

Time evolution of the reaction front in a subdiffusive system

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Using the quasistatic approximation, we show that in a subdiffusion-reaction system with arbitrary nonzero values of subdiffusion coefficients, the reaction front $x_f(t)$ evolves in time as $x_f(t) = Kt^{\alpha/2}$, with α being the subdiffusion parameter and K being controlled by the subdiffusion coefficients. To check the correctness of our analysis, we compare approximate analytical solutions of the subdiffusion-reaction equations with the numerical ones.

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I. INTRODUCTION

The diffusion-reaction system of two initially separated substances A and B reacting according to the formula $\lambda_A A + \lambda_B B \rightarrow P(\text{inert})$, where the stoichiometric coefficients λ_A and λ_B are positive integers, has been intensively studied during recent years [1–13]. As the diffusion-reaction equations describing the system are nonlinear, it is difficult to solve them and their general solutions remain unknown (except for very special cases). Thus, to simplify the calculations one usually uses various approximations, such as the quasistatic approximation [1–3], the scaling method [1,4–7], or the perturbation one [9,10]. Applying these methods, there were derived characteristic functions of the system that include the time evolution of the reaction front, $x_f(t)$, the width of the reaction region, $W_R(t)$, and the width of the depletion zone, $W_{\text{Dep}}(t)$ [1,2,4–6], which all appear to be power functions of time $f(t) = Kt^\gamma$. The results were partially confirmed by numerical calculations and simulations [3,5,6]. However, as the methods of extracting the power functions are not based on analytical solutions of subdiffusion-reaction equations (not even on their approximate forms), the proportionality coefficients K are usually unknown. The coefficients carry dynamic information about the system, e.g., how the diffusion coefficient influences the process. As far as we know, there were only a few attempts to determine K by means of the quasistatic approximation [2,3].

The situation is even more complicated in the case of subdiffusive systems, since the equations describing the systems contain derivatives of fractional order. Subdiffusion occurs in systems where mobility of particles is significantly hindered due to the internal structure of a medium, as it happens in porous media or gels [14,15]. The subdiffusion is characterized by a time dependence of the mean-square displacement of transported particle $\langle \Delta x^2 \rangle = 2Dt^\alpha / \Gamma(1 + \alpha)$, where D is the subdiffusion coefficient measured in units m^2/s^α and α is the subdiffusion parameter, which obeys $0 < \alpha < 1$. For $\alpha = 1$, one deals with the normal diffusion.

Since no explicit solutions of the nonlinear (sub)diffusion-reaction equations are known, one commonly considers a simplified system, for example the system in which diffusion coefficients of both reactants are assumed to be equal to each other [16,17]. However, the diffusion-reaction equations remain difficult to solve and approximate methods are still needed. The scaling method does not allow us to determine K unless special extra conditions are adopted. The perturbation method is of small efficiency because the first-order result is often insufficient, while the higher-order corrections are hard to obtain even in the case of normal diffusion. The quasistatic method is more promising. In the case of a normal diffusion-reaction system, it is based on the assumption that the process proceeds so slowly that changes of concentration of the transported substance are small in some regions [2,3]. Since the subdiffusion process is even slower than the normal diffusion, we expect that the quasistatic approximation is well suited to the subdiffusive systems. Therefore, we adopt the method in this study. The scaling method and the quasistatic approximation are often treated as equivalent to each other. We note, however, that the equivalence holds only in the long-time limit [17]. At shorter times, the applicability of the quasistatic method does not imply the applicability of the scaling one and vice versa.

In this paper, we show that the time evolution of the reaction front is given by the formula $x_f(t) = Kt^{\alpha/2}$ for a system with arbitrary nonzero values of the subdiffusion coefficients. We also derive an equation obeyed by the coefficient K . Our analytical results are confirmed by numerical solutions of the subdiffusion-reaction equations.

II. THE SYSTEM

A real system is usually three-dimensional, but we assume its homogeneity in the plane perpendicular to the x axis. Therefore, we use only one space variable x in our considerations. Throughout this paper, we assume that the subdiffusion parameter α is the same for both substrates. The physical meaning of this assumption is that the subdiffusion parameter is determined solely by the medium while the subdiffusion coefficient D depends on the transported substance. This assumption is supported by the experimental results

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presented in [15], where the same value of the parameter α was found for glucose and sucrose transported in an agarose-water gel, whereas the subdiffusion coefficients of the two substances were found to be different from each other. Additionally, we assume that both of the reactants are mobile, $D_A, D_B > 0$. The subdiffusion-reaction equations are

$$\frac{\partial}{\partial t} C_i(x, t) = D_i \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2}{\partial x^2} C_i(x, t) - d_i R_\alpha(x, t), \quad (1)$$

where C_i denotes the concentration of the diffusing particles of species i , D_i is the subdiffusion coefficient, $i=A, B$, $d_A = m$ and $d_B = n$, with the parameters m and n occurring in the reaction term [see Eq. (3)]; in the simplest kinetic reaction model, these coefficients are equal to the stoichiometric ones, $m=\lambda_A$ and $n=\lambda_B$, but experimentally determined parameters m and n are sometimes noninteger and different from the stoichiometric coefficients. The Riemann-Liouville fractional time derivative present in Eq. (1) is defined for the case of $0 < \alpha < 1$ as

$$\frac{d^\alpha f(t)}{dt^\alpha} = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t d\tau \frac{f(\tau)}{(t-\tau)^\alpha}.$$

We note that the choice of the reaction term is neither obvious nor unique [16–23]. The reaction term that we use here was applied earlier to the subdiffusion-reaction system in [16,17]. It is

$$R_\alpha(x, t) = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} R(x, t), \quad (2)$$

where the term $R(x, t)$ obtained within the mean-field approximation reads

$$R(x, t) = k C_A^m(x, t) C_B^n(x, t), \quad (3)$$

where k is the reaction rate.

We assume that the particles of reactants A and B are initially separated from each other. Thus, the initial conditions are

$$C_A(x, 0) = \begin{cases} C_{0A}, & x < 0 \\ 0, & x > 0, \end{cases} \quad (4)$$

$$C_B(x, 0) = \begin{cases} 0, & x < 0 \\ C_{0B}, & x > 0. \end{cases} \quad (5)$$

It was observed [1–6] that when the process starts, characteristic regions appear in the system (see Fig. 1): the *depletion zone* “Dep,” which is defined as a region where the concentrations are significantly smaller than the initial ones ($C_A \ll C_{0A}$ and $C_B \ll C_{0B}$), the *reaction region*, where the production of particles P is significant, and the *diffusion region* “Dif,” where the reaction term $R(x, t)$ is close to zero and the particle transport appears to be almost subdiffusive, i.e., without chemical reactions.

For the normal diffusion, the widths of the depletion zone W_{Dep} and the reaction region W_R grow as the power functions of time [1–7], $W_{\text{Dep}} \sim t^\theta$, with $\theta=1/2$, and $W_R \sim t^\mu$, where $\mu < \theta$. The value of the parameter μ depends on the system under study. In the case in which the reactants A and

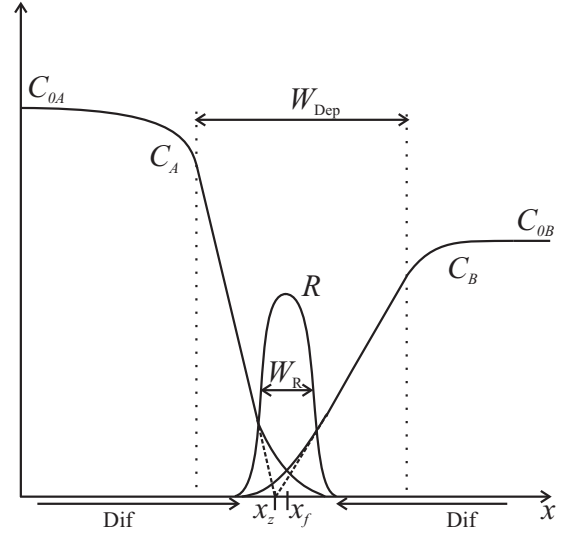


FIG. 1. Schematic view of the system under consideration; x_f is the reaction front, “Dif” is the diffusion region, W_{Dep} and W_R denote the width of the depletion zone and of the reaction region, respectively, and the point x_z is defined in Sec. VI.

B are mobile, there is $\mu=1/6$, and for the system with a mobile reactant A and a static reactant B we have $\mu=(m-1)/2(m+1)$, where m is the parameter occurring in the reaction term R in Eq. (3) [4] (see also [7,11]). As reported in [8,17], W_R evolves in time according to the power function with $\mu=\alpha/6$ also in the subdiffusive-reaction system with two mobile reactants.

An important characteristic of the system under consideration is the time evolution of the reaction front $x_f(t)$. It is defined as a point at which the reaction term $R(x, t)$ reaches its maximum $R(x_f(t), t) = \max$ or, as argued in [5], for $m=n=1$ it can be defined by the relation $C_A(x_f(t), t) = C_B(x_f(t), t)$, or, in a more general situation, by $C_A(x_f(t), t)/m = C_B(x_f(t), t)/n$ [7]. Unfortunately, these definitions are difficult to apply using the numerically obtained concentrations. In the following, we define the reaction front as

$$x_f(t) = \frac{\int x R(x, t) dx}{\int R(x, t) dx}. \quad (6)$$

Although the relations defining the reaction front are not exactly equivalent to each other, they all give x_f lying inside the reaction region, and in the long-time limit the definitions lead to the power function of time,

$$x_f(t) \sim t^\gamma, \quad (7)$$

with $\gamma=1/2$ for the normal diffusion case [1–6]. It was shown in [17] by means of the scaling method that the relation (7) with $\gamma=\alpha/2$ holds for the subdiffusive system where the subdiffusion coefficients of the reactants are equal to each other. The relation (7) for any values of the subdiffusion coefficients is derived here.

III. QUASISTATIC APPROXIMATION

The quasistatic approximation assumes that the concentration profile is a slowly varying function of time in a given

region. Thus, the time derivative is small and, consequently, the right-hand side (r.h.s.) of (sub)diffusion equation (1) is also small in the region. It requires

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2}{\partial x^2} C_{A,B}(x,t) \approx d_{A,B} R_\alpha(x,t). \quad (8)$$

Since the reaction term is relatively large in the reaction zone, the quasistatic approximation holds in this zone under the condition

$$D \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2}{\partial x^2} C_{A,B}(x,t) \gg \frac{\partial}{\partial t} C_{A,B}(x,t). \quad (9)$$

We note that the condition (9) is fulfilled when the concentration profiles are given in the scaling form [17].

In the diffusive region where $R_\alpha(x,t) \approx 0$, the quasistatic approximation is applicable when the concentration is a linear function of x , as the r.h.s. of Eq. (1) then vanishes. The regions outside the reaction zone, where the concentration linearly varies with x , determine the borders of the quasistatic region. The solution of the subdiffusion equation without chemical reactions works here.

In the studies of the normal diffusion with reactions, one introduces the quasistatic approximation referring to the so-called equilibration time τ_F [2,7,11]. We define τ_F as the average time needed for the substance to spread over the length W_R in the absence of reactions when the substance flows from the outside. For the normal diffusion-reaction system, this parameter was estimated using the relation $\langle \Delta x^2 \rangle \sim t$. Taking $\langle \Delta x^2 \rangle \sim W_R^2$ and $t \sim \tau_F$, one gets $\tau_F \sim W_R^2$. For the subdiffusive system, the relation $\langle \Delta x^2 \rangle \sim t^\alpha$ provides

$$\tau_F \sim W_R^{2/\alpha}. \quad (10)$$

As for the normal diffusion case, we also introduce a characteristic time τ_J of a noticeable change of the flux J in time dt defined through the relation $dJ/J = dt/\tau_J$, which gives

$$\frac{1}{\tau_J} = \frac{d(\log J)}{dt}. \quad (11)$$

The explicit expression of the subdiffusive flux is given later on by Eq. (33). The balance between the subdiffusion term and the reaction one is achieved when the equilibration time τ_F of the reaction region is negligibly small when compared to the time τ_J of the sizeable change of the flux, $\tau_F \ll \tau_J$. It was argued in [2,7,11] that this condition holds in the long-time limit for the normal diffusion case and the quasistatic approximation is applicable when the condition

$$\frac{\tau_F}{\tau_J} \xrightarrow{t \rightarrow \infty} 0 \quad (12)$$

is satisfied. The quasistatic region is usually defined as a region where at least one of the conditions (8) and (9), or (12) is fulfilled. As far as we know, the equivalence of these definitions has not been proven yet. In our considerations, we use the relation (8) as the definition of the quasistatic approximation, and we further show that Eq. (8) implies the condition (12).

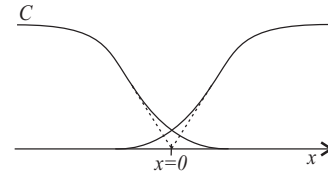


FIG. 2. The symmetrical system with static reaction front $x_f(t) = 0$. The solid lines denote the concentrations C for the system under considerations, the dashed ones for the system with a fully absorbing wall located at $x=0$.

IV. TIME EVOLUTION OF W_R AND W_{Dep}

We expect that, as in the case of the normal-diffusion reaction systems [5], the results obtained for $D_A = D_B$ and $C_{0A} = C_{0B}$ hold, at least qualitatively, for arbitrary values of the subdiffusion coefficients and initial concentrations. Sometimes the ratios D_A/D_B and C_{0A}/C_{0B} are even called “irrelevant parameters” [5]. In this section, we derive the time evolution of the widths of the reaction region W_R and of the depletion zone W_{Dep} assuming that $D_A = D_B \equiv D$ and $C_{0A} = C_{0B} \equiv C_0$.

At first, we argue that the assumption $\mu < \theta$ is correct not only for the diffusive but for the subdiffusive systems as well. In [17] it was found by means of the scaling method that $\theta = \alpha/2$ and $\mu = \alpha/6$. We confirm the above relations, using the method applied earlier to the normal diffusion-reaction system [13].

Since we assume that $C_{0A} = C_{0B}$ and $D_A = D_B$, the reaction front will not change its position, $x_f(t) = 0$, due to the symmetry arguments. Similarly as for the system with the normal diffusion [13], to further simplify the calculations, we assume that the concentrations of A and B particles can be expressed as

$$C_A(x,t) = C_{A\text{abs}}(x,t) + \delta C_A(x,t),$$

$$C_B(x,t) = C_{B\text{abs}}(x,t) + \delta C_B(x,t),$$

where $C_{A\text{abs}}$ and $C_{B\text{abs}}$ are the solutions of the pure subdiffusive equation in the system with a fully absorbing wall located at $x=0$ [the concentration profiles vanish at the wall $C_{A\text{abs}}(0,t) = C_{B\text{abs}}(0,t) = 0$], and δC_A and δC_B are correction terms (see Fig. 2). The symmetry of the system ensures that $C_A(x,t) = C_B(-x,t)$, which provides $\delta C_A(x,t) = \delta C_B(-x,t)$. Having explicit solutions of the subdiffusion equation for a system with a fully absorbing wall calculated from Eqs. (4), (5), (25), (28), and (A1), we obtain

$$C_{A\text{abs}}(x,t) = C_0 \left\{ 1 - \frac{2}{\alpha} H_{11}^{10} \left[\left(\frac{-x}{\sqrt{Dt}^\alpha} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 0 & 2/\alpha \end{vmatrix} \right] \right\} \quad (13)$$

for $x < 0$ and

$$C_{\text{Babs}}(x,t) = C_0 \left\{ 1 - \frac{2}{\alpha} H_{11}^{10} \left[\left(\frac{x}{\sqrt{Dt^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 0 & 2/\alpha \end{vmatrix} \right] \right\} \quad (14)$$

for $x > 0$, where H denotes the Fox function, which can be expressed as [24]

$$H_{11}^{10} \left(u \begin{vmatrix} 1 & 1 \\ p & q \end{vmatrix} \right) = \frac{1}{q} u^{p/q} \sum_{j=0}^{\infty} \frac{(-1)^j}{j! \Gamma(1-p/q-j/q)} u^{j/q}. \quad (15)$$

Substituting $C(x,t) \equiv C_i(x,t)$, $\delta C(x,t) \equiv \delta C_i(x,t)$, and $C_{\text{abs}}(x,t) \equiv C_{i\text{abs}}(x,t)$, where $i=A$ for $x < 0$ and $i=B$ for $x > 0$, into the subdiffusion-reaction equation and taking into account that C_{abs} obeys the subdiffusion equation without chemical reactions, we get

$$\frac{\partial}{\partial t} \delta C(x,t) = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \left[D \frac{\partial^2}{\partial x^2} \delta C(x,t) - k [C_{\text{abs}}(x,t) + \delta C(x,t)] \delta C(x,t) \right].$$

The borders of the reaction region occur for x where δC is close to zero. In this region, one can neglect the term $(\delta C)^2$ in the above equation. Moreover, in the long-time limit we can approximate the Fox functions present in Eqs. (13) and (14) by the first term of the series (15). Then, we get the expression $C_{\text{abs}}(x,t) = \kappa |x| / t^{\alpha/2}$, where $\kappa = C_0 k / \Gamma(1-\alpha/2) \sqrt{D}$. So, we find

$$\frac{\partial}{\partial t} \delta C(x,t) = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \left[D \frac{\partial^2}{\partial x^2} \delta C(x,t) - \frac{\kappa |x|}{t^{\alpha/2}} \delta C(x,t) \right]. \quad (16)$$

As in the case of a normal diffusion-reaction system, [13], we assume that

$$\frac{\partial}{\partial t} \delta C(x,t) = 0. \quad (17)$$

Then, from Eqs. (16) and (17), and the relation [25]

$$\frac{d^\beta t^\nu}{dt^\beta} = \frac{\Gamma(\nu+1)}{\Gamma(\nu+1-\beta)} t^{\nu-\beta}, \quad \nu > -1, \quad (18)$$

we obtain

$$D \frac{\partial^2}{\partial x^2} \delta C(x,t) - \frac{\kappa |x|}{t^{\alpha/2}} \delta C(x,t) = \frac{A(x)}{t^\alpha}, \quad (19)$$

where $A(x)$ is an arbitrary function of x only. In the long-time limit, the r.h.s. of Eq. (19) can be neglected.

Solving Eq. (19) with the right side equal to zero, we find

$$\delta C(x,t) = f(t) \text{Ai} \left(\lambda \frac{|x|}{t^{\alpha/6}} \right), \quad (20)$$

where Ai denotes the Airy function, which can be approximated by the following expression:

$$\text{Ai}(u) \approx \frac{1}{2\sqrt{\pi} u^{1/4}} \exp \left[-\frac{2u^{3/2}}{3} \right] \quad (21)$$

if $u \gg 1$. To obtain the function $f(t)$, we assume that it is a power function of time $f(t) \sim t^\lambda$. Putting the function f into

Eq. (16) and using Eq. (17), we obtain $\lambda = -\frac{\alpha}{3}$. Comparing Eq. (16) with Eqs. (1) and (2), we get

$$R(x,t) = \frac{\kappa |x|}{t^{\alpha/2}} \delta C(x,t). \quad (22)$$

Substituting Eqs. (20) and (21) into Eq. (22), we obtain

$$R(x,t) \sim t^{-2\alpha/3} \left(\frac{|x|}{t^{\alpha/6}} \right)^{3/4} \exp \left[-\frac{2}{3} \left(\frac{\lambda |x|}{t^{\alpha/6}} \right)^{3/2} \right]. \quad (23)$$

As the width of the reaction region is defined by the relation [7]

$$W_R^2(x,t) = \frac{\int [x - x_f(t)]^2 R(x,t) dx}{\int R(x,t) dx}, \quad (24)$$

we get $W_R \sim t^{\alpha/6}$ substituting Eq. (23) into Eq. (24) with $x_f \equiv 0$.

Because the width of the depletion zone is defined by the conditions $C_i \ll C_{0i}$, $i=A,B$, from Eqs. (13) and (14) we get $W_{\text{Dep}} \sim t^{\alpha/2}$. Thus, the relation $\mu < \theta$ is fulfilled for the system where the subdiffusion coefficients of the reactants are equal to each other. We assume that this relation holds for the system with any nonzero values of the subdiffusion coefficients.

V. CONCENTRATION PROFILE IN THE DIFFUSION REGION

Since $W_R \ll W_{\text{Dep}}$, the reaction region plays the role of a partially absorbing wall with respect to the depletion zone. We find the concentration profiles in the region outside the reaction zone as the solution of the subdiffusion equation [Eq. (1) with $R_\alpha(x,t) \equiv 0$] in the system with a partially absorbing wall. To calculate the concentration profiles, we use the integral formula

$$C(x,t) = \int G(x,t;x_0) C(x_0,0) dx_0, \quad (25)$$

where $G(x,t;x_0)$ denotes the Green's function for the subdiffusion equation. For the system with a partially absorbing wall located at $x=0$, the Green's functions are as follows (see Appendix A):

$$G_{A \text{ Dif}}(x,t;x_0) = G_{0A}(x,t;x_0) - \rho_A G_{0A}(x,t;-x_0) \quad (26)$$

and

$$G_{B \text{ Dif}}(x,t;x_0) = G_{0B}(x,t;x_0) - \rho_B G_{0B}(x,t;-x_0), \quad (27)$$

where the Green's function G_0 for the homogeneous system (without the wall) reads

$$G_{0i}(x,t;x_0) = \frac{1}{\alpha |x-x_0|} H_{11}^{10} \left[\left(\frac{|x-x_0|}{\sqrt{Dt^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 1 & 2/\alpha \end{vmatrix} \right], \quad (28)$$

$i=A,B$. The parameters ρ_A and ρ_B play here only an auxiliary role and do not occur in our final formulas. The physical meaning of ρ_A and ρ_B is discussed in Appendix A. Using the

integral formula (25) and initial conditions (4) and (5), we find (for details, see Appendix B)

$$C_{A \text{ Dif}}(x,t) = C_{0A} - \frac{2}{\alpha} \eta_A \times H_{11}^{10} \left[\left(\frac{-x}{\sqrt{D_A t^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 0 & 2/\alpha \end{vmatrix} \right], \quad (29)$$

where

$$\eta_A \equiv C_{A0}(1 + \rho_A)/2, \quad (30)$$

and

$$C_{B \text{ Dif}}(x,t) = C_{0B} - \frac{2}{\alpha} \eta_B \times H_{11}^{10} \left[\left(\frac{x}{\sqrt{D_B t^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 0 & 2/\alpha \end{vmatrix} \right], \quad (31)$$

where

$$\eta_B \equiv C_{B0}(1 + \rho_B)/2. \quad (32)$$

Let us note that when $C_{0A} = C_{0B} \equiv C_0$ and $D_A = D_B$, Eqs. (13) and (14) give $\rho_A = \rho_B = 1$.

Since the condition of validity of the quasistatic approximation, which is used in our further consideration, involves the fluxes, we derive here some formulas to be used in the next sections. The subdiffusive fluxes are given by the formula

$$J_i(x,t) = -D_i \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial C_i(x,t)}{\partial x}. \quad (33)$$

Using Eqs. (29) and (31), we obtain

$$J_{A \text{ Dif}}(x,t) = \frac{2}{\alpha} \sqrt{D_A} \eta_A \left(\frac{\sqrt{D_A}}{-x} \right)^{(2/\alpha)-1} \times H_{11}^{10} \left[\left(\frac{-x}{\sqrt{D_A t^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ -1 + 2/\alpha & 2/\alpha \end{vmatrix} \right], \quad (34)$$

$$J_{B \text{ Dif}}(x,t) = -\frac{2}{\alpha} \sqrt{D_B} \eta_B \left(\frac{\sqrt{D_B}}{x} \right)^{(2/\alpha)-1} \times H_{11}^{10} \left[\left(\frac{x}{\sqrt{D_B t^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ -1 + 2/\alpha & 2/\alpha \end{vmatrix} \right]. \quad (35)$$

In the following, we use the shorter notation for the fluxes (34) and (35),

$$J_{A \text{ Dif}}(x,t) = \frac{\sqrt{D_A} \eta_A}{t^{1-\alpha/2}} Q \left(\frac{-x}{\sqrt{D_A t^\alpha}} \right), \quad (36)$$

$$J_{B \text{ Dif}}(x,t) = -\frac{\sqrt{D_B} \eta_B}{t^{1-\alpha/2}} Q \left(\frac{x}{\sqrt{D_B t^\alpha}} \right), \quad (37)$$

where

$$Q(z) = \frac{\alpha}{2} \sum_{k=0}^{\infty} \frac{1}{k! \Gamma[\alpha(1-k)/2]} (-z)^k. \quad (38)$$

VI. TIME EVOLUTION OF THE REACTION FRONT

In this section, we derive the time evolution of the reaction front within the quasistatic approximation. The derivation is based on three assumptions that are expected to hold in the long-time limit.

(i) We assume that the relations

$$W_R \sim t^{\alpha/6}, \quad (39)$$

$$W_{\text{Dep}} \sim t^{\alpha/2}, \quad (40)$$

which are derived in Sec. IV for $D_A = D_B$ and $C_{0A} = C_{0B}$, hold for arbitrary values of the subdiffusion coefficients and initial concentrations.

(ii) The region around the reaction front, where the quasistatic approximation works, is assumed to extend beyond the reaction zone provided the relation

$$W_R(t) \ll |x - x_f(t)| \ll W_{\text{Dep}}(t) \quad (41)$$

holds.

(iii) In the diffusion region, the concentrations are given by Eqs. (29)–(32).

We note that the relations (39) and (40) were derived in [17] by means of the scaling method for the system where the subdiffusion coefficients of both reactants are equal to each other. The relation (39) was also found in [8] by means of the Monte Carlo simulations. We finally note that our numerical calculations confirm all our assumptions.

Starting with the above assumptions, we show at first the following:

(a) The concentration profiles (29) and (31) extended to the reaction region vanish at the points that are identified with the point x_z [shown in Fig. 1 and uniquely defined by Eq. (47)]. In the long-time limit, the point x_z is localized so close to x_f that x_z can be replaced by x_f in the obtained formulas.

(b) The fluxes J_A and J_B flowing into the reaction region from the left and from the right side, respectively, are balanced in such a way that m particles A and n particles B flow into the reaction region in the time unit.

After showing that the conditions (a) and (b) hold, we use Eqs. (29), (31), (36), and (37) to derive a relation describing the time evolution of the reaction front.

According to Eq. (8), the quasistatic approximation implies

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \left[D_A \frac{\partial^2}{\partial x^2} C_A(x,t) - mR(x,t) \right] = 0 \quad (42)$$

and

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \left[D_B \frac{\partial^2}{\partial x^2} C_B(x,t) - nR(x,t) \right] = 0, \quad (43)$$

which combined provide

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2}{\partial x^2} \Psi(x,t) = 0,$$

where

$$\Psi(x, t) \equiv \frac{1}{m} D_A C_A(x, t) - \frac{1}{n} D_B C_B(x, t). \quad (44)$$

Using the formula (18), we find that the function Ψ is of the form

$$\Psi(x, t) = E(x)t^{-\alpha} + F(t)x + G(t), \quad (45)$$

where E , F , and G are arbitrary functions that are determined in the following. Applying the operator $\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial}{\partial x}$ to Eqs. (44) and (45), we obtain

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} F(t) = \frac{1}{n} J_B(t) - \frac{1}{m} J_A(t). \quad (46)$$

The function Ψ changes its sign in the reaction zone from positive where $C_B \approx 0$ to negative where $C_A \approx 0$. Thus, there is the point $x_z(t)$ that lies inside the reaction zone, where the function Ψ vanishes. Therefore,

$$\Psi(x_z(t), t) = 0. \quad (47)$$

Since $x_f(t)$ also lies inside the reaction zone, there is

$$|x_z(t) - x_f(t)| \leq \Omega t^{\alpha/6}, \quad (48)$$

where Ω is a positive constant. After simple calculations, we get

$$\Psi(x, t) = \frac{E(x) - E[x_z(t)]}{t^\alpha} + F(t)[x - x_z(t)]. \quad (49)$$

Let us now consider the region where the region of diffusion approximation overlaps with the one of the quasistatic approximation for $x < x_f(t)$. The region occurs for such x that the condition

$$-W_{\text{Dep}}(x, t) \leq x - x_f(t) \leq -W_{\text{R}}(x, t) \quad (50)$$

is fulfilled. Here $C_A \approx C_{\text{ADif}}$, $C_B \approx 0$, $J_A \approx J_{\text{ADif}}$, and $J_B \approx 0$. So, we get from Eq. (44),

$$\Psi(x, t) = \frac{1}{m} D_A C_A \text{Dif}(x, t), \quad (51)$$

and from Eq. (46),

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} F(t) = -\frac{1}{m} J_A \text{Dif}(t). \quad (52)$$

Let us note that Ψ is given by the function of the variable $x/t^{\alpha/2}$ only [see Eq. (29)]. Therefore, we deduce that

$$E(x) = ax^2, \quad (53)$$

$$F(t) = \frac{b}{t^{\alpha/2}}, \quad (54)$$

and

$$G(t) = c, \quad (55)$$

where a , b , c are constants.

We denote

$$x_f(t) - x = \epsilon(t). \quad (56)$$

From Eqs. (39)–(41) and (56), we get

$$\Omega_1 t^{\alpha/6} \leq \epsilon(t) \leq \Omega_2 t^{\alpha/2},$$

where Ω_1 and Ω_2 are positive constants. When $t \rightarrow \infty$, the inequality provides $t^{\alpha/6}/\epsilon(t) \rightarrow 0$ and

$$\epsilon(t)/t^{\alpha/2} \rightarrow 0. \quad (57)$$

Combining Eqs. (29), (49), (51), and (53)–(56), we obtain

$$D_A \left\{ C_{0A} - \frac{2}{\alpha} \eta_A H_{11}^{10} \left[\left(\frac{\epsilon(t) - x_f(t)}{\sqrt{D_A t^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 0 & 2/\alpha \end{vmatrix} \right] \right\} = a \frac{[x_f(t) - \epsilon(t)]^2 - x_z^2(t)}{t^\alpha} + b \frac{x_f(t) - \epsilon(t) - x_z(t)}{t^{\alpha/2}}. \quad (58)$$

Since in the long-time limit $[x_f(t) - x_z(t) - \epsilon(t)]/t^{\alpha/2} \rightarrow 0$ [see Eqs. (48) and (57)], from Eq. (58) we get

$$C_{0A} - \frac{2}{\alpha} \eta_A H_{11}^{10} \left[\left(\frac{-x_f(t)}{\sqrt{D_A t^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 0 & 2/\alpha \end{vmatrix} \right] = 0. \quad (59)$$

Similar considerations performed in the region

$$W_{\text{R}}(x, t) \leq x - x_f(t) \leq W_{\text{Dep}}(x, t)$$

provide

$$\Psi(x, t) = -\frac{1}{n} D_B C_B \text{Dif}(x, t)$$

and

$$\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} F(t) = \frac{1}{n} J_B \text{Dif}(t), \quad (60)$$

which gives

$$C_{0B} - \frac{2}{\alpha} \eta_B H_{11}^{10} \left[\left(\frac{x_f(t)}{\sqrt{D_B t^\alpha}} \right)^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 0 & 2/\alpha \end{vmatrix} \right] = 0. \quad (61)$$

From Eqs. (52) and (60), we obtain

$$\frac{1}{m} J_A \text{Dif} = -\frac{1}{n} J_B \text{Dif}, \quad (62)$$

and from Eqs. (36), (37), and (62), we get

$$\frac{1}{m} \sqrt{D_A} \eta_A Q \left(\frac{-x_f(t)}{\sqrt{D_A t^\alpha}} \right) = \frac{1}{n} \sqrt{D_B} \eta_B Q \left(\frac{x_f(t)}{\sqrt{D_B t^\alpha}} \right). \quad (63)$$

Combining Eqs. (59), (61), and (63), and using the identity [28]

$$H_{11}^{10} \left(z^{2/\alpha} \begin{vmatrix} 1 & 1 \\ 0 & 2/\alpha \end{vmatrix} \right) = \frac{\alpha}{2} H_{11}^{10} \left(z \begin{vmatrix} 1 & \alpha/2 \\ 0 & 1 \end{vmatrix} \right), \quad (64)$$

we have

$$\Phi \left(\frac{-x_f(t)}{\sqrt{D_A t^\alpha}} \right) = \frac{n \sqrt{D_A} C_{0A}}{m \sqrt{D_B} C_{0B}} \Phi \left(\frac{x_f(t)}{\sqrt{D_B t^\alpha}} \right), \quad (65)$$

where $\Phi(z) \equiv H_{11}^{10}(z | \begin{smallmatrix} 1 & \alpha/2 \\ 0 & 1 \end{smallmatrix}) / Q(z)$. The unique solution of Eq. (65) is

$$x_f(t) = K t^{\alpha/2}, \quad (66)$$

where coefficient K is the solution of the following equation:

$$\Phi\left(\frac{-K}{\sqrt{D_A}}\right) = \frac{n}{m} \frac{\sqrt{D_A} C_{0A}}{\sqrt{D_B} C_{0B}} \Phi\left(\frac{K}{\sqrt{D_B}}\right). \quad (67)$$

Thus, the time evolution of the reaction front is the power function with the exponent depending on the subdiffusion parameter α only; the subdiffusion coefficients D_A and D_B control the parameter K . Equations (66) and (67) are the main results of our paper.

The procedure developed in this paper is the extension of the one used previously for the normal diffusion [2]. Repeating our consideration for $\alpha=1$, we obtain the results identical with those from [2]. Our formula (66) with K given by Eq. (67) is a generalization of Eq. (21) from Ref. [17].

VII. NUMERICAL SOLUTIONS

To verify the correctness of our procedure, we compare the analytical functions, which are derived in the previous sections, with numerical solutions of Eq. (1). The quasistatic approximation zone exists where the function Ψ is parabolic with respect to x , as required by Eqs. (45) and (53)–(55). We also show that there exists the region of overlap of the diffusion zone and the quasistatic one; in this region, C_{ADif} or C_{BDif} are the linear functions of x .

A. Numerical procedure

The functions C_A and C_B and their second derivatives with respect to x are assumed to be bounded. As we show in Appendix C, Eq. (1) is equivalent to

$$\frac{C}{\partial t^\alpha} C_i(x, t) = D_i \frac{\partial^2}{\partial x^2} C_i(x, t) - d_i R(x, t), \quad (68)$$

where $i=A, B$, $d_A=m$, $d_B=n$, and on the l.h.s. there is the Caputo fractional time derivative, which is defined for $0 < \alpha < 1$ as [29]

$$\frac{C}{dt^\alpha} f(t) = \frac{1}{\Gamma(1-\alpha)} \int_0^t d\tau \frac{f(\tau)}{d\tau} (t-\tau)^{-\alpha}.$$

Throughout this paper, we denote the Riemann-Liouville fractional derivative without any additional index as $d^\alpha f(t)/dt^\alpha$; the other kinds of the fractional derivatives are labeled by index C for the Caputo fractional derivative and GL for the Grünwald-Letnikov one.

In the papers [30,31], procedures were presented to solve numerically the subdiffusion equation without chemical reactions, when one can use the equation with Riemann-Liouville as well as Caputo fractional time derivative. The situation is different in the case of the subdiffusion-reaction equations. Since the operator of the Riemann-Liouville fractional derivative acts in Eq. (1) on the term representing chemical reactions, Eq. (68) is simpler for numerical treatment, as the operator of fractional derivative acts here only on the concentration on the l.h.s. of the equation.

To numerically solve the normal diffusion equation, one usually substitutes the time derivative by the backward difference $\frac{\partial f(t)}{\partial t} \approx \frac{f(t) - f(t-\Delta t)}{\Delta t}$. In the presented procedure, we proceed in a similar way. We use the Grünwald-Letnikov frac-

tional derivative, which is defined as the limit of the fractional-order backward difference [29]

$$\frac{GL}{dt^\alpha} f(t) = \lim_{\Delta t \rightarrow 0} (\Delta t)^{-\alpha} \sum_{r=0}^{[t/\Delta t]} (-1)^r \binom{\alpha}{r} f(t-r\Delta t), \quad (69)$$

where $\alpha > 0$, $[z]$ means the integer part of z , and

$$\binom{\alpha}{r} = \frac{\Gamma(\alpha+1)}{r! \Gamma(\alpha-r+1)} = \frac{\alpha(\alpha-1) \times \dots \times [\alpha-(r-1)]}{1 \times 2 \times 3 \times \dots \times r}.$$

When the function $f(t)$ of a positive argument has continuous derivatives of the first order, the Riemann-Liouville fractional derivative is equivalent to the Grünwald-Letnikov one for any parameter α ($0 < \alpha < 1$) [29]. So, we have

$$\frac{d^\alpha f(t)}{dt^\alpha} = \frac{GL}{dt^\alpha} f(t). \quad (70)$$

The relation between Riemann-Liouville and Caputo derivatives is more complicated and reads

$$\frac{d^\alpha f(t)}{dt^\alpha} = \frac{C}{dt^\alpha} f(t) + \Phi_{1-\alpha}(t) f(0), \quad (71)$$

where

$$\Phi_{q+1}(t) = \begin{cases} \frac{t^q}{\Gamma(q+1)}, & t > 0 \\ 0, & t \leq 0. \end{cases} \quad (72)$$

From Eqs. (69)–(72), we can express the Caputo fractional derivative in terms of the fractional-order backward difference,

$$\frac{C}{dt^\alpha} f(t) = \lim_{\Delta t \rightarrow 0} (\Delta t)^{-\alpha} \sum_{r=0}^{[t/\Delta t]} (-1)^r \binom{\alpha}{r} f(t-r\Delta t) - \frac{1}{t^\alpha \Gamma(1-\alpha)} f(0). \quad (73)$$

The standard way to approximate the fractional derivative, which is useful for numerical calculations, is to keep Δt in Eq. (73) finite and to replace the infinite series by the finite one,

$$\frac{C}{dt^\alpha} f(t) \approx (\Delta t)^{-\alpha} \sum_{r=0}^L (-1)^r \binom{\alpha}{r} f(t-r\Delta t) - \frac{1}{t^\alpha \Gamma(1-\alpha)} f(0), \quad (74)$$

where the “memory length” L is a natural number of arbitrary value ($L \leq [t/\Delta t]$).

Subdiffusion is a process with memory as the operators of fractional derivatives are not local in time. According to the *short memory principle*, the fractional derivative is approximated by the fractional derivative with moving lower limit $t-L$, where L is the “memory length” equal to a certain number of time steps [29]. However, we showed [32] that the numerical solutions of the subdiffusion equation with the initial conditions (4) and (5) are in agreement with the analytical ones only when the memory length is close to the actual number of time steps. So, the *short memory principle* does

not work and in numerical calculations we take the memory length L equal to the actual number of time steps.

Substituting Eq. (74) into Eq. (68) and using the following approximation of the second-order derivative:

$$\frac{d^2 f(x)}{dx^2} \approx \frac{f(x + \Delta x) - 2f(x) + f(x - \Delta x)}{(\Delta x)^2},$$

we obtain

$$\begin{aligned} C_i(x,t) = & - \sum_{r=1}^L (-1)^r \frac{\alpha(\alpha-1) \times \dots \times [\alpha-(r-1)]}{1 \times 2 \times 3 \times \dots \times r} \\ & \times C_i(x, t - r\Delta t) + \frac{(\Delta t)^\alpha}{t^\alpha \Gamma(1-\alpha)} C_i(x, 0) \\ & + D_i \frac{(\Delta t)^\alpha}{(\Delta x)^2} [C_i(x + \Delta x, t - \Delta t) - 2C_i(x, t - \Delta t) \\ & + C_i(x - \Delta x, t - \Delta t)] \\ & - d_i k (\Delta t)^\alpha C_A^m(x, t - \Delta t) C_B^n(x, t - \Delta t) \end{aligned} \quad (75)$$

for $i=A, B$, $d_A=m$, and $d_B=n$.

B. Numerical results

Here we compare the analytical results with the numerical ones. In all figures, there are presented functions calculated for the system where $\alpha=0.5$, $D_A=0.025$, $D_B=0.0125$, $C_{0A}=2$, $C_{0B}=1$, $k=1$, and $m=n=1$. For numerical calculations, we take $\Delta x=0.2$ and $\Delta t=0.05$ (all quantities are given in the arbitrary units). Additionally, in Figs. 5 and 6 we plot the borders of the reaction zone ($x_f - W_R/2, x_f + W_R/2$) calculated for the time $t=5000$. The position of the reaction front was calculated from the discrete version of Eq. (6),

$$x_f(t) = \frac{\sum_i x_i R(x_i, t)}{\sum_i R(x_i, t)}, \quad (76)$$

and it equals 0.71 for $t=5000$. The width of the reaction region calculated from a discrete version of Eq. (24),

$$W_R^2(t) = \frac{\sum_i [x_i - x_f(t)]^2 R(x_i, t)}{\sum_i R(x_i, t)},$$

equals 0.38 for $t=5000$. Thus, the reaction region occupies the interval (0.52; 0.90).

From Eq. (76), we find that

$$x_f(t) = 0.0838t^{0.251}. \quad (77)$$

This relation is similar to the relation (66) with K calculated from Eq. (67), which is

$$x_f(t) = 0.0825t^{0.25}. \quad (78)$$

Figures 3 and 4 present the concentration profiles C_A and C_B obtained numerically according to the formula (75) and the functions given by Eqs. (29)–(32) with $\rho_A=0.40$ and $\rho_B=3.64$, respectively; the parameters ρ_A and ρ_B are treated as fit parameters that ensure the best matching of the analytical solutions and numerical ones. We observe a good agreement of the analytical and numerical functions in the diffusion region.

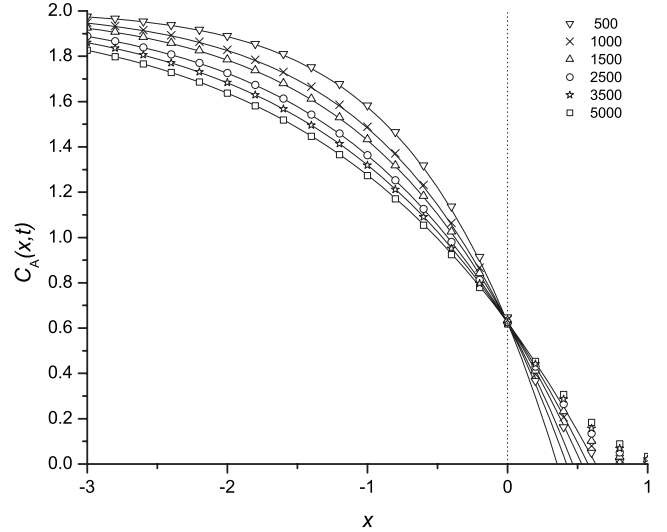


FIG. 3. The symbols represent the numerical solutions C_A of the subdiffusion-reaction equation; the solid lines are assigned to the analytic solutions C_{ADif} for the times given in the legend. All quantities are in arbitrary units.

In Fig. 5, we present the function $\Psi(x,t)$ calculated numerically and its parabolic fit $\Psi(x,t) = 0.297(x/t^{\alpha/2})^2 - 0.168(x/t^{\alpha/2}) + 0.015$ [the parameters a , b , and c occurring in Eqs. (45) and (53)–(55) are fit parameters]. We note that Ψ is well approximated by the parabolic function of x . The region where Ψ is parabolic determines the quasistatic approximation region. However, we expect that there are deviations from this approximation in a region located within the reaction zone, where the reaction term is significantly different from zero. This is because the concentrations C_A and C_B have different scaling properties in that region. We expect that the width of that region is so narrow, as compared with the width of the quasistatic approximation one, that the deviation from parabolic approximation is hard to observe in the plots presented in our paper. We conclude that the possibility of those deviations does not influence our main results.

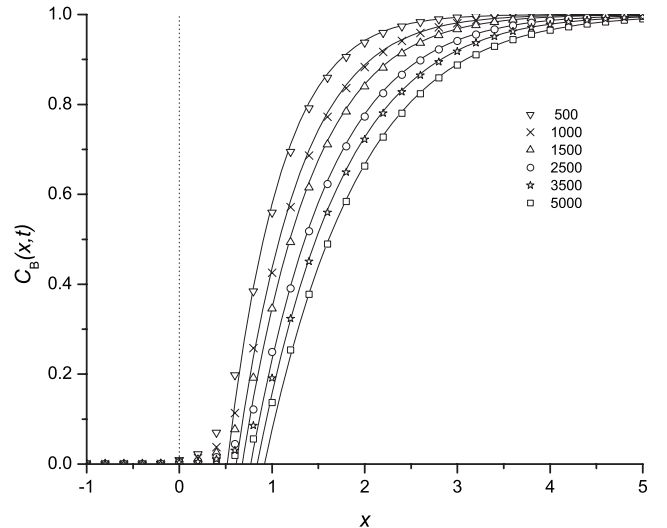


FIG. 4. The numerical solutions C_B (symbols) and the analytic solutions C_{BDif} (solid lines) for the times given in the legend.

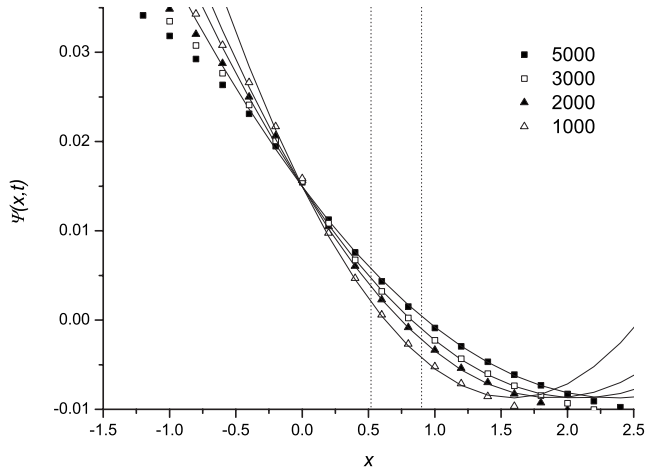


FIG. 5. The function Ψ (symbols) obtained numerically for the times given in the legend and their parabolic fits inside the quasistatic approximation region (solid line); the vertical lines represent the borders of the reaction zone calculated for $t=5000$.

In Fig. 6, we present the numerical solutions of the subdiffusion-reaction equations and their linear fit calculated from the formulas $C_A(x,t) \approx -0.816x + 0.616$ and $C_B(x,t) \approx 0.620x - 0.490$, respectively. The linear fit of C_A and C_B is satisfactory outside the reaction region. This confirms the correctness of the quasistatic approximation in the region enclosing the reaction region.

The numerical results give $W_R \sim t^{0.08}$ with the exponent which is very close to the one obtained analytically. As we mentioned in Sec. III, the quasistatic approximation can be applied to a region where the equilibrium time τ_F of the reaction region is negligibly small in comparison with the characteristic time of change of the flux τ_J in the long-time limit [2,7,11]. Let us note that this condition is fulfilled in the system under consideration. Since $W_R \sim t^{\alpha/6}$, we have τ_F

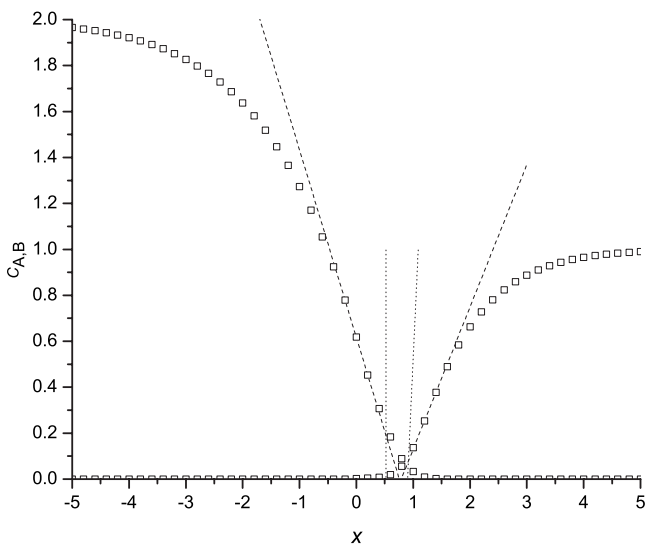


FIG. 6. The concentration profiles C_A and C_B obtained numerically (squares) calculated for time $t=5000$ and the linear fits (dashed lines); the vertical lines represent the borders of the reaction zone.

$\sim t^{1/3}$ from Eq. (10). Taking the definition (11), which for the subdiffusion flux $J \sim 1/t^{1-\alpha/2}$ gives $\tau_J \sim 1/t$ [see Eqs. (36) and (37)], we get $\tau_F/\tau_J \rightarrow t \rightarrow \infty$ for any value of the subdiffusive parameter α . So, the assumptions adopted in our paper agree with the quasistatic condition (12).

It can be concluded that our numerical results fully support the postulates of the quasistatic approximation.

VIII. FINAL REMARKS

Using the quasistatic approximation and utilizing the solution of the subdiffusion-reaction equations in the diffusive region, we show that the time evolution of the reaction front for the subdiffusion-reaction system is the power function (66) with the exponent $\alpha/2$ and the coefficient K controlled by the subdiffusion coefficients of the system. The function $x_f \sim t^{\alpha/2}$ can be obtained by means of the scaling method, but it is very hard within this method to find an explicit expression of the parameter K for the case of $D_A \neq D_B$.

We consider the process of subdiffusion controlled by chemical reactions. It means that the reactions proceed relatively fast, when compared with the characteristic time of meeting of particles A and B [1]. Under such an assumption, the quasistatic approximation is valid and the time evolution of the reaction front does not depend on the detailed form of the reaction term (except the dependence on the parameters m and n). This happens because the form of R does not change the relation $W_R \sim t^{\alpha/6}$. Thus, the width of the reaction zone appears to be relatively small in comparison with the width of the quasistatic approximation region. The time evolution of x_f is determined by the dynamics of transport of particles to the reaction zone. This statement is particularly important for the subdiffusion-reaction systems, where the reaction term is not uniquely defined (as the fractional derivative can be applied in a few ways [16–22]). Let us note that x_f depends on the parameters $\alpha, m, n, D_A, D_B, C_{0A}$, and C_{0B} , which can be measured experimentally and have a simple physical interpretation, but it is independent of the parameters ρ_A, ρ_B (and consequently η_A, η_B), which play only an auxiliary role in our considerations.

Equations (66) and (67), which are main results of our paper, can be used to extract the subdiffusion parameters from experimental data. However, as far as we know, the time evolution of the reaction front has not yet been measured experimentally in a subdiffusive system with two mobile reactants. The only example of the subdiffusion-reaction process that has been observed is, to the best of our knowledge, the process of progress of the carious lesion in tooth enamel [33,34]. The reaction front can then be identified with the border of the caries and its time evolution can be measured. In that case, the system consists of one reactant (acid) that is mobile, but the other (hydroxyapatite) is static. Since the quasistatic approximation cannot be then defined by Eqs. (42) and (43), this case is not considered here. However, our preliminary results show that in such a system, the time evolution of the reaction front is also given by the formula (66), but the equation defining the parameter K is different from Eq. (67). A quantitative comparison of the measured evolution of the reaction front with our theoretical

predictions is presented, and the parameters α and D_α are extracted in [33,34].

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APPENDIX A

Here we find the Green’s functions for a system with a partially absorbing wall by means of the generalized method of images, which was used earlier to find such functions for a system with a partially reflecting wall [27].

From a microscopic point of view, the Green’s function is interpreted as a concentration profile of the N particles (divided by N), which are instantaneously produced and start their random walk from the position x_0 at the initial moment $t=0$. It is also interpreted as a probability density of finding a particle in point x at time t under the condition, that the particle is located in the position x_0 at the initial moment $t=0$.

The standard method of images was applied for a diffusive system with a fully absorbing or a fully reflecting wall [26]. Then, one replaces the wall by a fictitious instantaneous point source of the particles (IPS) in such a manner that the concentration profile generated by all IPS behaves as in the system with the wall. In the case of a fully absorbing wall, the concentration vanishes at the wall. The Green’s function is then the difference of IPS placed at x_0 and $-x_0$, which gives

$$G(x, t; x_0) = G_0(x, t; x_0) - G_0(x, t; -x_0), \tag{A1}$$

where G_0 denotes the Green’s function for the homogeneous system without any wall; here the wall is located at $x=0$. The Green’s function for the system with the partially absorbing wall can be obtained from Eq. (A1) by reducing the IPS located at $-x_0$ by the parameter ρ . Then, we find

$$G(x, t; x_0) = G_0(x, t; x_0) - \rho G_0(x, t; -x_0). \tag{A2}$$

The parameter ρ is assumed to be a constant characterizing the wall and it has the following physical interpretation: *if during a given time interval N particles reach the wall, the fraction ρ of them will be absorbed.*

APPENDIX B

In this appendix, we present some details of the procedure of solving the subdiffusion equation. The calculations with Riemann-Liouville fractional time derivative are relatively simple in terms of the Laplace transform (LT) $\hat{L}[f(t)] \equiv \hat{f}(s) = \int_0^\infty dt f(t) e^{-st}$. The LT of the Green’s function for a homogeneous subdiffusive system without chemical reaction (28) reads [14,24]

$$\hat{G}_{0,i}(x, s; x_0) = \frac{1}{2\sqrt{D_i}s^{1-\alpha/2}} e^{-|x-x_0|\sqrt{s^\alpha/D_i}}, \tag{B1}$$

$i=A, B$. The LT commutes with the integration (with respect to the variable x). So, from Eq. (25) we get

$$\hat{C}(x, s) = \int \hat{G}(x, s; x_0) C(x_0, 0) dx_0. \tag{B2}$$

Putting Eq. (B1) into the LT of Eqs. (26) and (27), and next to Eq. (B2), we obtain

$$\hat{C}_A(x, s) = \frac{C_{0A}}{s} - \frac{\eta_A}{s} e^{-(-xs^{\alpha/2})/\sqrt{D_A}} \tag{B3}$$

with $\eta_A \equiv C_{0A}(1 + \rho_A)/2$, and

$$\hat{C}_B(x, s) = \frac{C_{0B}}{s} - \frac{\eta_B}{s} e^{-xs^{\alpha/2}/\sqrt{D_B}} \tag{B4}$$

with $\eta_B \equiv C_{0B}(1 + \rho_B)/2$. The inverse Laplace transform \hat{L}^{-1} , for $a > 0$ and $\beta > 0$, gives [24]

$$\hat{L}^{-1}(s^\nu e^{-as^\beta}) = \frac{1}{\beta a^{(1+\nu)/\beta}} H_{11}^{10} \left(\frac{a^{1/\beta}}{t} \left| \begin{matrix} 1 & 1 \\ 1+\nu & 1/\beta \end{matrix} \right. \right) \tag{B5}$$

and

$$\hat{L}^{-1}(s^\nu e^{-as^\beta}) = \frac{1}{t^{1+\nu}} \sum_{j=0}^\infty \frac{1}{j! \Gamma(-\nu - j\beta)} \left(-\frac{a}{t^\beta} \right)^j. \tag{B6}$$

Using the relation (B5) to calculate the inverse LT of Eqs. (B3) and (B4), we get Eqs. (29) and (31). Let us note that comparing the right-hand sides of Eqs. (B5) and (B6), after simple calculations, we get the useful relation (15).

The LT of the subdiffusive flux (33) reads

$$\hat{J}_i(x, s) = -D_i s^{1-\alpha} \frac{d\hat{C}_i(x, s)}{dx}. \tag{B7}$$

Putting Eqs. (B3) and (B4) into Eq. (B7) and next to Eq. (B5), we obtain Eqs. (34) and (35).

APPENDIX C

Here we show that Eqs. (1) and (68) are equivalent to each other when the concentration C and its second space derivative are bounded. The Laplace transforms of fractional derivatives are as follows [29] (here $0 < \alpha < 1$):

$$\hat{L} \left[\frac{d^\alpha f(t)}{dt^\alpha} \right] = s^\alpha \hat{f}(s) - \frac{d^{\alpha-1} f(t)}{dt^{\alpha-1}} \Big|_{t=0},$$

$$\hat{L} \left[\frac{C d^\alpha f(t)}{dt^\alpha} \right] = s^\alpha \hat{f}(s) - s^{\alpha-1} f(0).$$

The Laplace transform of Eq. (1) is

$$s\hat{C}(x,s) - C(x,0) = s^{1-\alpha} \left[D \frac{d^2\hat{C}(x,s)}{dx^2} - \hat{R}(x,s) \right] - \frac{d^{-\alpha}}{dt^{-\alpha}} \left[D \frac{d^2C(x,t)}{dx^2} - R(x,t) \right] \Big|_{t=0}, \quad (\text{C1})$$

whereas the Laplace transform of Eq. (68) reads $s^\alpha\hat{C}(x,s) - s^{\alpha-1}C(x,0) = D \frac{d^2\hat{C}(x,s)}{dx^2} - \hat{R}(x,s)$, which gives

$$s\hat{C}(x,s) - C(x,0) = s^{1-\alpha} \left[D \frac{d^2\hat{C}(x,s)}{dx^2} - \hat{R}(x,s) \right]. \quad (\text{C2})$$

We assume that the function C and its second space-variable derivative are bounded. So, there is a positive number M that fulfills the relation $|\Theta(x,t)| < M$, where $\Theta(x,t) \equiv D \frac{d^2C(x,t)}{dx^2}$

$-R(x,t)$, for any x and t . From the definition of Riemann-Liouville derivative of negative order

$$\frac{d^{-\alpha}}{dt^{-\alpha}} f(t) = \frac{1}{\Gamma(\alpha)} \int_0^t d\tau (t-\tau)^{\alpha-1} f(\tau),$$

we obtain

$$\left| \frac{d^{-\alpha}}{dt^{-\alpha}} \Theta(x,t) \right| \leq M \int_0^t d\tau (t-\tau)^{\alpha-1} = \frac{M}{\alpha} t^\alpha, \quad (\text{C3})$$

and from Eq. (C3) we get

$$\frac{d^{-\alpha}}{dt^{-\alpha}} \Theta(x,t) \Big|_{t=0} = 0,$$

which makes the Laplace transforms (C1) and (C2) equal to each other. Thus, Eqs. (1) and (68) are equivalent to each other for the bounded function Θ .

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