THE SOLUTION TO SUBDIFFUSION-REACTION EQUATION FOR THE SYSTEM WITH ONE MOBILE AND ONE STATIC REACTANT*

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We theoretically study the subdiffusion of B particles which can chemically react with A particles according to the formula $A + B \rightarrow \emptyset$(inert). The A particles are static and located at the wall which bounds the system. To describe the process, we use a fractional subdiffusion-reaction equation in which the character of the transport process is included in the reaction term. We find the exact solution to the equation for arbitrarily chosen initial conditions in terms of the Laplace transform. The inverse Laplace transform of this solution is calculated over a long time limit. We also briefly discuss the possibility of experimental verification of the model.

1. Introduction

A diffusion process in which particles of types A and B can chemically react has been intensively studied during recent years [1–10]. The equation describing this process is usually assumed to be a diffusion equation supplemented by the operator $\Pi(C_A, C_B)$ which represents the velocity of particles vanishing due to a chemical reaction; then, the diffusion-reaction

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equation reads $\partial C_{A,B}/\partial t - D_{A,B}\Delta C_{A,B} = -\Pi(C_A, C_B)$. Usually, operator Π is defined by the kinetic reaction equation $\Pi \equiv -dC_{A,B}/dt$. However, the above equation is derived under the condition that the particle solution is well mixed up. This situation is quite different when particles are transported by diffusion. A reaction term is then derived within the mean field approximation [1–3] and for the reaction

$$A + B \to \emptyset(\text{inert}) \tag{1}$$

reads

$$\Pi(x,t) = kC_A(x,t)C_B(x,t)\,, \tag{2}$$

where k is the reaction coefficient. Within the mean-field approximation, the process is considered in a 'cellular system' in which the cells are assumed to be sufficiently large to neglect the fluctuations of the particles' concentration and sufficiently small to assume that the solution is homogeneous within a cell [1]. Then, the chemical reactions within each cell can be approximately described by the kinetic reaction equation mentioned above.

The dynamics of the reaction are controlled by the 'mixing process' of the particles. When particles A and B meet each other (this means that both are located at a reaction distance at which the reaction is possible), they can chemically react. If the reaction is absent in some time interval, the particles can move away from the reaction zone and again return to it. Thus, the occurrence of a reaction in a time interval depends on the kind of particle transport (diffusion or subdiffusion). To find an influence of a transport process on a reaction, we should consider the reaction between two arbitrarily chosen diffusive particles A and B. The frequency of the particles' meetings depends on diffusion or subdiffusion parameters. Subdiffusive transport is usually described by means of an equation with a fractional time derivative. There were few attempts to determine the form of the subdiffusion-reaction equation. In paper [11] the authors have postulated the subdiffusion-reaction equation in which the reaction term — characteristic for normal diffusion — was only added to the subdiffusion equation, which provides the following equation $\partial C_{A,B}/\partial t - D_{A,B}\Delta\partial^{1-\alpha}C_{A,B}/\partial t^{1-\alpha} = -\Pi(C_A, C_B)$ (in this paper, we use the Riemann–Lioville fractional derivative definition). In papers [12, 13], the type of particle transport was included in the derivation of the subdiffusion-reaction equation. This model will be used in this paper. It was used in describing the subdiffusion-reaction process in which substances were separated at the initial moment [14, 15]. The subdiffusion-reaction equation in one-dimensional system reads

$$\frac{\partial C_{A,B}(x,t)}{\partial t} - D_{A,B}\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial^2 C_{A,B}(x,t)}{\partial x^2} = -\frac{\partial^{1-\alpha}\Pi(C_A, C_B)}{\partial t^{1-\alpha}}\,. \tag{3}$$

A different subdiffusion-reaction equation was proposed by Sokolov *et al.* [16] in which the process of simple molecular conversion $A \to B$ was considered. Therefore, the reaction term depends on the concentration of A at all previous times.

As far as we know, the correctness of the above mentioned models has not been experimentally decided upon to date. The lack of experimental verification seems to be caused technical difficulties. For example, the very useful interferometric method of the investigation of concentration profiles, which has been used to study normal diffusion and subdiffusion in various media [17–19], provides the concentration profiles $C_A + C_B$, and there is no possibility of finding the concentration of particles A and B separately. Thus, within this method, the influence of subdiffusion on the dynamic of reaction (1) can be found experimentally only when one of the substances is static. Let us note that there is additional difficulty in performing a comparison of experimental and theoretical results. Namely, since the subdiffusion-reaction equation is a fractional nonlinear one, therefore, it is difficult to solve and its general solutions have not yet been found (except in a few special cases). To find an approximate solution, one uses various method such as the perturbation method, the scaling method and the quasistatic approximation method. Unfortunately, the usefulness of all these methods is strongly limited (see, for example, [15, 20] and references cited therein).

In this paper, we will solve the subdiffusion-reaction equation for a system in which both one mobile and one static reactants are found. The static reactant is placed on the wall restricting the one-dimensional system. We add that a similar problem was considered in [21], where the stationary situation was analyzed. In our paper, we will study the non-stationary process. We will show the exact solution to the subdiffusion-reaction equation in terms of the Laplace transform. The inverse Laplace transform will be taken over the long time limit. The solutions which we will obtain could be compared to experimental results. The experiment can be conducted by means of the laser inferferometric method of concentration measurement.

2. The model

In our consideration, we adopt the model by Seki, Wójcik and Tachiya, which was used to describe the subdiffusive motion of a B particle which can chemically react with an A particle [12, 13]. The scheme of the model is the following: B particle moves randomly at the discrete lattice in a system in which an A particle is located at the origin of the system. The A particle is represented by the sphere of radius R centred at system's origin. The diffusion-reaction process is then considered as the random walk, in which the B particle can vanish when it enters into the vicinity of the sphere.

The various models which take specific boundary conditions at the sphere were considered. In the simplest Smoluchowski model, it was assumed that the sphere was fully absorbing. A more general model assumes that the sphere is partially absorbing or fully reflecting; in the latter case, the reaction takes place in the region $(R, R + \Delta R)$ (called the encounter region) with the probability density

$$\psi_{\text{rea}}(t) = \gamma \exp(-\tilde{\gamma}t)\,, \tag{4}$$

$\tilde{\gamma}$ is the reaction rate. If the B particle leaves this region (with the probability $\psi_{\text{out}}(t)$), then the chemical reaction cannot occur and the reaction can take place during next particle's visit inside the encounter region. In order to find the subdiffusion-reaction equation, the following assumptions are taken into consideration: the B particle moves at the discrete lattice and its every jump has the same length, $\tilde{b}$, each jump of the B particle located inside the encounter region moves the particle outside this region (in practice, this means that $\Delta R < \tilde{b}$) and the waiting time distribution of leaving the encounter distance is as follows

$$\psi_{\text{out}}(t) = \psi(t) \exp(-\tilde{\gamma}t)\,, \tag{5}$$

where $\psi(t)$ is the probability density of the waiting time to take the B particle's next step (it is assumed that this function is independent of chemical reactions and would be the same in a system without chemical reactions). The Laplace transform of Eq. (5) reads

$$\hat{\psi}_{\text{out}}(s) = \hat{\psi}(s + \tilde{\gamma})\,. \tag{6}$$

Under the above mentioned assumptions, the subdiffusion-reaction equation reads in terms of the Laplace transform

$$
\begin{aligned}
s\hat{\rho}\left(\vec{r}, s; \vec{r}_0\right) - \delta(\vec{r} - \vec{r}_0) &= \frac{\tilde{b}^2 s\hat{\psi}(s)}{2\left[1 - \hat{\psi}(s)\right]} \nabla^2 \hat{\rho}\left(\vec{r}, s; \vec{r}_0\right) \\
&\quad - \frac{\tilde{b}s\left[\hat{\psi}(s) - \hat{\psi}(s + \tilde{\gamma})\right]}{2\left[1 - \hat{\psi}(s)\right]} \delta(r - R)\hat{\rho}\left(\vec{r}, s; \vec{r}_0\right)\,, \quad (7)
\end{aligned}
$$

where $\rho(\vec{r}, t; \vec{r}_0)$ denotes the probability density of finding B particle at a position $\vec{r}$ at time t under the condition that the initial position of the particle is $\vec{r}_0$.

To find the subdiffusion-reaction equation for $\rho(\vec{r}, t; \vec{r}_0)$, one must calculate the inverse Laplace transform of Eq. (7). In practice, it is only possible to calculate the inverse transform for small values of s, which corresponds to the limit of long time t. In the following, we adapt the model to a one-dimensional system.

3. Subdiffusion-reaction in a one dimensional system

Let us assume that the system is homogeneous in the plane perpendicular to the x axis. Therefore, the system can be considered as one-dimensional. The system is bounded by a reflecting wall placed at $x = x_m$. The particles of substance A are uniformly located on this wall. A subdiffusive particle B moves randomly in the space interval $(-\infty, x_m)$. When B enters the reaction region $(x_m - \Delta x_m, x_m)$, it can chemically react according to the formula (1). Transforming Eq. (7) to the system considered here, we get

$$
s\hat{\rho}(x, s; x_0) - \delta(x - x_0) = \frac{b^2 s \hat{\psi}(s)}{2\left[1 - \hat{\psi}(s)\right]} \frac{d^2}{dx^2} \hat{\rho}(x, s; x_0)
$$
$$
- \frac{bs\left[\hat{\psi}(s) - \hat{\psi}(s + \gamma)\right]}{2\left[1 - \hat{\psi}(s)\right]} \delta(x - x_m)\hat{\rho}(x, s), \quad (8)
$$

where parameters b and γ correspond to the three-dimensional parameters $\tilde{b}$ and $\tilde{\gamma}$, respectively. The relations between the 'one-dimensional' and 'three-dimensional' parameters are not important here, and will be discussed in detail elsewhere. We mention here that γ depends on the value of $\tilde{\gamma}$ as well as the concentration of particles A on the wall which bounds the system.

We solve Eq. (8) by means of the Fourier transform method. After calculations, this solution reads, in terms of the Laplace transform, as

$$
\hat{\rho}(x, s; x_0) = \frac{a(s)}{2bs} e^{-\frac{a(s)|x - x_0|}{b}} - \frac{a(s)}{2bs} e^{-\frac{a(s)|2x_m - x - x_0|}{b}} \left[1 - \frac{1}{1 + \frac{\hat{\psi}(s) - \hat{\psi}(s + \gamma)}{4\sqrt{\hat{\psi}(s)\left[1 - \hat{\psi}(s)\right]}}} \right],
$$
$$
(9)
$$

where

$$
a(s) = \sqrt{\frac{1 - \hat{\psi}(s)}{\hat{\psi}(s)}} . \quad (10)
$$

In the following consideration, we take the Laplace transform of waiting time distribution in the following form

$$
\hat{\psi}(s) = e^{-\tau_\alpha s^\alpha} . \quad (11)
$$

For small values of s, there is

$$
\hat{\psi}(s) \approx 1 - \tau_\alpha s^\alpha . \quad (12)
$$

From Eqs. (9), (10), and (12), within the limit of small values of s, we obtain (here $x, x_0 < x_m$)

$$\hat{\rho}(x, s; x_0) = \frac{1}{2\sqrt{D_\alpha}s^{1-\alpha/2}}e^{-\frac{s^{\alpha/2}|x-x_0|}{\sqrt{D_\alpha}}}$$

$$-\frac{1}{2\sqrt{D_\alpha}s^{1-\alpha/2}}e^{-\frac{s^{\alpha/2}(2x_m-x-x_0)}{\sqrt{D_\alpha}}}\left[1 - \frac{4\sqrt{D_\alpha}s^{\alpha/2}}{1-e^{-\tau_\alpha\gamma^\alpha}}\right], \quad (13)$$

where $D_\alpha = b^2/\tau_\alpha$.

Concentration profiles can be calculated using the following formula $C(x, t) = \int_{-\infty}^{x_m} C(x_0, t)\rho(x, t; x_0)dx_0$, which in terms of Laplace transform reads

$$\hat{C}(x, s) = \int\limits_{-\infty}^{x_m} C(x_0, 0)\hat{\rho}(x, s; x_0)dx_0. \quad (14)$$

Let us assume that at the initial moment $C(x, 0) = C_0$, $-\infty < x < x_m$, so we obtain

$$\hat{C}(x, s) = \frac{C_0}{s} - \frac{C_0}{s}e^{-\frac{s^{\alpha/2}(x_m-x)}{\sqrt{D_\alpha}}}$$

$$+\frac{2C_0\sqrt{\tau_\alpha}}{s^{1-\alpha/2}\left[1-e^{-\tau_\alpha\gamma^\alpha}\right]}e^{-\frac{s^{\alpha/2}(x_m-x)}{\sqrt{D_\alpha}}}. \quad (15)$$

Let us note that the first term on the right-hand side of Eq. (15) corresponds to the initial concentration, which is reduced by two following terms.

The amount of substance which vanished in the time interval $(0, t)$ due to chemical reactions, denoted here by $M(t)$, can be calculated by means of the following formula $M(t) = \int_{-\infty}^{x_m}[C(x, 0) - C(x, t)]dx$, which in terms of Laplace transform reads $\hat{M}(s) = \int_{-\infty}^{x_m}[C(x, 0)/s - \hat{C}(x, s)]dx$. Using the above formula and Eq. (15), we obtain

$$\hat{R}(s) = \frac{C_0\sqrt{D_\alpha}}{s^{1+\alpha/2}} - \frac{4C_0\sqrt{D_\alpha}\tau_\alpha}{s^{1-\alpha/2}\left[1-e^{-\tau_\alpha\gamma^\alpha}\right]}. \quad (16)$$

To obtain the functions over a long time limit, which is what interested us the most, we compute the inverse Laplace transform of Eqs. (15) and (16) by means of the following formulae $\mathcal{L}^{-1}\left\{1/s^{\nu+1}\right\} = t^\nu/\Gamma(\nu+1)$, where $\nu > -1$, $\mathcal{L}^{-1}\left\{1/s\right\} = 1$ and [22]

$$\mathcal{L}^{-1}\left\{s^\nu e^{-as^\beta}\right\} \equiv f_{\nu,\beta}(t; a) = \frac{1}{t^{1+\nu}}\sum_{k=0}^{\infty}\frac{1}{k!\,\Gamma(-k\beta-\nu)}\left(-\frac{a}{t^\beta}\right)^k, \quad (17)$$

($a > 0$), $f_{\nu,\rho}(t;a)$ can be also expressed by the Fox function. Finally, we obtain

$$
\begin{aligned}
C(x,t) &= C_0 \left[1 - f_{-1,\alpha/2}\left(t; \frac{x_m - x}{\sqrt{D_\alpha}}\right) \right] \\
&\quad + \frac{2C_0\sqrt{\tau_\alpha}}{1 - e^{-\tau_\alpha\gamma^\alpha}} f_{-1+\alpha/2,\alpha/2}\left(t; \frac{x_m - x}{\sqrt{D_\alpha}}\right) ,
\end{aligned}
\tag{18}
$$

and

$$
M(t) = \frac{C_0\sqrt{D_\alpha}}{\Gamma(2 + \alpha/2)} t^{1+\alpha/2} - \frac{4C_0\sqrt{D_\alpha}\tau_\alpha}{\left[1 - e^{-\tau_\alpha\gamma^\alpha}\right]\Gamma(2 - \alpha/2)} t^{1-\alpha/2} .
\tag{19}
$$

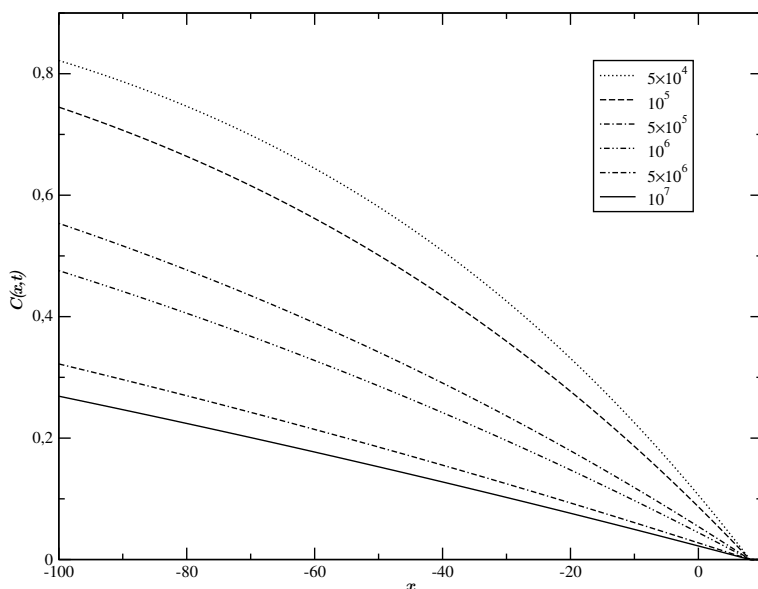The examples of the plots of functions (18) are presented in Fig. 1.

Fig. 1. The concentration profiles calculated for $\alpha = 0.6$, $D_\alpha = 1.2$, $\tau_\alpha = 12.0$, $\gamma = 0.1$ and for times given in the legend, all quantities are given in arbitrarily chosen units.

4. Final remarks

The main results presented in this paper are Eqs. (18) and (19). They show influence of the subdiffusive transport on the intensity of chemical reactions. Our theoretical study was based on the model adapted from the one presented in [12, 13]. Functions (18) and (19), which were obtained for

$t \gg 1/\gamma$ show that the crucial role on the subdiffusion-reaction process is played by the subdiffusion parameter α. The considerations were performed for chemical reaction (1), but we suppose that qualitatively similar results will be obtained for more complicated chemical reactions.

The choice of the system under consideration was not obvious. Namely, the concentration profiles calculated for this system can be verified experimentally, since experimental profiles can be obtained by means of the interferometric method of concentration measurements. We mention here that this method has been used in the experimental study of sugar subdiffusion in gel (water solution of agarose). We add that the functions (18) and (19) can be also used to describe subdiffusion in real biological systems, in which a membrane contains chemically active objects (see for example [23]).

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