PERSISTENT RANDOM WALK EFFECT IN THE SUBDIFFUSION-REACTION PROCESS*

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The persistent random walk model assumes a correlation between successive particles' steps. This model provides hyperbolic Cattaneo normal diffusion or subdiffusion equations for a system without chemical reactions. Utilizing the recently derived hyperbolic subdiffusion-reaction equation (T. Kosztołowicz, `arXiv:1306.3806 [cond-mat.stat-mech]`), we study the steps' correlation effect for the subdiffusion-reaction process. Based on the solutions to this equation, we discuss the influence of this effect on the subdiffusion coefficient and the reaction rate constant.

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1. Introduction

Subdiffusion can be treated as a random walk of particles in a medium where the mobility of particles is strongly hindered due to the complex structure of the medium. Subdiffusion can be described by the following 'parabolic' equation with the fractional Caputo time derivative

$$\frac{\partial_C^\alpha}{\partial t^\alpha} C(x,t) = D_\alpha \frac{\partial^2}{\partial x^2} C(x,t)\,, \tag{1}$$

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where

$$\frac{d_C^{\alpha}}{dt^{\alpha}} f(t) = \frac{1}{\Gamma(n-\alpha)} \int_0^t \left(t-t'\right)^{n-\alpha-1} \frac{d^n}{dt'^n} f\left(t'\right) dt' , \tag{2}$$

n is a natural number fulfilling $n-1 < \alpha \leq n$, $C(x,t)$ is a concentration of particles, α, D_α are the subdiffusion parameters defined by the relation describing the time evolution of the mean square displacement of a single particle [1]. We note that Eq. (1) can be transformed to its version with the Riemann–Liouville time fractional derivative [1]. The Green function, which is defined by its initial condition $P(x,t) = \delta(x-x_0)$ (δ denotes the Dirac-delta function), is interpreted as a probability density in order to find a random walker at point x after time t under the condition that its initial position is x_0. The Green function of Eq. (1) has non-zero values for any x at $t > 0$. This means that some of the particles move with an arbitrarily chosen large velocity. To avoid this non-physical property, the persistent random walk model was proposed [2–4]. Under the assumption that the actual random walker's step is correlated with the previous one, which means that the direction of successive steps remains the same with a certain probability, for the normal diffusion process one obtains the following differential hyperbolic Cattaneo equation

$$(1-2\beta)\tau \frac{\partial^2}{\partial t^2} P(x,t) + \frac{\partial}{\partial t} P(x,t) = D \frac{\partial^2}{\partial x^2} P(x,t) , \tag{3}$$

where D is the normal diffusion coefficient, the parameter β controls the correlation of jumps $\langle (\Delta x)_n (\Delta x)_{n+1} \rangle = (1-2\beta)(\Delta x)^2$, where $(\Delta x)_n$ is the particle's displacement during its n^{th} step [3, 5], τ is a parameter given in time units and defined by the Laplace transform of a waiting time probability density $\omega(t)$ needed to take a particle's next step, namely, over a long time limit (which corresponds to the limit of a small s) there is $\hat{\omega}(s) \equiv \int_0^{\infty} \exp(-st)\omega(t)dt \approx 1 - \tau s$. The case of $\beta = 1/2$ corresponds to the 'ordinary' non-persistent random walk, described by the 'parabolic' (sub)diffusion equation. The process can be also interpreted as the diffusive flux being delayed over time by parameter $(1-2\beta)\tau$ with respect to the concentration gradient. We add here that the generalization of Eq. (3) to the subdiffusion system is not clear (see [6]).

Since the parabolic diffusion (or subdiffusion) equation is relatively easy to solve (at least compared to the hyperbolic equation), it is most often used in the modelling of a diffusion process. In many systems, such as a membrane system, the solutions of both equations are very similar to each other [7]. However, in some systems the solutions obtained on the basis of a hyperbolic equation significantly differ from the solutions to a parabolic equation as, for example, with the problem of subdiffusive impedance [8].

The situation is more complicated when subdiffusing particles of species A and B can chemically react with each other according to the formula $n_A A + n_B B \to \emptyset$ (inert). The standard 'parabolic' equation which describes this process reads as follows [9–12]

$$\frac{\partial_C^\alpha}{\partial t^\alpha} C_i(x,t) = D_i \frac{\partial^2}{\partial x^2} C_i(x,t) - n_i k C_A^{n_A}(x,t) C_B^{n_B}(x,t)\,, \tag{4}$$

where $i = A, B$, k is a reaction rate, $C_{A,B}$ denotes substance concentrations.

There arise the following questions: is the persistent random walk effect important in the modelling of the subdiffusion-reaction process? If so, what is the main source of this effect? In order to find the answers, we consider subdiffusion in a system in which a subdiffusive particle A can chemically react with static particles B which are located at one point (here we consider a three-dimensional system which is homogeneous in a plane perpendicular to the x-axis, therefore it is effectively one-dimensional). Additionally, we assume that the reaction probability is independent of time. Such a system is convenient in analytical treatment. Formally, it corresponds to subdiffusive systems with a thin membrane; and at the membrane are located B particles which can react with A particle according to the rule $A + B \longrightarrow B$. We expect that the general properties of such a system concerning the persistent random walk effect will be in agreement to other subdiffusion-reaction processes in which mobile particles B can chemically react with A according to more complex rules. In our considerations, we use the recently derived Cattaneo-type subdiffusion-reaction equation and its solution [13].

2. 'Hyperbolic' subdiffusion-reaction equation

Let us assume that when a subdiffusive particle A reaches the site x_r (x_r is a position of the thin membrane with particles B located on it), it can react with static particles B according to the rule $A + B \longrightarrow B$. Then, the probability that a reaction occurs when A meets B does not change over time. The subdiffusion-reaction equation describing this process reads [13]

$$\begin{aligned}
&(1-2\beta)\tau_\alpha \frac{\partial_C^{2\alpha}}{\partial t^{2\alpha}} P(x,t) + 2\beta \frac{\partial_C^\alpha}{\partial t^\alpha} P(x,t) \\
&= 2(1-\beta) D_\alpha \frac{\partial^2}{\partial x^2} P(x,t) - (1-2\beta)\tau_\alpha D_\alpha \frac{\partial^2}{\partial x^2} \frac{\partial_C^\alpha}{\partial t^\alpha} P(x,t) \\
&- \tilde{R}\delta(x-x_r)\Big[2\beta P(x,t) + 2(1-2\beta)\tau_\alpha \frac{\partial_C^\alpha}{\partial t^\alpha} P(x,t) \\
&+ 2\tau_\alpha \frac{t^{-\alpha}}{\Gamma(1-\alpha)} P(x,0) - (1-2\beta)\tau_\alpha D_\alpha \frac{\partial^2}{\partial x^2} P(x,t)\Big]\,,
\end{aligned} \tag{5}$$

where $\tilde{R}$ is the 'subdiffusive' reaction constant defined as $\tilde{R} = R/\tau_\alpha$, R is the probability that the reaction takes place when A and B meet and τ_α is a parameter which, together with α, defines the probability distribution $\omega(t)$ for subdiffusion. Over the limit of a small s its Laplace transform $\hat{\omega}(s) = \int_0^\infty \exp(-st)\omega(t)dt$ reads

$$\hat{\omega}(s) \approx 1 - \tau_\alpha s^\alpha \,. \tag{6}$$

The probability R can be derived in the following standard way (see, for example, [12, 14]). Let us assume that the distribution function of the reaction is $\psi(t) = \gamma\exp(-\gamma t)$, where γ is the 'static' reaction constant. The waiting time distribution that the reaction will produce, $\psi_r(t)$, is as follows

$$\psi_r(t) = \gamma\exp(-\gamma t)\left[1 - \int_0^t \omega\left(t'\right)dt'\right] \,. \tag{7}$$

The term in the square bracket represents the probability that the particle A does not change its position at x_r over the time interval $(0, t)$. The probability that the particle reacts with a single particle B equals

$$R = \int_0^\infty \psi_r\left(t'\right)dt' = 1 - \hat{\omega}(\gamma) \,. \tag{8}$$

From the above relations, we obtain

$$\tilde{R} \equiv R/\tau_\alpha = \gamma^\alpha \,. \tag{9}$$

For the initial condition $P(x,t) = \delta(x - x_0)$, the solution to Eq. (5) reads over a long time limit (here $\tilde{R}, \beta \neq 0$ and $\beta \neq 1$)

$$\begin{aligned} P(x,t) \;=\; & \frac{1}{2\sqrt{\tilde{D}_\alpha}} f_{-1+\alpha/2,\alpha/2}\left(t; \frac{|x - x_0|}{\sqrt{\tilde{D}_\alpha}}\right) \\ & - \frac{1}{2\sqrt{\tilde{D}_\alpha}} \sum_{k=0}^{\infty} \left(-\frac{2\sqrt{\tilde{D}_\alpha}}{\tilde{R}_\beta}\right)^k \\ & \times f_{-1+(k+1)\alpha/2,\alpha/2}\left(t; \frac{|x| + |x_0|}{\sqrt{\tilde{D}_\alpha}}\right) \,, \end{aligned} \tag{10}$$

where

$$\begin{aligned} \tilde{D}_\alpha \;&=\; \frac{1-\beta}{\beta} D_\alpha \,, \\ f_{\nu,\alpha}(t; a) \;&=\; \frac{1}{t^{\nu+1}} \sum_{k=0}^{\infty} \frac{1}{k!\Gamma(-k\alpha - \nu)} \left(-\frac{a}{t^\alpha}\right)^k \,. \end{aligned} \tag{11}$$

3. Persistent random walk effect

The persistent random walk effect (PRWE) is manifested by changing the subdiffusion coefficient according to Eq. (11) and it can be observed in the models concerning pure subdiffusion (*i.e.* without chemical reactions). We expect that this effect also concerns the reaction rate. The reaction rate given by Eq. (9) is independent of parameter β. However, various theoretical models of bimolecular reactions assume that the particle A overcomes a potential barrier during its movement along the reaction coordinate axis [15, 16]. However, the probability of passing the barrier depends on a particle's energy. If the particle comes to the site x_r and its velocity sense is not changed after arriving at site, we assume that the reaction occurs with reaction rate γ_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 a reaction rate γ_2, $\gamma_2 < \gamma_1$. The probability of the 'choice' of the reaction rate depends on β. Thus, we postulate that

$$\tilde{R} = (1-\beta)\gamma_1^{\alpha} + \beta\gamma_2^{\alpha}\,. \tag{12}$$

The relation between the coefficients γ_1 and γ_2 is required in considering a detailed model of a chemical reaction, and this problem is not considered here.

Figures 1–6 present plots of function (10) made for various parameters characterized the model. The particle A is initially located at $x_0 = -1$, during its movement it can chemically react with the static particle B located at $x_r = 0$. In Fig. 1 one can observe a strong dependence of the solutions of Eq. (5) on the parameter β. In Fig. 2 the plots of function (10) are compared, calculated for $\tilde{R}$, given both by Eq. (9) (dashed lines) and by Eq. (12) (dotted lines) for various values of β. For the sake of simplicity, the values of γ_1 and γ_2 are assumed to be independent of β (although such a dependence cannot be excluded in a general case). It is seen that the plots for both cases coincide with each other for the given β. However, differences between the solutions are observed on a 'small scale', which is presented in Fig. 3; the plots are shown here in the region close to the position of the B particle. The dependence of function (10) on parameters γ_1 and γ_2 is presented in Figs. 4–6. It is shown that $P(x,t)$ decreases for increasing $\tilde{R}$ values, especially in the region near the location of the B particle. This effect suggests that with the bringing into consideration of the additional dependence of γ_1 and γ_2 on β, the PRWE can be noticeably strengthened.

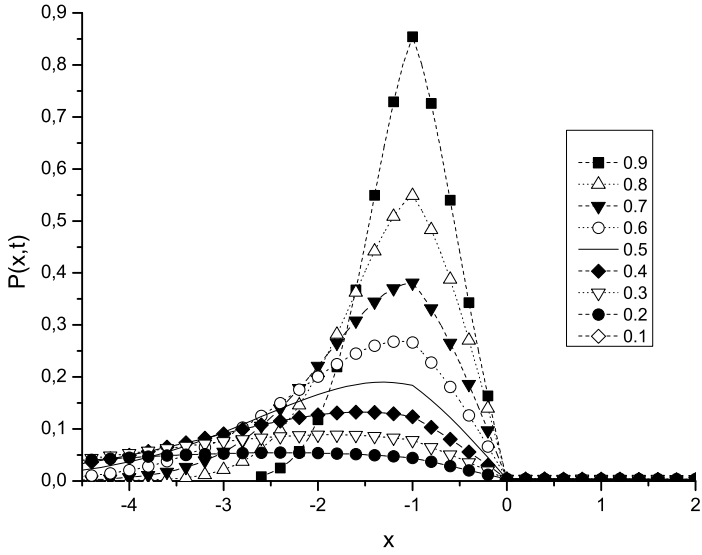


Fig. 1. Functions (10) for various values of the parameter β given in the legend for the case in which the reaction rate is independent of β (Eq. (9)), $\gamma = 0.5$, $D_\alpha = 0.01$, $\alpha = 0.9$, $x_0 = -1$, $x_r = 0$ (all quantities are given in arbitrary chosen units).

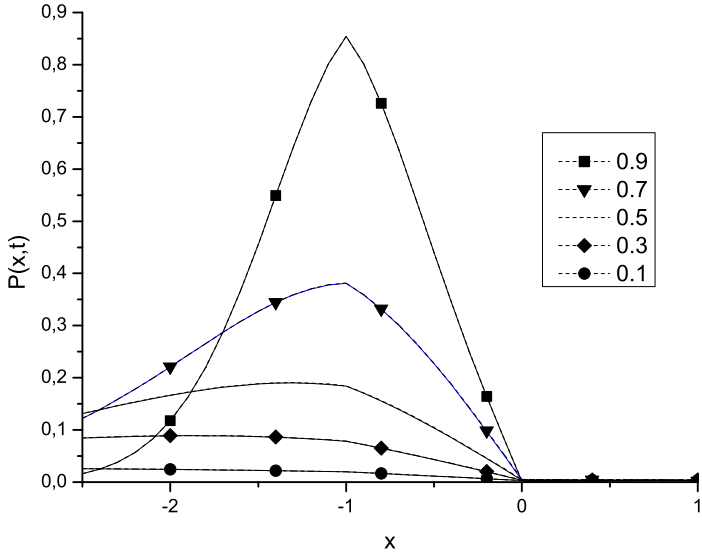


Fig. 2. Comparison of the solutions of Eq. (10) for $\tilde{R}$ given by Eq. (9) with $\gamma = 0.5$ (dashed lines) and for $\tilde{R}$ given by Eq. (12) (dotted lines) with $\gamma_1 = 0.5$ and $\gamma_2 = 0.3$, for various values of β given in the legend (here the dashed and dotted lines are very similar for given β), the other parameters are the same as in Fig. 1.

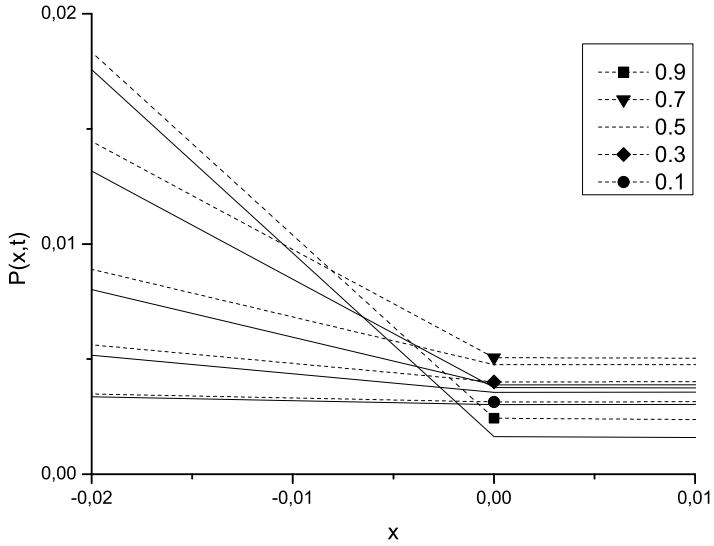


Fig. 3. The fragment of Fig. 2 plotted in the small scale.

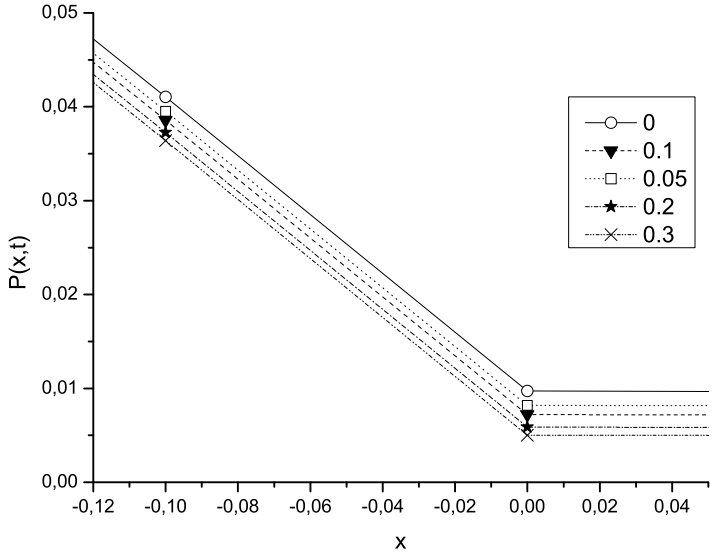


Fig. 4. Functions (10) in which $\tilde{R}$ is given by (12) for various values of γ_2 given in the legend, here $\gamma_1 = 0.5$, the other parameters are the same as in Fig. 1 (the plots are shown in the small scale).

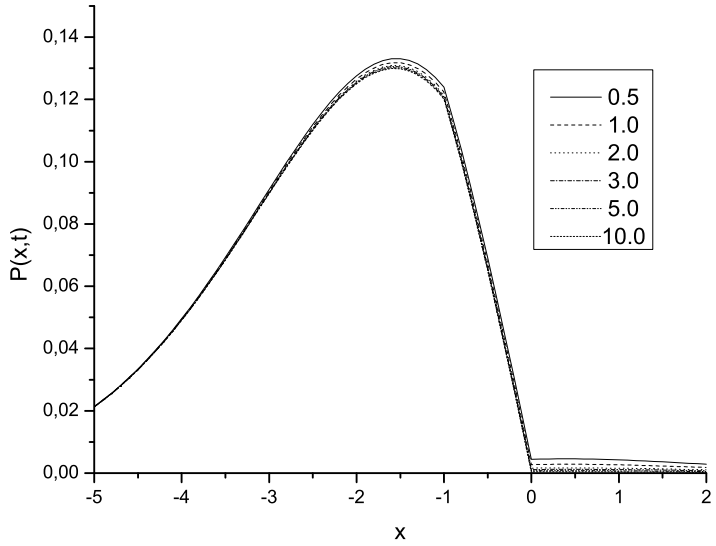


Fig. 5. Functions (10) in which $\tilde{R}$ is given by (12) for various values of γ_1 given in the legend, here $\gamma_2 = 0.3$, the other parameters are the same as in Fig. 1.

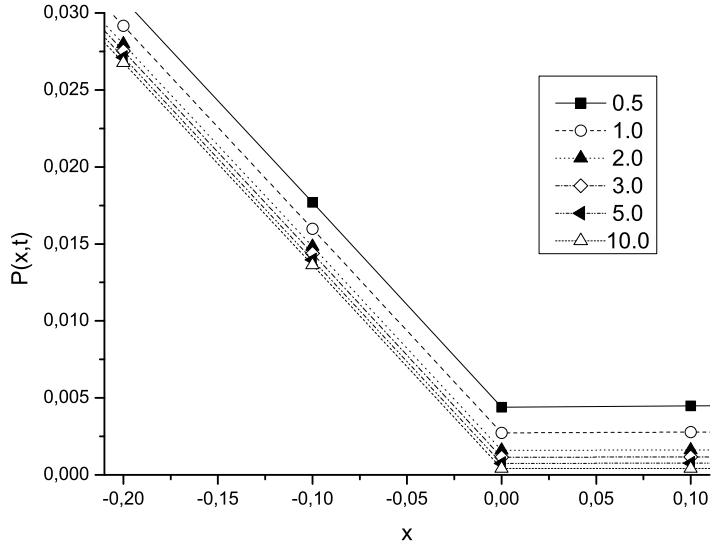


Fig. 6. The fragment of Fig. 5 plotted in the small scale.

4. Final remarks

The considerations presented in this paper show that the persistent random walk effect can be observed in a model of a subdiffusion-reaction process. In general, there are two sources of this effect. The first one is the dependence of subdiffusion coefficient D_α on β, and the second one consists in the making the reaction coefficient $\tilde{R}$ dependent on β. The first effect is stronger if β is smaller. The reason for this is that a particle changes its velocity sense with probability β, thus for small β the particle's mean square displacement grows faster over time compared to the case of a larger β. The origin of the second effect is more complex and consists in the dependence of $\tilde{R}$ on β. Equation (12) suggests that $\tilde{R}$ is a linear function of β. However, γ_1 and γ_2 depend on the potential barrier which should be overcome by the particle A (or by a complex containing this particle) during its movement along a reaction axis. The probability of overcoming the barrier depends on particles' energy, which can depend on β. Therefore, this means that the dependence of $\tilde{R}$ on β can be considered as nonlinear, at least within some reaction models [16].

In our paper, we show that the first effect dominates when the subdiffusion of single particle A (which can react with single particle B) is considered. A similar effect is expected in dilute solutions. When the concentrations of particles A and B are large, then the influence on the second effect grows, whereas the first effect does not change.

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