HYPERBOLIC SUBDIFFUSION IN A MEMBRANE SYSTEM*

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We discuss the physical meaning of three different version of hyperbolic anomalous diffusion equations with fractional time derivatives, which were derived in the paper A. Compte, R. Metzler, *J. Phys. A* **30**, 7277 (1997). We find that only one of them has clear physical interpretation and can be used to describe subdiffusion. We obtain the solutions of this equation and of the parabolic subdiffusion equation for a one-dimensional system with a thin membrane, where the flux flowing through the membrane is proportional to the concentration difference between membrane surfaces. We compare the solutions of hyperbolic and parabolic equations and briefly discuss their properties.

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1. Introduction

The subdiffusion is usually defined as a process where the mean square displacement of the particle $\langle \Delta x^2 \rangle$ is a power function of time [1]

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

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where the subdiffusion parameter α is less than one ($0 < \alpha < 1$) and D_α is the subdiffusion coefficient. The case of $\alpha = 1$ corresponds to the normal diffusion. The subdiffusion in a membrane system was recently studied experimentally and theoretically [2–4]. To model a transport process in such a system the parabolic subdiffusion equation (PSE) with fractional time derivative was usually applied. However, the PSE provides the Green functions (which is a probability density of finding a particle in the position x after time t under condition that at the initial moment the particle was located at x_0) have non-zero values for any x and $t > 0$; similar property has the Green function for the normal diffusion parabolic equation. This fact can be interpreted as an infinite speed propagation of some particles. To avoid this unphysical property Cattaneo proposed the hyperbolic normal diffusion equation, where the diffusion flux is delayed in time by τ with respect to the concentration gradient [5]. The Green function of this equation for $t \to 0$ is equal to zero for finite arguments, so the propagation velocity of the particles is finite.

In phenomenological way the subdiffusion hyperbolic equation (HSE) can be obtained by involving the fractional time derivative into a flux or continuity equation. In [6] there was derived three different hyperbolic anomalous diffusion equations, which are not equivalent to each other. In this paper we discuss properties of this equations and we show that only one of them has clear physical interpretation (this discussion is the extension of the one presented in our recent paper [7]).

The HSE is more difficult to solve than the PSE and its solutions can be usually obtained in the limits of short or long times only. Thus, there arises a question: is it worth the bother to find the solutions of HSE in the membrane system if the solution of PSE can be obtained in relatively simple way? The answer is not obvious, since in some systems (such as the electrochemical one) the solutions of HSE and PSE provide to results which are not equivalent to each other [7, 8]. Moreover, the delaying effect of the flux with respect to the concentration gradient seems to be stronger in a membrane system than in homogeneous one, since the flux can be involved into boundary conditions at the membrane. In our paper we find the solutions of the HSE for the one-dimensional system with a thin membrane, where the flux flowing through the membrane is proportional to the concentration difference between membrane surfaces, and we briefly study the differences between the solutions of hyperbolic and parabolic equations for the system under consideration.

2. Hyperbolic normal diffusion equation

To ensure the finite propagation velocity of the particle Cattaneo proposed the hyperbolic normal diffusion equation [5]

$$\frac{\partial C(x,t)}{\partial t} + \tau \frac{\partial^2 C(x,t)}{\partial t^2} = D \frac{\partial^2 C(x,t)}{\partial x^2} \,. \tag{2}$$

This equation can be derived phenomenologically by substituting the following flux equation

$$J(x,t) + \tau \frac{\partial J(x,t)}{\partial t} = -D \frac{\partial C(x,t)}{\partial x} \,, \tag{3}$$

into the continuity equation

$$\frac{\partial C(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} \,. \tag{4}$$

The left-hand side of Eq. (3) can be treated as an linear approximation of the following equation in the limit of small τ

$$J(x,t+\tau) = -D \frac{\partial C(x,t)}{\partial x} \,, \tag{5}$$

where τ is the delay time of the diffusion flux with respect to the concentration gradient; $\tau = 0$ provides the parabolic normal diffusion equation.

3. Parabolic subdiffusion equation

The parabolic subdiffusion equation reads

$$\frac{\partial C(x,t)}{\partial t} = D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2 C(x,t)}{\partial x^2} \,, \tag{6}$$

where the Riemann–Liouville fractional time derivative is defined for $\alpha > 0$ as

$$\frac{\partial^\alpha f(t)}{\partial t^\alpha} = \frac{1}{\Gamma(n-\alpha)} \frac{\partial^n}{\partial t^n} \int\limits_0^t dt' \frac{f(t')}{(t-t')^{1+\alpha-n}} \,, \tag{7}$$

the integer number n fulfills the relation $n-1 < \alpha \leq n$. Equation (6) can be derived by means of the Continuous Time Random Walk formalism [1] or on the phenomenological way. In the latter approach, to get Eq. (6), one puts the fractional flux

$$J(x,t) = -D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial C(x,t)}{\partial x} \,, \tag{8}$$

to the continuity equation (4).

4. Hyperbolic subdiffusion equation

As shown in [6], the phenomenological derivation of the hyperbolic anomalous diffusion equation can be performed in three different ways. Each of them consists in involving the fractional time derivative into a flux or the continuity equation. The obtained hyperbolic equations are not equivalent to each other. Below we discuss their physical meaning.

4.1. First equation

The natural way to generalize the parabolic subdiffusion equation to the hyperbolic one seems to be delaying the flux with respect to the concentration gradient in time by τ, analogically as for the normal diffusion case. In such a way one assumes the following flux equation

$$J(x,t)+\tau\frac{\partial J(x,t)}{\partial t}=-D\frac{\partial^{\alpha}}{\partial t^{\alpha}}\frac{\partial C(x,t)}{\partial x}\,. \tag{9}$$

Combining Eq. (9) with the continuity equation (4) one obtains

$$\tau\frac{\partial^2 C(x,t)}{\partial t^2}+\frac{\partial C(x,t)}{\partial t}=D_{\alpha}\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial^2 C(x,t)}{\partial x^2}\,. \tag{10}$$

Putting $\tau=0$ in Eqs. (9) and (10) we get the subdiffusive flux and parabolic subdiffusion equation, respectively. In this case the hyperbolic subdiffusion equation has the similar interpretation as the hyperbolic normal diffusion equation as the process where the flux is delayed with respect to the concentration gradient. The Green function of Eq. (10) provides the relation (1) for $t\gg\tau$ [6].

4.2. Second equation

The flux equation can be modified by replacing $\tau\frac{\partial}{\partial t}\rightarrow\tau^{\alpha}\frac{\partial^{\alpha}}{\partial t^{\alpha}}$ in the left-hand side of Eq. (9), what gives

$$J(x,t)+\tau^{\alpha}\frac{\partial^{\alpha}J(x,t)}{\partial t^{\alpha}}=-D\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial C(x,t)}{\partial x}\,. \tag{11}$$

Combining Eq. (11) with the continuity equation (4) one gets

$$\tau\frac{\partial^{1+\alpha}C(x,t)}{\partial t^{1+\alpha}}+\frac{\partial C(x,t)}{\partial t}=D_{\alpha}\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial^2 C(x,t)}{\partial x^2}\,. \tag{12}$$

This equation can be derived within the Continuous Time Random Walk scheme, where the flux is given in terms of Laplace and Fourier transforms as [6]

$$\hat{J}(k,s) = -2i\ell \frac{s}{1-\varphi(s)} \hat{C}(k,s) \int_0^\infty dx \hat{\psi}(x,s) \sin(kx)\,, \tag{13}$$

where $\psi(x,t)$ is the distribution of step lengths and waiting times between steps, $\varphi(t)$ is the distribution of time that the particle waits to make a step and ℓ is a microscopic length scale necessary to obtain the correct dimension for the flux. In our paper we denote the Fourier transform by $\mathcal{F}\{f(x)\} \equiv \int_{-\infty}^{\infty} e^{ikx} f(x) dx \equiv \hat{f}(k)$ and the Laplace one by $\mathcal{L}\{g(t)\} \equiv \int_0^\infty e^{-sx} g(t) dt \equiv \hat{g}(s)$. Assuming that

$$\psi(x,t) = \frac{1}{\sqrt{4\sigma^2\pi}} \exp\left(-\frac{x^2}{4\sigma^2}\right) \varphi(t)\,, \tag{14}$$

where $\varphi(t)$ is defined by its Laplace transform

$$\hat{\varphi}(s) = e^{-\theta^\alpha s^\alpha}\,, \tag{15}$$

(its inverse Laplace transform in the long time limit reads $\varphi(t) = \theta^\alpha/[t^{1+\alpha}\Gamma(-\alpha)]$, see Eq. (26) below). From Eq. (13)–(15) the following formula

$$\frac{e^{s^\alpha\theta^\alpha}-1}{s^\alpha\theta^\alpha} \hat{J}(k,s) = -ikD_\alpha s^{1-\alpha} \hat{C}(k,s)\,, \tag{16}$$

was derived in the limit of small k and s [6], where the subdiffusion coefficient is defined as

$$D_\alpha = \frac{\sigma^2}{\theta^\alpha}\,. \tag{17}$$

Putting

$$e^{s^\alpha\theta^\alpha} \approx 1 + s^\alpha\theta^\alpha + \frac{s^{2\alpha}\theta^{2\alpha}}{2}\,, \tag{18}$$

to Eq. (16) and using the formula $\mathcal{L}^{-1}(s^\alpha \hat{g}(s)) = \partial^\alpha g(t)/\partial t^\alpha$ $(0 < \alpha < 1)$, one gets Eq. (12), where

$$\tau = \frac{\theta}{2^{1/\alpha}}\,. \tag{19}$$

From Eqs. (17) and (19) we see that the subdiffusion coefficient D_α is controlled by the parameter τ and reads

$$D_\alpha = \frac{\sigma^2}{2\tau^\alpha}\,. \tag{20}$$

We find the difficulties in the interpretation of Eq. (12). The parabolic subdiffusion equation can be obtained from the hyperbolic one by putting $\tau = 0$ in Eq. (12). On the other hand vanishing of τ provides the infinite

speed of propagation as it should be. However, due to Eq. (20), for $\tau = 0$ one gets the infinite value of the subdiffusion coefficient. We note that the only way to obtain the parabolic subdiffusion equation within this model is to neglect the last term in right-hand side of Eq. (18). Then, we obtain the parabolic subdiffusion equation (with the infinite speed of propagation) under condition that τ is finite.

4.3. Third equation

Another fractional hyperbolic equation presented in [6] is the equation obtained by combining the continuity equation (4) and the following flux equation

$$J(x,t) + \tau^{\alpha} \frac{\partial^{\alpha} J(x,t)}{\partial t^{\alpha}} = -D_{\alpha} \frac{\partial^{\alpha-1}}{\partial t^{\alpha-1}} \frac{\partial C(x,t)}{\partial x}\,, \tag{21}$$

what gives

$$\tau \frac{\partial^{2-\alpha} C(x,t)}{\partial t^{2-\alpha}} + \frac{\partial^{\alpha} C(x,t)}{\partial t^{\alpha}} = D_{\alpha} \frac{\partial^2 C(x,t)}{\partial x^2}\,. \tag{22}$$

However, the Green function of Eq. (22) provides the relation $\left\langle \Delta x^2 \right\rangle = 2D_{\alpha} t^{2-\alpha}/\Gamma(3-\alpha)$ for $t \gg \tau$, which characterize superdiffusion, not subdiffusion. Thus, we do not treat Eq. (22) as the subdiffusion equation.

Summarize the considerations presented in this section we conclude, that only Eq. (10) has clear physical interpretation and can be used as hyperbolic subdiffusion equation. Thus, in the following we apply Eq. (10) in our study.

5. Green function

To find the solution of Eq. (10) we needs two initial conditions. For the Green function we choose the initial conditions as

$$G(x,t;0) = \delta(x)\,, \tag{23}$$

where δ is the Dirac-delta function, and

$$\left.\frac{\partial G(x,t;0)}{\partial t}\right|_{t=0} = 0\,. \tag{24}$$

The boundary conditions read $G(-\infty,t;0) = G(\infty,t;0) = 0$. The Laplace transform of the Green function is

$$\hat{G}(x,t;0) = \frac{\sqrt{1+\tau s}}{2\sqrt{D_{\alpha}} s^{1-\alpha/2}} \exp\left(-\frac{s^{\alpha/2}|x|\sqrt{1+\tau s}}{\sqrt{D_{\alpha}}} \right)\,. \tag{25}$$

The limit of long time corresponds to the limit of small parameter s. Expanding the right-hand side of Eq. (25) into the power series, assuming that $\tau s \ll 1$ (what corresponds to $t \gg \tau$), keeping the leading terms and using the following formula [9]

$$\mathcal{L}^{-1}\left(s^{\nu}e^{-as^{\rho}}\right) \equiv f_{\nu,\rho}(t;a) = \frac{1}{t^{1+\nu}}\sum_{n=0}^{\infty}\frac{1}{n!\Gamma\left(-n\rho-\nu\right)}\left(-\frac{a}{t^{\rho}}\right)^{n}, \qquad (26)$$

$(a > 0)$, we get

$$\begin{aligned} G(x,t;0) \;=\; & \frac{1}{2\sqrt{D_{\alpha}}}\left[f_{\alpha/2-1,\alpha/2}\left(t;\frac{|x|}{\sqrt{D_{\alpha}}}\right)+\frac{\tau}{2}f_{\alpha/2,\alpha/2}\left(t;\frac{|x|}{\sqrt{D_{\alpha}}}\right)\right. \\ & \left.-\frac{|x|\tau}{2\sqrt{D_{\alpha}}}f_{\alpha,\alpha/2}\left(t;\frac{|x|}{\sqrt{D_{\alpha}}}\right)\right]. \end{aligned} \qquad (27)$$

The plots of Eq. (27) for different τ are presented in Fig. 1. We see that the effect of delaying is hardly observed in the considered cases.

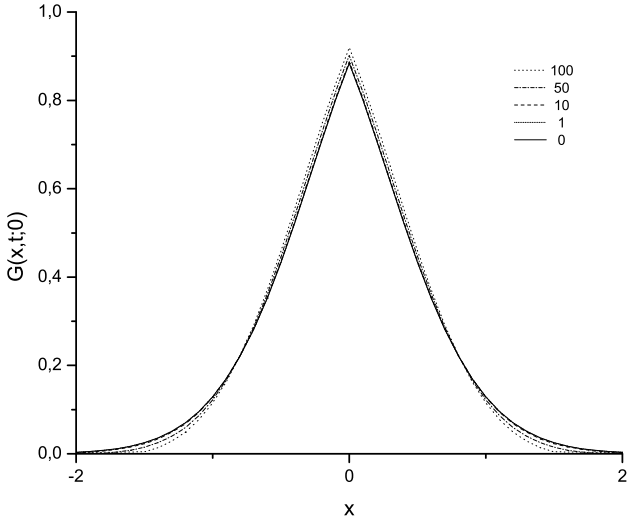

Fig. 1. The plots of the Green's functions (27) for different values of τ given in the legend; here $t = 500$, $D_{\alpha} = 10^{-3}$ and $\alpha = 0.8$ (all quantities are given in arbitrary units).

6. System with a thin membrane

We consider a system where a thin membrane is localized at $x = 0$. The concentrations and the fluxes in the region $x < 0$ we denote as $C_1(x,t)$ and $J_1(x,t)$ and for $x > 0$ as $C_2(x,t)$ and $J_2(x,t)$, respectively. Since the equa-

tion is of the second order with respect to the space variable, we need two boundary conditions in each of the region. Two of them demand finiteness of the solutions at $x \to -\infty$ and $x \to \infty$,

$$C_1(-\infty, t) = C_0, \qquad C_2(\infty, t) = 0\,, \tag{28}$$

and two other boundary conditions are fixed at the membrane. The first of them assumes the continuity of the flux at the membrane

$$J_1(0^-, t) = J_2(0^+, t) \equiv J(0, t)\,, \tag{29}$$

the second one reads

$$J(0, t) = \lambda[C_2(0^-, t) - C_1(0^+, t)]\,, \tag{30}$$

where λ is the membrane permeability coefficient. The initial condition is chosen as

$$C(x, 0) = \begin{cases} C_0, & x < 0\,, \\ 0, & x > 0\,. \end{cases} \tag{31}$$

The Laplace transforms of the solutions of Eq. (10) for the boundary and initial conditions (28)–(31) are

$$\hat{C}_1(x, s) = \frac{C_0}{s}\left[1 - \frac{\lambda}{2\lambda - \sqrt{D_\alpha} s^{1-\alpha/2}/\sqrt{1+\tau s}} \exp\left(x\sqrt{\frac{(1+\tau s)s^\alpha}{D_\alpha}}\right)\right]\,, \tag{32}$$

$$\hat{C}_2(x, s) = \frac{C_0}{s} \frac{\lambda}{2\lambda - \sqrt{D_\alpha} s^{1-\alpha/2}/\sqrt{1+\tau s}} \exp\left(-x\sqrt{\frac{(1+\tau s)s^\alpha}{D_\alpha}}\right)\,. \tag{33}$$

Assuming that $\tau s \ll 1$ and using Eq. (26) we get

$$\begin{aligned} C_1(x, t) \;=\; & C_0 - \frac{C_0}{2} \sum_{k=0}^{\infty} \left(-\frac{\sqrt{D_\alpha}}{2\lambda}\right)^k \left[f_{k(1-\alpha/2)-1,\alpha/2}\left(t; \frac{-x}{\sqrt{D_\alpha}}\right) \right. \\ & - \frac{k\tau}{2} f_{k(1-\alpha/2),\alpha/2}\left(t; \frac{-x}{\sqrt{D_\alpha}}\right) \\ & \left. + \frac{x\tau}{2\sqrt{D_\alpha}} f_{k(1-\alpha/2)+\alpha/2,\alpha/2}\left(t; \frac{-x}{\sqrt{D_\alpha}}\right) \right]\,, \end{aligned} \tag{34}$$

$$\begin{aligned} C_2(x, t) \;=\; & \frac{C_0}{2} \sum_{k=0}^{\infty} \left(-\frac{\sqrt{D_\alpha}}{2\lambda}\right)^k \left[f_{k(1-\alpha/2)-1,\alpha/2}\left(t; \frac{x}{\sqrt{D_\alpha}}\right) \right. \\ & + \frac{k\tau}{2} f_{k(1-\alpha/2),\alpha/2}\left(t; \frac{x}{\sqrt{D_\alpha}}\right) \\ & \left. - \frac{x\tau}{2\sqrt{D_\alpha}} f_{k(1-\alpha/2)+\alpha/2,\alpha/2}\left(t; \frac{x}{\sqrt{D_\alpha}}\right) \right]\,. \end{aligned} \tag{35}$$

The plots of functions (34) and (35) are presented in Fig. 2. As we can see, the differences between the solutions obtained for the parabolic subdiffusion equation are very close to the solution of hyperbolic equation (even for the largest time $\tau = 100$).

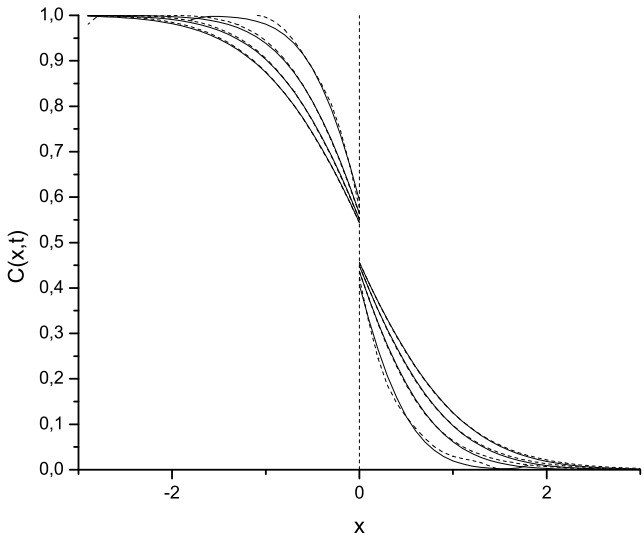

Fig. 2. The solutions calculated for $\lambda = 10^{-3}$, $\alpha = 0.9$, $D_\alpha = 5 \times 10^{-4}$ and for $t = 500,\ 1000,\ 1500,\ 2000$. Vertical line represents the membrane, dashed lines correspond to $\tau = 100$, continuous ones correspond to $\tau = 0$ (all quantities are given in arbitrary units).

7. Final remarks

The parabolic subdiffusion equation (6) has the 'unphysical' property manifested in the infinite speed of propagation. Introducing the hyperbolic subdiffusion equation (10) excludes this 'unphysical' property, but solving of this equation is significantly more complicated in comparison to the parabolic one. The plots presented in Figs. 1 and 2 suggest that the differences between the solution for the case $\tau \neq 0$ and $\tau = 0$ are too small in order to insist on using the hyperbolic subdiffusion equation in all situation. But there are systems (*e.g.* the electrochemical one) where using HSE is necessary [7].

Here the question arises: why the subdiffusion hyperbolic equation has not been applied to describe the experimental results in the subdiffusive membrane system, despite of proper 'physical quality' of the equation? Analyzing the plot (see Fig. 2) we conclude that in considered case there is no

reason to apply the hyperbolic subdiffusion equation instead of the parabolic one. The difference between the solutions is so small that both of them would certainly be laid within the error bars of the experimental concentration profiles. The order of values of the subdiffusion coefficient D_α taken into calculations agrees with the ones obtained experimentally for sugars in agarose gels [2] if as unit of time 1 sec is chosen and 1 mm is the unit of space variable. In these units the value $\tau = 100$ is certainly too large, nevertheless these differences are rather hard to observe, for smaller values of τ these differences are smaller.

REFERENCES

[1] R. Metzler, J. Klafter, *Phys. Rep.* **339**, 1 (2000).

[2] T. Kosztołowicz, K. Dworecki, S. Mrówczyński, *Phys. Rev. Lett.* **94**, 170602 (2005); *Phys. Rev.* **E71**, 041105 (2005).

[3] T. Kosztołowicz, *J. Membr. Sci.* **320**, 492 (2008).

[4] K. Dworecki, *Physica A* **359**, 24 (2006).

[5] G. Cattaneo, *Atti Sem. Mat. Fis. Univ. Mod.* **3**, 83 (1948).

[6] A. Compte, R. Metzler, *J. Phys. A* **30**, 7277 (1997).

[7] T. Kosztołowicz, K.D. Lewandowska, *J. Phys. A* **42**, 055004 (2009).

[8] K.D. Lewandowska, T. Kosztołowicz, *Acta Phys. Pol. B* **39**, 1221 (2008).

[9] T. Kosztołowicz, *J. Phys. A* **37**, 10779 (2004).