Hyperbolic versus parabolic equation with fractional derivative to describe subdiffusion in a membrane system

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Abstract. We use the parabolic and hyperbolic equation with fractional time derivative to describe the subdiffusion in a system with thin membrane. We find the Green’s function and solutions of the equation for the system where the homogeneous solution is separated by a thin membrane from the pure solvent. The solutions were obtained for two boundary conditions where the ratio of the concentrations at the membrane surfaces does not change in time and where the flux flowing through the membrane is proportional to the concentration difference between membrane surfaces. We discuss the difference between the solutions for parabolic and hyperbolic subdiffusion equations obtained for both boundary conditions.

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1. Introduction

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

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

where the subdiffusion parameter \( \alpha \) is less than one (0 < \( \alpha \) < 1), \( D_\alpha \) is the subdiffusion coefficient measured in the units \( m^2/s^\alpha \) [1]. The case of \( \alpha = 1 \) corresponds to the normal diffusion. The subdiffusion is related to an infinitely long average time that a random walker waits to make a finite jump. Then, its average displacement square, which is observed in a finite time interval, is dramatically suppressed. The subdiffusion occurs in systems with complex internal structure such as gels or porous media. To describe the subdiffusion the non-linear differential equation of natural order derived on the base of Tsallis formalism [2, 3] or the normal diffusion equation with diffusion coefficient which is assumed to be a power function of time \( D(t) = D_\alpha t^{\alpha-1} \) [4] were used. The Green’s functions obtained for these equations fulfill the relation (1), but the physical meaning of the assumptions providing to the equations is not always clear. For example, it is difficult to explain the decreasing of diffusion coefficient in time in a homogeneous system. The subdiffusion linear equation with fractional time derivative, derived on the base of Continuous Time Random Walk formalism [1, 5], has not got such disadvantages.

The subdiffusion in a membrane system was recently studied experimentally and theoretically. The motivation of the study is that the understanding of subdiffusion in a membrane system can help to model transport processes in systems so different as living cells and membrane microfilters (see for example [6]). The system with a membrane can also be used to measure subdiffusion parameters by comparing theoretical and empirical concentration profiles of substances of interest [7]. To model a transport process in such a system the parabolic subdiffusion equation was applied. However, the parabolic normal diffusion and parabolic subdiffusion equations give the solutions which posses the ‘unphysical’ property. Namely, for spatially unrestricted system the Green’s function \( G(x, t; x_0) \) (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 in \( x_0 \) ) have non-zero values for any \( x \) and \( t > 0 \). 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 based on the assumption that the diffusion flux is delayed in time \( \tau \) with respect to the concentration gradient [8]. The Green’s function of the equation is equal to zero for finite \( x - x_0 \), so the propagation velocity of the particles is finite. In phenomenological way the hyperbolic subdiffusion equation can be derived by involving the fractional time derivative into a flux or continuity equation. In the paper [9] there was noted that the hyperbolic subdiffusion equation can be derived in three different manners and the equations obtained are not equivalent to each other.

The delaying effect of the flux with respect to the concentration gradient seems to be stronger in a membrane system than in a homogeneous one, since the flux can be involved into boundary conditions at the membrane. So, the delaying effect can appear not only in the equation but also in the boundary conditions. As far as we know, the hyperbolic subdiffusion equation has not been applied to describe the subdiffusion in a membrane system yet. In our paper we compare the solutions of the parabolic and
hyperbolic subdiffusion equation in a homogeneous system and in a system with a thin membrane.

The problem of choosing a transport model in a membrane system is more complicated since one of the boundary conditions at the membrane is not set unambiguously. Two boundary conditions which are not equivalent to each other were used. First of them demands the constant ratio of the concentrations at the membrane surfaces [10, 11], the second one assumes that the flux is proportional to the concentration difference between membrane surfaces [12, 13]. The qualitatively difference between them is manifested in the long time limit because the concentrations calculated for second boundary condition goes to a continuous function at the membrane, unlike than for the first one.

In our paper we find the solutions of the hyperbolic equations for a system with a thin membrane for two boundary conditions mentioned above and compare them with the ones obtained from parabolic equation. We consider the system where the thin membrane separates a homogeneous solution from a pure solvent (we add that such a system was often used in experimental studies [7, 11, 14, 15]). In our study we assume that the system is one-dimensional where the diffusion or subdiffusion parameter as well as the parameter of membrane permeability do not depend on time and concentration, the first one is also independent of space variable.

The paper is organized as follows. In section 2 we present the phenomenological derivation of the hyperbolic equation for normal diffusion. We show plots of the Green’s functions obtained for the long times for the homogeneous system without a membrane. In section 3 we present the hyperbolic equation and the Green’s functions for the subdiffusive system. The boundary conditions at a thin membrane are derived in section 4. Solutions of the hyperbolic equation for the system where the homogeneous solution is separated by the thin membrane from pure solvent are presented in section 5. To illustrate our considerations the function obtained in sections 2, 3 and 5 are shown in several plots. Analyzing the plots we discuss the properties of the solutions in section 6.

2. Normal diffusion equation

2.1. Parabolic equation

It is well known that the normal diffusion equation
\[
\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2}
\]

with normal diffusion coefficient \(D\) (measured in the units \(m^2/s\)), can be derived phenomenologically by combining the first Fick’s law
\[
J(x, t) = -D \frac{\partial C(x, t)}{\partial x},
\]
and the continuity equation
\[
\frac{\partial C(x, t)}{\partial t} = - \frac{\partial J(x, t)}{\partial x}.
\]

The Green’s function is defined as a solution of the equation for the initial condition
\[
G(x, t; x_0) = \delta(x - x_0),
\]
and boundary conditions appropriate for considered system. When the system is not spatially restricted, there is
\[ G(-\infty, t; x_0) = G(\infty, t; x_0) = 0, \]
and the Green’s function reads
\[ G(x, t; x_0) = \frac{1}{2\sqrt{\pi Dt}} \exp \left( -\frac{(x-x_0)^2}{4Dt} \right). \]
The function \( G \) is different from zero for any \( x \) and \( t > 0 \). Utilizing the probability interpretation of the Green’s function one concludes that some particles are transported with the infinite speed propagation.

### 2.2. Hyperbolic equation

To ensure the finite velocity of the particle propagation one assumes that the flux is delayed with respect to the concentration gradient
\[ J(x, t + \tau) = -D \frac{\partial C(x, t)}{\partial x}, \]
where \( \tau \) is the delay time. Assuming that the parameter \( \tau \) is sufficiently small, the left hand side of equation (8) can be approximated by the first two terms of Taylor series with respect to \( \tau \)
\[ J(x, t) + \tau \frac{\partial J(x, t)}{\partial t} = -D \frac{\partial C(x, t)}{\partial x}. \]
Applying the operator \( \partial/\partial x \) to equation (9) and taking into considerations the continuity equation (4) one gets the hyperbolic diffusion equation
\[ \tau \frac{\partial^2 C(x, t)}{\partial t^2} + \frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2}. \]
We add that equation (10) can be derived from differential-difference equations with continuous time and discrete space variable [16]. The process can be interpreted as a process with ‘minimal’ memory which extends to one time step more than in ‘ordinary’ diffusion process described by parabolic diffusion equation.

Equation (10) ensures the finite propagation velocity of the particles \( v = \sqrt{D/\tau} \). In the limit \( \tau \to 0 \) we get parabolic diffusion equation with infinite \( v \). To solve equation (10) we must take two initial conditions. Let us assume that one of them is
\[ \frac{\partial C(x, t)}{\partial t} \Bigg|_{t=0} = 0, \]
what means that at an initial moment the concentration does not aim at its change and is effectively changed after time \( \tau \) since the particle flux is not generated before this time. The second boundary condition reads as \( C(x, 0) = f(x) \).

### 2.3. Green’s function

We obtain the Green’s function for equation (10) solving it by means of the Laplace \( L[f(t)] = \hat{f}(s) = \int_0^\infty f(t) \exp(-st)dt \) and Fourier \( F[g(x)] = \hat{g}(k) = \int_{-\infty}^{\infty} g(x) \exp(ikx)dx \) transforms method for the initial conditions (5) (with \( x_0 = 0 \)) and (11). After simple calculations we get the Green’s function in terms of Laplace and Fourier transforms
\[ \hat{G}(k, s; 0) = \frac{1 + \tau s}{s + \tau s^2 + Dk^2}. \]
The inverse Fourier transform of equation (12) reads
\[ \hat{G}(x, s; 0) = \frac{1}{2\sqrt{Ds}} \exp \left( -\frac{|x|\sqrt{s}}{\sqrt{D}} \right). \] (13)

The hyperbolic equation was derived on the assumption that we omit the terms which include the parameter \( \tau_k, k > 1 \), in the Taylor series of the flux (see equation (9)). We find similar approximation of equation (13), namely
\[ \hat{G}(x, s; 0) = \frac{1}{\sqrt{Ds}} \exp \left( -\frac{|x|\sqrt{s}}{\sqrt{D}} \right). \] (14)

The inverse Laplace transform of equation (14) is
\[ G(x, t; 0) = \frac{1}{\beta a} \left( 1 + \frac{|x|^2}{4Dt} \right) \exp \left( -\frac{|x|^2}{4Dt} \right) f_{\nu,1/2,1/2}(t; |x|/\sqrt{D}), \] (15)

where the function \( f \) is defined as \[ f_{\nu,\beta}(t; a) = L^{-1} \left[ s^{\nu} \exp \left( -as^{\beta} \right) \right], \]
for \( a, \beta > 0 \). This function can be expressed by the Fox function \( H \) and reads
\[ f_{\nu,\beta}(t; a) = \frac{1}{\beta a} \left( \frac{1}{1/\beta} \right) \left( \frac{1}{1+1/\beta} \right) \]
\[ = \frac{1}{t^{1+\nu}} \sum_{k=0}^{\infty} \frac{1}{k! \Gamma(-k\beta-\nu)} \left( -\frac{a}{t^{\beta}} \right)^k. \] (16)

**Figure 1.** The plots of the normal diffusion Green’s functions for different values of parameter \( \tau \) given in the legend, here \( t = 500, D = 10^{-3} \).

The plots of function (15) are presented in figure 1 for different values of the parameter \( \tau \). As we can see, only relatively large values of \( \tau \) make the noticeable difference between the Green’s functions obtained for the parabolic equation (represented by the solutions for \( \tau = 0 \)) and the hyperbolic one.
3. Subdiffusion equation

3.1. Parabolic equation

The hyperbolic subdiffusion equation can be derived by analogy with the derivation of the parabolic one. There are few ways to find the parabolic subdiffusion equation in phenomenological way. In the following we consider two of them which are natural generalization of the derivation of the parabolic normal diffusion equation. In the first one it is assumed that the subdiffusive flux reads as

\[ J(x, t) = -D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial C(x, t)}{\partial x}, \]  

(17)

where \( \partial^{\alpha}_{RL}/\partial t^{\alpha} \) denotes the Riemann-Liouville fractional time derivative defined as \[ \frac{d^{-\alpha}_{RL}f(t)}{dt^{-\alpha}} = \frac{1}{\Gamma(\alpha)} \int_0^t (t-u)^{\alpha-1} f(u)du, \]  

(18)

and \[ \frac{d^n_{RL}f(t)}{dt^n} = \frac{d_{RL}^{\alpha-n}f(t)}{dt^{\alpha-n}}, \]  

(19)

where \( n \) is the lowest natural number that fulfills \( n \geq \alpha \). The Laplace transform of the Riemann-Liouville derivative is

\[ L \left[ \frac{d_{RL}^{\alpha}f(t)}{dt^{\alpha}} \right] = s^{\alpha} \hat{f}(s) - \sum_{k=0}^{n-1} s^{k} \frac{d_{RL}^{\alpha-k-1}f(t)}{dt^{\alpha-k-1}} \bigg|_{t=0}, \]  

(20)

where \( n-1 \leq \alpha < n \). Combining equation (17) with equation (4) one gets the parabolic subdiffusion equation \[ \frac{\partial C(x, t)}{\partial t} = D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2 C(x, t)}{\partial x^2}. \]  

(21)

In general, to solve the differential equation with the fractional Riemann-Liouville derivative by means of the Laplace transform method, one should fix the initial condition for time derivatives of the fractional negative order (see equation (20)), what is beyond of physical interpretation. However, this remark does not concern the subdiffusion equation (21) since for a limited function there is (see Appendix)

\[ \frac{\partial^{\alpha-1}_{RL}C(x, t)}{\partial t^{\alpha-1}} \bigg|_{t=0} = 0, \]  

(22)

when \( 0 < \alpha < 1 \). The Laplace and Fourier transforms of (21) is

\[ s\hat{C}(k, s) - F[C(x, 0)] = -D_\alpha s^{1-\alpha}k^2 \hat{C}(k, s). \]  

(23)

For the Green’s function with the initial condition (23) we get \( F[C(x, 0)] = 1 \), what leads to the form of equation (23) obtained from the Continuous Time Random Walk formalism [1].

Another scenario provides to the subdiffusion equation consists in changing the time derivative of natural order to the fractional Caputo one in the continuity equation (4) according to the formula \( \partial/\partial t \rightarrow \theta \partial^{\alpha}_{\text{Caputo}}/\partial t^{\alpha} \), where \( \theta \) is a parameter which is involved to achieve an appropriate physical units. The Caputo fractional derivative is defined by the relation \[ \frac{d_{\text{Caputo}}^{\alpha}f(t)}{dt^{\alpha}} = \frac{1}{\Gamma(n-\alpha)} \int_0^t (t-u)^{\alpha-1} \frac{d^n}{dt^n} f(u)du, \]  

(24)
and its Laplace transform reads as

\[ L \left[ \frac{\partial^\alpha f(t)}{\partial t^\alpha} \right] = s^\alpha \hat{f}(s) - \sum_{k=0}^{n-1} s^{\alpha-k-1} \frac{d^k f(t)}{dt^k} \bigg|_{t=0}, \]

(25)

where \( n - 1 \leq \alpha < n \). Thus, we get

\[ \theta \frac{\partial^\alpha C(x, t)}{\partial t^\alpha} = -\frac{\partial J(x, t)}{\partial x}. \]

(26)

In the following we take

\[ \theta = \frac{D}{D_0}. \]

(27)

Combining (5), (26) and (27) one gets the subdiffusion equation

\[ \frac{\partial^\alpha C(x, t)}{\partial x^\alpha} = D_0 \frac{\partial^2 C(x, t)}{\partial x^2}. \]

(28)

Equation (28) is equivalent to equation (21) since their Laplace and Fourier transforms are expressed by (23).

3.2. Hyperbolic equation

The hyperbolic subdiffusion equation can be obtained by introducing the time derivative of fractional order to equations (4) or (9). As was noticed in the paper [9], where the Riemman-Liouville fractional derivative only was taken into considerations, it can be done in three different manners. Unlike in [9], we involve Caputo fractional derivative into the continuity equation (4). We assume that the flux is given as follow

\[ J(x, t + \tau) = -D_0 \frac{\partial^1_{RL} C(x, t)}{\partial t^1 - \alpha} \frac{\partial C(x, t)}{\partial x}. \]

(29)

Similarly to the previous case, let us approximate the left hand of equation (29) for \( \tau \ll t \) by the first two terms of Taylor series with respect to \( \tau \)

\[ J(x, t) + \tau \frac{\partial J(x, t)}{\partial t} = -D_0 \frac{\partial^1_{RL} C(x, t)}{\partial t^1 - \alpha} \frac{\partial C(x, t)}{\partial x}. \]

(30)

From equation (30) and equation (4) we get the hyperbolic subdiffusion equation

\[ \tau \frac{\partial^2 C(x, t)}{\partial t^2} + \frac{\partial C(x, t)}{\partial t} = D_0 \frac{\partial^1_{RL} \partial^2 C(x, t)}{\partial t^1 - \alpha}. \]

(31)

Let us note that from equations (3), (26) and (27) we get the hyperbolic subdiffusion equation with Caputo fractional derivatives

\[ \tau \frac{\partial^1_{C} C(x, t)}{\partial t^{1+\alpha}} + \frac{\partial^2 C(x, t)}{\partial t^\alpha} = D_0 \frac{\partial^2 C(x, t)}{\partial x^2}. \]

(32)

Equation (32) is fully equivalent to equation (31) since the Laplace and Fourier transforms of the equations are the same.
3.3. Green’s function

As previous, we take the initial conditions (5) (for \( x_0 = 0 \)) and (11) to solve equation (31). After calculations we get

\[
\hat{G}(k, s; 0) = \frac{1 + \tau s}{s + \tau s^2 + D_\alpha s^{1-\alpha} k^2},
\]

the inverse Fourier transform of equation (33) is

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

The hyperbolic equation was derived under the assumption that we take into account linear terms in the Taylor series of the flux (see equation (9)). Let us perform similar approximation for equation (13), what gives

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

The inverse Laplace transform of equation (35) is

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

Figure 2. Hyperbolic subdiffusion. The plots of the Green’s functions for different values of \( \tau \), here \( t = 500 \), \( D_\alpha = 10^{-3} \), \( \alpha = 0.5 \).

The plots of the Green’s functions (36) are presented in figures 2-4. Contrary to the normal diffusion case, the effect of delaying is hardly observed in the considered cases.
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Figure 3. The description as in figure 2 but for $\alpha = 0.8$.

Figure 4. The Green’s functions for $t = 500, 1000, 1500, 2000$, here $D_\alpha = 10^{-3}$, $\alpha = 0.8$, the dashed lines correspond to $\tau = 100$, continuous ones represent the Green’s functions with $\tau = 0$. 
4. Boundary conditions at thin membrane

We denote the concentration and flux in the region \( x < x_m \) as \( C_1 \) and \( J_1 \), and in the region \( x > x_m \) as \( C_2 \) and \( J_2 \), respectively, where \( x_m \) is the membrane position. Since the equation is of the second order with respect to the space variable, we need two boundary conditions in each of the region. Two boundary conditions demand finiteness of the solutions at \( x \to -\infty \) and \( x \to \infty \), two other ones are fixed at the membrane. The first of them is rather obvious and it assumes the continuity of the flux at the membrane

\[
J_1(x_m^-, t) = J_2(x_m^+, t) \equiv J(x_m, t). \tag{37}
\]

However, the problem of fixing the second boundary condition at the thin membrane is not unambiguously solved. The missing boundary condition at the membrane has been chosen in two ways. The first one demands the constant ratio of the concentrations at two opposite sides of the membrane \([7, 10, 11]\)

\[
C_2(x_m^+, t)/C_1(x_m^-, t) = \gamma = \text{const.} \tag{38}
\]

In the second one the flux flowing through the membrane is proportional to the difference of the concentrations at the opposite sides of the membrane \([7, 12, 13]\)

\[
J(x_m, t) = \lambda[C_2(x_m^-, t) - C_1(x_m^+, t)], \tag{39}
\]

where \( \lambda \) is the membrane permeability coefficient. Below we consider the possibility of application of the boundary conditions \([38] \) or \([39] \) for the case of the system described by the hyperbolic normal diffusion or hyperbolic subdiffusion equation.

4.1. Constant concentration ratio at the membrane

In the Smoluchowski’s papers (see for example \([20]\)) it was derived the boundary condition at the fully reflecting wall. Let the wall is placed at \( x_m \) and the system occupies the interval \((-\infty, x_m)\). Smoluchowski’s original approach utilized the assumptions that the amount of the substance in the system does not change in time

\[
\frac{\partial}{\partial t} \int_{-\infty}^{x_m} C(x,t) dx = 0, \tag{40}
\]

and the flux vanishes at \(-\infty\). Integrating the continuity equation \([4] \) over the interval \((-\infty, x_m)\) and using the above assumptions one gets

\[
J(x_m, t) = 0. \tag{41}
\]

Since equation \([4] \) works in hyperbolic subdiffusion equation case, we choose the boundary condition \([41] \) at the fully reflecting wall for the system described by the hyperbolic equation.

Chandrasekhar used the method of images to derive the Green’s function for this system \([21]\). The Green’s function can be interpreted as a concentration of large number of particles \( N \) (divided by \( N \)); the particles are located at point \( x_0 \) at the initial moment \( t = 0 \). So, the Green’s function can be treated as an instantaneous particle source (IPS) normalized to 1. Within the method one replaces the wall by additional IPS in such a manner that the concentration behaves exactly as in the system with the wall. Vanishing of the flux at the reflecting wall is achieved when one replaces the wall by the IPS located symmetrically to the initial point \( x_0 \) with respect to the wall. Then the instantaneous particle sources create fluxes of particles flowing
in opposite directions, which reduce each other at the point $x_m$. Thus, one finds (for $x < x_m$ and $x_0 < x_m$)

$$G(x, t; x_0) = G_0(x, t; x_0) + G_0(x, t; 2x_m - x_0),$$

(42)

where $G_0$ denotes the Green’s function for a homogeneous system (without the wall). Let us note that the Green’s function equation (42) leads to equation (41) in any system where the flux fulfills the following relation

$$J \sim \frac{\partial C}{\partial x}.$$  

(43)

In the papers [10] the method of images was generalized to the system with a partially permeable wall. Since the Green’s function (42) works in the system with fully reflecting wall, where a transport is described by hyperbolic diffusion or subdiffusion equation, similar generalization can be performed in such a system with thin membrane.

In the system with thin membrane the particles can pass through the membrane in both directions many times. Let us assume that the membrane is symmetric and the probabilities of passing through it do not depend on the direction of particle’s motion. To take into account selective properties of the membrane, we ‘weaken’ the additional IPS located at $2x_m - x_0$ by factor $\sigma$, which gives

$$G(x, t; x_0) = G_0(x, t; x_0) + \sigma G_0(x, t; 2x_m - x_0).$$

(44)

Assuming that the flux is continuous at the membrane, we get for $x > x_m$ and $x_0 < x_m$

$$G(x, t; x_0) = (1 - \sigma) G_0(x, t; x_0).$$

(45)

The functions (44) and (45) fulfill the boundary condition (38) with $\lambda = (1 - \sigma)/(1 + \sigma)$. To interpret the parameter $\sigma$ let us note that the probability of finding a particle (starting from $x_0$, where $x_0 < x_m$) in the region $x > x_m$ is equal to $P_\sigma = (1 - \sigma) \int_{x_m}^{\infty} G_0(x, t; x_0) dx$ for the membrane system, whereas the probability of finding the particle in this region for system without the membrane is equal to $P_0 = \int_{x_m}^{\infty} G_0(x, t; x_0) dx$. Comparing the above equations we obtain $\sigma = 1 - P_\sigma/P_0$, so the parameter $\sigma$ can be interpreted as a probability of finding the particle in the region $x < x_m$ under condition that in the system with removed membrane the particle will be in the region $x > x_m$. In other words, $\sigma$ is a conditional probability of stopping the particle by the membrane in unit time under condition, that in the similar system with no membrane this particle pass the position $x_m$. Thus, $\sigma$ is the parameter controlling the reflection of particles by the membrane, the parameter $1 - \sigma$ is the parameter of membrane permeability. The boundary condition (38) has simple physical interpretation: if $N$ diffusing particles are going to pass through the wall in unit time, then $\sigma N$ of them will be stopped by the wall whereas $(1 - \sigma)N$ pass through, where $\sigma = (1 - \lambda)/(1 + \lambda)$.

4.2. Radiation boundary condition

For the parabolic normal diffusion equation the radiation boundary condition [39] was derived from the model with discrete space variable [12] as well as for the considerations performed in a phase space where the diffusion is described by the Klein-Kramers equation [13]. Equation (39) can be interpreted as the natural continuation of the Fick equation applied to the membrane. According to equation (39), we can generalize equation (39) as follows

$$J(x_m, t + \tau) = \lambda [C_1(x_m^-, t) - C_2(x_m^+, t)].$$

(46)
In the following we will see that the boundary conditions (38) and (46) are not equivalent to each other.

5. Solutions of hyperbolic subdiffusion equation for a membrane system

Let us assume that the thin membrane is located at \( x_m = 0 \). We choose the initial condition as

\[
C(x, 0) = \begin{cases} 
C_0, & x < 0 \\
0, & x > 0.
\end{cases}
\]  

(47)

The boundary conditions demand finiteness of the solutions at infinity

\[
C_1(-\infty, t) = C_0, \quad C_2(\infty, t) = 0.
\]  

(48)

The first boundary condition at the membrane \([57]\) ensures that the flux is continuous at the one, the second boundary condition at the membrane we take in general form

\[
b_1 C_1(0^-, t) + b_2 C_2(0^+, t) + b_3 J(0, t + \tau) = 0.
\]  

(49)

We note that the Laplace transform of the flux reads

\[
\hat{J}(x, s) = -D_\alpha s^{1-\alpha} \frac{d \hat{C}(x, s)}{dx}.
\]  

(50)

The Laplace transforms of solutions for boundary conditions \((37), (48), (49)\) and initial condition \((47)\) are as follows

\[
\hat{C}_1(x, s) = \frac{C_0}{s} \left[ 1 - \frac{b_1}{b_1 - b_2 - b_3 \sqrt{D_\alpha} s^{1-\alpha/2}/\sqrt{1 + \tau s}} \exp \left( x \sqrt{\frac{(1 + \tau s)s^\alpha}{D_\alpha}} \right) \right],
\]  

(51)

\[
\hat{C}_2(x, s) = \frac{C_0}{b_1 - b_2 - b_3 \sqrt{D_\alpha} s^{1-\alpha/2}/\sqrt{1 + \tau s}} \exp \left( -x \sqrt{\frac{(1 + \tau s)s^\alpha}{D_\alpha}} \right).
\]  

(52)

Below we find the solutions for two boundary conditions described in section 4.

5.1. Constant ratio of the solutions at the membrane

Putting \( b_1 > 0, \ b_2 < 0 \) and \( b_3 = 0 \) in \((49)\) we get equation \((38)\) with \( \gamma = -b_2/b_1 \). The solutions are as follows

\[
C_1(x, t) = C_0 \left[ 1 - \sigma f_{-1,\alpha/2} \left( t; \frac{-x}{\sqrt{D_\alpha}} \right) - \sigma \frac{\tau x}{2 \sqrt{D_\alpha}} f_{\alpha/2,\alpha/2} \left( t; \frac{-x}{\sqrt{D_\alpha}} \right) \right],
\]  

(53)

\[
C_2(x, t) = C_0 \sigma \left[ f_{-1,\alpha/2} \left( t; \frac{x}{\sqrt{D_\alpha}} \right) - \sigma \frac{\tau x}{2 \sqrt{D_\alpha}} f_{\alpha/2,\alpha/2} \left( t; \frac{x}{\sqrt{D_\alpha}} \right) \right],
\]  

(54)

where \( \sigma = 1/(1 + \gamma) \). The plots of functions \((53)\) and \((54)\) are presented in figure 5.

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 \( \tau = 100 \)).
5.2. Radiation boundary condition

Here \( b_1 = -b_2 > 0, \; b_3 < 0 \). The boundary condition takes the form of equation (46) where \( \lambda = -b_1/b_3 \). To obtain the inverse transforms of equations (51) and (52) we assume that \( \tau s \ll 1 \) (what corresponds to \( t \gg 1/\tau \)) and we extend the transforms into the power series with respect to the parameter \( s \). Achieving only the linear terms with respect to \( \tau \) we get

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

(55)

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

(56)

The plots of functions (55) and (56) are presented in figures 6 and 7.

6. Final remarks

We present here the solutions of the parabolic and hyperbolic subdiffusion equations for the homogeneous system and for the membrane one. The solutions were found
under assumption that we take into account the terms linear with respect to the parameter $\tau$. We applied two different boundary conditions at the membrane. Our
considerations are illustrated by few plots presenting the solutions for both of the boundary conditions. The plots were prepared for the parameters which values are of the order of the ones already found for real systems on the basis of experimental results [7]. The detailed remarks extracted from the plots are not fully conclusive, but it suggested few regularities, which - in our opinion - are general. They are as follows.

(i) For the boundary condition (38)

• The solutions at the membrane do not change in time and read as $C_1(0^-, t) = (\gamma C_0)/(1+\gamma)$, $C_2(0^+, t) = C_0/(1+\gamma)$. This property seems to be ‘unphysical’, but let us note that the solution obtained for the system without membrane (for which $b_1 = -b_2$ and $b_3 = 0$) with initial condition (47) are constant for $x = 0$ and reads as $C(0, t) = C_0/2$.

• The delay effect does not occur at the membrane, consequently it is weak at the membrane neighborhood.

(ii) For radiation boundary condition (46)

• The concentration difference between the surfaces decreases in time (see figure 6). From equations (51) and (52) it is easy to see that $C_1(0, t) \rightarrow C_2(0, t)$ when $t \rightarrow \infty$, since the long time limit corresponds to the limit of small $s$.

• For $\lambda \sim 10^{-1}$ the membrane loses its selectivity.

(iii) The main qualitative difference between the above boundary conditions is noticeable in the long time limit as boundary condition (39) leads to the solutions of hyperbolic subdiffusion equation which are going to the continuous function at the barrier, unlike than the solutions obtained for (38).

(iv) In all cases the delayed effect is connected with the subdiffusion parameter $\alpha$ (this property is clearly seen in figure 1 - figure 3 for the Green’s functions). When $\alpha$ increases, the delaying effect is stronger.

(v) For large times the delaying effect is negligibly small. Let us note that for large time the term $\tau/t$ vanishes (it corresponds to the limit $\tau s \rightarrow 0$ in equations (51) and (52)).

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 plots 2 - 7 we conclude that in considered cases 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 $D_\alpha$ taken into calculations agrees with the ones obtained experimentally for sugars in agarose gels [7] 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 $\tau$ these differences are smaller.

There is a problem with choosing the boundary condition at the membrane. Seemingly there is no problem with choosing the condition since the real system is limited by external walls and the concentration goes to equilibrium functions which is continuous at the membrane. This property posses the radiation boundary condition only. However, experimental study performed on two membrane system show that the concentration profiles have the scaling property, which is limited to the theoretical
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solutions obtained for the boundary conditions only. Namely, changing the variables according to the relation \((x, t) \rightarrow (p^\alpha x, pt)\), \(p > 0\) the experimental profiles does not display noticeable changes. So, if the particles flowing through the membrane do not ‘feel’ the presence of external walls of the system, the boundary conditions can be used.

Although our conclusion is rather odd in respect to the membrane system, there are systems where the solutions of the hyperbolic and parabolic equations considerably differ from each other. Such a situation occurs for the boundary conditions where the concentration of the particles oscillates with high frequency, as for example in the problem of impedance spectroscopy.

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Appendix

Here we proof the relation \(22\). Let us assume that \(|C(x, u)| \leq A\) for \(u \in (0, t]\) and \(C(x, t) \to 0\) when \(t \to 0\). Then,

\[
\frac{\partial^{\alpha-1}C(x, t)}{\partial x^{\alpha-1}} \leq \frac{A}{\Gamma(1-\alpha)} \int_0^t (t-u)^{-\alpha}du = \frac{A}{\Gamma(1-\alpha)} t^{1-\alpha}.
\]

From the above equation we get equation \(22\).

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