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

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A dynamic reaction zone is produced in the $A+B\rightarrow C$ reaction-diffusion system with initially separated components. Our perturbation analysis results predict a rich behavior for the kinetics of the reaction front in the short-time limit, with variety of universality classes. In particular, we show that the center of the front can change its direction of motion. Our experimental data support this prediction and demonstrate that this behavior is measurable over a time scale of *hours* in bimolecular reactions at room temperature.

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Reaction-diffusion processes of the type $A+B\rightarrow C$ with initially separated components are more readily amenable to experimental studies than similar nonconvective systems with initially uniformly mixed reactants, a condition which is difficult to achieve in a real chemical system. The initial separation of reactants leads to the formation of a mobile reaction front, which is a spatially confined region with nonzero reaction production. The presence of an interface is a characteristic of many reactions in physics, chemistry, and biology [1–8].

The dynamics of the reaction front can be described by several quantities such as the location of the center of the front, the local production rate at that point, or the width of the reaction zone. Asymptotic scaling arguments for the properties of such a front, valid only in the long-time limit, have been suggested by Gálfi and Rácz [9], based on a mean-field approximation to the reaction-diffusion equations. They found that the center (x_f) and the width (w) of the front scale with time as $x_f\sim t^{1/2}$ and $w\sim t^{1/6}$, whereas the production rate at x_f is proportional to $t^{-2/3}$. These predictions have been verified both numerically [10,11] and experimentally [10,12]. A recent study by Cornell, Droz, and Chopard [13] argues that this mean-field description is valid above the upper critical dimension which is $d_{\mathrm{up}}=2$.

Gálfi and Rácz [9], and later Cornell, Droz, and Chopard [13], make the simplifying assumption that the diffusion constant is identical for both species A and B. They argue that the ratio of the diffusion constants D_a/D_b is an irrelevant parameter with respect to the asymptotic scaling behavior and provides only unimportant corrections to the scaling function. Indeed, it has been shown [10,11] that the asymptotic scaling results are valid also for unequal diffusion constants and are not affected by concentration fluctuations or the discrete (particle) nature of the reactants.

In this paper we study analytically and experimentally the kinetic behavior of the reaction front for the initially separated system, focusing on the short-time limit, where the system parameters have a crucial role in determining the kinetic properties. Our theoretical results predict a variety of nontrivial crossovers and different universality classes for the dynamics of the reaction center. Our experimental data support the crossover predictions and show that the so-called short-time limit can range over scales of *hours* in real systems with a small microscopic reaction constant. The interesting behavior in this formal short- (practically quite *long*) time limit cannot be described by the earlier asymptotic scaling predictions.

The system under consideration is assumed to obey the following set of mean-field type reaction-diffusion equations for the mean local concentrations per unit length 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 k is the microscopic reaction constant. The mean-field nature of these equations is expressed in the reaction term which is assumed to be proportional to the product of the mean particle densities. The equations are subject to the initial separation condition along the x axis,

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

where a_0 and b_0 are the initial densities, and $H(x)$ is the Heaviside step function. At early times, due to the relatively small amount of mixing of A's and B's, reactive effects are small compared to those of diffusion. Hence we can describe this behavior using a dimensionless reaction parameter

$$\epsilon=\frac{k}{\sqrt{a_0b_0D_aD_b}}\ , \tag{2}$$

which will be assumed to be small in subsequent analysis. In order to apply perturbation theory, we define the following dimensionless parameters [14]: $\alpha(x,t)=a_0^{-1}\rho_a(x,t)$, $\beta(x,t)=b_0^{-1}\rho_b(x,t)$, $\xi=x\sqrt{a_0b_0}$, and $\tau=ta_0b_0\sqrt{D_aD_b}$. We also define parameters in terms of the ratio of the diffusion constants $D=\sqrt{D_a/D_b}$, and the ratio of initial concentrations $r=\sqrt{a_0/b_0}$, assuming that D and r are $O(1)$. Equation (1) will now have the dimensionless form

$$\frac{\partial\alpha}{\partial\tau}=D\frac{\partial^2\alpha}{\partial\xi^2}-\frac{\epsilon}{r}\alpha\beta\ , \tag{3a}$$

$$\frac{\partial\beta}{\partial\tau}=\frac{1}{D}\frac{\partial^2\beta}{\partial\xi^2}-\epsilon r\alpha\beta\ . \tag{3b}$$

On the assumption $\epsilon\ll 1$, we can apply perturbation theory to solve Eq. (3), by expanding α and β in the series

$$\alpha=\sum_{j=0}^{\infty}\alpha_j\epsilon^j\ ,\quad \beta=\sum_{j=0}^{\infty}\beta_j\epsilon^j\ , \tag{4}$$

where α_0 and β_0 satisfy an ordinary diffusion equation under the initial separation condition in terms of dimensionless Heaviside step functions. The solution of Eq. (3) for the zeroth order in ϵ is then found to be [14]

$$\begin{aligned}\alpha_0(\xi,\tau)&=\frac{1}{2}\left[1+\operatorname{erf}\left[\frac{\xi}{2\sqrt{D\tau}}\right]\right]\ ,\\ \beta_0(\xi,\tau)&=\frac{1}{2}\left[1-\operatorname{erf}\left[\frac{\xi}{2}\frac{\sqrt{D}}{\sqrt{\tau}}\right]\right]\ ,\end{aligned} \tag{5}$$

where erf(z) is the error function. The next order terms can be shown to be approximated by

$$\alpha_1(\xi,\tau)\simeq-\frac{1}{r\sqrt{D}\sqrt{4\pi}}\tau\exp\left\{-\frac{1}{4}\left[\frac{\xi}{\sqrt{D\tau}}-\left[\frac{1}{\sqrt{D}}-\sqrt{D}\right]\right]^2-\frac{1}{4D}\right\}\ , \tag{6a}$$

$$\beta_1(\xi,\tau)\simeq-\frac{r\sqrt{D}}{\sqrt{4\pi}}\tau\exp\left\{-\frac{1}{4}\left[\frac{\xi}{\sqrt{\tau}}\sqrt{D}-\left[\frac{1}{\sqrt{D}}-\sqrt{D}\right]\right]^2-\frac{D}{4}\right\}\ . \tag{6b}$$

The local production rate of C in this system is assumed to be given through the reaction term in Eqs. (1a) and (1b), namely

$$R(\xi,\tau)=a_0b_0(D_aD_b)^{1/2}\epsilon\alpha(\xi,\tau)\beta(\xi,\tau)\ , \tag{7}$$

with the suitable series expansions for $\alpha(\xi,\tau)$ and $\beta(\xi,\tau)$.

The center of the reaction front ξ_f is defined as the position at which the local production rate $R(\xi,\tau)$ is a maximum. Previous studies [9,13] claim that this is equivalent to the point at which the concentration profiles of the two species are equal. This alternative definition is true when the diffusion constants are equal, and the initial densities do not differ too much, but these conditions are not necessarily satisfied for real systems. The consequence of such a mathematical simplification is that the center of the front moves with a velocity proportional to $t^{1/2}$ which is naturally expected on the basis of the diffusion mechanism [5,6,9,13], and is indeed valid in the asymptotic regime. It should also be noted that Cornell, Droz, and Chopard [13] have considered only the case in which the initial concentrations are also equal, and the front is stationary.

In the following we show that the perturbation analysis for ξ_f yields an unexpectedly rich kinetic behavior, with variety of universality classes, depending on the system parameters. The general expression for ξ_f is found after maximization of $R(\xi,\tau)$ and expansion around $\xi=0$ due to the short-time limit. The result is

$$\xi_f(\tau)\simeq\frac{\frac{1}{\sqrt{\pi}}\left[\frac{1}{\sqrt{D}}-\sqrt{D}\right]\tau^{-1/2}+\epsilon M\tau^{1/2}}{\frac{1}{\pi}\tau^{-1}+\epsilon N}\ , \tag{8}$$

where M and N are time-independent constants, related to the coefficients of the expansion for small ξ, and are found to depend in a nontrivial manner on the values of D and r. To lowest order in ϵ, $\xi_f\sim\tau^{1/2}$, but this occurs only provided that $D\neq 1$.

For $D=1$ (and $r\neq 1$), the first term in the numerator vanishes, and the center of the front remains fixed in position at the earliest times. As time increases, the second term in the numerator becomes significant, so that $\xi_f\sim\epsilon\tau^{3/2}$, finally changing to the asymptotic $\tau^{1/2}$ behavior. Thus, practically, there can be as many as three distinct regions for the kinetic behavior of ξ_f for $D=1$ and $r\neq 1$. If also $r=1$, then M is found to vanish as it should, yielding $\xi_f=0$ for all τ, due to the symmetry.

The most striking feature of ξ_f is the possibility of a change in its direction of motion along the separation axis. The mathematical expression of this feature is that the function $\xi_f(\tau)$ possesses an extremum point for some *positive* time ($\tau > 0$). The time τ^*, for which $\xi_f(\tau)$ has an extremum point, depends in a complicated manner on D and r, through the rather cumbersome expressions for M and N. These indicate that τ^* will be positive, provided that the parameters D and r satisfy the conditions $\{D > 1$ and $r < 1\}$ or, equivalently, $\{D < 1$ and $r > 1\}$. However, when D is greater than $2+\sqrt{3} \approx 3.73$ or less than $2-\sqrt{3} \approx 0.27$, τ^* will be negative, and ξ_f will not have a physical extremum point, no matter the value of r. But if we restrict ourselves to values of $\frac{1}{2} < D < 2$ [recall that $D = O(1)$], then the extremum condition $\{D > 1,\ r < 1\}$ (or the opposite) ensures a change of the direction of motion of the front.

This result can be physically understood. Suppose, for example, 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. This result is based on an expansion to second order in ϵ. Therefore one expects that the transition of the front from one direction to the other will occur at a rate proportional to $\tau^{3/2}$.

We confirmed our theoretical analysis by solving Eq. (1) numerically, using a split-step algorithm that uncouples the diffusion and the reaction at each time unit [14,15]. The diffusion part was solved by the exact enumeration method [16], which is equivalent to discretizing the evolution equation, whereas the reaction effect was calculated according to the reaction term in Eq. (1).

The experimental system used to test this intriguing phenomenon is composed of the reactants xylenol orange and Cr^{3+} in a 0.9% gel solution at room temperature, initially totally separated along a 500-mm glass reactor with 4×2 mm^2 cross section. Further details about the experimental technique are described for related systems in Ref. [12]. We used $5 \times 10^{-5} M$ xylenol orange (diffusion constant 3.5×10^{-10} m^2/sec), and $7.5 \times 10^{-4} M$ Cr^{3+} (diffusion constant 2.7×10^{-10} m^2/sec), so that $D = 1.14$ and $r = 0.26$ in accord with the requirements for an extremum position. The results are shown in Fig. 1. One can clearly see that the change of direction occurs at a rate much higher than the asymptotic $\tau^{1/2}$. This formal short-time limit behavior takes place at time $t = 223$ min, which is definitely quite long. This is because of the small reaction constant k in the system, so that the corresponding dimensionless parameter ϵ defined in Eq. (2) is very small, and the short-time limit is extended over a long measurable time interval.

The small reaction constant is typical for a class of experimental systems [12]. It is also reflected in a crossover of the global reaction rate from $\tau^{1/2}$ to $\tau^{-1/2}$ which occurs at time inversely proportional to the reaction constant [14], thus providing a possibility of eliminating this microscopic reaction constant from crossover behavior in macroscopic measurements.

For $D > 1$ and $r > 1$, we found from Eq. (8) that ξ_f is monotonic in time. However, for small values of k, there are three regions of different kinetic behavior: at the very earliest times $\xi_f \sim \tau^{1/2}$, at later times $\tau^{3/2}$ (corresponding to the order of the perturbation expansion), and finally one obtains the asymptotic $\tau^{1/2}$.

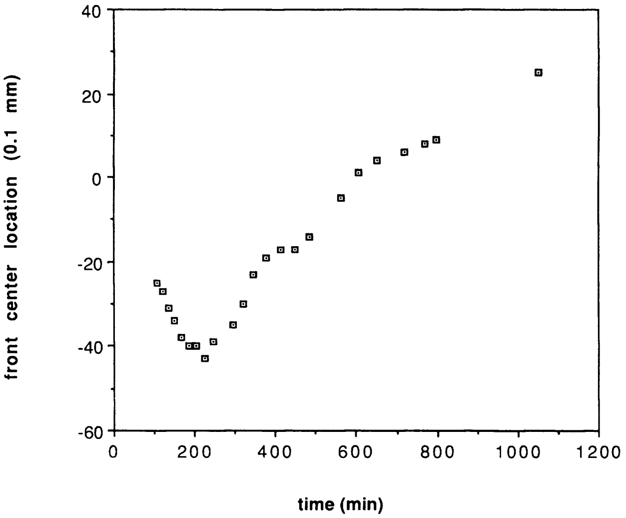

FIG. 1. Experimental results of the reaction center location x_f (in units of 0.1 mm), as a function of time (min). The initial position is $x_f(t=0)=0$, and the system parameters are $D = 1.14 > 1$ and $r = 0.26 < 1$, which give rise to an extremum point of x_f. The change of direction is seen to occur at a higher rate than the asymptotic behavior.

In Table I we summarize the various possibilities for the time dependences of ξ_f, as a function of the parameters D and r. We can see that apart from the symmetric trivial case ($\xi_f = 0$ for all times), there are four different universality classes describing the kinetics of the front center in the formal short-time limit. All these results were confirmed by the numerical solution of Eq. (1), with appropriate parameter combinations.

The local production rate at the center of the front $R(\xi_f, \tau)$ is calculated by substituting ξ_f into Eq. (7). An immediate consequence of the previous results for ξ_f is that the general form of the time dependence of $R(\xi_f, \tau)$ is

$$R(\xi_f,\tau) = a_0 b_0 (D_a D_b)^{1/2} \epsilon [K_0 + \epsilon K_1 \tau] , \tag{9}$$

where the specific values of the constants K_0 and K_1 depend on D and r. For most sets of $\{D, r\}$ only the lowest-order constant regime is observed (prior to the asymptotic solution), but for some other sets it would be possible to observe deviations from the constant to the next-order linear term of Eq. (9). The numerical solution for the entire time scale confirms the crossover from the result (9) to the asymptotic $\tau^{-2/3}$ found by Gálfi and Rácz on the basis of a scaling ansatz.

Before concluding, we note that further aspects of the reaction front properties in similar and related systems have been studied very recently by several investigators [17,18].

In summary, we have studied analytically, numerically, and experimentally, the kinetics of the reaction front in

TABLE I. A summary of the various time dependences of ξ_f, the center of the reaction front, as a function of the system parameters D and r.

$\{D,r\}$	Short times	Intermediate times	Long times
$\{D=1,r=1\}$	0	0	0
$\{D=1,r\neq 1\}$	0	$\tau^{3/2}$	$\tau^{1/2}$
$\{D\neq 1,r=1\}$	$\tau^{1/2}$	$\tau^{1/2}$	$\tau^{1/2}$
$\{2+\sqrt{3}>D>1,r<1\}$ or $\{1>D>2-\sqrt{3},r>1\}$	$\tau^{1/2}$	$\tau^{3/2}$ with extremum	$\tau^{1/2}$
$\{D>1,r>1\}$ or $\{D<1,r<1\}$	$\tau^{1/2}$	$\tau^{3/2}$	$\tau^{1/2}$

the $A+B\rightarrow C$ reaction-diffusion system with initially separated components. We found that the motion of the reaction center can be classified into four different universality classes, depending on the system parameters. These classes describe the kinetic behavior over times which are within easy experimental reach. In particular, we showed that under appropriate choice of the diffusion constants and initial densities, the front exhibits a change of its movement direction, a phenomenon which we have experimentally confirmed.

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