

Crossover from nonclassical to classical chemical kinetics in an initially separated $A+B\leftrightarrow C$ reaction-diffusion system with arbitrary diffusion constants

Misha Sinder and Joshua Pelleg

Department of Materials Engineering, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel

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The asymptotic long-time properties of the reaction front formed in a reversible reaction-diffusion process $A+B\leftrightarrow C$ with initially separated reactants are investigated. The case of arbitrary nonzero values of the diffusion constants D_A, D_B, D_C of the components A, B, C and the initial concentrations a_0 and b_0 of A and B is considered. The system is studied in the limit of $g\rightarrow 0$, where g is the backward reaction rate constant. In accordance with previous work, the dynamics of the reaction front is described as a crossover between the ‘‘irreversible’’ regime at times $t\ll g^{-1}$ and the ‘‘reversible’’ regime at times $t\gg g^{-1}$. It is shown that through this crossover the macroscopic properties of the reaction front, such as the global rate of C production, the motion of the reaction zone center, and the concentration profiles of the components outside the reaction front, are unchanged. The concentration profiles of the components inside the reaction zone are described by quasi-static equations. The results of the theoretical consideration are confirmed by computing the mean-field kinetics equations.

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I. INTRODUCTION

The reaction front formed in an $A+B\rightarrow C$ reaction-diffusion system with initially separated reactants is of great interest since it represents a pattern for a wide class of processes in physics, chemistry, and biology [1–3]. The possibility of testing the theoretical predictions by experimental studies in this system is also important. Since the article of Gálfi and Rácz [4] much work has been devoted to studying this problem by different approaches [5–28]. The main interest in these studies was concentrated on the spatiotemporal behavior of the reactants A and B and on the production rate of C . C is usually assumed to be motionless. The traditional approach is to consider a system of partial differential equations for the mean local concentrations $\rho_A(x,t)$ and $\rho_B(x,t)$, which contain the macroscopic reaction rate $R(x,t)$ [4]. Some techniques have been developed to study these equations, for the cases of space dimension $d>d_c=2$, when the mean-field expression $R\propto\rho_A\rho_B$ is valid, and for $d\leq d_c$, when the explicit form of R is unknown [23,16,25–27]. These techniques consider the asymptotic long-time limit of the reaction-diffusion system and include renormalization group analysis [26–28], the scaling ansatz [4,24], the quasistationary approximation [13,23], and the approach developed by Koza [11].

According to the scaling ansatz [4], the long-time behavior of the reaction-diffusion system inside the reaction zone may be represented in the form

$$\rho_A(x,t) = \eta_A t^{-\gamma_A} S_A \left(\frac{x-x_f(t)}{w(t)} \right), \quad (1)$$

$$\rho_B(x,t) = \eta_B t^{-\gamma_B} S_B \left(\frac{x-x_f(t)}{w(t)} \right), \quad (2)$$

$$R = \eta_R t^{-\gamma_R} S_R \left(\frac{x-x_f(t)}{w(t)} \right), \quad (3)$$

where S_A, S_B , and S_R are some scaling functions, $x_f\propto t^{1/2}$ is the point where the reaction rate R has a maximum value, $w(t)\propto t^\alpha\ll t^{1/2}$ is the width of the reaction zone, η_A, η_B , and η_R are some parameters independent of x and t , and the exponents $\alpha, \gamma_A, \gamma_B$, and γ_R are some positive constants. The values of $\alpha=\frac{1}{6}$, $\gamma_A=\gamma_B=\frac{1}{3}$, $\gamma_R=\frac{2}{3}$ were obtained in the mean-field approximation for the nonzero diffusion constants D_A and D_B . The values of $\alpha, \gamma_A, \gamma_B$, and γ_R and the form of S_A, S_B , and S_R do not depend on D_A and D_B and the initial concentrations a_0 and b_0 if the values of these parameters are nonzero [4,26,27,14,11].

In the quasistationary approximation [13,23], it is assumed that for sufficiently long times the front reaction is described by two characteristic time scales. One time scale, $\tau_J\propto[d(\ln J)/dt]^{-1}\propto t$, determines the rate of change in the diffusive current $J=J_A=J_B$ of the reactants A and B arriving at the reaction zone. The second time scale, $\tau_F\propto w^2/D\propto t^{2\alpha}$, is the equilibration time of the reaction front. For $\alpha<\frac{1}{2}$, $\tau_F/\tau_J\rightarrow 0$ as $t\rightarrow\infty$, i.e., the reaction in the reaction zone quickly converges to the currents of the reactants. If D_A and D_B are nonzero, the asymptotic forms of ρ_A and ρ_B inside the reaction zone are described by simple quasistatic equations. The characteristic feature of the quasistatic equations is that they include time only as a parameter, through the time-dependent boundary currents $J_A=J_B=J$. The dependence of J on t, D_A, D_B, a_0 , and b_0 may be determined analytically [11].

Recently, Koza applied the quasistationary approximation to the investigation of the asymptotic properties of the system outside the reaction zone [11]. Without knowing the concrete form of R , in the framework of a few physically based assumptions, controlled by simulation or experimentally, many interesting quantities were determined exactly as a function of the external parameters D_A, D_B, a_0 , and b_0 . In particular, the existence of long-time limits of $x_f(t), J(t)$, and $R(t)$ was shown, i.e., as $t\rightarrow\infty$, $x_f(t)/\sqrt{t}\rightarrow C_f, J(t)\sqrt{t}\rightarrow C_J$, and $R(t)\sqrt{t}\rightarrow C_J$. Here $R(t)$ is the global reaction rate of C production. The value C_f can be computed from the equations

$$\Phi\left(\frac{-C_f}{2\sqrt{D_A}}\right) = \frac{a_0\sqrt{D_A}}{b_0\sqrt{D_B}}\Phi\left(\frac{C_f}{2\sqrt{D_B}}\right), \quad (4)$$

$$\Phi(x) \equiv [1 - \operatorname{erf}(x)]\exp(x^2), \quad (5)$$

where $\operatorname{erf}(x) \equiv 2\pi^{-1/2}\int_0^x \exp(-\eta^2)d\eta$ is the error function.

C_J can be calculated from the expressions

$$C_A = a_0 / [\operatorname{erf}(C_f/2\sqrt{D_A}) + 1], \quad (6)$$

$$C_B = -b_0 / [\operatorname{erf}(C_f/2\sqrt{D_B}) - 1], \quad (7)$$

$$\begin{aligned} C_J &= C_A\sqrt{D_A/\pi}\exp(-C_f^2/4D_A) \\ &= C_B\sqrt{D_B/\pi}\exp(-C_f^2/4D_B). \end{aligned} \quad (8)$$

The constants C_A and C_B control the form of ρ_A and ρ_B outside the reaction zone. For $x \ll x_f - w$,

$$\rho_A(x, t) = a_0 - C_A[\operatorname{erf}(x/\sqrt{4D_A t}) + 1], \quad (9)$$

and for $x \gg x_f + w$,

$$\rho_B(x, t) = b_0 + C_B[\operatorname{erf}(x/\sqrt{4D_B t}) - 1]. \quad (10)$$

A major part of the works [4–6, 8–21, 23–28] was concerned with the irreversible reaction $A + B \rightarrow C$, but commonly the chemical reactions are reversible at sufficiently large time. In Refs. [22, 29] the case of the reversible reaction $A + B \leftrightarrow C$ with initially separated reactants was studied for long times $t \rightarrow \infty$ and for small values of g , where g is the backward reaction rate constant. It was established that the dynamics of the front can be described in terms of a crossover between the “irreversible” regime at times $gt \ll 1$ and the “reversible” regime at times $gt \gg 1$ [22]. In the “irreversible” regime, the front dynamics coincides with those predicted by Gálfi and Rácz [4]. In the “reversible” regime, a local equilibrium at the reaction front exists, and only the diffusion process governs the dynamics. It was established that the concentrations A , B , and C near the reaction zone may be described in the form of Eqs. (1)–(3) with the exponents γ_A , γ_B , γ_C , and γ_R equal to zero, whereas the reaction front width w given by $w \sim t^{1/2}$ is independent of the space dimension [22].

In Ref. [29] the refined rate of C production $R_r(x, t)$, including forward and backward reactions, was studied on the basis of the mean-field equations for mobile C . It was shown that the reversible regime ($gt \gg 1$) is characterized by scaling of the local rate of C production as $R_{r_{\text{local}}} \sim t^{-1}$ and by scaling of the global rate of C production as $R_{r_{\text{global}}} \sim t^{-1/2}$. Furthermore, a surprising property was observed in the crossover from the “irreversible” to the “reversible” regime, namely, that the macroscopic properties of the reaction-diffusion process, such as the time dependence of the global rate of C production and the distributions of the components, are unchanged outside the reaction front. In Ref. [29] only the specific case of equal diffusion constants of A , B , and C and equal initial concentrations of the reactants was considered. It was assumed, similarly to the irreversible reaction case [4], that the equality of the diffusion constants and the initial reactant concentrations does not af-

fect the scaling exponents. On the other hand, it is not clear whether under more general conditions the macroscopic properties of the crossover remain unaltered.

The objective of this work is to study for $t \rightarrow \infty$ and $g \rightarrow 0$ the crossover from the irreversible ($gt \ll 1$) to the reversible ($gt \gg 1$) regime with arbitrary nonzero diffusion constants and with arbitrary initial reactant concentrations. The analysis will be performed in the framework of Koza’s approach [11], extended to the case of the reversible $A + B \leftrightarrow C$ reaction. It will be supplemented by numerical and analytical computations of the equations in the mean-field approximation.

The paper is organized as follows. In the next section the analysis of the limiting cases of the irreversible and reversible regimes and the crossover from one to the other is presented. The behavior of the system in the case of a thin reaction zone is studied numerically and analytically on the basis of the mean-field kinetic equations in Sec. III. Section IV is devoted to the reversible regime when the reaction occurs in a wide region. Section V summarizes the results of our work.

II. IRREVERSIBLE AND REVERSIBLE REGIMES AND THE CROSSOVER BETWEEN THEM

The reversible reaction-diffusion system $A + B \leftrightarrow C$ is described by the following equations [22]:

$$\begin{aligned} \frac{\partial \rho_A}{\partial t} &= D_A \frac{\partial^2 \rho_A}{\partial x^2} - R + g\rho_C, \\ \frac{\partial \rho_B}{\partial t} &= D_B \frac{\partial^2 \rho_B}{\partial x^2} - R + g\rho_C, \\ \frac{\partial \rho_C}{\partial t} &= D_C \frac{\partial^2 \rho_C}{\partial x^2} + R - g\rho_C, \end{aligned} \quad (11)$$

with the initial state given by

$$\begin{aligned} \rho_A(x, t=0) &= a_0 H(-x); \quad \rho_B(x, t=0) = b_0 H(+x); \\ \rho_C(x, t=0) &= 0, \end{aligned} \quad (12)$$

where ρ_A , ρ_B , ρ_C , D_A , D_B , and D_C are the local concentrations and diffusion constants of A , B , and C , respectively.

For times of $gt \ll 1$, we have $g\rho_C \ll \partial \rho_C / \partial t$ and therefore the backward reaction term in Eqs. (11) may be neglected [22], resulting in

$$\begin{aligned} \frac{\partial \rho_A}{\partial t} &= D_A \frac{\partial^2 \rho_A}{\partial x^2} - R, \\ \frac{\partial \rho_B}{\partial t} &= D_B \frac{\partial^2 \rho_B}{\partial x^2} - R, \\ \frac{\partial \rho_C}{\partial t} &= D_C \frac{\partial^2 \rho_C}{\partial x^2} + R. \end{aligned} \quad (13)$$

Let us begin with the behavior of the reaction-diffusion system (12) and (13) at asymptotically long times of $t \rightarrow \infty$, following Koza’s approach with our modification, which

takes into account the nonzero diffusion constant of C . Our modification does not change the basic line of Koza's consideration [11]. We shall discuss only some key points, which are essential for further use.

The long-time limit properties of the reaction-diffusion system will be deduced in the light of a few physical assumptions, which were comprehensively discussed and verified by Koza [11].

(i) R , the production rate of C , attains its maximal value at point $x_f(t)$. There is a point x_0 where $D_A\rho_A(x_0,t) = D_B\rho_B(x_0,t)$. At asymptotically long times $t \rightarrow \infty$, $x_f(t) \approx x_0(t)$ [11].

(ii) The reaction occurs mainly in a region $|x - x_f| \sim w(t) \sim t^\alpha$, where $0 < \alpha < \frac{1}{2}$. Outside this region, at $x \ll x_f - w$, we have $\rho_A, \rho_C \gg \rho_B$, and at $x \gg x_f + w$, $\rho_B, \rho_C \gg \rho_A$ is obtained.

(iii) The dynamics of ρ_A and ρ_C in the region $x \ll x_f - w$ may be described by Eqs. (9) and (14):

$$\rho_C(x,t) = C_{C1}[\text{erf}(x/\sqrt{4D_C t}) + 1], \quad (14)$$

where C_A and C_{C1} are constants. For $x \gg x_f + w$ the dynamics of ρ_B and ρ_C may be described by Eqs. (10) and (15):

$$\rho_C(x,t) = -C_{C2}[\text{erf}(x/\sqrt{4D_C t}) - 1], \quad (15)$$

where C_B and C_{C2} are constants.

(iv) The quasistatic approximation [i.e., when the left sides of Eqs. (13) are neglected] is true in the region $-(D_A t)^{1/2} \ll x \ll (D_B t)^{1/2}$. These quasistatic equations are supplemented by the following boundary conditions:

$$\begin{aligned} D_A \partial \rho_A / \partial x \rightarrow -J_A(t), \quad \rho_B \rightarrow 0, \quad D_C \partial \rho_C / \partial x \rightarrow J_{C1}(t), \\ x \rightarrow -\infty, \\ \rho_A \rightarrow 0, \quad D_B \partial \rho_B / \partial x \rightarrow J_B(t), \quad D_C \partial \rho_C / \partial x \rightarrow -J_{C2}(t), \\ x \rightarrow +\infty, \end{aligned} \quad (16)$$

where $J_A(t)$, $J_B(t)$, $J_{C1}(t)$, and $J_{C2}(t)$ are some functions describing the currents of the components A , B , and C , respectively, toward the reaction zone.

With these assumptions the solution of Eq. (13) is reduced to solutions of more simple solvable equations. The regions in which these simple solutions are valid overlap and this enables them to merge into a complete solution. In particular, from assumption (ii) it follows that the reaction proceeds only inside a thin zone, while outside this zone independent diffusion of the components occurs. Therefore, the concentration profiles outside the reaction zone may be calculated by standard diffusion equations as presented in assumption (iii). Note that these forms ensure that the concentration limits for $x \rightarrow \pm \infty$ implied by the initial conditions (16) are fulfilled. For example, $\lim \rho_C = 0$ if $x \rightarrow \pm \infty$.

From the quasistatic equations linear expressions in x can be obtained in the region $-(D_A t)^{1/2} \ll x \ll (D_B t)^{1/2}$ according to assumptions (i) and (iv) as given by

$$D_A \rho_A + D_C \rho_C \approx J_1(t)[x - x_0(t)] + \Psi(t), \quad (17)$$

$$D_B \rho_B + D_C \rho_C \approx J_2(t)[x - x_0(t)] + \Psi(t). \quad (18)$$

$J_1(t)$, $J_2(t)$, and $\Psi(t)$ are some time functions, which are related to the functions from the boundary conditions (16) by $J_A(t) = J_B(t) = J(t) = J_2(t) - J_1(t)$, $J_{C1} = J_2(t)$, and $J_{C2} = -J_1(t)$. On the other hand, assumption (iii) determines expressions (9) and (14) for ρ_A and ρ_C in region $x \ll x_f - w$. By coordinating expressions (9) and (14) with Eqs. (17) and (18) and applying the same analysis for ρ_B and ρ_C in the region $x \gg x_f + w$, Eqs. (4)–(10), (19), and (20) are obtained for computation of the constants C_f , C_J , C_{J1} , C_{J2} , C_A , C_B , C_{C1} , and C_{C2} :

$$\begin{aligned} C_{C1} &= C_J \sqrt{\pi/4D_C} \Phi\left(\frac{C_f}{2\sqrt{D_C}}\right), \\ C_{C2} &= C_J \sqrt{\pi/4D_C} \Phi\left(\frac{-C_f}{2\sqrt{D_C}}\right), \end{aligned} \quad (19)$$

$$\begin{aligned} C_{J1} &= -0.5C_J \left[1 + \text{erf}\left(\frac{C_f}{2\sqrt{D_C}}\right)\right], \\ C_{J2} &= 0.5C_J \left[1 - \text{erf}\left(\frac{C_f}{2\sqrt{D_C}}\right)\right]. \end{aligned} \quad (20)$$

C_f , C_J , C_{J1} , and C_{J2} are constants that determine the long-time behavior of the reaction front coordinate x_f and the currents to the reaction front of the components $J(t) = J_2(t) - J_1(t)$, $J_1(t)$, and $J_2(t)$ by the following expressions: $\lim x_f(t)/\sqrt{t} \rightarrow C_f$, $\lim J(t)\sqrt{t} \rightarrow C_J$, $\lim J_1(t)\sqrt{t} \rightarrow C_{J1}$, and $\lim J_2(t)\sqrt{t} \rightarrow C_{J2}$. The constants C_A , C_B , C_{C1} , and C_{C2} are related to the form of the concentration profiles outside the reaction zone. The function Ψ from Eqs. (17) and (18) does not depend on the time and is given by

$$\begin{aligned} \Psi &= D_C C_{C1} \left[\text{erf}\left(\frac{C_f}{2\sqrt{D_C}}\right) + 1 \right] \\ &= D_C C_{C2} \left[-\text{erf}\left(\frac{C_f}{2\sqrt{D_C}}\right) + 1 \right]. \end{aligned} \quad (21)$$

Our analysis is extended as compared to the work of Koza [11] by taking into account the diffusion of the product C . Outside the reaction zone, C diffuses independently of the reactants A and B , and therefore the C profiles can be calculated on the basis of the diffusion equation $\partial \rho_C / \partial t = D_C \partial^2 \rho_C / \partial x^2$. The form of the C profile outside the reaction zone is shown in Fig. 1. It describes the exit of C from the moving reaction zone. The break in the C profile near the reaction front is related to the production of C in this zone.

For times of $gt \gg 1$ and $t \rightarrow \infty$ the system reaches a state of local equilibrium, $R(x,t) = g\rho_C(x,t)$, and Eqs. (11) transform to reversible regime equations [29,30] given as

$$0 = -R + g\rho_C, \quad (22)$$

$$\frac{\partial \rho_A}{\partial t} + \frac{\partial \rho_C}{\partial t} = D_A \frac{\partial^2 \rho_A}{\partial x^2} + D_C \frac{\partial^2 \rho_C}{\partial x^2},$$

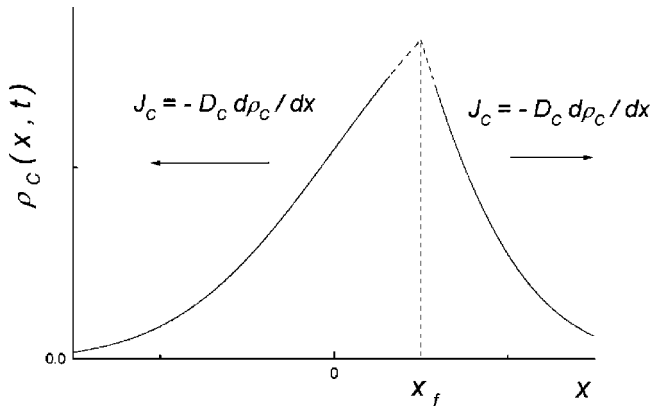


FIG. 1. The form of the C profile calculated on the basis of Eqs. (14), (15), and (19) given in arbitrary units of ρ_C and x . The dashed line marks the region near the reaction front $\sim x_f$, where the above equations cannot be applied.

$$\frac{\partial \rho_B}{\partial t} + \frac{\partial \rho_C}{\partial t} = D_B \frac{\partial^2 \rho_B}{\partial x^2} + D_C \frac{\partial^2 \rho_C}{\partial x^2}.$$

Equations (22) describe the correlated diffusion of the components in the “reversible” regime, but they are not equivalent. Whereas the first equation $R(x, t) = g\rho_C(x, t)$ is valid only asymptotically for $t \rightarrow \infty$, the second and the third equations are precise. These two equations can be obtained from Eq. (11) by adding the first and second equations to the third one, respectively.

Calculation of the refined rate of C production, $R_r \equiv R - g\rho_C$, cannot be performed directly from Eqs. (22). It can be calculated by substituting the solution of Eqs. (22) into any of the original equations (11) [29] resulting in

$$\begin{aligned} R_r &= D_A \frac{\partial^2 \rho_A}{\partial x^2} - \frac{\partial \rho_A}{\partial t}, \\ R_r &= D_B \frac{\partial^2 \rho_B}{\partial x^2} - \frac{\partial \rho_B}{\partial t}, \\ R_r &= D_C \frac{\partial^2 \rho_C}{\partial x^2} + \frac{\partial \rho_C}{\partial t}. \end{aligned} \quad (23)$$

This substitution is equivalent to the second step of the perturbation theory on a large time scale [29].

Consider the behavior of the reaction system $A + B \leftrightarrow C$ in the reversible regime assuming that $g \rightarrow 0$ [30]. In this case the dynamic equilibrium of the reaction $A + B \leftrightarrow C$ sharply shifts to the right, namely, the direct reaction $A + B \rightarrow C$ is preferential to the backward reaction $A + B \leftarrow C$, and in most points along the x axis only components A and C or B and C exist, i.e., $\rho_A, \rho_C \gg \rho_B$ or $\rho_B, \rho_C \gg \rho_A$. There exists a thin zone where $\rho_A \approx \rho_B$ and the production of C is concentrated only in this place, while in other regions independent diffusion of the components occurs. The reaction zone width w , evaluated on the basis of Eqs. (22) in the mean-field approximation [29,30], has a scaling $w \sim \sqrt{gt}$ if $g \rightarrow 0$. As in the irreversible regime, the relation between the characteristic times τ_J and τ_F can be written in the reversible regime as $\tau_F \sim w^2/D \sim tg \ll \tau_J \sim [d(\ln J)/dt]^{-1} \sim t$. The relation $\tau_F/\tau_J \rightarrow 0$ if $g \rightarrow 0$ is also valid when the dependence of w on g has

a more general form, i.e., $w \sim t^{1/2} g^\beta$, where β is some positive constant. This relation (as in the irreversible regime) justifies the simplified quasistatic equations in the region $-(D_B t)^{1/2} \ll x \ll (D_A t)^{1/2}$, where the local equilibrium relation $R = g\rho_C$ is used. The equations are

$$\begin{aligned} 0 &= -R + g\rho_C, \\ 0 &= D_A \frac{\partial^2 \rho_A}{\partial x^2} + D_C \frac{\partial^2 \rho_C}{\partial x^2}, \\ 0 &= D_B \frac{\partial^2 \rho_B}{\partial x^2} + D_C \frac{\partial^2 \rho_C}{\partial x^2}. \end{aligned} \quad (24)$$

Let us replace assumptions (i), (ii), and (iv) of the irreversible case by the modified assumptions (i-m), (ii-m), and (iv-m) given below for the reversible case: in assumption (i-m) the rate of C production, R , is changed to the refined rate of C production, R_r ; in assumption (ii-m) the dependence $w \sim t^\alpha$ is replaced by $w(t) \sim t^{1/2} g^\beta$, where β is a positive constant; in assumption (iv-m) the quasistatic equations of the irreversible reaction are replaced by the quasistatic equations of the reversible reaction (24). On the basis of these assumptions the analysis performed for the irreversible regime ($gt \ll 1$) can be repeated without variations for the reversible regime ($gt \gg 1$), provided the limit $g \rightarrow 0$ is added to the limit $t \rightarrow \infty$. This is based on the analogy between the two regimes. Thus we can make the following statements.

(a) The linear dependence on x of $D_A \rho_A + D_C \rho_C$ and $D_B \rho_B + D_C \rho_C$ is a consequence of the modified quasistatic equations (24). This dependence is the same as in the irreversible regime [see Eqs. (17) and (18)].

(b) Outside the reaction zone the concentration profiles have the same form because assumption (iii) was not modified. This is the outcome of the independent diffusion of the components outside the reaction zone in the reversible regime also.

(c) The analytical expressions describing the reaction dynamic outside the reaction zone are the same in both the irreversible and reversible regimes. This is a result of coordinating the solutions considered in (a) and (b).

Consequently, the asymptotic expressions for the component profiles outside the reaction zone, the global rate of the reaction, and the front reaction coordinate are the same in the irreversible and reversible regimes.

We have shown above that, when $t \rightarrow \infty$ and $g \rightarrow 0$ simultaneously, the descriptions of the reaction-diffusion system outside the reaction zone coincide in the two regimes: in the irreversible regime $gt \ll 1$ [under the assumptions (i)–(iv)] and in the reversible regime $gt \gg 1$ [under the assumptions (i-m), (ii-m), (iii), and (iv-m)]. Two major properties are used in the analysis of both regimes. (a) The first is the applicability of the quasistatic approximation. On this basis the linear dependence on x of the expressions $D_A \rho_A + D_C \rho_C$ and $D_B \rho_B + D_C \rho_C$ was derived. (b) The second is the monotonic decrease of the reaction zone width with respect to the diffusion length. Consequently, in the region where the quasistatic approximation can be used, independent diffusion of the components also occurs. Both requirements (a) and (b) are fulfilled when the ratio $\tau_F/\tau_J \sim w^2(t)/Dt \rightarrow 0$ as $t \rightarrow \infty$ and $g \rightarrow 0$. This is the case when a

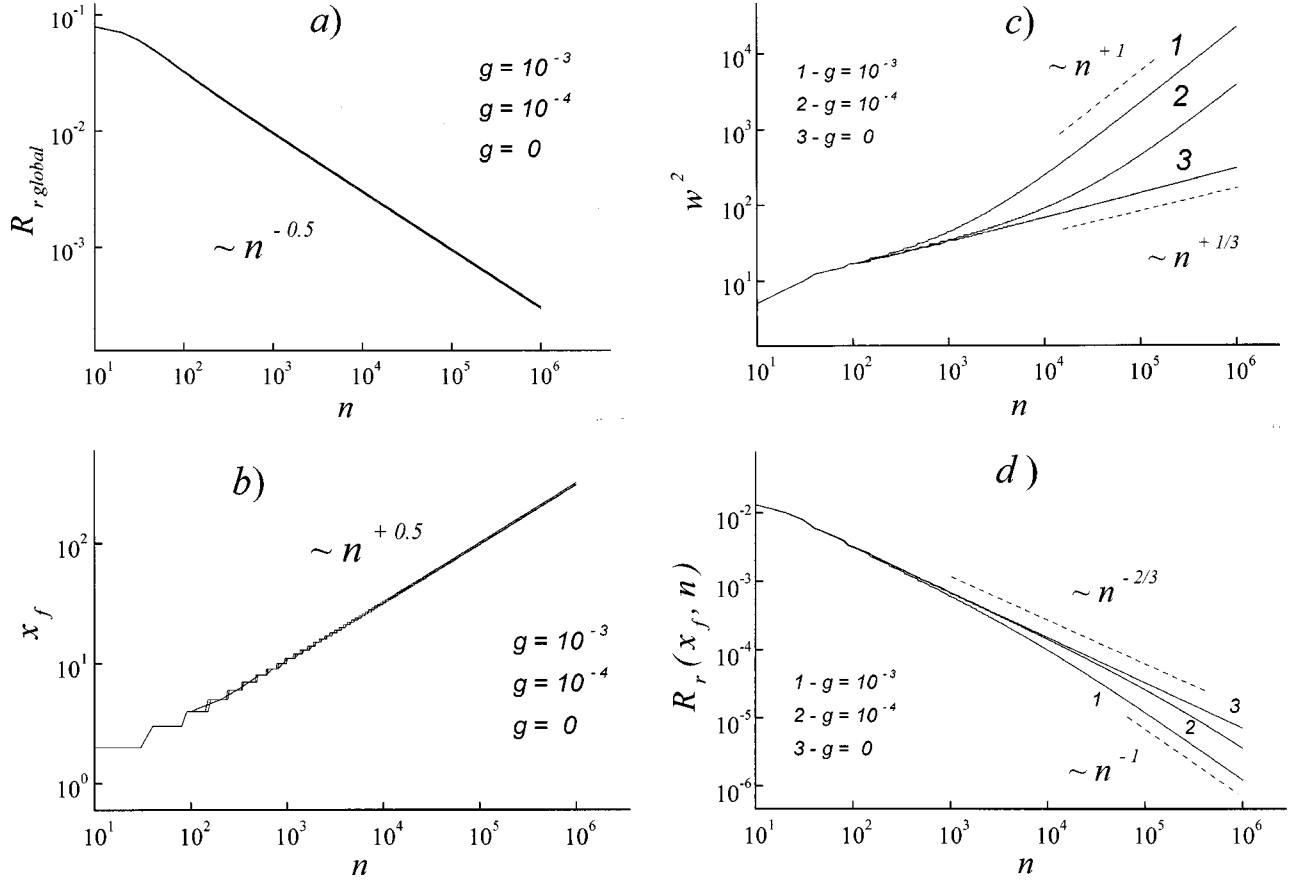


FIG. 2. Reaction characteristics: (a) the global rate of C production, $R_{r, \text{global}}$; (b) the coordinate of the reaction zone center, x_f ; (c) the width of the reaction zone, w ; (d) the local rate of C production, $R_{r, \text{local}}$ at $x = x_f$, all as functions of the time step number n . $R_{r, \text{global}}$ and $R_{r, \text{local}}$ are in units of τ^{-1} . x_f and w are measured by the number of space steps j . Three values of g were used, namely, $g = 10^{-3}$, 10^{-4} , and 0 (in units of τ^{-1}).

general monotonic dependence of the reaction zone width is assumed: $w(t, g) \sim t^\alpha$ for $gt \ll 1$, $w(t, g) \sim g^\beta t^{1/2}$ for $gt \gg 1$, and these limiting dependencies are monotonically linked for $gt \sim 1$. The numerical simulation presented in Refs. [22,29] and the calculation described below support the validity of a monotonic dependence of w on time in the region $gt \sim 1$. Thus, from the dependence of $w = w(t, g)$ it follows that the formulas describing the behavior of the system outside the reaction front apply to arbitrary values of gt . In other words, the macroscopic properties of the reaction-diffusion system do not change with time through the crossover from the irreversible to the reversible regime. The above description linking the two domains of $gt \ll 1$ and $gt \gg 1$ may be formulated by remodifying the assumptions (ii-m) and (iv-m) as follows. In assumption (ii-mm) the dependence $w(t) \sim t^{1/2} g^\beta$ is replaced by $w(t, g)$, where $w(t, g)$ is a time-dependent monotonic function having the properties described above. In assumption (iv-mm) the quasistatic equations of the reversible reaction (24) are replaced by the quasistatic equations obtained by equating to zero the left side of Eqs. (11). These quasistatic equations control the crossover near the reaction zone.

Assumptions (i-m), (ii-mm), (iii), and (iv-mm) for $t \rightarrow \infty$ and $g \rightarrow 0$ are applied to arbitrary values of gt and determine the properties of the crossover from the irreversible $gt \ll 1$ to the reversible $gt \gg 1$ regime. This means that the component profiles outside the reaction zone, the global rate of the re-

action, and the front reaction coordinate motion are unchanged at all times during the crossover.

It should be emphasized that, as in Ref. [11], our assumptions do not restrict the form of R , and therefore our results are true for all cases when the indicated assumptions are valid. In particular, they are true for the case of $d \leq d_c$, when the mean-field expression for R is not valid.

III. MEAN-FIELD APPROXIMATION: THE CASE OF A THIN REACTION ZONE

Consider Eqs. (11) with the mean-field expression $R = k\rho_A\rho_B$, where k is the direct reaction constant, as the simplest case of a system to which the above theoretical approach may be applied. To test the assumptions and the properties of the crossover from the irreversible to the reversible regime, the equations were solved numerically by an exact enumeration method [9,10,29,31,32], which is essentially equivalent to discretization of Eqs. (11) in both time and space. A one-dimensional discrete lattice is considered. First the diffusion step is calculated and only then is the reaction taken into account. The equations describing the reaction step were obtained on the basis of Eqs. (11) without the diffusion terms. The local reaction rate is calculated as $R_{r, \text{local}}(j) \equiv R_r(j)$, where j is a discrete spatial point. As in Ref. [9], the time step τ equals 1, whereas ρ_A , ρ_B , and ρ_C are the dimensionless probabilities of locating A , B , and C ,

respectively, at a discrete point. This means that the values of R_r , k , and g are in units of τ^{-1} and they are nondimensional. The constants $k=0.1$ and $g=10^{-3}$, 10^{-4} , and 0 were used. The global rate of C production was calculated as the sum over all discrete spatial points,

$$R_{r_{\text{global}}} = \sum_j R_r(j). \quad (25)$$

Figures 2 and 3 show the results of the numerical calculation for $a_0=b_0=1.0$ and $D_B=0.25D_A=0.5D_C$. In particular, the dependencies of the local and global rates of C production, the coordinate of the reaction zone center, and the width of the reaction zone on the number of time steps n are shown in Fig. 2. In Figs. 2(a) and 2(b) no changes through the crossover of the global rate and in the coordinate of the reaction zone center may be seen. By contrast, similarly to Refs. [22,29], the crossover of the local rate of C production and the width of the reaction zone are accompanied by a change in the exponents, from $\sim n^{-2/3}$ to $\sim n^{-1}$ and from $\sim n^{+1/6}$ to $\sim n^{+1/2}$, respectively, as seen in Figs. 2(c) and 2(d). Note that the function $w=w(n)$ grows monotonically as assumed in (ii-mm), i.e., one of the important assumptions is true in the case of the mean-field approximation.

The concentration profiles of the components for three times $0.1g^{-1}$, $10g^{-1}$, and g^{-1} ($g=10^{-4}$) are shown in Fig. 3. The chosen values represent the irreversible regime, the reversible regime, and the crossover between them, respectively. In accordance with expressions (9), (10), (14), and (15), the concentration profiles coincide in the region outside the reaction zone when expressed in terms of the diffusion-like coordinate $x/\sqrt{t} \sim j/\sqrt{n}$. In the reaction zone, in accordance with our theoretical predictions, the profiles do not coincide.

Knowing the concrete form of $R=k\rho_A\rho_B$, the expressions for ρ_A , ρ_B , ρ_C , and R_r inside the reaction zone in the reversible regime $gt \gg 1$ for $g \rightarrow 0$ have been computed directly from Eqs. (24) and are given below:

$$\rho_A = (g\Psi D_B/kD_A D_C)^{1/2} f_0(x/w_0), \quad (26)$$

$$\rho_B = (g\Psi D_A/kD_B D_C)^{1/2} f_0(-x/w_0), \quad (27)$$

$$\rho_C = k\rho_A\rho_B/g = \Psi/D_C, \quad (28)$$

$$R_r = (kD_C/g\Psi D_A D_B)^{1/2} (J_2 - J_1)^2 f_1(x/w_0). \quad (29)$$

Here

$$w_0 = \sqrt{g\Psi D_A D_B/kD_C} (J_2 - J_1),$$

$$w_1 = \sqrt{g\Psi D_A D_B/kD_C} (-J_1),$$

$$f_0(y) \equiv 0.5(\sqrt{y^2 + 4} - y),$$

and

$$f_1(y) \equiv 2/(y^2 + 4)^{3/2}.$$

These expressions show that for the concentrations A , B , and C and for R_r , neither the scaling exponents nor the scaling functions depend on the diffusion constants and on

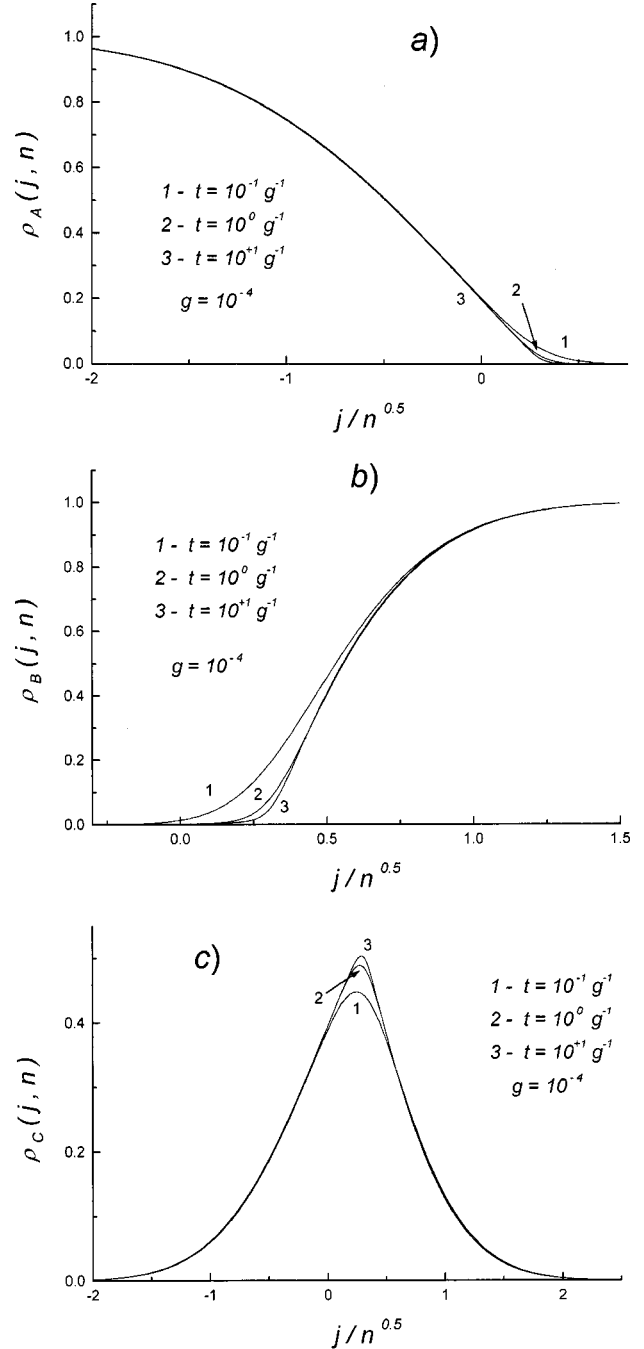


FIG. 3. The simulated concentration profiles of (a) A , (b) B , and (c) C for three times $10^{-1}g^{-1}$, g^{-1} , and $10g^{-1}$ (in units of the discrete time step τ) expressed in the diffusionlike dimensionless coordinate j/\sqrt{n} ($k=0.1$, $g=10^{-4}$). Here, ρ_A , ρ_B , and ρ_C are the dimensionless probabilities of locating A , B , and C , respectively, at a discrete point.

the initial reactant concentrations. This is similar to the case of the irreversible regime [Eqs. (1)–(3)].

In Fig. 4, the simulation data for $R_r(x,t)$ are compared with expression (29). The data fit the curve obtained from Eq. (29) reasonably well.

IV. MEAN-FIELD APPROXIMATION: THE CASE OF A WIDE REACTION ZONE

In Secs. II and III the reaction-diffusion system with small g values was discussed [22,29]. For this case, the complete

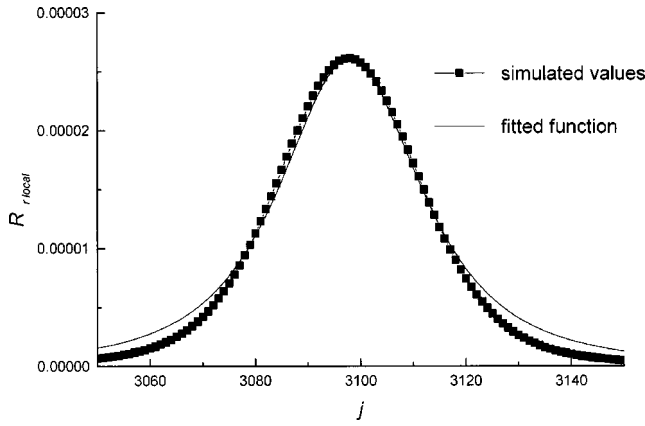


FIG. 4. Simulated profile of $R_{r_{\text{local}}}(x,t)$ at time 10^{-1} ($k=0.1$, $g=10^{-4}$) fitted by $f_1(y) \equiv 2[(x/w_0)^2 + 4]^{3/2}$. $f_1(y)$ is proportional to the asymptotic expression (29). Here j is a discrete space step number. $R_{r_{\text{local}}}(x,t)$ is in units of τ^{-1} .

dynamics of the reversible reaction-diffusion system $A + B \leftrightarrow C$, with initially separated reactants A and B , may be described as a crossover through three regimes, namely, the short-time regime, the long-time irreversible regime, and the long-time reversible regime. At short times $t \ll t_c \sim k^{-1}$ the initially separated reactants A and B start to mix [6,9]. The reaction is not influenced by the A and B profiles and occurs in a region of width w which is approximately equal to the diffusion length $\sim \sqrt{D_A t}, \sqrt{D_B t}$. For intermediate time $t \sim t_c$, the direct reaction $A + B \rightarrow C$ becomes more dominant, and for times $t \gg t_c$, long-time asymptotic behavior appears [6,8,12,21]. This state, describing the long-time irreversible regime, is characterized by a relatively small reaction zone width $w \ll \sqrt{D_A t}, \sqrt{D_B t}$. At time $t \sim t_r = g^{-1}$ the backward reaction sets in, and for times $t \gg t_r$ the system converts to the long-time reversible regime [22]. In Table I the quantities characterizing these regimes in the reaction-diffusion system are summarized. The data relating to times $gt \ll 1$ were taken from Ref. [8], taking into account that for these times $R_r(x,t) \approx R(x,t)$.

The classification in Table I is valid only if $t_c \ll t_r = g^{-1}$, i.e., for small values g . If g is not sufficiently small and $t_c \sim t_r$ the irreversible regime has not enough time to appear; therefore for long times $t \gg t_c, t_r$, the system transforms to the reversible regime directly, bypassing the irreversible regime. In this case the quasiequilibrium expression $k\rho_A(x,t)\rho_B(x,t) = g\rho_C(x,t)$ is valid and the system may be described by Eqs. (22) also. Thus, the reversible regime with large reaction width $w \sim \sqrt{D_A t}, \sqrt{D_B t}$ is described by Eqs. (22).

TABLE I. The reaction front properties of the crossover in the initially separated reversible $A + B \leftrightarrow C$ reaction-diffusion system.

Quantity	Notation	Short-time regime $t \ll t_c \sim k^{-1}$	Long-time irreversible regime $gt \ll 1$	Long-time reversible regime $gt \gg 1$
Global rate	$R_{r_{\text{global}}}(t)$	$t^{1/2}$	$t^{-1/2}$	$t^{-1/2}$
Center of front	$x_f(t)$	nonuniversal	$t^{1/2}$	$t^{1/2}$
Width of front	$w(t)$	$t^{1/2}$	$t^{1/6}$	$t^{1/2}$
Local rate at x_f	$R_{r_{\text{local}}}(x_f, t)$	constant	$t^{-2/3}$	t^{-1}

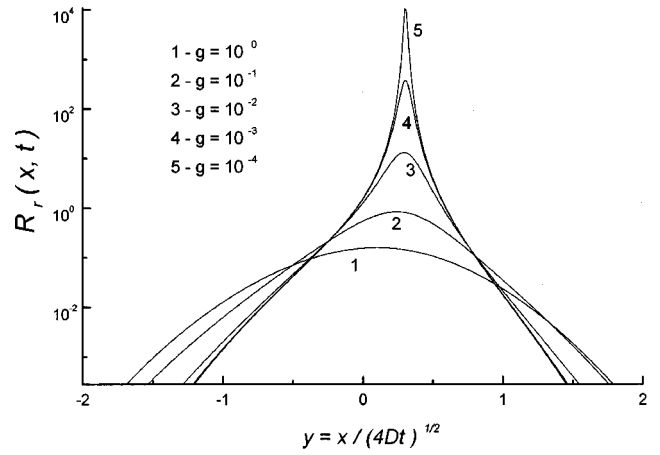


FIG. 5. The local rate of C production $R_r(x,t)$ (in units of ka_0^2) as a function of the nondimensional diffusionlike coordinate $x/2\sqrt{Dt}$ for values of $g = 10^0 - 10^{-4}$ [computed from Eqs. (23) and (30) with values $k=0.1$, $a_0=1.0$, and $b_0=0.25$]. Here g is in units of ka_0 .

Taking into account the diffusionlike character of Eqs. (22) in the mean-field approximation and the initial conditions of Eq. (12), the asymptotic solution of these equations may be presented in the form $\rho_A = \rho_A(x/\sqrt{t})$, $\rho_B = \rho_B(x/\sqrt{t})$, and $\rho_C = \rho_C(x/\sqrt{t})$ [29]. From these forms the universal properties of the reversible regime equations, $w \sim t^{1/2}$, $R_{r_{\text{local}}} \sim t^{-1}$, $R_{r_{\text{global}}} \sim t^{-1/2}$, and $x_f \sim t^{1/2}$, immediately follow. This is true for the wide reaction zone case also. These scale dependencies are important indications that a reaction-diffusion system occurs in the reversible regime, which may be used for the analysis of experimental data.

Equations (22) have a simple analytical solution for equal diffusion constants $D_A = D_B = D_C = D$ and arbitrary values of the initial concentrations and reaction constants k and g [29,30]:

$$\begin{aligned} \rho_A + \rho_C &= 0.5a_0[1 - \text{erf}(x/2\sqrt{Dt})], \\ \rho_B + \rho_C &= 0.5b_0[1 + \text{erf}(x/2\sqrt{Dt})], \end{aligned} \quad (30)$$

$$k\rho_A\rho_B = g\rho_C.$$

In Fig. 5 the change of R_r with varying g from the thin reaction zone state to the wide reaction zone state is illustrated on the basis of Eqs. (30) and (23).

Our approach, by which the reversible reaction regime $A + B \leftrightarrow C$ was considered, may be applied in an analogous manner to other reactions such as $mA + nB \leftrightarrow C$ or mA

$+nB \leftrightarrow pC + qD$ and can be generalized to an arbitrary number of such components and reversible reactions [33]. Taking into account that the macroscopic characteristics of the reaction-diffusion system in the irreversible regime coincide with those of the reversible regime, the equations of the reversible regime and their solutions (in the thin reaction zone limit) can conveniently be used for analysis of the irreversible regime dynamics.

V. SUMMARY

The diffusion-reaction system $A + B \leftrightarrow C$ with initially separated reactants was investigated for arbitrary nonzero values of the diffusion constants D_A , D_B , and D_C of the components A , B , and C and the initial concentrations a_0 and b_0 of A and B , respectively. The results of the investigation are the following.

(1) It was found that for $g \rightarrow 0$, $t \rightarrow \infty$, and arbitrary values of gt the concentration profile of C outside the reaction zone for nonzero values of D_C may be described by the analytical expressions (14) and (15).

(2) It was found that for $g \rightarrow 0$, $t \rightarrow \infty$, the reversible regime $gt \gg 1$ is characterized by the same macroscopic properties as the irreversible regime $gt \ll 1$. Moreover, the analytical expressions for the concentration profiles outside the reaction zone, the global rate of C production, and the law of motion of the reaction zone center coincide with those in the irreversible regime. All these are true if some of the natural assumptions are valid. The important assumptions are (a) the dependence of the reaction zone width on time t and constant

g , $w \sim \sqrt{t}g^\beta$, (b) the use of the refined expression $R_r \equiv R - g\rho_C$ for calculation of the reaction rate, and (c) the quasistatic equations (24), which take into account the local equilibrium relation $R = g\rho_C$.

(3) In the framework of the generalized assumptions, which can be tested experimentally or by computation, it was found that the macroscopic properties of the reaction front for $g \rightarrow 0$, $t \rightarrow \infty$ are conserved not only in the limiting regimes $gt \ll 1$ and $gt \gg 1$, but also at all times through the crossover from the irreversible regime to the reversible regime. In other words, the same analytical expressions can be used for arbitrary values of gt . The first important conjecture here relates to the type of the dependence $w = w(t, g)$. Two regions of the function $w(t, g)$ are linked monotonically at $gt \sim 1$: $w \sim t^\alpha$ at times $gt \ll 1$ and $w \sim \sqrt{t}g^\beta$ at times $gt \gg 1$. The second important result is the use of the quasistatic equations for describing the reaction-diffusion system inside the reaction zone.

(4) Numerical computation of the mean-field equations confirms the assumed dependence of $w = w(t, g)$ and the properties of the crossover from the irreversible to the reversible regime.

(5) It is shown that within the framework of the mean-field equations for sufficiently large values of g , the irreversible regime is not achieved, and the reaction-diffusion system has a crossover from the short-time regime $t \ll t_c \sim k^{-1}$ directly to the long-time reversible regime $t \gg g^{-1}$ with a wide reaction zone. The general properties of the reversible regime, such as $R_r(x_f, t) \sim t^{-1}$, $R_r(t) \sim t^{-1/2}$, $x_f \sim t^{1/2}$, and $w \sim t^{1/2}$, are maintained also.

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- [1] S. A. Rice, *Diffusion Limited Reactions* (Elsevier, Amsterdam, 1985).
- [2] J. S. Langer, *Rev. Mod. Phys.* **52**, 1 (1980).
- [3] G. T. Dee, *Phys. Rev. Lett.* **57**, 275 (1986).
- [4] L. Gálfi and Z. Rácz, *Phys. Rev. A* **38**, 3151 (1988).
- [5] Y. E. Koo and R. Kopelman, *J. Stat. Phys.* **65**, 893 (1991).
- [6] H. Taitelbaum, Y. E. Koo, S. Havlin, R. Kopelman, and G. H. Weiss, *Phys. Rev. A* **46**, 2151 (1992).
- [7] A. Yen, Y. E. Koo, and R. Kopelman, *Phys. Rev. E* **54**, 2447 (1996).
- [8] H. Taitelbaum and Z. Koza, *Philos. Mag. B* **77**, 1389 (1998).
- [9] H. Taitelbaum, S. Havlin, J. E. Kiefer, B. Trus, and G. H. Weiss, *J. Stat. Phys.* **65**, 873 (1991).
- [10] H. Larralde, M. Araujo, S. Havlin, and H. E. Stanley, *Phys. Rev. A* **46**, 855 (1992); **46**, R6121 (1992).
- [11] Z. Koza, *J. Stat. Phys.* **85**, 179 (1996); *Physica A* **240**, 622 (1997); *Philos. Mag. B* **77**, 1437 (1998).
- [12] V. Malyutin, S. Rabinovich, and S. Havlin, *Phys. Rev. E* **56**, 708 (1997).
- [13] E. Ben-Naim and S. Redner, *J. Phys. A* **25**, L575 (1992).
- [14] Z. Jiang and C. Ebner, *Phys. Rev. A* **42**, 7483 (1990).
- [15] B. Chopard and M. Droz, *Europhys. Lett.* **15**, 459 (1991).
- [16] S. Cornell, M. Droz, and B. Chopard, *Phys. Rev. A* **44**, 4826 (1991).
- [17] S. Cornell, M. Droz, and B. Chopard, *Physica A* **188**, 322 (1992).
- [18] S. Cornell, *Phys. Rev. E* **51**, 4055 (1995).
- [19] S. Cornell and M. Droz, *Physica D* **103**, 348 (1997).
- [20] S. Havlin, M. Araujo, Y. Lereah, H. Larralde, A. Shehter, H. E. Stanley, P. Trunfio, and B. Vilensky, *Physica A* **221**, 1 (1995).
- [21] Z. Koza and H. Taitelbaum, *Phys. Rev. E* **56**, 6387 (1997).
- [22] B. Chopard, M. Droz, T. Karapiperis, and Z. Rácz, *Phys. Rev. E* **47**, R40 (1993).
- [23] S. Cornell and M. Droz, *Phys. Rev. Lett.* **70**, 3824 (1993); S. Cornell, *ibid.* **75**, 2250 (1995).
- [24] S. Cornell, Z. Koza, and M. Droz, *Phys. Rev. E* **52**, 3500 (1995).
- [25] P. L. Krapivsky, *Phys. Rev. E* **51**, 4774 (1995).
- [26] B. P. Lee and J. Cardy, *Phys. Rev. E* **50**, R3287 (1994); *J. Stat. Phys.* **80**, 971 (1995).
- [27] M. Howard and J. Cardy, *J. Phys. A* **28**, 3599 (1995).
- [28] G. T. Barkema, M. Howard, and J. Cardy, *Phys. Rev. E* **53**, R2017 (1996).
- [29] M. Sinder and J. Pelleg, *Phys. Rev. E* **60**, R6259 (1999).
- [30] V. I. Fistul and M. I. Sinder, *Fiz. Tekh. Poluprovodn.* **17**, 2003 (1983) [*Sov. Phys. Semicond.* **17**, 1278 (1983)].
- [31] F. J. Muzzio and J. M. Ottino, *Phys. Rev. A* **40**, 7182 (1989).
- [32] S. Havlin and D. Ben-Avraham, *Adv. Phys.* **36**, 695 (1987).
- [33] M. I. Sinder, *Fiz. Tekh. Poluprovodn.* **20**, 373 (1986) [*Sov. Phys. Semicond.* **20**, 233 (1986)].