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Motion of the reaction front in the $A+B\rightarrow C$ reaction-diffusion system

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We examine the parameters that govern the motion of the reaction front in the $A+B\rightarrow C$ reaction-diffusion system with initially separated reactants. We claim that three different parameters determine the direction of motion of the front at different time regions. We predict the surprising possibility of *two* switches in the direction of motion of the front, as well as a situation of a stationary front after a single change of direction. [S1063-651X(96)52008-8]

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The kinetic behavior of the reaction front in initially separated reaction-diffusion systems has attracted much research interest in the last few years [1–22]. This is mainly since, unlike other initial conditions, the initial separation of the reactants is an initial condition that can be experimentally achieved [2,3,6,15,22]. Gálfi and Rácz [1] introduced a scaling theory for the simple $A+B\rightarrow C$ system, based on mean-field equations for the local concentrations ρ_a, ρ_b,

$$\frac{\partial \rho_a}{\partial t}=D_a\nabla^2\rho_a-k\rho_a\rho_b, \tag{1a}$$

$$\frac{\partial \rho_b}{\partial t}=D_b\nabla^2\rho_b-k\rho_a\rho_b, \tag{1b}$$

where D_a and D_b are the diffusion coefficients and k is the microscopic reaction rate constant. For the initially separated system, the initial condition reads

$$\rho_a(x,0)=a_0H(x), \quad \rho_b(x,0)=b_0[1-H(x)], \tag{1c}$$

where a_0, b_0 are the initial densities and $H(x)$ is the Heaviside step function, so that the A's are initially uniformly distributed on the right side $(x>0)$, and the B's on the left side $(x<0)$ of the initial boundary.

Later on, Taitelbaum *et al.* [5] presented a perturbation analysis to study the early-time regime, which is relevant to the case of a noninstantaneous reaction (i.e., k is finite and small). It has been shown that there exists a series of crossovers from the initial to the asymptotic kinetic behavior of the reaction front. These crossovers depend on the microscopic reaction constant, as well as on the diffusion coefficients and initial densities of the two species. For example, the global reaction rate changes dramatically from an initial $t^{1/2}$ increase to a final $t^{-1/2}$ decrease, at a time proportional to k^{-1} [5]. In practice, these crossovers take place on a real time scale of *hours*, thus providing a useful means to extract microscopic parameters from macroscopic experiments. The experimental results have confirmed the general crossover predictions, and provided more data which can be explained on the grounds of a slightly more complicated reaction scheme [22].

The quantities that describe the kinetic behavior of the reaction front are defined through the reaction term $R(x,t)=k\rho_a(x,t)\rho_b(x,t)$, and are the global reaction rate, $R(t)$, the location of the reaction front center, $x_f(t)$, the front width, $w(t)$, and the production rate of C at the center, $R(x_f,t)$. Among these, the reaction front center, $x_f(t)$, which is defined as the position where the production rate of C is maximal, has been found to have the most interesting and nontrivial behavior. This is reflected in the *nonuniversal* behavior in early times, where there can be as many as four different universality classes, and more than two regions in time, depending on the system parameters a_0, b_0, D_a, and D_b. In particular, it has been shown [6] that the front can exhibit a nonmonotonic motion along the separation axis. The switch in the direction of motion occurs in the early-time regime, and has been obtained both theoretically and experimentally. The question is, however, what happens to these four universality classes when the system enters into its asymptotic time phase? How does the front location attains its $t^{1/2}$ asymptotic behavior? What happens at the crossover time?

In this Rapid Communication, we study in detail the crossover behavior of the position of the reaction front center. We do so by examining the conditions which govern the direction of motion of x_f, and show that different parameters affect this motion in different time regimes. In particular, we show that there exists a surprising possibility of a *second* change of direction, and we define the appropriate conditions for this phenomenon.

In the pioneering paper by Gálfi and Rácz [1], they obtained the asymptotic time behavior $x_f\sim t^{1/2}$ which follows intuitively from the diffusive nature of the reaction-diffusion system. They also pointed out that in the symmetric system, i.e., $a_0=b_0$ (assuming that $D_a=D_b$), the front does not move and $x_f=0$ for all time t. In a later publication, Jiang and Ebner [4] showed that the more general condition for the center of the front to be stationary is

$$a_0\sqrt{D_a}=b_0\sqrt{D_b}. \tag{2}$$

This is based on the observation that in the long-time limit the reaction zone is fed by the diffusive fluxes of A and B, which at time t are given by $a_0\sqrt{D_a/t}$ and $b_0\sqrt{D_b/t}$, respectively. Equality of these fluxes would result in a stationary

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front, while unequal fluxes will cause a motion of the front from the side in which the species' flux is bigger towards the side which has the smaller flux. Jiang and Ebner support their findings by numerical calculations. The validity of (2) has been recently confirmed analytically by Koza [21].

These arguments pertain to the long-time limit only, or, equivalently, to the case of instantaneous reaction (infinite k). When k is finite, the reactants do not necessarily react on each encounter. As a result, they have the possibility of diffusing through one another, until they become effectively mixed. This leads to an early-time kinetic behavior which is characterized by completely different properties [5,6]. In this region one can treat the little reaction as a perturbation relative to the diffusion, using a perturbation parameter ϵ, which represents a small dimensionless reaction constant, and is given by

$$\epsilon=\frac{k}{\sqrt{a_0 b_0 D_a D_b}}. \tag{3}$$

The general expression for x_f in the early-time region has been found by Taitelbaum *et al.* [6] to be given by

$$x_f(t)\simeq\frac{\frac{1}{\sqrt{\pi}}\left(\frac{1}{\sqrt{D}}-\sqrt{D}\right)t^{-1/2}+\epsilon M(D,r)t^{1/2}}{\frac{1}{\pi}t^{-1}+\epsilon N(D,r)} \tag{4}$$

where

$$D=\sqrt{\frac{D_a}{D_b}}, \quad r=\sqrt{\frac{a_0}{b_0}}, \tag{5}$$

and M and N are time-independent constants, which depend in a nontrivial manner on D and r. A detailed examination of the expression (4) as a function of D and r results in four different universality classes in the early-time regime [6,14].

To the lowest order in ϵ one obtains $x_f\sim t^{1/2}$, but this is provided that $D\neq 1$. When $D=1$ (and $r\neq 1$), the first term in the numerator vanishes, the front is stationary to the lowest order, and when the next order term becomes significant, one obtains $x_f\sim \epsilon t^{3/2}$. If $D=1$ and $r=1$, then M vanishes as it should, and $x_f=0$ for all t, due to symmetry.

The most interesting behavior of the function $x_f(t)$ is that it can have an extremum point with the physical implication of a *nonmonotonic* motion along the separation axis. The time t^*, for which $x_f(t)$ has such an extremum point, depends in a complicated manner on D and r, through rather cumbersome expressions for M and N. The condition for a *positive* t^*, and thus for a physical meaning of switching directions, is $\{D>1$ and $r<1\}$, or, equivalently, $\{D<1$ and $r>1\}$, provided that the value of D is relatively close to 1, as is discussed in detail in [6]. This result is understood as follows. Suppose, e.g., that $D_a>D_b$ and $a_0<b_0$. At very early times diffusion effects are dominant, and the direction of motion is determined by the penetration of the A species to the left, B side of the system. Later on, the reaction comes into play, and the species with higher concentration, B, will govern the direction of motion, which will be towards the right, A side. Note that this result involves both two lowest orders in ϵ, so one expects the transition of the front from one direction to the other to occur at a rate proportional to $t^{3/2}$. Experimental results reported in [6] confirm the nonmonotonic motion for $D=1.14$ and $r=0.26$.

For $D>1$ and $r>1$ (or both less than 1), Eq. (4) predicts that x_f is monotonic in time, where at the very earliest times $x_f\sim t^{1/2}$, and at later times $x_f\sim t^{3/2}$, corresponding to the order of the perturbation expansion.

Consider now the most interesting case of the nonmonotonic behavior in the early-time regime, with $D>1$ and $r<1$ (or vice versa). If these parameters fulfill also the relation $r^2D=1$, then due to (2) we can expect the front to become asymptotically (as $t\rightarrow\infty$) stationary. So is it possible that the front would start to move, change its direction, and finally stop? If not, will it continue in the same direction?

In what follows we propose that three different parameters govern the direction of motion as time evolves. Based on the above discussion of the nonmonotonic case, it is reasonable to assume that at the very earliest times the direction depends on D only, where later, still within the short-time regime, it is r that determines the direction. In the asymptotic time regime we suggest that the dominant parameter is the combination r^2D, following from Eq. (2). In each time region, if the relevant parameter of this region (D, r, or r^2D) is greater than 1, the front will move from the A side to the B side. If it is less than 1, the motion will be in the opposite direction, from the B side to the A side, and if it is equal to 1, the front will be stationary or temporarily stationary. Thus, various combinations of these parameters are expected to yield rich kinetic behavior of the reaction front, in particular unusual nonmonotonic properties.

We have performed numerical calculations based on the standard, finite-difference method, to check our claim. In these computations we have used the following method to calculate the location of x_f. First we find the point x_m of the finite-difference grid at which the production rate R attains the maximal value. Then we use five points, $x_{m-2},\ldots,x_{m+2}$, to find the quadratic function $y(x)=ax^2+bx+c$ that would minimize $\chi^2=\Sigma_i[R(x_i)-y(x_i)]^2$, where the sum is to be taken over $i=m-2,\ldots,m+2$. Finally we estimate x_f as the point maximizing the value of y. This form of interpolation enabled us to investigate the evolution of x_f very precisely. The calculations have been performed for a wide range of the system parameters. The numerical results confirm our claim that D, r, and r^2D determine the direction of motion of the front in the short, intermediate, and asymptotic time regions, respectively. In what follows we present the exotic consequences of this general description.

In Fig. 1 we show our results for a system whose parameters are chosen so that $D<1$, $r>1$, for various possibilities of r^2D. The specific values are $k=0.01$, initial densities $a_0=0.2$, $b_0=0.1$ ($r=1.414$), diffusion coefficients $D_a=0.1$ and various $D_b=0.38$, 0.4, 0.42, so that $D=0.513$, 0.5, 0.488 and $r^2D=1.026$, 1, 0.976, respectively. Since $D<1$ and $r>1$, the directions of the front motion will be $B\rightarrow A$ and then $A\rightarrow B$ in the short-time regime. After the asymptotic time region sets in, we have all three possibilities: continuation in the $A\rightarrow B$

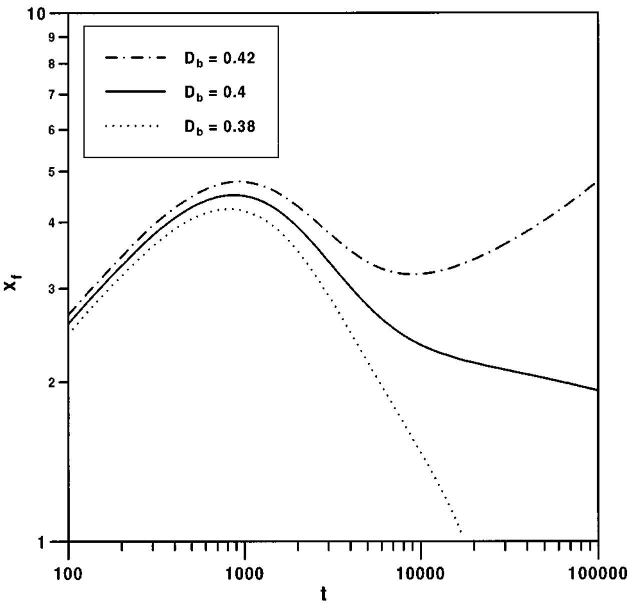

FIG. 1. The reaction front center x_f as a function of time as obtained numerically for fixed initial densities $(r>1)$ and various values of $D(D<1)$ and r^2D. Parameter values are $k=0.01$, densities $a_0=0.2$, $b_0=0.1$ $(r=1.414)$, diffusion constants $D_a=0.1$ and D_b as is indicated in the figure $(D<1)$. The initial motion from left (B) to right (A) is reflected in an initial *increase* of $x_f(t)$.

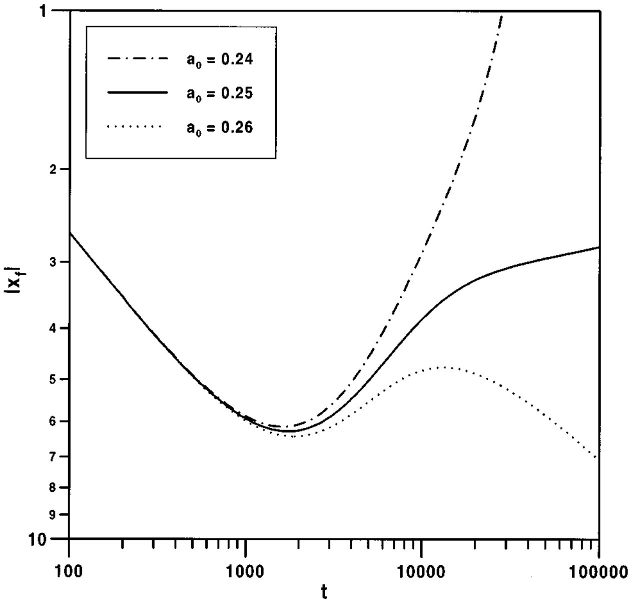

FIG. 2. The reaction front center x_f as a function of time as obtained numerically for fixed diffusion constants $(D>1)$ and various values of r $(r<1)$ and r^2D. Parameter values are $k=0.002$, diffusion constants D_a=0.4, $D_b=0.1$ $(D=2)$, densitites $b_0=0.5$ and a_0 as is indicated in the figure $(r<1)$. The initial motion from right (A) to left (B) is reflected in an initial *decrease* of $x_f(t)$.

direction (for $r^2D>1$); approaching a stationary position (for $r^2D=1$); and the most surprising phenomenon—a *second* switch to $B \rightarrow A$ (for $r^2D<1$), which is reflected by a second extremum point in the curve for $x_f(t)$. All these three asymptotic curves belong to the same universality class, and exhibit an asymptotic $t^{1/2}$ behavior with different prefactors.

In Fig. 2 we show similar data for $D>1$, $r<1$ and the three possibilities for r^2D. The specific parameters are $k=0.002$, diffusion constants $D_a=0.4$, $D_b=0.1$ $(D=2)$,initial concentrations $b_0=0.5$ and various a_0=0.24, 0.25, 0.26 (r=0.69, 0.707, 0.721), so that $r^2D=0.96$, 1, 1.04, respectively. The directions of motion are $A \rightarrow B$ $(D>1)$, $B \rightarrow A$ $(r<1)$, and then according to the value of r^2D. It can be seen that at the earliest times the three curves for the various values of r are indistinguishable, which confirms that at this region the behavior depends on D only. As is evident from the figures, the starting of the asymptotic region occurs at a time which is about an order of magnitude larger than the first switch of direction. The latter occurs at a time of order k^{-1}, which is the typical time for the beginning of the asymptotic region in systems with a monotonic motion of the front.

It is interesting to note that other relevant quantities in this reaction-diffusion system with initially separated reactants, such as the local or global production rates or the width of the reaction zone, do not exhibit such a rich spatiotemporal behavior. They do cross over from short-time to asymptotic behavior [14], but do not possess any nonuniversal or nonmonotonic properties as does x_f, the location of the reaction front center.

The significance of these results from the experimental point of view is that they can be used to control the motion of the front. Generally one cannot do much to change the values of the diffusion coefficients of the reactants which are determined by the type of solution in which the reaction takes place [3]. However, the initial densities can be controlled more easily, allowing one to obtain some preset values for r and particularly r^2D, in order, for example, to stabilize the front motion, or to have it moving in any preferred direction. In the experiment described by Taitelbaum *et al.* [6], the parameters were $D=1.14$ and $r=0.26$, so that $r^2D=0.08$, and indeed only one switch of direction has been observed, in agreement with the above conclusions. It remains an experimental challenge to obtain the second switch or the stationary state as well.

In summary, we have presented a surprising behavior of the reaction front in the initially separated $A+B \rightarrow C$ reaction-diffusion system, which is the possibility of *two* direction changes during its motion, as well as a stationary front after a single switch of direction. These phenomena result from the fact that three different parameters determine the direction of motion of the reaction front in different time regimes.

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