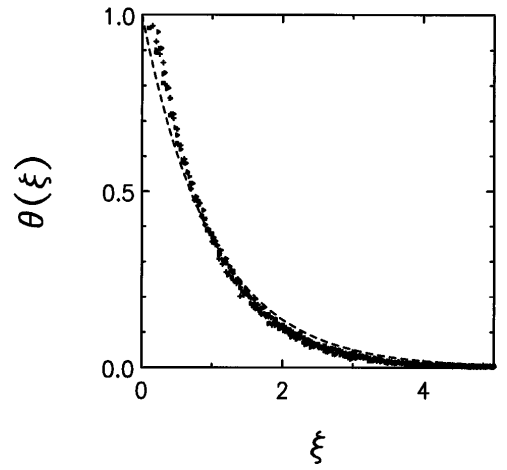

FIG. 3. Same as in Fig. 2, but now for the distribution $\theta(\xi)$ of distances between the rightmost A particle and its nearest (A) neighbor to the left.

The boundary conditions are $g(x \to \infty) = c$ and $g(x_f) = 0$ at the instantaneous front position x_f. Now the motion of the front is a relay race, during which the rightmost position passes from one particle to another. The front motion can be viewed as a drift with an averaged velocity ν on which a random process with zero mean is superimposed. For the analysis we now focus on the drift and assume that the front moves with a constant velocity ν. Turning to a description in the coordinate frame moving with ν and introducing both the dimensionless density $n(x) = g(x)/c$ and the dimensionless length variable $\xi = cx$, we obtain from Eq. (4)

$$\frac{\partial}{\partial t} n - \nu c n' = D c^2 n'', \tag{5}$$

where the primes mean differentiation with respect to ξ. The boundary conditions are now $n(0) = 0$ and $n(+\infty) = 1$. In a stationary situation the time derivative vanishes, so that dividing both sides of Eq. (5) by cD we have

$$n'' = -\alpha n', \tag{6}$$

where $\alpha = \nu/cD$, as introduced above. The solution of Eq. (6) for the given boundary conditions reads

$$n(\xi) = 1 - e^{-\alpha\xi}, \tag{7}$$

which gives the density of B particles to the right of the front. Equation (6) also describes the concentration profile of the A particles to the left of the front. Now the boundary condition is $n(-\infty) = 1$, which leads automatically (note the prefactor of α) to $n(\xi) = 1 = \text{const}$ for $\xi < 0$. This implies an exponential (Hertz) distribution of all AA distances, including the one between the rightmost A particle and its left neighbor. Thus $\theta(\xi) = c^{-1} p_{AA}(x) = \exp(-\xi)$ is independent of α, a fact corroborated by Fig. 3.

Note that for any value of ν the condition of the equality of the particle fluxes to the left $[j_- = \nu c n(-0)]$ and to the right $[j_+ = Dc^2(\partial/\partial\xi)n(+0)]$ of the boundary is identically fulfilled (due to the fact that $\nu c = Dc^2\alpha$); thus in the Smoluchowski (continuous) picture the velocity of the front is not fixed: Each propagation velocity has its own front form. This parallels the situation described by the Fisher equation in higher dimensions, and leads to the stable propagation of fronts with different forms. Contrary to this prediction, our numerical simulations show that only one stable front propagation mode occurs in 1D. The value of ν and the corresponding front form $n(\xi)$ are then well defined.

Although the mean-field approximation does not lead to a unique value of ν, we can obtain from $n(\xi)$ analytically the p_{AB} distribution (of nearest-neighbor A-B pairs) quite well, provided that the actual value of ν is known otherwise (i.e., from simulations). As stated above, the distributions of distances between the neighboring B particles are of Hertz type. This implies that the probability density $m(\eta)$ to find a B particle at the (dimensionless) distance η to the right of the leftmost

B particle is constant: $m(\eta) = 1$. Evidently, for $\eta < 0$ one has $m(\eta) = 0$. The values of $n(\xi)$ and $\rho(\xi)$ are then connected via the integral equation:

$$n(\xi) = \rho(\xi) + \int_0^\xi m(\xi - \eta)\rho(\eta)d\eta = \rho(\xi) + \int_0^\xi \rho(\eta)d\eta\,, \tag{8}$$

an expression of Ornstein-Zernike form, whose solution is

$$\rho(\xi) = \frac{\alpha}{1-\alpha}(e^{-\alpha\xi} - e^{-\xi})\,, \tag{9}$$

which in the limiting case $\alpha \to 1$ gives

$$\rho(\xi) = \xi e^{-\xi}. \tag{10}$$

As our simulations give $\alpha \approx 1$, we compare in Fig. 2 the numerical findings to Eq. (10). Note that the agreement is good and that here, as well as in Fig. 3, no fitting procedure is involved. The small but statistically significant deviations can be traced to the fact that it takes some time for the newly created A particle to lose memory of its creation next to an already existing A.

We conclude by summarizing our findings: We analyzed both numerically and analytically the irreversible $A + B \to 2B$ autocatalytic reaction in 1D. The simulations show that the front propagates with a stable velocity ν, given by Eq. (1) with $\alpha \cong 1$. The microscopic front form does not change with time; the corresponding distributions are universal functions of the dimensionless interparticle distances. Analytically the continuous-medium approximation does not fix the value of ν, but reproduces quite well the properties of the local ordering, provided that ν is known by other means (say from simulations); the (inevitable) statistical fluctuations of ν from realization to realization give rise to the (reported) growth of the apparent (ensemble-averaged) front width with time.

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