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Exponential temporal asymptotics of the $A+B\rightarrow 0$ reaction-diffusion process with initially separated reactants

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We study theoretically and numerically the irreversible $A+B\rightarrow 0$ reaction-diffusion process of initially separated reactants occupying the regions of lengths L_A, L_B comparable with the diffusion length ($L_A,L_B\sim\sqrt{Dt}$, here D is the diffusion coefficient of the reactants). It is shown that the process can be divided into two stages in time. For $t\ll L^2/D$ the front characteristics are described by the well-known power-law dependencies on time, whereas for $t>L^2/D$ these are well-approximated by exponential laws. The reaction-diffusion process of about 0.5 of initial quantities of reactants is described by the obtained exponential laws. Our theoretical predictions show good agreement with numerical simulations.

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I. INTRODUCTION

The irreversible reaction $A+B\rightarrow 0$ of two initially separated and diffusing reactants A and B is concentrated in a dynamic zone known as the reaction front. The formation of the reaction front is simulated in the following way: initially two kinds of reactants A and B are separated by an impenetrable barrier which is removed at time $t=0$ and the reactants start to form the reaction front. The reaction-diffusion model is applied to describe a wide spectrum of processes in physics, chemistry, biology, and material science [1,2]. Well-known examples of the application of the reaction front conception are analyses of diffusion flames [3], gas absorption with chemical reaction in liquids [4,5], diffusion with chemical reactions in liquids [6,7], chemical diffusion in semiconductors [8], internal oxidation of the metals [9], and electron-hole gases in semiconductors [10].

A standard way to treat the problem is to solve the system of equations [1,2,11]

$$\frac{\partial N_A}{\partial t}=D_A\frac{\partial^2 N_A}{\partial x^2}-R, \tag{1a}$$

$$\frac{\partial N_B}{\partial t}=D_B\frac{\partial^2 N_B}{\partial x^2}-R \tag{1b}$$

with the initial conditions

$$N_A(x,0)=N_{A0}\theta(-x),\quad N_B(x,0)=N_{B0}\theta(x),$$

where N_A and N_B are the concentrations of the reactants A and B, respectively, and N_{A0} and N_{B0} are their initial concentrations, D_A and D_B are the diffusion coefficients of the reactants, $\theta(x)$ is the Heaviside step function, and R is the macroscopic reaction rate. Analysis of the reaction-diffusion processes shows that in one-dimensional (1D) systems fluctuations play the dominant role and in the general case the explicit form of R remains unknown [12,13]. It was shown [14] that the fluctuations become essential starting with a characteristic time. At times less than the characteristic time the mean-field approximation

$$R=kN_AN_B \tag{2}$$

is fulfilled (k is the reaction rate constant). The role of fluctuations decreases with an increase of the system dimension d and the mean-field approximation can be used in the systems with dimension $d>2$ [12,13].

It was shown using the scaling ansatz that within the mean-field approximation the long-time behavior of the front is described by the following temporal dependencies [11]:

$$w\sim t^{1/6},\quad R_f\sim t^{-2/3}, \tag{3}$$

where w is the width of the reaction front, and R_f is the maximum local reaction rate.

Dependencies (3) have been also obtained using the quasistatic approximation (QSA) for an infinite space problem [12–15], where it was assumed that the lengths L_A and L_B of the regions occupied by A and B reactants are much larger than the diffusion length, i.e., at any time $L_A,L_B\gg\sqrt{Dt}$, where D is the diffusion coefficient of the reactants. Expressions (3) were obtained for the same diffusion coefficients of the reactants, $D_A=D_B=D$. This approximation is based on the assumption that for sufficiently long times the kinetics of the front is governed by two characteristic times. One characteristic time, $t_J=-J/(dJ/dt)$, controls the rate of change in the diffusive current J of the particles arriving at the reaction zone. The second characteristic time, $t_f=w^2/D$, is the equili-

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bration time of the reaction front. Assuming $t_f/t_J \ll 1$, one can neglect the change in the particle currents on the boundaries of the reaction zone and QSA gives [15]

$$w \sim (D^2/J)^{1/3}, \tag{4}$$

$$R_f \sim J/w. \tag{5}$$

The most important feature of QSA is that both w and R_f depend on time only due to the time dependence of the current $J(t)$. The dependence of the current on time is determined as a solution of the external task: diffusion of the reactants outside the reaction zone. Using QSA, the spatiotemporal behavior of the system $A+B\rightarrow 0$ has been extended for arbitrary nonzero diffusion coefficients and initial concentrations of the reactants [16]. Dependencies (3) were well-confirmed by the experimental results [6,7,17–20]. The influence of the concentrations of both the reactants and reaction product on the diffusion coefficients was taken into account in the theoretical investigation in [21]. In this case the reaction front characteristics are well-approximated by temporal power laws also.

All the dependences have been obtained within the infinite space approach. The infinite space approach is the first approximation: real physics systems (for example, electron-hole recombination in semiconductor devices, vortex-antivortex annihilations in superconductors, and vacancy-interstitial annihilations in solids) have finite sizes. Actuality of these tasks is increasing with the development of the micro- and nanotechnologies. The behavior of an A reactant island in the B reactant sea was investigated in [22]. The time dependences of the reaction front characteristics obtained in [22] differ from the dependences for the infinite task. And what is more, these dependences can be nonmonotonic.

In this paper we theoretically investigate another important case: the irreversible reaction of initially separated reactants A and B occupying the finite regions of lengths comparable with the diffusion length ($L_A, L_B \sim \sqrt{Dt}$). The one-dimension reaction-diffusion process, where products are massless (reaction of the annihilation type), is considered.

II. MEAN-FIELD APPROXIMATION

A. Mobile reactants

Let us consider first the symmetric case: $D_A=D_B=D$, $L_A=L_B=L$ and the same initial concentrations of the reactants $N_{A0}=N_{B0}=N_0$. Note that the reaction front is immobile due to symmetry. We will analyze the reaction front using QSA, i.e., the reaction characteristic time t_f is much less than the diffusion characteristic time t_J. Two characteristic stages can be separated in the diffusion process. The first is a period when $t \ll L^2/D$ and expressions (3) are valid. The second stage is characterized by $t > L^2/D$. At time $t \sim L^2/D$, the reactants start to exhaust and the concentration of reactant A is obtained as a solution of the diffusion external task with other boundary conditions. We assume that the reactant currents at $x=\pm L$ are zero:

$$\left.\frac{\partial N_i}{\partial x}\right|_{x=\pm L} = 0, \tag{6a}$$

where $i=A,B$.

Under the approximation that the reaction front width w is much less than L and the reactant completely reacts in the reaction zone, the second boundary condition at $x=0$ is

$$N_i = 0. \tag{6b}$$

The solution can be obtained by the method of the separation of variables and presented in the form of a series [23]:

$$N_A = -\frac{4N_{A0}}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\exp\left[-\frac{D(2n+1)^2\pi^2 t}{4L^2}\right] \times \sin\frac{(2n+1)\pi x}{2L}. \tag{7}$$

The reaction front is at $x=0$ and reactant A is placed at $x<0$. A similar expression can be written for the concentration of reactant B.

One can see that the ratio of the second term ($n=1$) to the first ($n=0$) in Eq. (7) is proportional to the first term power of 8, i.e., to $\exp(-8at)$, where $a=\pi^2 D/4L^2$. At $at=0.58$ the second term is less than 1% of the first one. At $t>t_b=0.58/a$ we consider only the first term:

$$N_A = -\frac{4N_{A0}}{\pi}\exp(-at)\sin\left(\frac{\pi}{2L}x\right). \tag{8}$$

Following QSA the front width and maximum reaction rate are given by Eqs. (4) and (5) and their temporal dependencies are determined by the temporal dependence of the current $J(t)$. From Eqs. (4), (5), and (8) at $t>L^2/D$ the front width and maximum local reaction rate can be presented as

$$w(t) \sim \exp\left(+\frac{1}{3}at\right), \tag{9}$$

$$R_f(t) \sim \exp\left(-\frac{4}{3}at\right). \tag{10}$$

The total reaction rate is determined by the reactant current at $x=0$ and is given by

$$R(t) \sim \exp(-at). \tag{11}$$

For the finite space reaction-diffusion task we first obtained that the distribution of the reactant concentrations are fitted by sines and the concentrations decrease with time according to the exponential law. This leads to the exponential temporal dependences of the characteristic of the reaction front. The dependences obtained by us differ from the known power dependences.

Note that, in the infinite space problem, the reaction front width w and characteristic diffusion length, $L_D=\sqrt{Dt}$, are increasing proportionally to $t^{1/6}$ and $t^{1/2}$, respectively. The condition $L_D \gg w$ is fulfilled for all time. In the considered case the reaction front width w increases with time [see Eq. (9)] but the lengths L of the regions occupied by the reactants are time-independent values. Hence expressions (9)–(11) are valid for a limited time while $w(t) \ll L$. Using Eq. (8) the characteristic time $t_J = -J/(dJ/dt)$ of a change in the diffusive current J of the particles arriving at the reaction zone can be estimated as $t_J = 4L^2/\pi^2 D$. The equilibration time of the reaction front is $t_f = w^2/D$. The assumption $w(t) \ll L$ is equivalent to the criterion of applicability of QSA $t_f/t_J \ll 1$.

The obtained result can be expanded to the case of different diffusion coefficients, $D_A \neq D_B$. In the case of an immobile front the reactant currents to the reaction zone, at $x=0$, are equal. From Eq. (8) the equal currents at $x=0$ can be obtained at

$$N_{A0}\sqrt{D_A} = N_{B0}\sqrt{D_B}, \tag{12}$$

$$N_{A0}L_A = N_{B0}L_B. \tag{13}$$

The obtained condition (12) is the same as the known condition of an immobile front for the infinite problem [16,24]. Condition (13) means that the initial quantities of the reactants A and B are equal. At $t \sim L^2/D$ the temporal dependencies of the reaction front width w, the maximum reaction rate R_f, and the total reaction rate R are given by Eqs. (9)–(11), respectively. In these expressions D and L have to be replaced by D_A and L_A or by D_B and L_B.

B. Immobile reactant *B*

Let us consider the special case where reactant B is immobile, i.e., $D_B = 0$. The concentrations N_A and N_B of the reactants in a dynamic zone can be described by a solution of the following system [24–26]:

$$\frac{\partial N_A}{\partial t} = D_A \frac{\partial^2 N_A}{\partial x^2} - kN_A N_B, \tag{14a}$$

$$\frac{\partial N_B}{\partial t} = -kN_A N_B. \tag{14b}$$

The process can be divided in time into two characteristic stages similarly as it was done above for the case of equal diffusion coefficients. At $t \ll L_A^2/D_A$, one can use the well-known approximation obtained for the infinite space task [24–26]. In this approximation the width of the reaction front is a constant, independent of time, and the maximum reaction rate R_f is proportional to $t^{-1/2}$ at the asymptotic long-time approximation.

At $t > L_A^2/D_A$ we will consider two ranges: the external task and the reaction zone. At long-time period reactant A exhausts and in the first approximation the reaction front is immobile. In this case the external task has a solution for the concentration of reactant A in the form of Eqs. (7) and (8), where L is replaced by the maximum length L_f of the range occupied by reactant A. The maximum length can be estimated as

$$L_f = L_A(1 + N_{A0}/N_{B0}).$$

The current at the dynamic zone boundary is proportional to $\exp(-\pi^2 D_A t/4L_f^2)$. In the reaction zone following the scaling ansatz approach [11,26], the solution of the equation system (14) can be found in the form

$$N_i = e^{-a_i t} F\left(\frac{x - x_f(t)}{w(t)}\right), \tag{15}$$

where $x_f(t)$ is the coordinate of the reaction front, $i = A, B$. Here the point of origin is placed at a distance L_f from the left boundary.

We assume that the width of the reaction front and its coordinate are given also by an exponential law. Substitution of expression (15) into Eq. (14) gives that at the long-time approximation the constants $a_A = \pi^2 D_A/4L_f^2$, $a_B = 0$. The width w is independent of time like in the well-known case of the infinite task, $t \ll L_A^2/D_A$. However, at $t > L_A^2/D_A$, the total and maximum local reaction rates decrease with time according to the exponential law, $\sim\exp(-a_A t)$. The coordinate x_f of the reaction front tends to zero also according to the exponential law. Our results differ from the results obtained in the framework of the infinite space approach [26] where the total and maximum reaction rates are proportional to $t^{-1/2}$ and $x_f \sim t^{1/2}$ and increases without limit.

III. NUMERICAL CALCULATION

To confirm the obtained results, a numerical simulation of the reaction has been carried out. Numerical solution of Eq. (1) in the framework of the mean-field approximation using the usual finite element method gives a good agreement with our analytical results. This approach does not take into account fluctuation processes. It was shown that fluctuations could play an important role in one-dimensional (1D) reaction-diffusion infinite tasks and therefore the mean-field approximation and the reaction rate in the form (2) are not valid in the general case [12–14]. However, influence of the fluctuations for the finite tasks considered in the present paper were not analyzed yet. Therefore we use the Monte Carlo methods which do not contain any explicit form of the macroscopic reaction rate.

Our model consists of a one-dimensional lattice with $L_A = L_B$. The particles of A and B are located on the lattice points. The initial concentrations of the particles can be specified as various values independent of the coordinate. The developed software allows us to place a large number (up to 10^5) of particles in every point. The motion of the particle is simulated by a unit jump of each particle to the left or to the right with a given probability at each time step, $\Delta t = 1$. The probabilities of the jump of the A and B particles can be different. Each particle A can react with a B particle on the same lattice cell with the reaction probability α. The probability is independent of the number of particles in the cell. After each reaction both particles are removed from the lattice.

Here we numerically simulate two cases.

(1) Diffusion coefficients for the A and B particles and their initial concentrations are equal ($D_A = D_B$, $N_{A0} = N_{B0}$).

(2) The B particles are immovable and their initial concentration is twice the concentration of the A particles ($D_B = 0$, $N_{B0} = 2N_{A0}$).

The probabilities of unit jumps to the left and to the right are taken as being equal and as 0.5 for the moving particles. This corresponds to the diffusion coefficient equal to 0.5 in

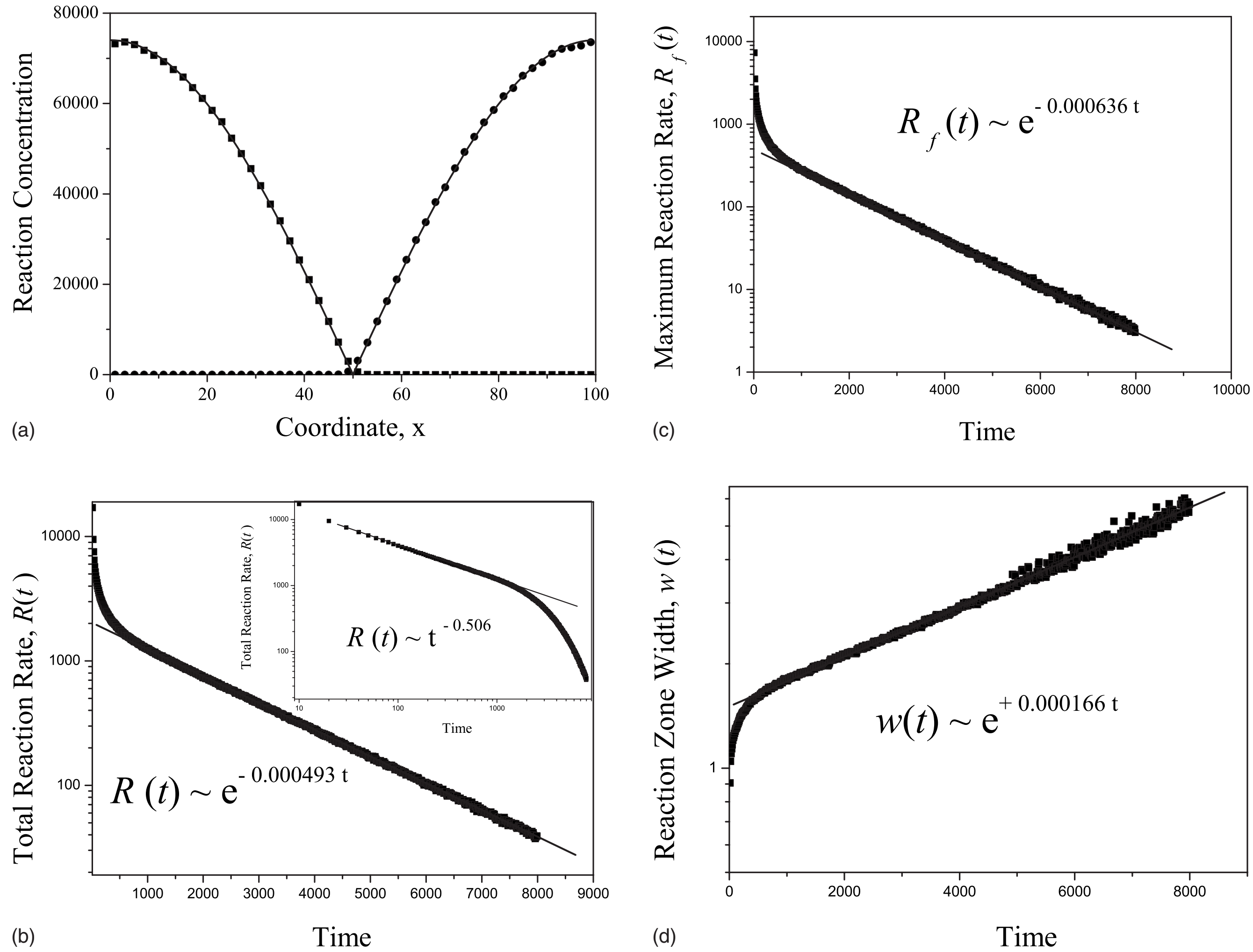

FIG. 1. Numerical simulation of the reaction-diffusion process for the case of equal diffusion coefficients, $D=D_A=D_B=0.5$ (the probabilities of unit jumps to the left and to the right are 0.5) and $L_A=L_B=L=50$: (a) the distribution of the particle density at $t=1100$ [solid lines are given by Eq. (8)]; (b) the temporal dependencies of the total and (c) maximum reaction rates; and (d) the reaction zone width. Inset in (b) presents the temporal dependence of the total reaction rate at $t < \sim t_b$. Reaction probability is 0.0001; the initial particle concentrations are 100 000. Note that for the chosen parameters D and L the coefficient a in Eqs. (9)–(11) is 0.000 493 and analytically predicted the exponent indexes of $R(t)$, $R_f(t)$, and $w(t)$ are −0.000 493, −0.000 657, and +0.000 164, respectively.

the chosen units. The results of the numerical simulation are presented in Figs. 1 and 2. In both cases, the numerical simulation properly confirms the obtained asymptotical temporal dependencies of the reaction front characteristics. When $t \ll L^2/D$, the numerical results are well-fitted by the known power expressions obtained in the framework of the infinite space approximation. For example, in both considered cases, the total reaction rate $R(t)$ is proportional to $t^{-1/2}$ [insets of Figs. 1(b) and 2(b)]. At a longer time, $t > L^2/D$, the temporal dependencies of the reaction front characteristics are fitted by exponential laws as predicted above.

IV. DISCUSSION

We first analytically and numerically showed that in a one-dimensional approximation for the finite space tasks there are two stages for the irreversible reaction $A+B \rightarrow 0$ front. In the first stage the front characteristics are described by the well-known power-law dependencies on time, whereas the second one is characterized by the exponential laws.

The numerical calculations well-confirm not only qualitatively (power and exponential laws) but also quantitatively the predictions obtained analytically. The power-law approximations obtained for the infinite tasks are fulfilled at time t less than a boundary value t_b. For the case $D_A=D_B$, this value can be determined from the condition: the second term in the series (7) is much less than the first one $t_b \approx 0.6/a$. The estimation carried out in Sec. II A predicts that the transition from the power-law description to the exponential one is at a time of about 1100 for the first numerical considered case. The numerical simulation gives that this transition occurs in the range from 900 to 1200 (Fig. 1). Figure 1(a) presents the distribution of the reactant concentrations at $t=1100$. One can see good agreement between Eq. (8) (solid lines) and the results of the numerical simulation (circles and squares). Note that at $t=t_b$, when the power laws

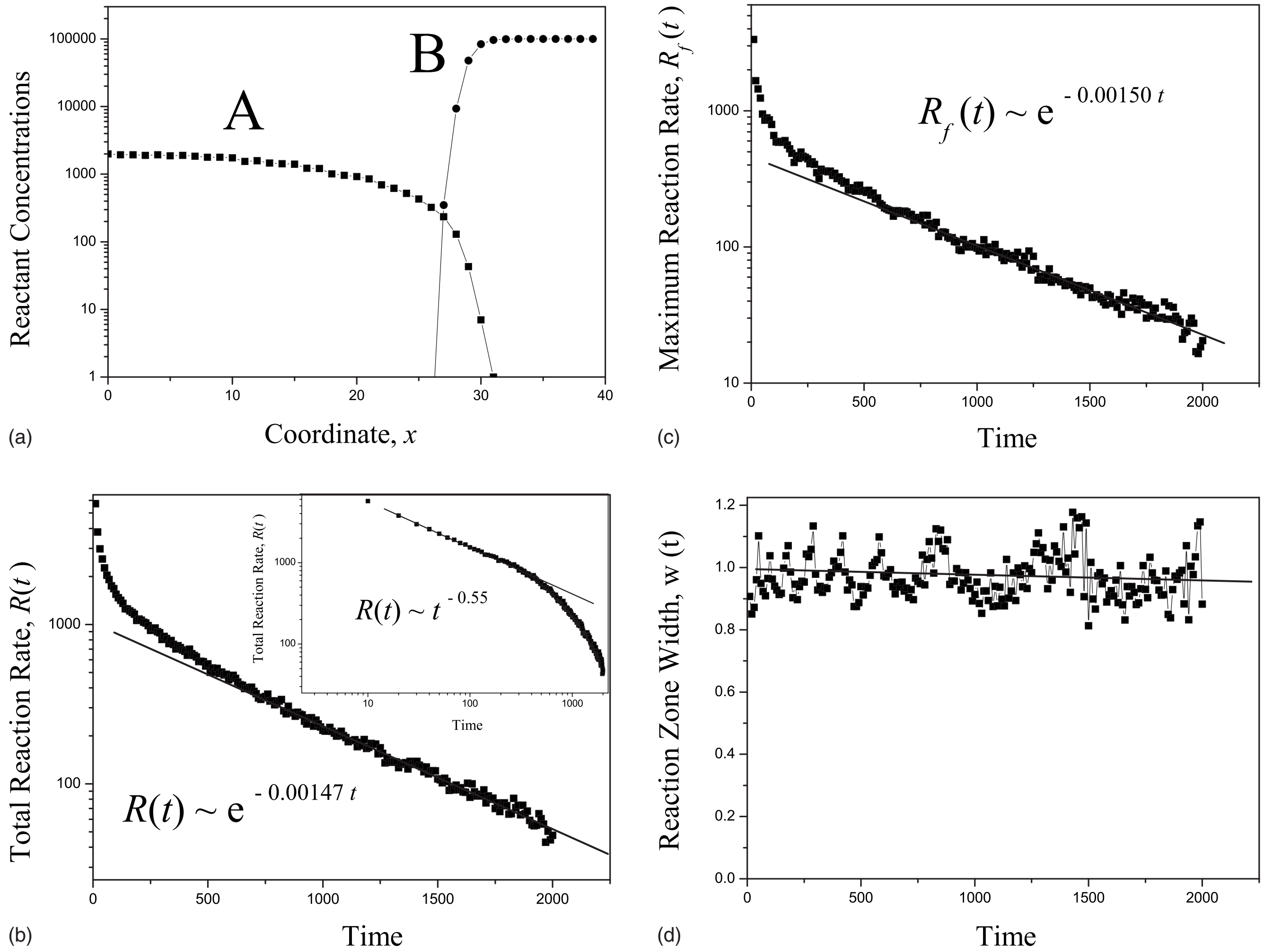

FIG. 2. Numerical simulation of the reaction-diffusion process for the case of immovable B particles. The initial particle concentrations are $N_{B0}=100\,000$, $N_{A0}=50\,000$, and $D_B=0$, $D_A=0.5$, and initial lengths $L_A=L_B=20$. The distribution of the particle density at $t=2000$: (a) the temporal dependencies of the total (b) and maximum (c) reaction rates and of the reaction zone width (d). Inset in (b) presents the temporal dependence of the total reaction rate at $t \lesssim t_b$. Reaction probability is 0.000 01. In the asymptotic time regime the length occupied by the A reactant is about 29 [see (a)]. The analytically estimated exponent index a_A of $R(t)$ and $R_f(t)$ is 0.001 47 for the chosen parameters D and L_A and the front width is independent of time

change to the exponential laws, the reactant concentrations at $x=\pm L$ are about 0.75 of the initial concentrations and the total quantities of the reactants [integral of Eq. (8) through x] are about 0.5 of their initial quantities. These ratios are independent of lengths of the regions occupied by reactants and of the diffusion coefficient. The concentrations at $x=\pm L$ and the total reactant quantities decrease with time according to the exponential laws at $t>t_b$ and should be easily measured.

In the special case where one reactant, B, is immovable, the boundary value can be estimated as $t_b=4L_A^2/\pi^2 D_A$. For the numerically simulated case this estimation gives $t_b=325$ while numerical calculation $-t_b \approx 400$ [Fig. 2(b), inset]. The transition from the power laws to the exponential ones is observed in the range from $t=400$ to ≈ 800 (Fig. 2). The concentration of mobile reactant A on the region boundary is about 0.5 at $t=400$ and 0.25 at $t=800$ of the initial concentration. If one of the reactants is immobile, the reaction front moves. This explains the widening of the transition range in comparison with the case when both reactants are mobile.

The numerically obtained exponents in the power laws and constants in the exponent indexes well agree with the constants predicted by the analytical expressions. At $t<t_b$ theory predicts exponents of 0.5 for the fitting of the total reaction rates [11,26]. Our calculation gives 0.506 and 0.55 [insets in Figs. 1(b) and 2(b)]. At $t>t_b$ in the first simulated case, the constant a in the exponent indexes in Eqs. (9)–(11) is calculated as 0.000 493, and the numerical simulation gives $a=0.000\,477-0.000\,498$ (Fig. 1). In the second case the parameter a_A in Eq. (15) is estimated as 0.00 147, and the numerical calculation gives $a_A=0.00\,147-0.00\,150$ at time above 750 (Fig. 2). The numerical calculation with help of the Monte Carlo methods confirms the applicability of the mean-field approximation for 1D finite space tasks in the wide temporal range.

V. CONCLUSION

Two stages for the irreversible reaction $A+B\rightarrow 0$ front have been found in a one-dimensional approximation for the finite space tasks with the mean-field reaction rate. For $t \ll L^2/D$ the front characteristics are described by the well-known power-law dependencies on time, whereas for $t > L^2/D$ the unexpected results are obtained: the characteristic temporal dependencies are properly approximated by the exponential laws. At the time when the power laws change by the exponential laws, the reactant concentrations at the region boundary are about 0.75 of the initial concentrations and the total quantities of the reactants are about 0.5 of their initial quantities. These ratios are independent of the diffusion coefficient and of lengths of the regions occupied by reactants.

Our theoretical predictions qualitatively and quantitatively agree well with numerical simulations carried out by the Monte Carlo methods. It was shown that the mean-field approximation can be applied for simulation of reaction-diffusion processes in 1D finite space tasks in a wide temporal range.

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