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Properties of the reaction front in a reversible $A+B\underset{g}{\overset{k}{\rightleftharpoons}}C$ reaction-diffusion process

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We study the properties of the reaction front formed in a reversible reaction-diffusion process, $A+B\underset{g}{\overset{k}{\rightleftharpoons}}C$, with initially separated reagents. It is shown that the dynamics of the front can be described in terms of a crossover between "irreversible" scaling at short times ($t \ll g^{-1}$) and "reversible" scaling at long times ($t \gg g^{-1}$). The reversible regime is dominated by diffusion and the critical exponents characterizing the properties of the front are independent of dimension.

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Reaction fronts formed in diffusion-limited $A+B\rightarrow C$ type reactions have been much investigated recently [1–12]. The interest stems partly from the fact that moving reaction fronts are important in a variety of physical and chemical phenomena where pattern formation occurs [13,14], and one of the few examples where the properties of the front can be studied in detail is the $A+B\rightarrow C$ process. There is also a more practical reason for the interest: When investigating chemical reactions in nonconvective media (e.g., in gel), it is easier to prepare an initial state with spatially separated components than to mix the reagents uniformly. Initial separation leads to a reaction front (i.e., to a spatially localized region where the production rate of C is nonzero) that can be visualized and the time dependence and the spatial dependence of the reaction rate can be measured. Thus the experiments provide information not only about the rate law but also about the segregation of the reagents [4] and, consequently, they allow direct testing of such ideas in reaction kinetics as the idea of self-ordering of reactants [15–17].

In a simple geometry where the density of the reagents depends only on one spatial coordinate, one can characterize the reaction zone by the location of its center, $x_f(t)$, by its width, $W(t)$, and by rate of production of C at the center, $R(x_f,t)$. The solution of rate equations as well as simple scaling arguments suggest [1] that the time evolution of these quantities obeys scaling in the long-time limit and one has $x_f \sim t^{1/2}$, $W(t) \sim t^{1/6}$, and $R(x_f,t) \sim t^{-2/3}$. These results are expected to be valid above an upper critical dimension [6] $d_u=2$ and, indeed, they have been verified both experimentally [4] and by simulation studies [2,3,5,6].

Scaling behavior is usually limited in extent and one expects that there exist lower and upper cutoffs in time (τ_l and τ_u) where the power-law behavior discussed above breaks down. The physical origin of the short-time ($t<\tau_l$) breakdown has been discussed recently [7,12]. At times smaller than the inverse reaction rate, the particles mainly mix instead of reacting and thus the observed results are due to diffusion rather than reaction. Accordingly, an initial behavior that is rich in detail [12] emerges from both theoretical considerations and experiments.

There is no upper cutoff to scaling ($\tau_u=\infty$) in case of a strictly irreversible reaction. In reality, however, every reaction is reversible and the rate g of the back reaction $C\rightarrow A+B$ introduces a new time scale (g^{-1}) into the problem. In this paper, the reversibility effects are studied using scaling arguments, numerical integration of the rate equations, and cellular-automata simulations. The results indicate that the "irreversible" scaling discussed above crosses over into a "reversible" scaling at times $t>\tau_u \approx g^{-1}$ and the exponents in the reversible regime are mean-field-like ($W \sim t^{1/2}$, $R \sim$ const) independently of dimension.

A mathematical description of the reversible reaction-diffusion process we are interested in, $A+B\underset{g}{\overset{k}{\rightleftharpoons}}C$, can be given by the following equations:

$$\begin{aligned} \partial_t a &= D_A \nabla^2 a - kR + gc \;, \\ \partial_t b &= D_B \nabla^2 b - kR + gc \;, \\ \partial_t c &= D_C \nabla^2 c + kR - gc \;, \end{aligned} \tag{1}$$

where a, b, and c are the local concentrations of A, B, and C, respectively, and D_j is the diffusion constant of the species j. For simplicity, we assume that

$D_A = D_B = D$. It is expected that, just as in the case of the irreversible reactions [2,3], the long-time scaling properties are not affected by this assumption. The reaction term R is proportional to the joint probability of having an A and a B particle simultaneously present at a given location. The forward and backward reaction rates are k and g, respectively.

As an initial condition, the reagents A and B are chosen to be separated with no C present. We assume constant densities for both $x<0$ ($a=a_0$, $b=0$) and $x>0$ ($a=0$, $b=b_0$) and we also assume that $a_0=b_0$. With these initial conditions, the system becomes effectively one dimensional since the densities depend only on x at all time. Furthermore, the center of the reaction front remains motionless $[x_f(t)=0]$. It is expected again that the motion of the center does not affect the $t\to\infty$ scaling properties of $W(t)$ and $R(x_f,t)$.

We start analyzing Eqs. (1) by applying a scaling theory that has been developed for the irreversible case [6]. In order to contrast the reversible and irreversible reactions, let us first review the irreversible case ($g=0$). The basic assumption is that for $x \ll L_d$, where $L_d \sim t^{1/2}$ is the width of the depletion zone (defined as the region where both a and b are significantly smaller than their initial values), the densities and the reaction rate can be written in the following scaling forms:

$$\rho_i(x,t)=t^{-\gamma}\hat{\rho}_i(xt^{-\alpha}) \ , \quad R(x,t)=t^{-\beta}\hat{R}(xt^{-\alpha}) \ , \tag{2}$$

where ρ_i is a,b,c for $i=1,2,3$, respectively. The exponent α characterizes the width of the reaction zone ($W\sim t^{\alpha}$), while β is the exponent of the production rate at the center of the zone $[R(0,t)\sim t^{-\beta}]$. Substituting the scaling forms into Eqs. (1), one finds that the three exponents α, β, and γ are related by two scaling laws:

$$\gamma+\alpha=\tfrac{1}{2} \ , \quad \gamma+2\alpha=\beta \ , \tag{3}$$

and there is only one independent exponent. The above scaling relations are still quite general, since no explicit form of the reaction term R has been used. Further approximation can be made by neglecting the fluctuations and assuming that R factorizes into a product of the local concentrations of A and B. Then the mean-field form of the reaction rate $R_{\mathrm{MF}}\sim ab$ leads to another relation among the exponents, $\beta=2\gamma$, and all the exponents are determined. The results obtained in this way $\alpha_{\mathrm{MF}}=\frac{1}{6}$ and $\beta_{\mathrm{MF}}=\frac{2}{3}$ are in agreement with those of Gálfi and Rácz [1].

The situation is simpler in the reversible ($g\neq0$) case. For large times, $t\gg g^{-1}$, the reversibility of the reaction starts to play a role and a "local equilibrium" domain is formed around the center. In this domain, the concentrations of all species approach a stationary value and only the extrema of the flat region evolve in time. Thus if scaling is assumed to hold in the reaction zone then the exponents β and γ in (2) should be zero:

$$\rho_i(x,t)=\hat{\rho}_i^{g}(xt^{-\alpha_r}) \ , \quad R(x,t)=\hat{R}^{g}(xt^{-\alpha_r}) \ . \tag{4}$$

Let us substitute the above forms into Eqs. (1) and consider first the equation for $c(x,t)$. Assuming that the scaling function $\hat{\rho}_3^{g}$ is smooth, and that $\alpha_r>0$, the terms $\partial_t c$ and $\nabla^2 c$ go to zero as $t\to\infty$, while the two other terms remain finite. Thus the last two terms should compensate each other, and this means that the system reaches a state of local equilibrium for which

$$kR(x,t)=gc(x,t) \ . \tag{5}$$

Returning now to the equations of motion for $a(x,t)$ and $b(x,t)$, one can see that due to the local equilibrium, they reduce to independent diffusion equations:

$$\partial_t a = D\nabla^2 a \ , \quad \partial_t b = D\nabla^2 b \ . \tag{6}$$

Since these equations have solutions of the form (4) with $\alpha_r=\frac{1}{2}$, we conclude that in the reversible case, and in the long-time regime ($gt\gg1$), the front properties are governed diffusion, and the exponent of the width of the reaction zone α_r is given by

$$\alpha_r=\tfrac{1}{2} \ . \tag{7}$$

Note that no explicit form of R has been assumed and the above arguments are not related to a mean-field approximation.

The result $\alpha_r=\frac{1}{2}$ is easily understandable in case of $D_C\neq0$: Once the C's have been produced, they diffuse and, because of the reversibility of the reaction, generate reaction events in a region of the size proportional to $t^{1/2}$. Thus the width of the reaction zone increases as $W\sim t^{1/2}$ and we have $\alpha_r=\frac{1}{2}$. Less obvious is that $\alpha_r=\frac{1}{2}$ remains valid for $D_C=0$. Thus in order to test the validity of the above scaling assumptions, we solved numerically the reaction-diffusion equations in the mean-field approximation ($R\sim ab$) and performed simulations of the process on a cellular automata model. In both cases, we mainly concentrated on the immobile C ($D_C=0$) limit.

Equations (1) with the approximation $R\sim ab$ were solved by standard finite-difference methods for the initial conditions described in the paragraph following (1). Measuring length, time, and particle density in units of $l=\sqrt{D/(ka_0)}$, $\tau=1/(ka_0)$, and a_0, respectively, and setting $D_C=0$, one was left with g as the only control parameter. It was chosen to be $g=10^{-n}$ [in units of $\tau=1/(ka_0)$], with $n=2,3,4,5$. The width of the reaction zone $W(t)$ was calculated as

$$W^2(t)=\sum_j j^2 c(j,t) \Big/ \sum_j c(j,t) \ , \tag{8}$$

where the sums were over the discretized spatial points. In Fig. 1, we plot the raw data for $W(t)$. An initial transient ($t<\tau_i\approx50$) as well as the crossover at $t\approx g^{-1}$ is clearly seen in this figure. Excluding the initial transient from the data, one can obtain an excellent collapse of the curves if $g^{1/6}W(t)$ is plotted against gt as shown in Fig. 2. Thus, for $t>\tau_i$, $W(t)$ can be written in the following scaling form:

$$W(t)=g^{-1/6}\Phi(gt) \ , \tag{9}$$

and the asymptotic behavior of the scaling function $\Phi(z)\sim z^{1/6}$ for $z\ll1$ and $\Phi(z)\sim z^{1/2}$ for $z\gg1$ can be seen in Fig. 2. These results demonstrate our claims that

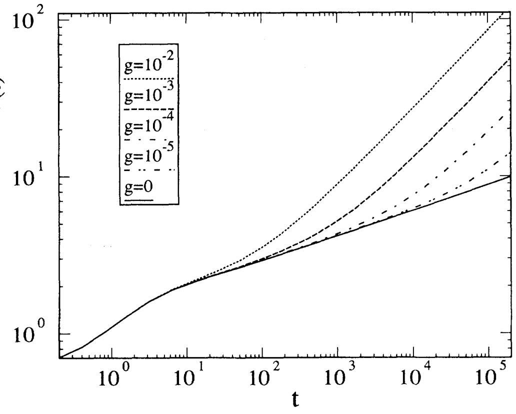

FIG. 1. Width of the reaction zone $W(t)$, obtained by solving the rate equations numerically for several values of the rate g of the back reaction $C \rightarrow A + B$. All the quantities $W(t)$, t, and g are dimensionless since they are measured in units of $(D/ka_0)^{1/2}$, $(ka_0)^{-1}$, and ka_0, respectively [for definitions see paragraph after Eq. (1)]. One can observe that there is an initial transient $t < \tau_i \approx 50$ before the "irreversible regime" [$W(t) \sim t^{1/6}$] sets in for $g = 0$. The crossover between the "irreversible regime" and the "reversible regime" [$W(t) \sim t^{1/2}$] can be seen to occur at $t \sim g^{-1}$.

there is a crossover at $gt \sim 1$ between the "irreversible" $W \sim t^{1/6}$ and the "reversible" $W \sim t^{1/2}$ regimes and that the reversible regime is dominated by diffusion ($\alpha_r = \frac{1}{2}$).

The mean-field results derived above are supposed to be valid above some upper critical dimension d_u that is 2 for the irreversible regime [6]. In order to find d_u for the reversible reaction, the process has also been described in terms of a cellular-automata model: particles of type A, B, or C perform a random walk along the main directions of a regular lattice. When an A particle collides with a B particle moving in the opposite direction, a reaction occurs and a C particle is produced with probability k. We allow for no more than one particle of a given species per site and per direction (exclusion principle). In this approach the reaction term R is not assumed to factorize as a product of a and b; thus the microscopic fluctuations are taken into account.

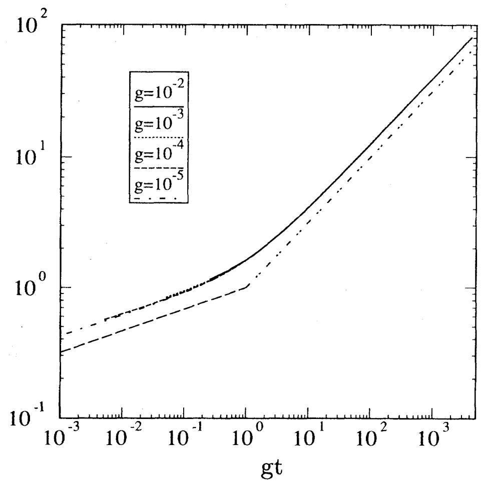

FIG. 2. Scaling of the data presented in Fig. 1. The initial transient ($t < \tau_i \sim 50$) is excluded from this plot. The two straight lines correspond to the asymptotic $W(t) \sim t^{1/6}$ and $W(t) \sim t^{1/2}$ behaviors.

The dynamics is quite similar to that used previously to study the irreversible case and the details can be found in Refs. [6] and [18]. The new ingredient is that the C particles can transform back to an A and a B, with a probability g. Note that the $A + B \rightarrow C$ and $C \rightarrow A + B$ reactions take place with probability k and g, respectively, only when they are allowed by the exclusion principle. The values of k and g as defined here are proportional to the k and g of the rate equations. The proportionality factors (of order 1) can be derived following the procedure explained in Ref. [5]. Their actual value is not important in what follows.

The simulations have been performed in one and two dimensions. The expected crossover for the one-dimensional case can be seen in Fig. 3. In the long-time regime, it is found for several values of k and g that the width of the reaction zone increases with an exponent $\alpha_r = 0.495$, in agreement with the predicted $\alpha_r = \frac{1}{2}$. The exponent associated with the short-time regime, however, is not equal to that of the irreversible case ($\alpha = 0.29$ in one dimension [6]). This is not surprising since $\alpha = 0.29$ corresponds to a very-long-time behavior [5,6] that is never attained because of the crossover to the reversible regime. The behavior in two dimensions is also found to be in agreement with the scaling predictions.

In summary, our study of the reversible $A + B \rightleftharpoons C$ reaction-diffusion process shows that the asymptotic properties of the reaction front are in some sense simpler than in the purely irreversible case. Due to local equilibrium, the long-time limit of the dynamics is governed by

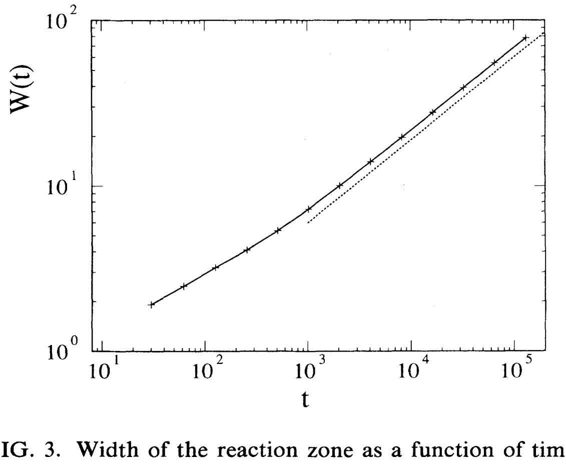

FIG. 3. Width of the reaction zone as a function of time in the one-dimensional cellular-automata simulations of the $A + B \leftrightarrow C$ process. The probabilities of the forward and of the backward reactions are 1 and 0.0001, respectively. Length is measured in units of the lattice spacing while time is scaled by the number of moves per particle. The system size is 8192, and the diffusion coefficient of the C particles is $D_C = 0$. An average is made over 128 systems. The straight line represents asymptotic behavior $W(t) \sim t^{1/2}$. The short-time ($t \sim 50$) behavior of $W(t)$ is approximately given by $W(t) \sim t^{0.36}$.

diffusion and, consequently, the critical exponents characterizing the scaling properties are correctly given by the mean-field approximation. The fluctuations do not modify the exponents even in one dimension, only the nonuniversal properties are affected. The trace of the irreversible regime can be seen in the early-time dynamics, however, provided the crossover time $\tau_c = g^{-1}$ is large enough for the irreversible regime to set in. Since there is at least one experiment [4] where the irreversible regime is seen during all of the observation time, one should be able to find experimental circumstances where the crossover between the irreversible and reversible regimes can also be observed.

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