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# Cattaneo-type subdiffusion-reaction equation

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Subdiffusion in a system in which mobile particles $A$ can chemically react with static particles $B$ according to the rule $A + B \to B$ is considered within a persistent random-walk model. This model, which assumes a correlation between successive steps of particles, provides hyperbolic Cattaneo normal diffusion or fractional subdiffusion equations. Starting with the difference equation, which describes a persistent random walk in a system with chemical reactions, using the generating function method and the continuous-time random-walk formalism, we will derive the Cattaneo-type subdiffusion differential equation with fractional time derivatives in which the chemical reactions mentioned above are taken into account. We will also find its solution over a long time limit. Based on the obtained results, we will find the Cattaneo-type subdiffusion-reaction equation in the case in which mobile particles of species $A$ and $B$ can chemically react according to a more complicated rule.

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## I. INTRODUCTION

Subdiffusion-reaction equations have been studied extensively during the last decade [1–14]. Subdiffusion occurs in a medium where the mobility of particles is strongly hindered due to the internal structure of the medium as, for example, in porous media or gels [15,16]. Subdiffusion can be treated as a random-walk process, which is characterized by the relation

$$\langle(\Delta x)^2\rangle = \frac{2D_\alpha}{\Gamma(1+\alpha)}t^\alpha , \qquad (1)$$

for $0 < \alpha < 1$, for $\alpha = 1$, one deals with normal diffusion, $\langle(\Delta x)^2\rangle$ denotes a mean square displacement of a random walker, $D_\alpha$ is a subdiffusion coefficient, $\Gamma$ denotes the Gamma function. Subdiffusion is non-Markovian stochastic process, different from normal diffusion. However, as was shown in Ref. [17], there is a non-Markovian process that provides the relation Eq. (1) in which $\alpha = 1$. Thus, it seems to be a good idea to include a stochastic interpretation in the definition of anomalous diffusion together with the relation Eq. (1). Such a simple interpretation has a random walk, which is used in our considerations. We mention here that the random-walk model is universal; for example, it has been used to derive normal diffusion-reaction equations [18–20] or subdiffusion-reaction equations [9,12–14,21–23].

The most commonly used differential equation describing anomalous diffusion is the following equation with the Riemann-Liouville fractional derivative:

$$\frac{\partial}{\partial t}P(x,t) = D_\alpha \frac{\partial^{1-\alpha}_{\mathrm{RL}}}{\partial t^{1-\alpha}}\frac{\partial^2}{\partial x^2}P(x,t). \qquad (2)$$

The derivative is defined for $\alpha > 0$ as follows [24,25]:

$$\frac{d^\alpha_{\mathrm{RL}}}{dt^\alpha}f(t) = \frac{1}{\Gamma(n-\alpha)}\frac{d^n}{dt^n}\int_0^t (t-t')^{n-\alpha-1}f(t')dt', \qquad (3)$$

where $n$ is a natural number fulfilled, $\alpha \leqslant n < \alpha + 1$. Equation (2) was derived within the continuous-time random-walk formalism [15,26]. This equation can be transformed to the following equation with the Caputo fractional derivative [see Eqs. (A7) and (A8), Appendix A]:

$$\frac{\partial^\alpha_C}{\partial t^\alpha}P(x,t) = D_\alpha \frac{\partial^2}{\partial x^2}P(x,t), \qquad (4)$$

where [25]

$$\frac{d^\alpha_C}{dt^\alpha}f(t) = \frac{1}{\Gamma(n-\alpha)}\int_0^t (t-t')^{n-\alpha-1}\frac{d^n}{dt'^n}f(t')dt', \qquad (5)$$

where $n-1 < \alpha \leqslant n$. The fundamental solution to Eqs. (2) and (4) (the Green function), which is defined by its initial condition $P(x,t;x_0) = \delta_{x,x_0}$ (in the following $\delta_{x,x_0}$ denotes both the Dirac-$\delta$ function for continuous variables and the Kronecker symbol for discrete ones), is interpreted as a probability density to find a random walker at point $x$ after time $t$ under the condition that its initial position is $x_0$. However, it is well known that the Green function of Eq. (2) has a nonphysical property. Namely, it has nonzero values for any $x$ at $t > 0$. This means that some of the particles move with an arbitrarily chosen large velocity. To avoid this absurdity the persistent random-walk model was proposed [27–29]. Under the assumption that the actual random walker's step is correlated with the previous one, which means that the direction of successive steps is retained with some probability, for the normal diffusion process, one obtains the following differential hyperbolic Cattaneo equation:

$$\tau\frac{\partial^2}{\partial t^2}P(x,t) + \frac{\partial}{\partial t}P(x,t) = D\frac{\partial^2}{\partial x^2}P(x,t), \qquad (6)$$

where $D$ is the normal diffusion coefficient. A solution to this equation is above zero in a finite domain only, which ensures that a random walker's velocity is limited. We mention here that one of the simplest interpretations of this process is that the probability flux is delayed over time by parameter $\tau$ with respect to the probability gradient,

$$J(x,t+\tau) = -D\frac{\partial}{\partial x}P(x,t). \qquad (7)$$

Assuming $\tau \ll t$, there is

$$J(x,t) + \tau\frac{\partial}{\partial t}J(x,t) = -D\frac{\partial}{\partial x}P(x,t). \qquad (8)$$

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Combining the above equation with the continuity equation,

$$\frac{\partial}{\partial t}P(x,t)=-\frac{\partial}{\partial x}J(x,t), \tag{9}$$

one obtains Eq. (6). For $\tau=0$, we have the normal diffusion equation. The generalization of Eq. (6) to the subdiffusion system is not obvious. As was discussed in Ref. [30], there are various forms of such a generalization, which are not equivalent to each other.

The situation is more complicated when diffusing particles of species $A$ and $B$ can chemically react with each other according to the formula $n_A A+n_B B\longrightarrow\emptyset$ (inert). Phenomenologically, the diffusion-reaction equations are derived on the basis of a normal diffusion equation (without the persistent effect, $\tau=0$) by subtracting a reaction term $\Pi(C_A,C_B)$ from the right-hand side of Eq. (6). Within the mean-field approximation the reaction term reads [2]

$$\Pi(C_A,C_B)=kC_A^{n_A}C_B^{n_B}, \tag{10}$$

where $k$ is a reaction rate, and $C_{A,B}$ denotes substance concentrations. Such a procedure provides the standard normal diffusion-reaction equation,

$$\frac{\partial}{\partial t}C_i(x,t)=D_i\frac{\partial^2}{\partial x^2}C_i(x,t)-n_i kC_A^{n_A}C_B^{n_B}, \tag{11}$$

where $i=A,B$. A similar procedure was applied to obtain a subdiffusion-reaction equation. However, there arose a problem concerning which of the subdiffusion equations, Eq. (2) or Eq. (4), should be taken into account. In Ref. [6] the reaction term was subtracted from the right-hand side of Eq. (2), whereas in Ref. [5] it was shown that this term should be subtracted from the right-hand side of Eq. (4). The above-mentioned versions of subdiffusion-reaction equations describe the processes whose dynamics differ from each other (see Appendix B). The latter version of the equation has been considered in many papers, for example, in Refs. [3,4]. We mention here that another version of the subdiffusion-reaction equation was derived in Ref. [8].

The character of transport processes (normal diffusion or subdiffusion) strongly influences the dynamics of chemical reactions [5,7]. There arises a question concerning the influence of the persistent random walk effect on the subdiffusion-reaction process. In some physical systems this effect plays an important role. For example, as we showed in Ref. [31], in electrochemical systems the Nyquist plots of subdiffusive impedance strongly depend on parameter $\alpha$ as well as on the parameter described by persistent random walk effect. A similar effect can occur in a system in which subdiffusive particles of species $A$ can chemically react with particles $B$. The reason is that the reaction efficiency depends on the particle's concentration. The probability that the reaction between particles $A$ and $B$, which are located close to each other, occurs in some time interval strongly depends on the character of particles' transport mechanism [5]. Moreover, as we will discuss later, the reaction rate for the persistent random walk is changed compared to the nonpersistent one.

In our paper, we derive a Cattaneo-type subdiffusion-reaction equation that describes the persistent subdiffusive random walk with a chemical reaction of type $A+B\rightarrow B$. We assume that the three-dimensional system is homogeneous in the plane perpendicular to the $x$ axis, so it can be treated as a one-dimensional system. The particles $B$ are assumed to be immobile and all of them are located at the position $x_r$. In practice, this problem can be treated as a particle's random walk on a lattice with a single immobile trap. This system was chosen for theoretical study for the following reasons. First, the concentration of particles $B$ does not change over time; thus, the analytical treatment of the problem is relatively simpler than for other systems. The results obtained can be treated as the background to finding a more general equation for the case of chemical reactions $n_A A+n_B B\rightarrow\emptyset$ in a system with both mobile $A$ and $B$ species. Second, the model can be used for a theoretical description of the process in a system in which the reaction is ruled according to $A+B\rightarrow\emptyset$ if the concentration of static particles $B$ (located at the permeable membrane) remains "almost constant," which is achieved if the concentration is very large compared to the concentration of particles $A$ [32]. Such a model can be useful to describe transport in a porous medium with a chemical reaction occurring at the medium surface [33]. Moreover, the time evolution of the concentration of $A$ particles can be measured experimentally, for example, by means of the laser interferometric method [16], which gives the possibility of the experimental verification of the theoretical subdiffusion-reaction model. We add that the experimental method of concentration measurement mentioned above is effective for the (sub)diffusion-reaction systems with only one mobile substance.

The paper is organized as follows. In Sec. II we consider a nonpersistent random walk in a system in which a particle $A$ can be absorbed with some probability into an arbitrary chosen site (this situation corresponds to the reaction $A+B\rightarrow B$ occurring at this site). Starting from difference equations with discrete time and space variables, we will derive the fractional subdiffusion-reaction equation for continuous variables. Next, we will generalize the obtained equation for the case of mobile $A$ and $B$ particles, which can chemically react according to a more complicated rule. The main aim of this section is to check if the method used in this paper provides the subdiffusion-reaction equation, which was derived in Ref. [5] for the nonpersistent random-walk model. In Sec. III we will use a procedure to find the subdiffusion-reaction equation within the persistent random walk model. We will also find the solution to the equation over a long time limit for the case of the reaction $A+B$ (static) $\rightarrow B$ (static). The discussion of various aspects of the model will be presented in Sec. IV. The details of the calculations and some useful formulas will be presented in the four Appendices.

## II. SUBDIFFUSION-REACTION EQUATION

We consider the nonpersistent random walk in a discrete system in which a random walker $A$ can react with a static particle $B$ located at $m_r$, according to the formula $A+B\rightarrow B$. The subdiffusion-reaction equation was already derived using the random-walk model with a continuous time, and here we will show that the lattice random-walk model with discrete time (which is represented by the number of steps) provides the subdiffusion-reaction equation equivalent to the one derived in Ref. [5].

### A. General equation

Let $P_n(m;m_0)$ denote a probability of finding a particle $A$, which arrives at site $m$ at the $n$th step, $m_0$ is the initial position of the particle, $P_0(m;m_0)=\delta_{m,m_0}$. If a particle arrives at the site $m_r$ then it can react during its stay at site $m_r$ with a particle $B$ with the probability $R$. This process is described by the following difference equation:

$$P_{n+1}(m;m_0)=\tfrac{1}{2}P_n(m+1;m_0)+\tfrac{1}{2}P_n(m-1;m_0)\\ -\delta_{m,m_r}RP_n(m;m_0). \tag{12}$$

This equation is usually solved by means of the generating function method [34,35]. The generating function is defined as

$$S(m,z;m_0)=\sum_{n=0}^{\infty}z^nP_n(m;m_0). \tag{13}$$

From Eqs. (12) and (13), we obtain

$$S(m,z;m_0)-P_0(m;m_0)\\ =\frac{z}{2}S(m+1,z;m_0)+\frac{z}{2}S(m-1,z;m_0)\\ -z\delta_{m,m_r}RS(m,z;m_0). \tag{14}$$

The probability of finding the particle at site $m$ for a continuous time equals $P(m,t;m_0)=\sum_{n=0}^{\infty}P_n(m;m_0)\Phi_n(t)$, where $\Phi_n(t)$ is the probability that a particle, starting from $m_0$, reaches site $m$ in $n$ steps. The function $\Phi_n$ depends on the waiting time probability density $\omega(t)$ needed to take the particle's next step. In terms of the Laplace transform, $L[f(t)]\equiv\hat{f}(s)=\int_0^{\infty}\exp(-st)f(t)dt$, one obtains [15] $\hat{\Phi}_n(s)=[1-\hat{\omega}(s)]\hat{\omega}^n(s)/s$, which, together with Eq. (13), provides

$$\hat{P}(m,s;m_0)=\frac{1-\hat{\omega}(s)}{s}S[m,\hat{\omega}(s);m_0]. \tag{15}$$

When a particle $A$ reaches the site $m_r$, it can react with a particle $B$ if these particles meet in a reaction region. We note that a discrete system is an approximation of a continuous one; a discrete site represents an interval in the continuous model. Thus, it is not obvious that the particles really meet even when they are assigned to the same discrete site (this problem was discussed in more detail in Ref. [23]).

Let us assume that the distribution function of the reaction is

$$\psi(t)=\gamma\exp(-\gamma t), \tag{16}$$

where $\gamma$ is the reaction rate. The choice of Eq. (16), which seems to be the most often used distribution to describe the reaction process, is motivated by the Kramer's reaction rate model. The waiting-time distribution that the reaction will produce if particles $A$ and $B$ meet in a reaction region is as follows:

$$\psi_r(t)=\gamma\exp(-\gamma t)\left[1-\int_0^t\omega(t')dt'\right], \tag{17}$$

the last term on the right-hand side of the above equation (in the square brackets) represents the probability that the particle does not change its position in the time interval $(0,t)$. The probability that the particle reacts with single-particle $B$ equals

$$R=p\int_0^{\infty}\psi_r(t')dt'=p[1-\hat{\omega}(\gamma)], \tag{18}$$

where $p$ is the probability that particle $A$, which has jumped to the site $m_r$, meets a particle $B$ in a reaction region. Let us assume that the distance between discrete sites equals $\Delta x$. To pass from a discrete to a continuous space variable one puts $x=m\Delta x$, $P(m,t;m_0)=(\Delta x)P(x,t;x_0)$, and assumes that $\Delta x$ goes to zero. Taking into account the following approximation

$$P(x\pm\Delta x,t;x_0)=P(x,t;x_0)\pm(\Delta x)\frac{\partial}{\partial x}P(x,t;x_0)\\ +\frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}P(x,t;x_0), \tag{19}$$

and Eqs. (14)–(18), with $z=\hat{\omega}(s)$, we obtain the following equation:

$$[1-\hat{\omega}(s)]\hat{P}(x,s;x_0)-\frac{1-\hat{\omega}(s)}{s}P(x,0;x_0)\\ =\hat{\omega}(s)\frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{P}(x,s;x_0)\\ -\delta_{x,x_r}R\hat{\omega}(s)\hat{P}(x,s;x_0). \tag{20}$$

The above equation, written in terms of Laplace transform, is the basis for further considerations. In the next subsection we will find the equation for a continuous time variable.

### B. Continuous-time random-walk approach

Subdiffusion can be interpreted as a random walk in which the mean waiting time between a particle's successive steps is infinite, whereas all the moments of the step length distribution are finite. Within the continuous-time random-walk formalism, function $\hat{\omega}(s)$ is considered in a limit of small $s$, which, according to the Tauberian theorems, corresponds to the limit of a large time $t$, is

$$\hat{\omega}(s)\approx 1-\tau_\alpha s^\alpha. \tag{21}$$

In our approach, the length of the particle's step is not a random variable, but we can choose the parameter $\Delta x$ in such a way that the coefficient $(\Delta x)^2/2$ equals the variation of step-length distribution, which can be involved into a stochastic model. The definition of the subdiffusion coefficient then reads

$$D_\alpha=\frac{(\Delta x)^2}{2\tau_\alpha}. \tag{22}$$

The parameters $\alpha$ and $D_\alpha$ control subdiffusion and are measured experimentally [16]. The parameter $\Delta x$ is related to $\tau_\alpha$ by Eq. (22). Thus, we consider both $\Delta x$ and $\tau_\alpha$ as "small parameters". From Eqs. (18) and (21), over the limit of small values of $\tau_\alpha$ we obtain $\tilde{R}\equiv R/\tau_\alpha=\gamma^\alpha$. From Eqs. (20)–(22), keeping the terms of the first order with respect to $\tau_\alpha$, after simple calculations we obtain

$$\frac{\partial_C^\alpha}{\partial t^\alpha}P(x,t;x_0)=D_\alpha\frac{\partial^2}{\partial x^2}P(x,t;x_0)-\tilde{R}P(x,t;x_0). \tag{23}$$

Let us generalize Eq. (23) to a system containing a large number of particles $A$ and $B$. Using the relation $C_A(x,t)=N_AP(x,t)$, where $C_A$ is the concentration of the particles $A$, $N_A$ denotes the initial number of particles $A$ in the system ($N_A \gg 1$), we find that Eq. (23) is fulfilled by concentration $C_A$ and the reaction term reads $\Pi(C_A) = \tilde{R}C_A(x,t)$. The function $\tilde{R}$ is now proportional to the concentration of $B$ particles, thus we obtain $\Pi(C_A,C_B) = \gamma^\alpha C_A(x,t)C_B(x_r)$. The essential assumption is that the above reaction term is correct in the case of mobile particles $B$, which react with particle $A$ according to the more general formula $n_A A + n_B B \to \emptyset$. In general, within the mean-field approach the reaction term is proportional to the probability that $n_A$ particles of species $A$ and $n_B$ particles of species $B$ meet in such a small volume that chemical reaction is possible with a probability controlled by the reaction rate $k$ (in the considerations presented above we have $k = \gamma^\alpha$). Thus, the arguments presented above suggest that the equation

$$\frac{\partial_C^\alpha}{\partial t^\alpha} C_i(x,t) = D_\alpha \frac{\partial^2}{\partial x^2} C_i(x,t) - n_i \Pi(C_A,C_B), \qquad (24)$$

where $i = A,B$ and the reaction term is given by Eq. (10), is the generalization of Eq. (23).

## III. CATTANEO-TYPE SUBDIFFUSION-REACTION EQUATION

### A. General equation

Let $P_n^+(m)$, $P_n^-(m)$ denote probabilities that the particles arrive at site $m$ at step $n$ with a positive or negative velocity, respectively (in the following we will skip the symbol $m_0$ for shortening the notation); $\beta$ is a probability that a particle changes its velocity sense after arriving at site $m$. The persistent random walk with a reaction with a particle $B$ located at $m_r$ is described by the following equations [29]:

$$\begin{aligned} P_{n+1}^+(m) &= (1-\beta)P_n^+(m-1) + \beta P_n^-(m-1) \\ &\quad - R_\beta P_n^+(m)\delta_{m,m_r}, \end{aligned} \qquad (25)$$

$$\begin{aligned} P_{n+1}^-(m) &= (1-\beta)P_n^-(m+1) + \beta P_n^+(m+1) \\ &\quad - R_\beta P_n^-(m)\delta_{m,m_r}. \end{aligned} \qquad (26)$$

As in the previous section, we solve the equations by means of the generating function method.

The $\beta$ parameter strongly influences the random walk. Consequently, it is natural to consider the influence of this parameter on the reaction rate coefficient. To do this we should refer to a particular model of a chemical reaction. Various theoretical reaction models applied to the reaction $A + B\,(\text{static}) \to B\,(\text{static})$ assume that the particle $A$ overcomes a potential barrier during its movement along the reaction coordinate axis [36,37]. In many models, such as the transition state theory, the coefficient is proportional to the Arhenius factor $e^{-\Delta E_b/(k_B T)}$, where $\Delta E_b$ is the height of a potential barrier (measured from the level of particle's energy), which should be passed through the particle for a reaction to occur, $k_B$ is the Boltzmann constant, $T$ denotes temperature. However, the probability of passing the barrier depends on a particle's energy. If the particle comes to the site $m_r$ and its velocity sense is not changed after arriving at this site, we assume that the reaction occurs with reaction rate $\gamma_1$, but if the particle's velocity sense is changed, the energy of the particle will be lower than in the previous case, thus the reaction occurs with the reaction rate $\gamma_2$, $\gamma_2 < \gamma_1$. The probability of the "choice" of the reaction rate depends on $\beta$. Thus, we postulate that

$$R_\beta = p(1-\beta)[1 - \hat{\omega}(\gamma_1)] + p\beta[1 - \hat{\omega}(\gamma_2)]. \qquad (27)$$

The motivation of Eq. (27) based on a more detailed phenomenological model is as follows [36–48]. The position of nuclei of $N$ particles, which constitute reactants $A$ and $B$, is represented by a point $\mathbf{r} = (r_1,r_2,\dots,r_{3N})$. In the reaction region the particles interact with each other by means of the internal potential $U(\mathbf{q})$, where $\mathbf{q}$ is a vector of particles' internal coordinates. The state of molecules is then represented by a point $Q$ on a hypersurface in ($\mathbf{q}$, energy) coordinate system, $Q$ performs random walk due to energy fluctuations. Initially this point is located at $Q_0$ inside a reactant well on the hypersurface. The reaction rate can be defined as $\gamma = 1/(2t_M)$, where $t_M$ is a mean first-passage time from $Q_0$ to a separatrix located between the reaction well and a product well. The velocity sense of particle $A$ located in its initial position $Q_0$ influences the mean first time to achieve the separatrix, and consequently influences the reaction rate. The specially chosen way, which minimizes the energy, is called the reaction way. This way joins the points $Q_0$ and $Q_P$ (which is located in a product well) on the energy hypersurface. The random walk of point $Q$ on this way is described by the Klein-Kramers equation. This equation provides two values of the reaction rate $\gamma_1$ and $\gamma_2$, which depend on a particle's velocity sense at point $Q_0$.

Proceeding similarly as in the previous case (see Sec. II), Eqs. (25) and (26), transformed to the continuous variables $(x,t)$, in terms of Laplace transform read

$$\begin{aligned} \hat{P}^+(x,s) - \frac{1-\hat{\omega}(s)}{s}P^+(x,0) &= \hat{\omega}(s)\Bigg\{(1-\beta)\left[\hat{P}^+(x,s) - (\Delta x)\frac{\partial}{\partial x}\hat{P}^+(x,s) + \frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{P}^+(x,s)\right] \\ &\quad + \beta\left[\hat{P}^-(x,s) - (\Delta x)\frac{\partial}{\partial x}\hat{P}^-(x,s) + \frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{P}^-(x,s)\right]\Bigg\} - R_\beta \hat{P}^+(x,s)\delta_{x,x_r}, \end{aligned} \qquad (28)$$

$$\begin{aligned} \hat{P}^-(x,s) - \frac{1-\hat{\omega}(s)}{s}P^-(x,0) &= \hat{\omega}(s)\Bigg\{(1-\beta)\left[\hat{P}^-(x,s) + (\Delta x)\frac{\partial}{\partial x}\hat{P}^-(x,s) + \frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{P}^-(x,s)\right] \\ &\quad + \beta\left[\hat{P}^+(x,s) + (\Delta x)\frac{\partial}{\partial x}\hat{P}^+(x,s) + \frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{P}^+(x,s)\right]\Bigg\} - R_\beta \hat{P}^-(x,s)\delta_{x,x_r}. \end{aligned} \qquad (29)$$

The probability density of finding a particle at site $x$ is

$$\hat{P}(x,s)=\hat{P}^{+}(x,s)+\hat{P}^{-}(x,s). \tag{30}$$

Let us define the flux as follows:

$$\hat{J}(x,s)=\hat{P}^{+}(x,s)-\hat{P}^{-}(x,s). \tag{31}$$

Adding and next subtracting Eqs. (28) and (29), taking into account Eqs. (30) and (31), we obtain

$$\begin{aligned}&[1-\hat{\omega}(s)]\hat{P}(x,s)-\frac{1-\hat{\omega}(s)}{s}P(x,0)\\&\quad=\hat{\omega}(s)\left[\frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{P}(x,s)-(1-2\beta)(\Delta x)\frac{\partial}{\partial x}\hat{J}(x,s)\right]\\&\qquad-\hat{\omega}(s)\delta_{x,x_r}R_\beta\hat{P}(x,s),\end{aligned} \tag{32}$$

and

$$\begin{aligned}&[1-(1-2\beta)\hat{\omega}(s)]\hat{J}(x,s)-\frac{1-\hat{\omega}(s)}{s}J(x,0)\\&\quad=-\hat{\omega}(s)(\Delta x)\frac{\partial}{\partial x}\hat{P}(x,s)+(1-2\beta)\hat{\omega}(s)\\&\qquad\times\frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{J}(x,s)-\hat{\omega}(s)\delta_{x,x_r}R_\beta\hat{J}(x,s).\end{aligned} \tag{33}$$

The assumption that the probability of a particle's first step being taken with negative velocity is equal to the probability of a particle's first step being taken with positive velocity gives $J(x,0)=0$. Combining Eqs. (32) and (33), we obtain the following equation, which is the base for the derivation of differential subdiffusion-reaction equations for various probability densities $\omega$:

$$\begin{aligned}&[1-\hat{\omega}(s)][1-(1-2\beta)\hat{\omega}(s)]\left[\hat{P}(x,s)-\frac{P_0(x)}{s}\right]\\&\quad=\hat{\omega}(s)[1+(1-2\beta)\hat{\omega}(s)]\frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{P}(x,s)\\&\qquad+(1-2\beta)\hat{\omega}(s)[1-\hat{\omega}(s)]\frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\left[\hat{P}(x,s)-\frac{P_0(x)}{s}\right]\\&\qquad-R_\beta\delta_{x,x_r}\hat{\omega}(s)\left\{[1-\hat{\omega}(s)]\left[\hat{P}(x,s)-\frac{P_0(x)}{s}\right]\right.\\&\qquad+[1-(1-2\beta)\hat{\omega}(s)]\hat{P}(x,s)\\&\qquad\left.-\,2(1-\beta)\frac{(\Delta x)^2}{2}\frac{\partial^2}{\partial x^2}\hat{P}(x,s)-\hat{\omega}(s)R_\beta\delta_{x,x_r}\hat{P}(x,s)\right\}.\end{aligned} \tag{34}$$

In Eq. (34) we have omitted a term containing the fourth-order derivative of the function $\hat{P}(s,t)$ with respect to the $x$ variable. The reason is this term is much smaller compared to the term with a derivative of a second order, which can be easily noted when continuous-time random-walk formalism is used to derive a (sub)diffusion equation [15].

### B. Continuous-time random-walk approach

Parameter $\beta$ controls the correlation of jumps, namely the correlation coefficient is $\mathrm{cor}=\langle(\Delta x)_n(\Delta x)_{n+1}\rangle=(1-2\beta)(\Delta x)^2$, where $(\Delta x)_n$ is the particle's displacement during its $n$th step [28,49]. Thus, the case of $\beta=1/2$ corresponds to the "ordinary" nonpersistent random walk, described by the (sub)diffusion equation. In the various forms of the Cattaneo subdiffusion equation, a parameter analogous to $\tau$ occurring in Eq. (6) is present (in the following we denote this parameter by $\tilde{\tau}_\alpha$). Motivated by the above-mentioned facts, we assume that all terms containing $\tilde{\tau}_\alpha$ in the Cattaneo subdiffusion-reaction equation should vanish if $\beta=1/2$ and the equation obtained take the form of a "standard" subdiffusion-reaction Eq. (24) with the reaction term Eq. (10). Moreover, in different versions of the Cattaneo subdiffusion equation that have been considered until now, the terms of the order $\Theta(\tilde{\tau}_\alpha^2)$ do not occur [30].

In order to derive a new equation from Eq. (34), which fulfills the above conditions, we set the following rules:

(1) the approximation of the function $\hat{\omega}(s)$ is given by Eq. (21);

(2) the parameters $\alpha$ and $D_\alpha$ [the last one is defined by Eq. (22)] are the same for both persistent and nonpersistent models, moreover

$$(\Delta x)^2=2D_\alpha\tau_\alpha; \tag{35}$$

(3) according to Eqs. (21) and (27), for small $\tau_\alpha$,

$$R_\beta=\tau_\alpha\tilde{R}_\beta, \tag{36}$$

where $\tilde{R}_\beta=p(1-\beta)\gamma_1^\alpha+p\beta\gamma_2^\alpha$;

(4) in the obtained equation, we keep all terms up to the first order with respect to $\tau_\alpha$; the terms of the second order with respect to $\tau_\alpha$ are kept only in terms which vanish at $\beta=1/2$. The other terms are neglected.

Taking into account the above points, inverse Laplace transform Eqs. (A4) and (A5) (Appendix A), and the following formula (here $0<\alpha<1$) [25],

$$\frac{\partial^\alpha_{\mathrm{RL}}}{\partial t^\alpha}P(x,t)=\frac{\partial^\alpha_C}{\partial t^\alpha}P(x,t)+\frac{t^{-\alpha}}{\Gamma(1-\alpha)}P(x,0), \tag{37}$$

we obtain from Eq. (34) the following subdiffusion-reaction equation:

$$\begin{aligned}&(1-2\beta)\tau_\alpha\frac{\partial^{2\alpha}_C}{\partial t^{2\alpha}}P(x,t)+2\beta\frac{\partial^\alpha_C}{\partial t^\alpha}P(x,t)\\&\quad=2(1-\beta)D_\alpha\frac{\partial^2}{\partial x^2}P(x,t)-(1-2\beta)\tau_\alpha D_\alpha\frac{\partial^2}{\partial x^2}\frac{\partial^\alpha_C}{\partial t^\alpha}P(x,t)\\&\qquad-\tilde{R}_\beta\delta_{x,x_r}\left[2\beta P(x,t)+(1-2\beta)\tau_\alpha\frac{\partial^\alpha_{RL}}{\partial t^\alpha}P(x,t)\right.\\&\qquad\left.-(1-2\beta)\tau_\alpha D_\alpha\frac{\partial^2}{\partial x^2}P(x,t)\right].\end{aligned} \tag{38}$$

### C. The solution

The general form of the solution to Eq. (38) in terms of Laplace and Fourier transforms is given in Appendix C, Eq. (C1). Over a long time limit, the solution given in terms of Laplace transform reads (here $x_r=0$ and $\tilde{R}\neq 0$)

$$\begin{aligned}\hat{P}(x,s)&=\frac{s^{-1+\alpha/2}}{2\sqrt{\tilde{D}_\alpha}}\exp\left(-\frac{|x-x_0|s^{\alpha/2}}{\sqrt{\tilde{D}_\alpha}}\right)\\&\quad-\frac{s^{-1+\alpha/2}}{2\sqrt{\tilde{D}_\alpha}}\frac{\exp\left(-\frac{(|x|+|x_0|)s^{\alpha/2}}{\sqrt{\tilde{D}_\alpha}}\right)}{1+(2\sqrt{\tilde{D}_\alpha}s^{\alpha/2}/\tilde{R})}.\end{aligned} \tag{39}$$

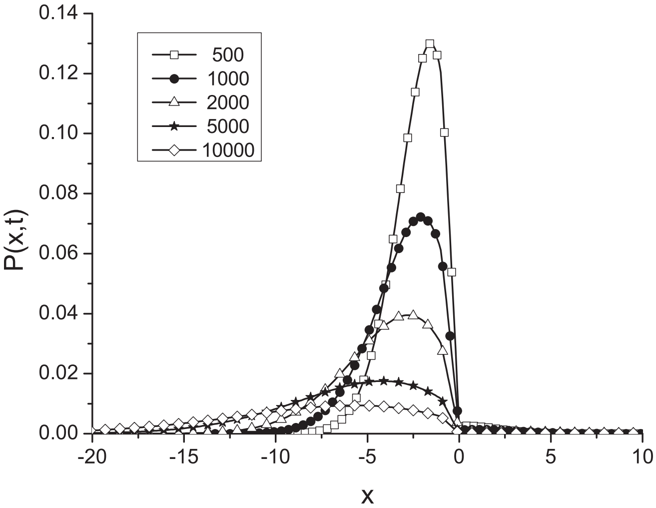

FIG. 1. Function Eq. (41) for various values of time $t$ given in the legend, $D_\alpha = 0.01$, $\alpha = 0.9$, $\beta = 0.6$, $p = 1.0$, $\gamma_1 = 0.5$, $\gamma_2 = 0.2$, $x_0 = -1$, $x_r = 0$ (all quantities are given in arbitrary chosen units).

Using the following formula [50],

$$L^{-1}\{s^\nu \exp(-as^\gamma)\} \equiv f_{\nu,\gamma}(t;a) = \frac{1}{t^{\nu+1}} \sum_{k=0}^{\infty} \frac{1}{k!\Gamma(-k\gamma-\nu)} \left(-\frac{a}{t^\gamma}\right), \tag{40}$$

where $a,\gamma > 0$, we obtain

$$\begin{aligned} P(x,t) = {} & \frac{1}{2\sqrt{\tilde{D}_\alpha}} f_{-1+\alpha/2,\alpha/2}\left(t; \frac{|x-x_0|}{\sqrt{\tilde{D}_\alpha}}\right) \\ & - \frac{1}{2\sqrt{\tilde{D}_\alpha}} \sum_{k=0}^{\infty} \left(-\frac{2\sqrt{\tilde{D}_\alpha}}{\tilde{R}_\beta}\right)^k \\ & \times f_{-1+(k+1)\alpha/2,\alpha/2}\left(t; \frac{|x|+|x_0|}{\sqrt{\tilde{D}_\alpha}}\right), \end{aligned} \tag{41}$$

where

$$\tilde{D}_\alpha = \frac{1-\beta}{\beta} D_\alpha. \tag{42}$$

We add that the mathematical condition of a long time limit is briefly described in Appendix A, in the comment just after Eq. (A9). In Figs. 1 and 2, example plots of function Eq. (41) are presented. Figure 1 shows that the solutions to Eq. (38) over the long time limit behave "almost" in the same way as for the system with an absorbing wall located at $x_r$. The plots presented in Fig. 2 show that the solutions strongly depend on parameter $\beta$.

### D. More general form of subdiffusion-reaction equation

Let us generalize Eq. (38) to a many-particle system containing substances $A$ and $B$. The generalization is based on the interpretation of the subdiffusion-reaction process. If particles $A$ move independently of each other, the particle's concentration, defined as $C_A(x,t) = N_A P(x,t)$, also fulfils Eq. (38), but now the reaction probability $\tilde{R}_\beta$ depends on the concentration of particles $B$. For the reaction $A + B\,(\text{static}) \rightarrow B\,(\text{static})$, if all particles $B$ are located at $x_r$, then $\tilde{R}_\beta = kC_B(x_r)$. To simplify the description let us introduce the function $\Psi$, whose value is proportional to the probability of particles $A$ and $B$ meeting in such a small volume that a chemical reaction is possible; the probability of the reaction is then controlled by the reaction rate $k$. For the considered reaction we have

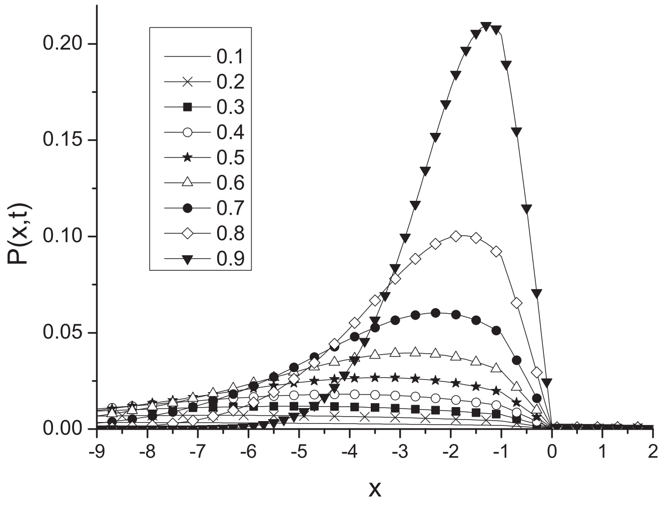

FIG. 2. Function Eq. (41) for various values of probability $\beta$ given in the legend, $t = 2\,000$, the other parameters are the same as described in the legend of Fig. 1.

$$\Pi(C_A,C_B) = k\Psi(x,t), \tag{43}$$

with $\Psi(x,t) = C_A(x,t)C_B(x_r)$. When particles $B$ are mobile, the crucial assumption is that Eq. (43) is still valid and

$$\Psi(x,t) = C_A(x,t)C_B(x,t). \tag{44}$$

Equation (44) is also assumed to be valid for the reaction $A + B \rightarrow \emptyset$.

The parameters $D_\alpha$, $\beta$, and $\tau_\alpha$ are assumed to be defined separately for substances $A$ and $B$, whereas the parameter $\alpha$ is assumed to be the same for both substances. The last assumption is motivated by experiments [16], which suggest that $\alpha$ is determined by the properties of a medium, whereas the others depend on properties of both the particles and medium. As suggested by Eq. (38), for $\beta_{1,2} \neq 0$, the general form of the Cattaneo-type subdiffusion-reaction equation reads

$$\begin{aligned} & \tilde{\tau}_{\alpha,i} \frac{\partial_C^{2\alpha}}{\partial t^{2\alpha}} C_i(x,t) + \frac{\partial_C^\alpha}{\partial t^\alpha} C_i(x,t) \\ & \quad = \tilde{D}_{\alpha,i} \frac{\partial^2}{\partial x^2} C_i(x,t) - \tilde{\tau}_{\alpha,i} D_{\alpha,i} \frac{\partial^2}{\partial x^2} \frac{\partial_C^\alpha}{\partial t^\alpha} C_i(x,t) \\ & \qquad - \Pi_i[C_A,C_B], \end{aligned} \tag{45}$$

where $i = A,B$, $\tilde{\tau}_{\alpha,i} = (1-2\beta_i)\tau_{\alpha,i}/(2\beta_i)$, $\tilde{D}_{\alpha,i} = (1-\beta_i)D_{\alpha,i}/\beta_i$, $C_i(x,t) = N_i P_i(x,t)$, $P_i(x,t)$ is the probability density of finding a particle of species $i$ at position $x$ and time $t$, and $N_i$ denotes the initial number of particles $i$.

There is a problem in finding a proper reaction term $\Pi$. It is not obvious if the position of $\tilde{R}_\beta \equiv \Psi/C_A$ (now depending on the variables $x$ and $t$) is within the reaction term occurring in Eq. (38). More particularly, one should find out whether the derivative operators act on the product $\tilde{R}_\beta C_A$ or on function

$C_A$ alone. To solve this problem, we recall the interpretation of the subdiffusion equation.

Subdiffusion is a non-Markovian process generated by the anomalously long time of a particle's remaining in one position. On the other hand, it looks like some of the particles apparently temporarily "vanish," which means that they temporarily do not take part in the random-walk process. This interpretation is supported by the phenomenological method of deriving the fractional Cattaneo equation. Namely, involving the fractional derivative into the flux equation $J(x,t)+\tau\frac{\partial_C^\alpha}{\partial t^\alpha}J(x,t)=-D\frac{\partial}{\partial x}P(x,t)$, and combining the above equation with the fractional continuity equation $\frac{\partial_C^\alpha}{\partial t^\alpha}P(x,t)=-\frac{\partial}{\partial x}J(x,t)$, we obtain a simplified form of the Cattaneo subdiffusion Eq. (38) without chemical reactions. However, the fractional continuity equation does not achieve the number of particles, which can be interpreted as follows. The approximation of the fractional Caputo derivative Eq. (5) reads [4,24,25]

$$\frac{\partial_C^\alpha}{\partial t^\alpha}C_A(x,t)=\frac{1}{(\Delta t)^\alpha}\left[C_A(x,t)-C_A(x,t-\Delta t)-\sum_{k=1}^{L}w_kC_A(x,t-k\Delta t)\right]-\frac{1}{t^\alpha\Gamma(1-\alpha)}C_A(x,0),\tag{46}$$

where $w_1=\alpha-1, w_k=\alpha(1-\alpha)\ldots(k-1-\alpha)/k!, k\geqslant 2$, $L$ is the memory length. The "apparently vanishing particles" effect is represented by a fractional derivative in Eq. (38) [more particularly, by the last term in square brackets in Eq. (46)] and provides a reduced effective concentration of particles that can be involved in chemical reactions. Thus, the subdiffusive effect regards the functions on which the fractional differential operator acts.

Let us return for a moment to Eq. (38), putting $P(x,t)\to C_A(x,t)$, $\tilde{R}_\beta\to kC_B(x,t)$. If we assume that the second term in the square bracket on the right-hand side of this equation is in the form $kC_B(x,t)\partial_C^\alpha C_A(x,t)/\partial t^\alpha$, the subdiffusion effect does not concern the particles $B$ during the reaction process. The derivative of the second order with respect to $x$ can be approximated as $\partial^2C_i(x,t)/\partial x^2\sim[C_i(x+\Delta x,t)+C_i(x-\Delta x,t)]/2-C_i(x,t)$. This term describes temporal changes in concentration generated by the concentration difference between the concentration measured in $x$ and the mean concentration measured in its vicinity; the velocity of this process is controlled by the subdiffusion coefficient. In this term, the memory effect is not present, but taking into account that a chemical reaction can be present at point $x$ as well as in its vicinity, we assume the following term occurring in Eq. (38) $\partial^2[C_A(x,t)C_B(x,t)]/\partial x^2$. Summarizing the above considerations, in order to keep the subdiffusive effect in both substances we assume the following form of the reaction term

$$\Pi_i(C_A,C_B)=\Psi(x,t)+\tilde{\tau}_{\alpha,i}\frac{\partial_{RL}^\alpha}{\partial t^\alpha}\Psi(x,t)-\tilde{\tau}_{\alpha,i}D_{\alpha,i}\frac{\partial^2}{\partial x^2}\Psi(x,t),\tag{47}$$

where $\Psi(x,t)$ is given by Eq. (44).

The generalization in the more general chemical reaction $n_AA+n_BB\to\emptyset$ (inert) seems to be natural within the mean field approximation and is given by the following equation:

$$\tilde{\tau}_{\alpha,i}\frac{\partial_C^{2\alpha}}{\partial t^{2\alpha}}C_i(x,t)+\frac{\partial_C^\alpha}{\partial t^\alpha}C_i(x,t)=\tilde{D}_{\alpha,i}\frac{\partial^2}{\partial x^2}C_i(x,t)-\tilde{\tau}_{\alpha,i}D_{\alpha,i}\frac{\partial^2}{\partial x^2}\frac{\partial_C^\alpha}{\partial t^\alpha}C_i(x,t)-n_i\Pi_i[C_A,C_B],\tag{48}$$

where $i=A,B$, and the reaction term is given by Eq. (47), with

$$\Psi(x,t)=C_A^{n_A}(x,t)C_B^{n_B}(x,t).\tag{49}$$

### E. Comparison to other models

It is interesting to compare the obtained Eq. (38) with the subdiffusion-reaction equations derived in other papers [8,12], in which various equations of a rather unexpected form were derived for the case of a "parabolic" subdiffusion-reaction process (for which $\beta=1/2$) in which particle $A$ vanishes with a probability that is assumed to be independent of any space and time variables. The more general case, in which a particle's vanishing probability depends on the particle's position, was considered in Ref. [22]. To find a connection between the models considered in the above cited papers and the model presented in this paper, we refer to Ref. [23], in which various models of subdiffusion with reactions $A\longrightarrow B$ and $A+B\longrightarrow B$ were considered with constant rates independent of time and space variables. It was shown in this paper that a Laplace transform of the subdiffusion-reaction equation reads

$$\frac{1-\hat{\omega}_M(s)}{\hat{U}_M(s)}\hat{P}(x,s)-P(x,0)=\frac{\hat{\omega}_M(s)(\Delta x)^2}{2\hat{U}_M(s)}\frac{\partial^2}{\partial x^2}\hat{P}(x,s),\tag{50}$$

which contains the Laplace transforms of the following functions: $\omega_M(t)$, which is a waiting time probability density which is needed for a particle $A$ to take its next step and continue to exist until time $t$ and $U_M(t)$, which is the probability that the particle has not performed any step over time interval $(0,t)$ and continues to exist at time $t$. When a reaction can occur with a constant per capita rate during the time that the particle waits before taking its next step, then

$$\hat{\omega}_M(s)=(1-p)\hat{\omega}(s)+p\hat{\omega}(s+\gamma),\tag{51}$$

and

$$\hat{U}_M(s)=(1-p)\frac{1-\hat{\omega}(s)}{s}+p\frac{1-\hat{\omega}(s+\gamma)}{s+\gamma}.\tag{52}$$

Inserting the approximation Eq. (21) of $\hat{\omega}(s)$ and the following approximation,

$$\hat{\omega}(s+\gamma)=1-\tau_\alpha(s+\gamma)^\alpha,\tag{53}$$

into Eqs. (50)–(52) and next calculating the inverse transform of obtained equation, we get (the details of the calculation are presented in Appendix D)

$$(1-p)\frac{\partial_C^\alpha P(x,t)}{\partial t^\alpha}+pe^{-\gamma t}\frac{\partial_C^\alpha}{\partial t^\alpha}e^{\gamma t}P(x,t)=D_\alpha\frac{\partial^2 P(x,t)}{\partial x^2}. \tag{54}$$

The relation Eq. (21) is valid under the condition that $\tau_\alpha s^\alpha \ll 1$, which corresponds to the condition $t \gg \tau_\alpha^{1/\alpha}$. Due to Eq. (22), supposing that $\Delta x$ is small, we can treat $\tau_\alpha$ as a small coefficient. The relation Eq. (53) should be treated as an approximation of $\hat{\omega}(s+\gamma)$, which is acceptable if $\tau_\alpha(s+\gamma)^\alpha \ll 1$, this condition provides $s \ll (1/\tau_\alpha^{1/\alpha})-\gamma$ (which is correct under the condition that the right-hand side of the above inequality is positive, i.e., for $\gamma\tau_\alpha^{1/\alpha}<1$), and finally to

$$t \gg \tau_\alpha^{1/\alpha}/\left(1-\gamma\tau_\alpha^{1/\alpha}\right). \tag{55}$$

Thus, Eq. (54) works for time given by Eq. (55).

For the case in which $p=1$ the particle's vanishing process corresponds to the reaction $A \longrightarrow B$. Then, Eq. (54) is equivalent to Eq. (60) in Ref. [12] and to the subdiffusion-reaction equation derived in Ref. [8]. When $p<1$, for

$$t \gg \max\left[\frac{\tau_\alpha^{1/\alpha}}{1-\gamma\tau_\alpha^{1/\alpha}},\frac{1}{\gamma},\frac{1}{\gamma}\left(\frac{p}{1-p}\right)^{1/(1-\alpha)}\right], \tag{56}$$

where $\max[a,b,c]$ represents the largest number from the set $\{a,b,c\}$, Eq. (54) is equivalent to the following equation (see Appendix D):

$$\frac{\partial P(x,t)}{\partial t}=\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\left[\bar{D}_\alpha\frac{\partial^2 P(x,t)}{\partial x^2}-\mu^2 P(x,t)\right], \tag{57}$$

where

$$\bar{D}_\alpha = D_\alpha/(1-p), \quad \mu=\sqrt{p\gamma^\alpha/(1-p)}. \tag{58}$$

We add that a derivation of Eq. (57) from Eq. (54) is not obvious. However, both of the equations have been derived form Eqs. (50)–(53) for various domains of parameter $s$ (which is assumed to be small), which corresponds to various domains of time $t$. Since both Eqs. (54) and (57) are derived from the same general Eq. (50), but to derive the latter the additional condition has been taken into account (see Appendix D), Eq. (57) can be treated as a special case (or "useful approximation") of the more general Eq. (54). We note that for $\gamma > 1/(2\tau_\alpha^{1/\alpha})$ and $p<1/2$, both the above-mentioned equations are valid for the same time interval. Let us also note that for $p \longrightarrow 1$, Eq. (57) loses its validity for finite times due to Eq. (56).

Equation (54) has been derived under the assumption that a reaction can occur at every moment of time between the particle's jumps with the probability density Eq. (16). Assuming that a reaction can occur just before the jump of particle $A$, the random walk with reaction $A+B \longrightarrow B$ can be described by the following difference equation:

$$P_{n+1}(m;m_0)=\tfrac{1}{2}P_n(m-1;m_0)+\tfrac{1}{2}P_n(m+1;m_0) - RP_n(m;m_0), \tag{59}$$

which can be treated as an "extension" of Eq. (12) (or of Eqs. (25) and (26) for $\beta=1/2$) to the case in which reaction occurs in a whole system. It was shown [23] that in this case the process is described by Eq. (50) in which

$$\hat{\omega}_M(s)=\frac{\hat{\omega}(s)}{1+R\hat{\omega}(s)}, \tag{60}$$

and

$$\hat{U}_M(s)=\frac{\hat{U}(s)}{1+R\hat{\omega}(s)}. \tag{61}$$

Equations (50), (60), and (61) give the subdiffusion-reaction equation, which is the same as Eq. (57) after replacing $\bar{D}_\alpha \longrightarrow D_\alpha$ and $\mu \longrightarrow \sqrt{D_\alpha}\kappa$, $\kappa=\sqrt{2R}/\Delta x$.

The case $p=1$, which is characteristic of a reaction $A \longrightarrow B$, is qualitatively different from the case $p<1$, in which particles $A$ and $B$ must first meet (with probability $p$) for a reaction $A+B \longrightarrow B$ to take place. Thus, the equations describing both processes mentioned above are not equivalent to each other (unless $p=1$). The Cattaneo-type subdiffusion reaction Eqs. (38), (45), and (48) derived in this paper correspond to the case of $p<1$.

## IV. FINAL REMARKS

The Cattaneo-type subdiffusion reaction Eq. (38) for the reaction $A+B\,(\text{static}) \to B\,(\text{static})$ was derived within the continuous-time random-walk formalism using the persistent random-walk model, but its generalization in the cases of more complicated reactions was made using a "heuristic" method based on a stochastic interpretation of the subdiffusion-reaction process. Thus, Eqs. (45) and (48) should be treated rather as postulates. Nevertheless, we believe that this equation will be useful in modeling subdiffusion-reaction processes occurring in nature, since it has a relatively simple stochastic interpretation.

Let us note that parameter $\beta$ changes the effective subdiffusion coefficient. Namely, from Eq. (C2) (Appendix C) for the system without chemical reactions ($\tilde{R}_\beta=0$), we obtain

$$\langle(\Delta x)^2\rangle=\frac{2\tilde{D}_\alpha}{\Gamma(1+\alpha)}t^\alpha, \tag{62}$$

where $\tilde{D}_\alpha$ is defined by Eq. (42). We note that there are two definitions of subdiffusion coefficients. The first one, defined by Eq. (62), shows how fast particles spread out over a long time limit (in this case every particle performs large number of steps); this coefficient we call the "effective subdiffusion coefficient." It is obvious that it depends on parameter $\beta$. For example, if $\beta=1$, then a particle changes its velocity sense at every step with a probability of 1. In practice, the particle does not change its position over time, which provides $\tilde{D}_\alpha=0$. The second subdiffusion coefficient refers to a particle's single step and is defined by Eq. (22) within the continuous-time random-walk formalism and is independent of $\beta$. Both of them are equal to each other for $\beta=1/2$.

Persistent random walk is a process with memory, as well as subdiffusion. There arises a question: are these two effects simultaneously worth considering? The subdiffusive memory effect, controlled by the parameter $\alpha$, is long and vanishes in the case of normal diffusion. The persistent random-walk memory effect, which arises from the correlation of the successive random walker's steps, is relatively short. This is controlled by parameter $\beta$, which is assumed to be independent of $\alpha$. As we can see in Fig. 2, parameter $\beta$ significantly influences the solutions to Eq. (38). The considerations presented in this paper show that the effect of step correlations changes the effective subdiffusion parameter $\tilde{D}_\alpha$ and provides new terms in the subdiffusion-reaction equation, which can change the dynamic of the process (at least in some situations).

The dynamic of the process depends on parameter $\beta$. For $\beta < 1/2$ a particle prefers the direction of its previous step. This occurs when the particle inertia effect is taken into account. For $1/2 < \beta < 1$, one obtains the effect of the rapid changing of a particle's step direction, which occurs more frequently than in the case of the uncorrelated random walk. This effect can be caused by the interaction of diffusing particles and it is expected to be in a system with large particle concentration. Diffusion or subdiffusion in dense systems, in which the effective diffusion coefficient depends on the concentration, is usually described by nonlinear equations, but we suppose that—at least in some situations—such a process can be described by the Cattaneo-type subdiffusion equation with $\beta > 1/2$.

The simplest approximation of the reaction term seems to neglect the terms occurring in Eq. (38), in which the small parameter $\tau_\alpha$ is contained. In this way, parameter $\beta$ will be involved in the reaction rate constant alone. However, by consequently neglecting similar terms in the remaining parts of the equation, we lose the steps' correlation effect. The reaction rate for the reaction $A + B$ (static) → $B$ (static) is given by Eq. (27). However, this is the simplest situation in which the persistent random-walk effect can be explicitly taken into account in derivation of the reaction rate coefficient. In the case of mobile $B$, and for more complicated reactions, the reaction rate cannot be defined in such a simple form. The generalization can be done using, for example, the diffusion model of chemical reactions described by difference-differential equations [51,52], in which rates depend on parameter $\beta$.

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## APPENDIX A: LAPLACE TRANSFORMS

The Laplace transform of the Riemann-Liouville fractional derivative reads

$$L\left\{\frac{d^\alpha_{\mathrm{RL}} f(t)}{dt^\alpha}\right\} = s^\alpha \hat{f}(s) - \sum_{k=0}^{n-1} s^k \left.\frac{d^{\alpha-k-1} f(t)}{dt^{\alpha-k-1}}\right|_{t=0}, \tag{A1}$$

where $n-1 \leqslant \alpha < n$, and where $(\gamma > 0)$

$$\frac{d^{-\gamma}_{\mathrm{RL}} f(t)}{dt^{-\gamma}} = \frac{1}{\Gamma(-\gamma)} \int_0^t (t-t')^{-\gamma-1} f(t')dt'. \tag{A2}$$

Let $0 < \alpha < 1$ and $f$ is bounded over the time interval $(0,t)$, $|f(t)| < A$, $t \in (0,t)$. Thus,

$$\left|\frac{d^{\alpha-1}_{\mathrm{RL}} f(t)}{dt^{\alpha-1}}\right| < \frac{A}{\Gamma(\alpha-1)} \int_0^t (t-t')^{\alpha-1} dt' = \frac{At^\alpha}{\alpha\Gamma(\alpha-1)} \overset{t\to 0}{\to} 0. \tag{A3}$$

Equations (A1)–(A3) provide

$$L\left\{\frac{d^\alpha_{\mathrm{RL}} f(t)}{dt^\alpha}\right\} = s^\alpha \hat{f}(s). \tag{A4}$$

The above equation is also applied for the initial distribution function, which is given formally by the $\delta$-Dirac function, since this unbounded function is only an idealization of a realistic initial condition and can be approximated by a bounded one.

The Laplace transform of the Caputo fractional derivative reads

$$L\left\{\frac{d^\alpha_C f(t)}{dt^\alpha}\right\} = s^\alpha \hat{f}(s) - \sum_{k=0}^{n-1} s^{\alpha-k-1} \left.\frac{d^k f(t)}{dt^k}\right|_{t=0}, \tag{A5}$$

where $n-1 < \alpha \leqslant n$.

Using

$$F\left\{\frac{\partial^2}{\partial x^2} P(x,t)\right\} = -k^2 \hat{P}(k,t), \tag{A6}$$

for $P(x,0) = \delta_{x,0}$ the Fourier and Laplace transforms of Eq. (2) reads

$$s\hat{P}(k,s) - 1 = -s^{1-\alpha} k^2 D_\alpha \hat{P}(k,s). \tag{A7}$$

Transforming the above equation to the form

$$s^\alpha \hat{P}(k,s) - s^{\alpha-1} = -k^2 D_\alpha \hat{P}(k,s), \tag{A8}$$

and using Eqs. (A5) and (A6), one obtains Eq. (4).

Using Eq. (40) and the exponent function $\exp(u) = \sum_{k=0}^\infty u^n/n!$, we obtain

$$L^{-1}\left\{s^\nu \sum_{k=0}^\infty \left[\frac{(-as^\gamma)^k}{k!}\right]\right\} = \frac{1}{t^{\nu+1}} \sum_{k=0}^\infty \frac{1}{k!\Gamma(-\gamma k-\nu)} \left(-\frac{a}{t^\gamma}\right)^k. \tag{A9}$$

From Eq. (A9) we obtain the condition $s \ll 1/a^{1/\gamma}$ corresponding to $t \gg a^{1/\gamma}$.

## APPENDIX B: SUBDIFFUSION-REACTION EQUATIONS

The subdiffusion-reaction equation can be obtained heuristically by adding the reaction term to the subdiffusion equation. Putting $C_A(x,t) = N_A P_A(x,t)$ and $C_B(x,t) = N_B P_B(x,t)$, where $N_i$ denotes the initial number of particles of species $i$. Therefore, Eqs. (2) and (4) are fulfilled also by concentrations

$C_A$ and $C_B$. In Ref. [6] the equation of the form was postulated

$$\frac{\partial}{\partial t}C_i(x,t) = D_\alpha \frac{\partial^{1-\alpha}_{\mathrm{RL}}}{\partial t^{1-\alpha}}\frac{\partial^2}{\partial x^2}C_i(x,t) - \Pi(C_A,C_B), \tag{B1}$$

where $i = A,B$. Thus, subdiffusion does not influence the reaction process directly, since the reaction term is located outside the fractional Riemann-Liouville derivative.

In Ref. [5] the derivation of the subdiffusion-reaction equation provides the following equation:

$$\frac{\partial}{\partial t}C_i(x,t) = \frac{\partial^{1-\alpha}_{\mathrm{RL}}}{\partial t^{1-\alpha}}\left[D_\alpha \frac{\partial^2}{\partial x^2}C_i(x,t) - \Pi(C_A,C_B)\right]. \tag{B2}$$

In this case the kinetic of reactions is controlled by parameter $\alpha$. Equation (B2) can be transformed to

$$\frac{\partial^\alpha_C}{\partial t^\alpha}C_i(x,t) = D_\alpha \frac{\partial^2}{\partial x^2}C_i(x,t) - \Pi(C_A,C_B). \tag{B3}$$

## APPENDIX C: GENERAL SOLUTION TO EQ. (38)

We assume that $\frac{\partial^2}{\partial x^2}P(x,t)|_{x=x_r} = 0$; this assumption is motivated by a quasistatic approximation of the solution of the subdiffusion-reaction equation, which works near a point where a reaction term takes its maximal value (see Ref. [4]). The general solution to Eq. (38) in terms of Laplace and Fourier transforms, $F\{f(x)\} \equiv \hat{f}(k) = \int_{-\infty}^{\infty}\exp(ikx)f(x)dx$, is (here $x_r = 0$)

$$\hat{P}(k,s) = \frac{(1-2\beta)\tau_\alpha s^{2\alpha-1}e^{ikx_0} + 2\beta s^{\alpha-1}e^{ikx_0} - k^2(1-2\beta)\tau_\alpha s^{\alpha-1} - \tilde{R}_\beta[2\beta + (1-2\beta)\tau_\alpha s^\alpha]\hat{P}(0,s)}{(1-2\beta)\tau_\alpha s^{2\alpha} + 2\beta s^\alpha + k^2 D_\alpha[2(1-\beta) - (1-2\beta)\tau_\alpha s^\alpha]}. \tag{C1}$$

In the limit of small $s$, keeping the leading terms in Eq. (C1), we obtain

$$\hat{P}(k,s) = \frac{s^{\alpha-1}e^{ikx_0} - \tilde{R}_\beta \hat{P}(0,s)}{s^\alpha + k^2\tilde{D}_\alpha}, \tag{C2}$$

where $\tilde{D}_\alpha = (1-\beta)D_\alpha/\beta$. Using the inverse Fourier transform ($a > 0$) to Eq. (C2),

$$F^{-1}\left\{\frac{1}{a^2+k^2}\right\} = \frac{1}{2a}e^{-a|x|}, \tag{C3}$$

we get

$$\hat{P}(x,s) = \frac{1}{2\sqrt{\tilde{D}_\alpha s^\alpha}}\left[s^{\alpha-1}e^{-\frac{|x-x_0|}{\sqrt{\tilde{D}_\alpha}}s^{\alpha/2}} - \tilde{R}\hat{P}(0,s)e^{-\frac{|x|}{\sqrt{\tilde{D}_\alpha}}s^{\alpha/2}}\right]. \tag{C4}$$

Calculating $\hat{P}(0,s)$ from Eq. (C4), we finally obtain Eq. (39).

## APPENDIX D: DERIVATION OF EQS. (54) and (57)

This section partially covers the results presented in Ref. [23]. Putting Eqs. (21) and (53) into Eqs. (51) and (52), we obtain

$$\hat{\omega}_M(s) = 1 - (1-p)\tau_\alpha s^\alpha - p(s+\gamma)^\alpha, \tag{D1}$$

and

$$\hat{U}_M(s) = \tau_\alpha[(1-p)s^{\alpha-1} + p(s+\gamma)^{\alpha-1}]. \tag{D2}$$

From Eqs. (50), (D1), and (D2), keeping the leading terms [as previously the parameters $s$ and $\tau_\alpha$ are assumed to be small; in the following we assume that $\tau_\alpha \ll 1/(p\gamma^\alpha)$], we get

$$\begin{aligned}&(1-p)[s^\alpha \hat{P}(x,s;x_0) - s^{\alpha-1}P(x,0;x_0)]\\&\quad + p[(s+\gamma)^\alpha \hat{P}(x,s;x_0) - (s+\gamma)^{\alpha-1}P(x,0;x_0)]\\&= D_\alpha \frac{\partial^2 \hat{P}(x,s;x_0)}{\partial x^2}.\end{aligned} \tag{D3}$$

Calculating the inverse Laplace transform of Eq. (D3) and using the formula

$$\begin{aligned}&\mathcal{L}\left\{e^{-\gamma t}\frac{\partial^\alpha_C}{\partial t^\alpha}e^{\gamma t}P(x,t)\right\}\\&\quad = (s+\gamma)^\alpha \hat{P}(x,s) - (s+\gamma)^{\alpha-1}P(x,0),\end{aligned} \tag{D4}$$

we obtain Eq. (54).

For $s \ll \gamma$ (which corresponds to $t \gg 1/\gamma$), we use the following approximation:

$$(s+\gamma)^\alpha \approx \gamma^\alpha\left(1 + \frac{\alpha s}{\gamma}\right). \tag{D5}$$

Substituting Eq. (D5) into Eqs. (D1) and (D2), and leaving the leading terms in the limit of small $s$, we get

$$\hat{\omega}_M(s) = 1 - p\tau_\alpha\gamma^\alpha - (1-p)\tau_\alpha s^\alpha, \tag{D6}$$

and $\hat{U}_M(s)=\tau_\alpha[(1-p)s^{\alpha-1} + \gamma^{\alpha-1}]$. Supposing $s \ll \gamma[(1-p)/p]^{1/(1-\alpha)}$ [which corresponds to $t \gg (1/\gamma)[p/(1-p)]^{1/(1-\alpha)}$], we have

$$\hat{U}_M(s) = \frac{(1-p)\tau_\alpha}{s^{1-\alpha}}. \tag{D7}$$

From Eqs. (50), (D6), and (D7), in the limit of small $s$, we get

$$\begin{aligned}&\left[\frac{p\gamma^\alpha}{1-p}s^{1-\alpha} + s\right]\hat{P}(x,s;x_0) - s^{\alpha-1}P(x,0;x_0)\\&\quad = s^{1-\alpha}\frac{D_\alpha}{1-p}\frac{\partial^2 \hat{P}(x,s;x_0)}{\partial x^2}.\end{aligned} \tag{D8}$$

The inverse Laplace transform of Eq. (D8) provides Eq. (57). The considerations presented in this Appendix and in Sec. III E lead to the conclusion that Eq. (54) is valid for the time defined by Eq. (55) and can be simplified to Eq. (57) for the time given by Eq. (56).

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