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Theory for competing reactions with initially separated components

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The asymptotic long-time properties of a system with initially separated components and two competing irreversible reactions $A_1+B\to C_1$ and $A_2+B\to C_2$ are studied. It is shown that the system is characterized by a single reaction zone, with width growing like $t^{1/6}$, in which both reactions occur. Numerical computations of the mean-field kinetic equations confirm these asymptotic results.

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The behavior of irreversible reaction-diffusion systems with initially separated reactants has attracted much research interest in the last decade [1–22]. The elementary irreversible reaction $A+B\to C$ with initially separated reactants leads to the formation of a distinctive reaction zone. Gálfi and Rácz [1] have shown that in the long-time limit the reaction zone properties scale as $x_f\sim t^{1/2}$, $w\sim t^{1/6}$, $R(x_f,t)\sim t^{-2/3}$, and $R(t)\sim t^{-1/2}$, where x_f and w are the center coordinate and the width of the reaction front, respectively, $R(x_f,t)$ and $R(t)\equiv\int R(x,t)dx$ are the local and the global reaction rate, respectively. These scaling relations, obtained from the mean-field equations [1], are valid for space dimension d greater than the critical dimension $d_c=2$ [6]. These results have been confirmed by a variety of approaches [1,7,9–12,14,15], including experiments [2,3,5,16–20]. More complex reactions such as $mA+nB\to C$ were studied in Refs. [6,9,12,21].

A possible level of complexity of the single irreversible reaction system is the system with two competing elementary irreversible reactions $A_1+B\to C_1$ and $A_2+B\to C_2$. This system exhibits rich spatiotemporal reaction zone pattern observed in experiment [18,19]. New patterns of properties of this system, such as two reaction centers, and distinctive spatiotemporal behavior of $R(t)$ and $R(x,t)$, are predicted by numerical calculations.

In this Brief Report we study analytically and numerically the long-time asymptotic behavior of the system of two irreversible reactions $A_1+B\to C_1$ and $A_2+B\to C_2$. It is shown that the long-time dynamics is similar to the single irreversible reaction pattern, i.e., both irreversible reactions on the macroscopic scale $\sim\sqrt{Dt}$ occur in one reaction zone. Inside the reaction zone the local properties of the reactions are scaled as $\sim t^{1/6}$, and are determined by quasistatic equations.

Consider a system of the two competing irreversible reactions, with initially separated reactants (A_1, A_2 from the right side and B from the left side),

$$A_1+B\to C_1, \tag{1}$$

$$A_2+B\to C_2. \tag{2}$$

The initial concentrations of A_1, A_2, and B are a_{10}, a_{20}, and b_0, respectively.

The process is described by the following set of reaction-diffusion equations for the concentrations of A_1, A_2, B, C_1, and C_2:

$$\partial a_1/\partial t=D\partial^2 a_1/\partial x^2-R_1, \tag{3}$$

$$\partial a_2/\partial t=D\partial^2 a_2/\partial x^2-R_2, \tag{4}$$

$$\partial b/\partial t=D\partial^2 b/\partial x^2-R_1-R_2, \tag{5}$$

$$\partial c_1/\partial t=D\partial^2 c_1/\partial x^2+R_1, \tag{6}$$

$$\partial c_2/\partial t=D\partial^2 c_2/\partial x^2+R_2, \tag{7}$$

with initial conditions

$$\begin{aligned}a_1(x,0)&=a_{10}H(x),a_2(x,0)=a_{20}H(x),b(x,0)\\&=b_0[1-H(x)],c_1(x,0)=c_2(x,0)=0.\end{aligned} \tag{8}$$

$H(x)$ is the Heaviside step function. In the mean-field approximation we have $R_1=k_1a_1b$, $R_2=k_2a_2b$, where k_1 and k_2 are the forward reaction kinetics constants for reactions (1) and (2), respectively. For simplicity, the same diffusion constant D of all components is assumed. Since the sums a_1+c_1, a_2+c_2, and $b+c_1+c_2$ are controlled by ordinary diffusion equations, they are given by

$$a_1+c_1=a_{10}[1+erf(z)]\equiv F_1(z), \tag{9}$$

$$a_2+c_2=a_{20}[1+erf(z)]\equiv F_2(z), \tag{10}$$

$$b+c_1+c_2=b_0[1-erf(z)]\equiv F_3(z). \tag{11}$$

Here $z\equiv x/\sqrt{4Dt}$, $erf(z)=(2/\sqrt{\pi})\int_0^z\exp(-u^2)du$. The functions $F_1(z)$, $F_2(z)$, and $F_3(z)$ are shown in Fig. 1(a).

In the long-time limit let us assume that the solution may be presented on two scales [1]: the diffusion length scale $\sim\sqrt{Dt}$ and the reaction width scale $w\sim t^{1/6}\ll\sqrt{Dt}$. Likewise the pure kinetic consideration [i.e., on the basis of the Eqs. (3)–(7) without diffusion terms] the long-time behavior of the system is determined by the values a_1+c_1, a_2+c_2, and $b+c_1+c_2$ and relations between them. One can define a relation between the A_1 and A_2 components from one side and the B component from the other side a_1+a_2-b, which equals to $F_1(z)+F_2(z)-F_3(z)$. This quantity can be greater, less, or approximately equal to zero, depending on the dimensionless coordinate z.

Let us denote the dimensionless location by z_0 for which $a_1+a_2-b=0$, namely, it satisfies

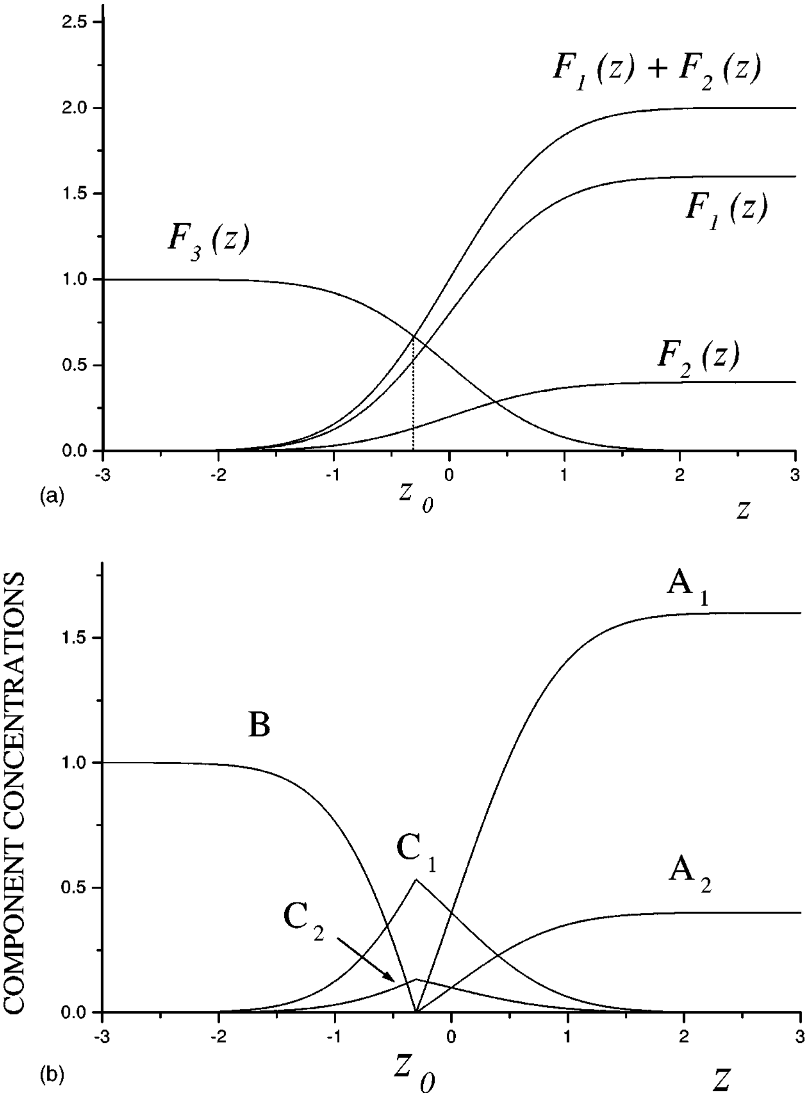

FIG. 1. (a) Forms of the $F_1(z)$, $F_2(z)$, and $F_3(z)$ functions as defined in Eqs. (9)–(11); (b) the asymptotic profiles of the components calculated on the basis of Eqs. (13)–(15) and (18) and (19) on the $\sim\sqrt{Dt}$ scale, i.e., as a function of z. All component concentrations are expressed in units of b_0. The values of $a_{10}/b_0=1.6$ and $a_{20}/b_0=0.4$ are used.

$$a_1+a_2-b=F_1(z_0)+F_2(z_0)-F_3(z_0)=0. \tag{12}$$

For $z<z_0$, i.e., $a_1+a_2-b<0$, i.e., there is an excess of B compared to A_1 and A_2. Since in the long-time period, the quantities of A_1 and A_2 are small, one can assume $a_1\approx a_2\approx 0$. Then we have from Eqs. (9)–(11)

$$b\approx F_3(z)-F_1(z)-F_2(z), \tag{13}$$

$$c_1\approx F_1(z), \tag{14}$$

$$c_2\approx F_2(z), \tag{15}$$

which describe the independent diffusion of B, C_1, and C_2 next to the region $z\cong z_0$.

For $z>z_0$ ($a_1+a_2-b>0$) the value of b is small compared to a_1 and a_2. Then in the long-time period it follows from Eqs. (9)–(11) that

$$a_1+a_2\approx F_1(z)+F_2(z)-F_3(z). \tag{16}$$

Eliminating b from Eqs. (3) and (4), one obtains

$$(\partial a_1/\partial t-D\partial^2 a_1/\partial x^2)/k_1 a_1=(\partial a_2/\partial t-D\partial^2 a_2/\partial x^2)/k_2 a_2, \tag{17}$$

so that from Eqs. (16) and (17) the profiles of A_1 and A_2 next to the region $z\cong z_0$ are controlled by diffusion equations and given by the expressions

$$a_1\approx a_{10}\{1-[1-erf(z)]/[1-erf(z_0)]\}, \tag{18}$$

$$a_2\approx a_{20}\{1-[1-erf(z)]/[1-erf(z_0)]\}. \tag{19}$$

From Eq. (16) the sum of A_1 and A_2 concentrations tends to zero for $z\to z_0$ and thus the values of A_1 and A_2 concentrations tend to zero as well. The expressions for c_1 and c_2 can be calculated from Eqs. (9) and (10).

For the region $z\cong z_0$, i.e., where $a_1+a_2-b\approx 0$, one can follow Koza's approach [15] and write down the following quasistatic equations:

$$0=D\partial^2 a_1/\partial x^2-R_1, \tag{20}$$

$$0=D\partial^2 a_2/\partial x^2-R_2, \tag{21}$$

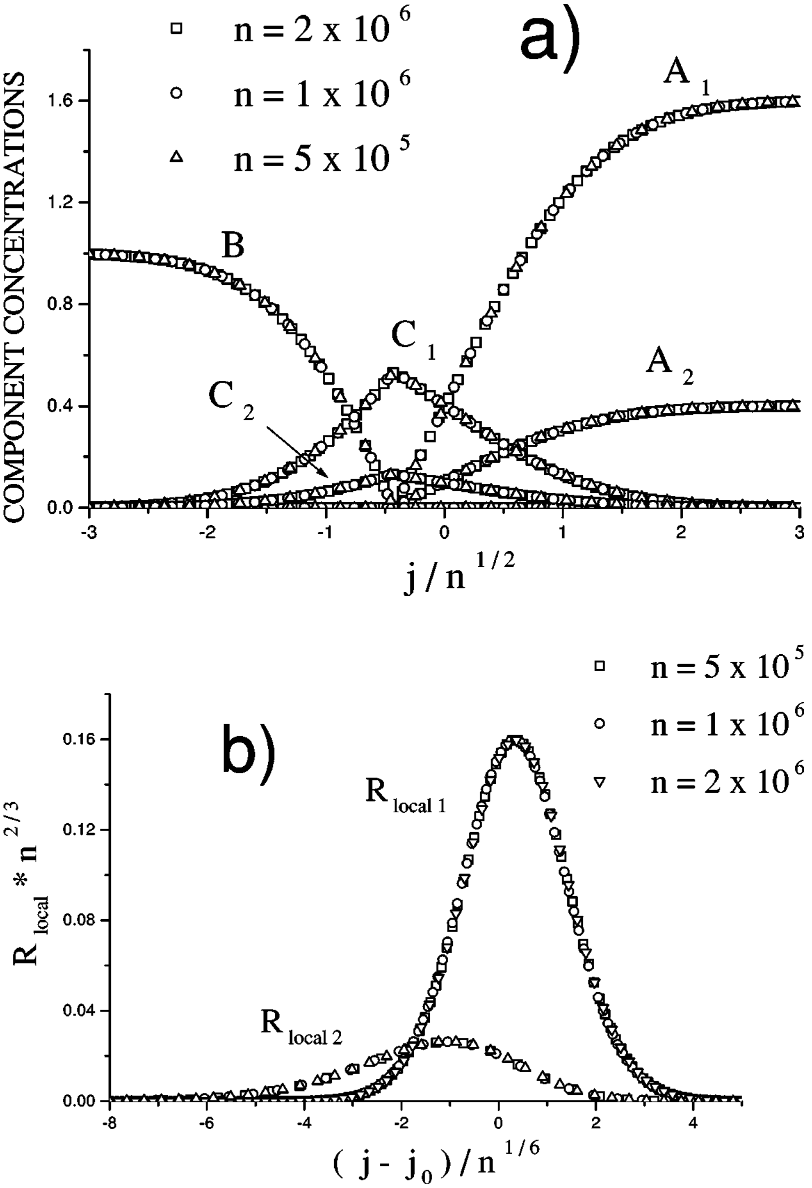

FIG. 2. A_1, A_2, B, C_1, and C_2 component profiles (a) and the local reaction rate $R_1(j,n)$ and $R_2(j,n)$ profiles (b) calculated by direct simulation of the reaction-diffusion equations (3)–(7) ($k_1=1.0$ and $k_2=0.1$) at times $n=5\times10^5$, 10^6, 2×10^6 are shown. All component concentrations are expressed in units of b_0. The values of $a_{10}/b_0=1.6$ and $a_{20}/b_0=0.4$ are used in calculations.

$$0=D\partial^2 b/\partial x^2-R_1-R_2, \tag{22}$$

$$0=D\partial^2 c_1/\partial x^2+R_1, \tag{23}$$

$$0=D\partial^2 c_2/\partial x^2+R_2. \tag{24}$$

The boundary conditions for Eqs. (20)–(24) can be expressed in the form of $-D\partial a_1/\partial x=\text{const.}\ t^{-1/2}$, etc. This form follows from the condition that near z_0 the solution of Eqs. (20)–(24) must coincide with Eqs. (13)–(15) and with Eqs. (18)–(19). The same form of equations and boundary conditions as in the single irreversible $A+B\rightarrow C$ reaction-diffusion system determines the same dependences of the reaction zone characteristics on time $w_0\sim t^{1/6}$, $R_1(x_{f1},t)\sim t^{-2/3}$, $R_2(x_{f2},t)\sim t^{-2/3}$, $a_1\sim t^{-1/3}$, $a_2\sim t^{-1/3}$, and $b\sim t^{-1/3}$.

So there is one reaction zone with complex structure in long-time irreversible regime. The component profiles on the scale $\sim\sqrt{Dt}$ obtained on the basis of the asymptotic expressions (13)–(15) and (18)–(19) are presented in Fig. 1(b).

The above heuristic consideration is based on the analysis of the kinetics equations. It is possible to present a qualitative analysis of the system from a physical point of the view. It is known that for initially separated components both single irreversible reactions create reaction fronts. This shows that for considered system with two competing irreversible reactions both reaction fronts must be located only in one place to an accuracy of reaction front widths $\sim t^{1/6}$. Indeed, if the reaction fronts are located in different places, then in the region between fronts there is no component B, such as there is no component B to the right of the left front. However, component B must exist to the left of the right front. The contradiction demonstrates that both reaction fronts must be located in one place. Taking this into account all the long-time characteristics of the system can be calculated in the lines of approach developed for single irreversible reaction case.

The validity of the properties of the process can be tested by numerically solving the reaction-diffusion equations (3)–(7). They were solved by the exact enumeration method [4,8], which is basically equivalent to discretization of equations, both in time and in space. A discrete lattice in one dimension is considered. At first the diffusion step is calculated and then only the reactions are taken into account. The equations describing the reaction step were obtained on the basis of approximation without the diffusion terms: $a_1(j,n+1)=a_1(j,n)+R_{local}(j)$, where j is the discrete spatial point. As in Ref. [4] the time step equals 1. The constants used are $k_1=1.0$ and $k_2=0.1$.

In Figs. 2(a) and 2(b) the results of the numerical calculation of the component profiles and reaction rate profiles $R_1(x,t)$ and $R_2(x,t)$ are shown, respectively. The profiles for times $n=5\times10^5$, 10^6, 2×10^6 are presented in coordinates $j/n^{1/2}$ and $(j-j_0)/n^{1/6}$ for the components and reaction rates, respectively. The coincidence of the profiles for the different periods of time confirms the asymptotic form of the analytical solution. For comparison of the asymptotic solutions Eqs. (12)–(14) and (17) and (18) component profiles on scale $\sim\sqrt{Dt}$ are also presented. The analysis of the asymptotic behavior of the system for times $n\leqslant2\times10^{+6}$ show the following time dependences: $w_1^2\sim n^{-0.34}$, $w_2^2\sim n^{-0.33}$, $R_{rlocal1}(x_{f1},n)\sim n^{-0.67}$, $R_{local2}(x_{f2},n)\sim n^{-0.67}$, $R_{rlocal1}(x_{f1},n)\sim n^{-0.67}$, $R_{local2}(x_{f2},n)\sim n^{-0.67}$, $R_{global1}\sim R_{global2}\sim n^{-0.50}$, and $(x_{f1}-x_{f2})\sim n^{+0.171}$. The calculated time exponents are like the asymptotic solution values.

Notice that the problem being considered in this paper was studied in the framework of the mean-field approximation. It is natural to assume that this approximation is valid only for the spatial dimension larger than the definite critical value d_c, like the single irreversible reaction $A+B\rightarrow C$. The detailed analysis of restrictions on use of the mean-field approximation and the determination of the correct value of d_c require taking into account fluctuations and this is not carried out here. At the same time, if $k_1=k_2$, then our problem coincides with a single $A+B\rightarrow C$ reaction case and so the rough evaluation of d_c may be taken as 2.

It is shown that the solution can be constructed as the combination of the two scale solutions: on diffusion length scale $\sim\sqrt{Dt}$ and on reaction zone width $\sim w\ll\sqrt{Dt}$. Heuristic analysis of mean-field reaction-diffusion equations confirmed by numerical simulation shows that the patterns are similar to a single-reaction case. It can be presented as one-reaction zone pattern. Generalization on arbitrary values of diffusion constants can be performed in the line of Koza's approach [15,22].

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