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Properties of the crossover from nonclassical to classical chemical kinetics in a reversible $A+B\leftrightarrow C$ reaction diffusion process

Misha Sinder and Joshua Pelleg
Department of Materials Engineering, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel

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We study the properties of the reaction front formed in a reversible reaction diffusion process $A+B\leftrightarrow C$, with initially separated reactants. The case of the mobile C component is considered. In accordance with Chopard *et al.* [Phys. Rev. E **47**, R40 (1993)] the dynamics of the front is described as a crossover between the ''irreversible'' regime at short times and the ''reversible'' regime at long times. A refined definition for the rate of C production is suggested, taking into account both the forward and the backward reaction rates. By this definition within the framework of the mean-field equations it is shown that the reversible regime is characterized by scaling of the local rate of C production as $R_{\mathrm{local}}\sim t^{-1}$ and by scaling of the global rate of C production as $R_{\mathrm{global}}\sim t^{-1/2}$. It is also established that in the considered special case of equal diffusion coefficients and equal initial concentrations, the macroscopic properties of the reaction front, such as the global rate of the C production R_{global} and the concentration profiles of the components outside the front reaction, are unchanged through this crossover. [S1063-651X(99)50212-2]

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The unusual dynamical properties of a reaction diffusion system with initially separated reactants have attracted much research interest in the last decade [1–37]. For an irreversible reaction $A+B\rightarrow C$, the initial separation of the reactants leads to the formation of a dynamic reaction front, which is a characteristic feature of a variety of physical and chemical phenomena where pattern formation occurs [38,39]. The practical interest in the initial separation of the reactants is associated with the fact that it can be achieved experimentally [2,3,6,17,26–30].

Galfi and Racz [1] developed a theory for the $A+B\rightarrow C$ reaction diffusion system, based on mean-field equations for the local concentrations of A and B. They showed that in the long-time limit the center of the reaction front x_f and the width of the front, w, obey a scaling $x_f\sim t^{1/2}$, $w\sim t^{1/6}$, while the production rate of C at x_f, scales as $R(x_f,t)\sim t^{-2/3}$. These results have been verified both experimentally [3] and by simulation studies [2,4,7,8]. It was shown that this mean-field description is valid above an upper critical dimension, $d_{\mathrm{up}}=2$ [8].

Most of the works were concerned with irreversible reaction $A+B\rightarrow C$, but the major part of the chemical reactions is reversible if sufficient time is given for the process. This case of the reversible process $A+B\leftrightarrow C$ with initially separated components was considered by Chopard *et al.* [13]. By using scaling arguments, numerical integration of the rate equations and cellular-automata simulation, they showed that the dynamics of the front can be described in terms of a crossover between ''irreversible'' regime at short times and a ''reversible'' regime at long times. In the irreversible regime the front dynamics coincides with those predicted by Galfi and Racz [1]. In the reversible regime a local equilibrium at the reaction front is present and only the diffusion process governs the dynamics. The critical exponents are correctly given by the mean-field approximation $w\sim t^{1/2}$, $R(x_f,t)\sim\mathrm{const}$, which are independent of the dimension. The results of the experiments in a convectionless capillary [26] are in agreement with values predicted by the theory and the simulations of Chopard *et al.* [13].

In this Rapid Communication, we study the local rate of C production in the reversible regime, when the component C is mobile. It is shown that the definition of the rate of C production used in Ref. [13] is not complete and does not correspond to the experimentally measured quantity in the ''reversible'' regime. Both the forward and the backward reaction rates must be included for the computation of the rate of C production. By this definition the dependence on time of the local product reaction rate is modified, and it will be shown in the framework of the mean-field equations that in the reversible regime the rate of C production, $R_r(x_f,t)$, scales to $R_r(x_f,t)\sim t^{-1}$. Defining the global rate, as the integral of the local reaction rate $R_r(x,t)$ over the x coordinate, provides $R_r(t)\sim t^{-1/2}$. The numerical integration of the mean-field equations shows good agreement with the predicted values of the exponents. The theoretical time dependence of the global rate of C production, $R_r(t)\sim t^{-1/2}$, obtained in this work, is inconsistent with the experimentally observed expression of $R_{\mathrm{exp}}(t)\sim t^{+1/2}$ [26]. Therefore, the discrepancy between our suggested scaling exponents and the experimental data is a subject for future work.

It should be noted that the time dependence $R_r(t)\sim t^{-1/2}$ in the reversible regime is similar to the analogous dependence of the global rate in the irreversible regime $R(t)\sim t^{-1/2}$ [1]. Calculation of the global rate in the irreversible regime and in the reversible regime for the special case, when $a_0=b_0$ and $D_A=D_B=D_C$, showed that $R(t)$ equals to $R_r(t)$. The calculated macroscopic distributions of the components outside the vicinity of the reaction front, both in the irreversible regime and in the reversible regime, are also identical each other. Thus, in this specific case, the crossover from irreversible to reversible regime is characterized only by a change in the local properties of the reaction front, namely, the temporal dependencies of the front width, $w(t)$, and the local rate of the C production $R_r(x_f,t)$. The macroscopic properties of the reaction front, i.e., the global rate of the C production $R_r(t)$ and the macroscopic distribution of the components outside the front reaction, are unchanged.

The reversible reaction diffusion process $A+B \leftrightarrow C$ can be described by the following equations [13]:

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

where a, b, c and D_A, D_B, D_C are the local concentrations and the diffusivities of A, B, and C, respectively. The rate of the forward reaction of the C particles production, R, is proportional to the joint probability of an A and a B particle simultaneously being present at a given location, and g is the backward reaction rates constant. For simplicity we suppose $D_A = D_B = D_C = D$. It is expected that the long-time scaling properties are not affected by this assumption [1,13].

The reactants A and B are separated and no C is present in the beginning. These initial conditions can be written as

$$a(x,0) = a_0 H(x), \quad b(x,0) = b_0[1 - H(x)], \quad c(x,0) = 0, \tag{2}$$

where a_0, b_0 are the initial concentrations and $H(x)$ is the Heaviside step function. We assume $a_0 = b_0$ and therefore the center of the reaction front is motionless $[x_f(t) = 0]$. Along the lines of Ref. [1,13], it is again expected that the motion of the center does not affect the long-time scaling properties of the reaction front.

At short times $t \ll g^{-1}$ the backward reaction can be neglected and the system is in the irreversible regime, which was considered by Galfi and Racz [1]. For long times, $t \gg g^{-1}$, because of the reversibility of the reaction, a local equilibrium is formed. The forward and the backward reactions compensate each other and the system reaches a state of local equilibrium for which

$$R(x,t) = gc(x,t). \tag{3}$$

Equation (3) is an approximate equation, which is valid only asymptotically for long times. By this it is meant that the difference between R and gc is much smaller than the values R and gc themselves, and this difference decreases as time increases. Because of the approximate character of Eq. (3), its direct substitution in Eqs. (1) is not correct. Such substitution would result in zero whereas $R - gc$ has a small but finite value.

For the description of the dynamics of the $A+B \leftrightarrow C$ reaction diffusion process two additional equations beyond the local equilibrium equation (3) are required. These can be obtained from Eqs. (1) by adding the first and the second equations to the third, resulting in

$$\partial_t a + \partial_t c = D_A \nabla^2 a + D_C \nabla^2 c, \tag{4a}$$

$$\partial_t b + \partial_t c = D_B \nabla^2 b + D_C \nabla^2 c. \tag{4b}$$

It should be stressed that all terms in Eqs. (4) are of the same order [40]. These diffusionlike equations (3) and (4) describe the correlated diffusion of the reactants in the ''reversible'' regime.

Let us assume the mean-field expression R

$$R \equiv kab, \tag{5}$$

where k is the forward reaction constant. Then the solutions of Eqs. (3)–(5) can be presented in the scaling form $a(x,t) = a(xt^{-\alpha_r})$, $b(x,t) = b(xt^{-\alpha_r})$, and $c(x,t) = c(xt^{-\alpha_r})$ with $\alpha_r = 0.5$. Consequently, the exponent of the width of the reaction zone α_r is given by $\alpha_r = 0.5$ as shown in [13], i.e., $w \sim t^{1/2}$. Note that this form of the solution is consistent with the conditions $\lim_{x\to+\infty} a(x,t) = 0$, $\lim_{x\to-\infty} a(x,t) = a_0$ etc., which is implicit in the initial conditions (2).

To analyze the rate of C production it is convenient to transform Eqs. (1) to Eqs. (6) as given below:

$$\begin{aligned} \partial_t a &= D_A \nabla^2 a - R_r, \\ \partial_t b &= D_B \nabla^2 b - R_r, \\ \partial_t c &= D_C \nabla^2 c + R_r. \end{aligned} \tag{6}$$

Here, R_r is the complete reaction rate of C formation,

$$R_r = R - gc. \tag{7}$$

In the irreversible regime R_r coincides with R, because the backward reaction term gc is neglected. But in the reversible regime this is not true, since the backward reaction cannot be neglected. In this regime due to the local equilibrium the forward reaction term and the backward reaction term compensate each other and the calculation of R_r by direct substitution of Eq. (3) to Eq. (7) is again not correct [because of the approximate character of Eq. (3)]. R_r is determined only by the complete system of Eqs. (3)–(6). R_r can be calculated by substitution of $a(x,t)$, $b(x,t)$, or $c(x,t)$ in Eqs. (6). Taking into account the scaling form of the concentrations of the reactants from Eqs. (6) we obtain that $R_r(x,t) \sim t^{-1} F(xt^{-\alpha_r})$, where F is some function. The local rate of C production at the reaction front $x_f = 0$ has a scaling $R_r(x_f,t) \sim t^{-1}$ and the global production rate of C scales to $R_r(t) \sim t^{-1/2}$.

The value of the scaling exponents can be interpreted by the following simple qualitative consideration. Because of local equilibrium the concentration of C in the thin reaction zone is approximately constant, $c(x_f,t) = c(x_f t^{-\alpha_r}) \approx c(0)$, i.e., does not depend on time. The global rate of C production, which is determined as the amount of C produced in the reaction zone per unit time, may be evaluated by $R_{\text{global}}(t) \approx d[c(0)w(t)]/dt \sim t^{-1/2}$. The value of the scaling exponent of the local rate of C production, γ, follows directly from the relation between the local and the global rates of C production $R_{\text{global}}(t) \approx \int R_{\text{local}}(x)dx \approx wR_{\text{local}}(x_f,t) \sim wt^{\gamma} \sim t^{\gamma+1/2}$. Taking into account that $R_{\text{global}}(t) \sim t^{-1/2}$ we have $\gamma = -1$.

In the above analysis the diffusionlike form of the solution of Eqs. (3)–(5) was used, and therefore it relates to the mean-field approximation. It should be noted that in Ref. [13], on the basis of the heuristic arguments and numerical simulations it was conjectured that in the reversible regime

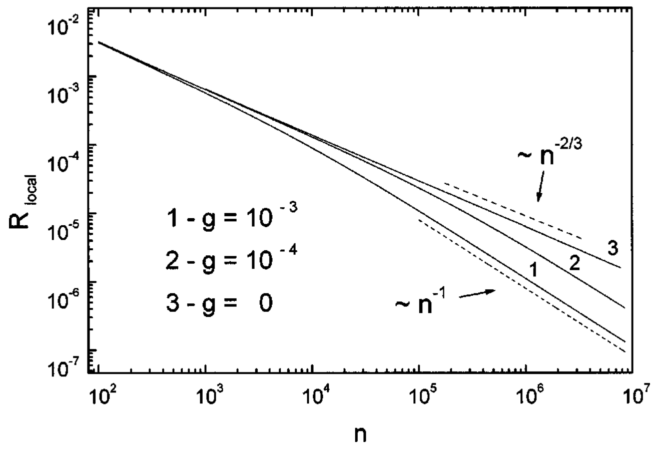

FIG. 1. Local rate of C production R_{local} at $x=0$, as the function of n time steps, for several values of the rate g of the back reaction $C\rightarrow A+B$.

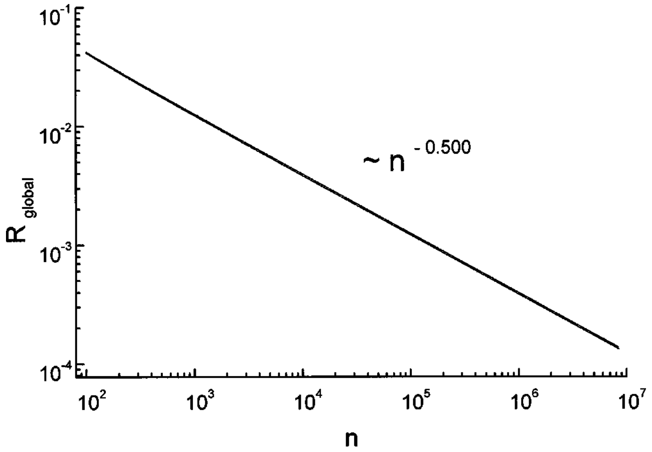

FIG. 2. Global rate of C production R_{global}, as the function of n time steps, for two values of the rate g of the back reaction $C\rightarrow A+B$ $g=10^{-3},10^{-4}$ [in units of $\tau=1/(ka_0)$].

the mean-field approximation is always the case. This occurs even for the space dimension $d\leqslant d_c=2$, when the mean-field expression $R\equiv kab$ is not valid. Therefore, the application of our analysis can possibly be extended for $d\leqslant d_c=2$.

Note that the time dependence of the global rate of C production in the reversible regime is similar to the dependence of the global rate in the irreversible regime, i.e., $R(t)\sim t^{-1/2}$ [1]. The relationship between them may be obtained by computing the dynamics of our system ($a_0=b_0$ and $D_A=D_B=D_C=D$). From Eqs. (4) we obtain

$$a+c=0.5[1+\text{erf}(x/2\sqrt{t})], \tag{8a}$$

$$b+c=0.5[1-\text{erf}(x/2\sqrt{t})]. \tag{8b}$$

The length, time, and concentrations are measured in units of $l=\sqrt{D/ka_0}$, $\tau=1/(ka_0)$, and a_0, respectively. The erf(x) is $\text{erf}(x)\equiv 2/\sqrt{\pi}\int_0^x \exp(-y^2)dy$. Adding to Eqs. (8) the local equilibrium Eqs. (4) and (5) $ab=gc$ (g in units of ka_0), we have the complete description of the system in the reversible case. Taking into account the condition of the reaction front formation $g\ll 1$ [40] we can see that A, B, and C distributions have two scales: the large macroscopic diffusion scale $L_d\sim\sqrt{t}$ and the small microscopic front reaction scale $L_w\sim w\sim\sqrt{gt}$. The asymptotic expressions ($g\rightarrow 0$) of the component concentrations on large scale L_d are given by

$$\begin{aligned} a&=H(x)\text{erf}(x/2\sqrt{t}),\\ b&=[1-H(x)]\text{erf}(-x/2\sqrt{t}),\\ c&=H(x)0.5[1-\text{erf}(x/2\sqrt{t})]\\ &\quad+[1-H(x)]0.5[1+\text{erf}(x/2\sqrt{t})],\\ R_r(t)&=1/\sqrt{\pi t}. \end{aligned} \tag{9}$$

It should be noted that Eqs. (9) coincide with the long-time asymptotic in the irreversible regime obtained in Refs. [1,25]. So, the macroscopic properties of the reaction diffusion system under consideration are the same in the irreversible and in the reversible regimes.

The validity of the crossover properties can be tested by solving numerically the reaction diffusion equations (1) and (2) in the mean-field approximation (5). We concentrated on the temporal dependencies of the C production rate. Equations (1) were solved by the exact enumeration method [5,12,41,42], which is basically equivalent to discretization of Eqs. (1), both in time and space. A discrete lattice in one dimension is considered. First the diffusion step is calculated, and then only the reaction is taken into account. The equations describing the reaction step were obtained on the basis of Eqs. (1) without the diffusion terms. The local reaction rate is calculated by $R_{\text{local}}(j)\equiv R_r(j)$, where j is the discrete spatial point. As in Ref. [5] the time step is equaled to 1. The constant used is $k=0.1$. The control parameter g was chosen as 10^{-m}, with $m=3,4$. The global rate of C production was calculated as the sum over all discrete spatial points,

$$R_{\text{global}}=\sum_j R_r(j), \tag{10}$$

where j is the discrete spatial point.

Figures 1 and 2 show crossover from $\sim n^{-2/3}$ to $\sim n^{-1}$ for the local rate of C production, $R_{\text{local}}(0)$, and the conservation of the scaling of $\sim n^{-1/2}$ for the global rate of C production, R_{global}. The time dependence of the front reaction depth $w(n)$ coincides with the one obtained in Ref. [1].

In summary, on the basis of the refined definition of the rate of C production, which includes the forward and the backward reaction rates, it is shown that in the mean-field approximation the reversible regime of the reaction diffusion process is characterized by scaling the local rate of C production as $R_r(x_f,t)\sim t^{-1}$ and by scaling of the global rate of the C production as $R_r(t)\sim t^{-1/2}$. The resulting theoretical value of the time scaling exponent, for the global rate of the C production, $-\frac{1}{2}$, is inconsistent with the one measured experimentally [26] and which is $+\frac{1}{2}$. It is also established that for the considered special case of equal diffusion coefficients and equal initial concentrations, the macroscopic properties of the reaction front, such as the global rate of C production, $\sim t^{-1/2}$, and the macroscopic distribution of the components outside the front reaction, are conserved through the crossover from the irreversible to the reversible regime.

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