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SPECIAL ISSUE PAPER

Boundary conditions at a thin membrane for normal diffusion, classical subdiffusion, and slow subdiffusion processes†

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Summary

We consider three different diffusion processes in a system with a thin membrane: normal diffusion, classical subdiffusion, and slow subdiffusion. We conduct the considerations following the rule: *If a diffusion equation is derived from a certain theoretical model, boundary conditions at a thin membrane should also be derived from this model with additional assumptions taking into account selective properties of the membrane*. To derive diffusion equations and boundary conditions at a thin membrane, we use a particle random walk model in one-dimensional membrane system in which space and time variables are discrete. Then we move from discrete to continuous variables. We show that the boundary conditions depend on both selective properties of the membrane and a type of diffusion in the system.

KEYWORDS:
subdiffiusion, membrane boundary conditions, fractional calculus

1 | INTRODUCTION

Normal diffusion and anomalous diffusion are stochastic processes that can be described by partial differential equations derived from various stochastic models[1,2,3,4,5,6,7]. Diffusion is usually characterized by the time evolution of mean square displacement of a particle

$$\left\langle (\Delta x)^2(t) \right\rangle \sim f(t). \tag{1}$$

The function f is very often used to define a type of diffusion, $f(t) = t^\alpha$ with $\alpha > 1$ for superdiffusion, $\alpha = 1$ for normal diffusion, $0 < \alpha < 1$ for classical subdiffusion, when $f(t)$ is a slowly varying function we have slow subdiffusion (which is also called ultraslow diffusion)[8,9]. In the following we consider normal diffusion and subdiffusion processes in a one–dimensional system. Formally, normal diffusion can be treated as a special case of subdiffusion for which $\alpha = 1$. However, the physical interpretation of normal diffusion differs from the interpretation of subdiffusion. Namely, in the Continuous Time Random Walk (CTRW) model[4,6], the average waiting time of a diffusing particle for a jump is finite for normal diffusion and infinite for both types of subdiffusion. Subdiffusion occurs in media where the movement of molecules is very hindered comparing to diffusion in 'ordinary' liquids. Classical subdiffusion can occur in gels or porous media[10,11]. This process is observed in various biological systems, see for example[12,13,14,15,16,17]. To distinguish between classical subdiffusion and slow subdiffusion, it is required to include in the considerations fractional moments of the distribution of time which is needed to take particle's next step; this issue is discussed in[18]. We mention that these processes are qualitatively different. It is supposed that slow subdiffusion can occur in crowded disordered media, such as narrow membrane channels[19].

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[0]**Abbreviations:** CTRW, Continuous Time Random Walk

Usually, modelling normal or anomalous diffusion in the natural sciences differential or differential-integral diffusion equations are derived from certain theoretical models. An example is the fractional subdiffusion equation derived from the CTRW model[4,6]. In biological systems, the diffusion of particles is additionally hindered by the presence of membranes. It is essential to determine the boundary conditions at a thin membrane which is treated here as a partially absorbing or partially reflecting wall. However, membrane boundary conditions are often just assumed. In our opinion, the boundary conditions should take into account the characteristic features of the process that have been considered when deriving the diffusion equation. We therefore postulate: *If the diffusion equation is derived from a certain theoretical model, the boundary conditions at the thin membrane should also be derived from this model with additional assumptions taking into account the selective properties of the membrane*. In other words, the boundary conditions should take into account not only the permeability of the membrane, but also a type of particle transport in the system. In particular, the boundary conditions commonly used for normal diffusion should not be applied, without any justification, for a system in which subdiffusion occurs. Assuming that particles diffuse independently of each other, the diffusion equation can be derived from the model describing the random walk of a single particle. To derive membrane boundary conditions, random walk of a particle models on a discrete lattice with continuous time have been often used[20,21,22,23,24,25]. We mention that the classification of boundary conditions at a partially permeable or absorbing wall for the diffusion process, especially using the Feller semigroup method, has been widely considered, see[26,27,28].

In this paper we present a simple particle random walk model in a one-dimensional system with a thin membrane, which leads to both diffusion equations and boundary conditions at the membrane. Unlike in the papers cited above, we assume that a particle is not temporarily retained at a point representing the membrane. The results obtained are qualitatively different from the results presented in the above cited papers. We show that the boundary conditions depend on both a membrane permeability coefficient and a type of diffusion. First, we consider a particle's random walk in a system in which spatial and time variables are discrete. Then we move from discrete to continuous variables. The model differs from the CTRW model because a random variable is only the time between particle's jumps, while the jump length is a parameter. We show that this model is useful for modelling diffusion in a membrane system. In our considerations, we first derive the probability distributions of finding a diffusing particle in both parts of the system separated by a thin membrane. Then, we derive boundary conditions from the obtained distributions. We mention that such a way of deriving boundary conditions at fully reflecting or fully absorbing wall for normal diffusion has been presented in[29]. The model presented in this paper has been used to model different diffusion processes in systems with a thin membrane[18,30,31,32,33,34]. The aim of this paper is to show that boundary conditions at the membrane should depend on the type of diffusion. We also present the new form of boundary condition at the membrane for the slow subdiffusion process.

The organization of paper is as follows. In Sec. 2 we show equations for different types of diffusion and their fundamental solutions derived by means of the Laplace transform method. In Sec. 3 we show that the equations and their fundamental solutions can be derived from a simple random walk model of a particle in a discrete system. In Sec. 4 we show that this model can be simply generalized to a system with a thin membrane. We also derive fundamental solutions for the membrane system by means of the method presented in Sec. 3, taking into account the selective properties of the membrane. From the solutions we obtain general forms of boundary conditions at a thin membrane. Explicit forms of fundamental solutions and boundary conditions at the membrane for normal diffusion, classical subdiffusion, and slow subdiffusion are presented in Sec. 5. A brief discussion of the results is in Sec. 6.

2 | NORMAL DIFFUSION AND SUBDIFFUSION EQUATIONS AND THEIR FUNDAMENTAL SOLUTIONS

We assume that the general form of subdiffusion equation reads (to shorten the description, we treat here normal diffusion as a special case of subdiffusion for $\alpha = 1$)

$$\int_0^t F(t-t')\frac{\partial P(x,t';x_0)}{\partial t'}dt' = D\frac{\partial^2 P(x,t;x_0)}{\partial x^2}\ , \tag{2}$$

where $P(x,t;x_0)$ denotes a probability of finding a diffusing particle at a point x at time t, x_0 denotes the initial position of the particle, D is a diffusion coefficient,

$$P(x;0;x_0) = \delta(x-x_0), \tag{3}$$

δ is the delta–Dirac function. A solution to diffusion equation which fulfils the initial condition (3) is usually called a fundamental solution. Considering diffusion in the interval $(-\infty, \infty)$ the boundary conditions are assumed to be

$$P(\pm\infty; t; x_0) = 0. \tag{4}$$

If the Laplace transform, $\mathcal{L}[f(t)] = \hat{f}(s) = \int_0^\infty \mathrm{e}^{-st} f(t)dt$, of the function F exists, in terms of the Laplace transform Eq. (2) reads

$$\frac{\upsilon(s)}{s}\left[s\hat{P}(x, s; x_0) - P(x, 0; x_0)\right] = D\frac{\partial^2 \hat{P}(x, s; x_0)}{\partial x^2}\ . \tag{5}$$

where

$$\upsilon(s) = s\hat{F}(s). \tag{6}$$

The fundamental solution to Eq. (5) with initial condition (3) and the Laplace transform of boundary conditions (4) is

$$\hat{P}(x, s; x_0) = \frac{\sqrt{\upsilon(s)}}{2s\sqrt{D}}\ \mathrm{e}^{-|x-x_0|\sqrt{\frac{\upsilon(s)}{D}}}\ . \tag{7}$$

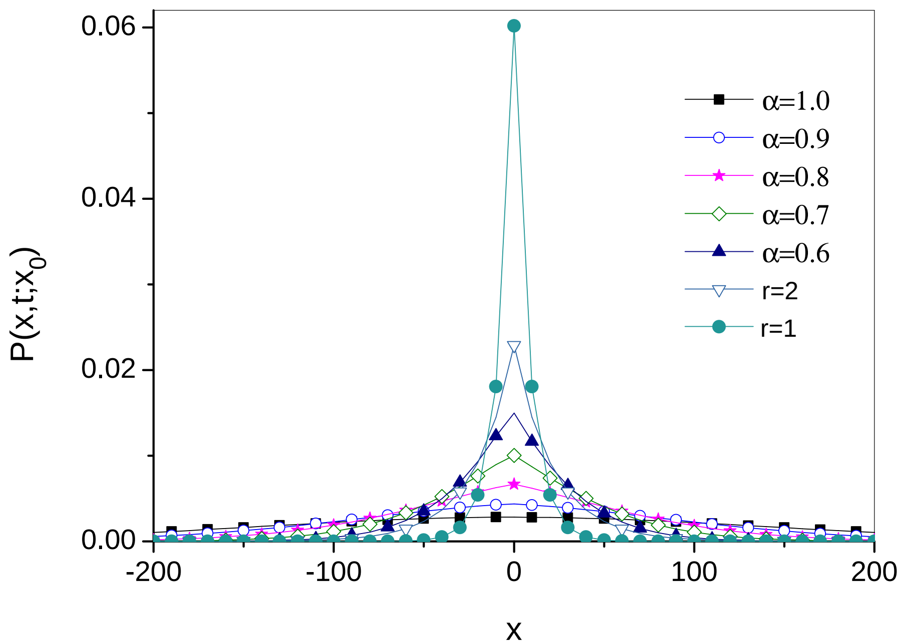

FIGURE 1 Plots of fundamental solutions to normal diffusion (9), classical subdiffusion (12), and slow subdiffusion (20) equations for a homogeneous system without a membrane, $D = 10$, $x_0 = 0$, and $t = 1000$, the values of other parameters are given in the legend, the lines labelled by α and by r represent the solutions to classical subdiffusion and slow subdiffusion equation, respectively, the case of $\alpha = 1$ corresponds to normal diffusion. All quantities are given in arbitrarily chosen units.

The function υ defines a diffusion type. We choose this function so that it leads to the relation (1) defining an appropriate type of diffusion, $\left\langle(\Delta x)^2(t)\right\rangle = \int_{-\infty}^{\infty}(x - x_0)^2 P(x, t; x_0)dx$. For normal diffusion we assume $\upsilon(s) = s$. Then, $F(t - t') = \delta(t - t')$ and we get the well–known normal diffusion equation

$$\frac{\partial P(x,t;x_0)}{\partial t} = D\frac{\partial^2 P(x,t;x_0)}{\partial x^2} \ . \tag{8}$$

The fundamental solution to Eq. (8) is the Gaussian distribution

$$P(x,t;x_0) = \frac{1}{2\sqrt{\pi D t}}\,\mathrm{e}^{-\frac{(x-x_0)^2}{4Dt}} \ . \tag{9}$$

Eq. (9) provides $\left\langle (\Delta x)^2(t)\right\rangle = 2Dt$.

Considering classical subdiffusion we suppose $v(s) = s^\alpha$, $0 < \alpha < 1$. Using the formula $\mathcal{L}^{-1}[s^\alpha \hat{f}(s) - s^{\alpha-1}f(0)] = d^\alpha_C g(t)/dt^\alpha := (1/\Gamma(1-\alpha))\int_0^t dt'(df(t')/dt')/(t-t')^\alpha$, $0<\alpha<1$, where $d^\alpha_C g(t)/dt^\alpha$ is the Caputo fractional derivative, we obtain the classical subdiffusion equation

$$\frac{\partial^\alpha_C P(x,t;x_0)}{\partial t^\alpha} = D\frac{\partial^2 P(x,t;x_0)}{\partial x^2} \ , \tag{10}$$

$0<\alpha<1$. In this case we have $F(t-t') = 1/\Gamma(1-\alpha)(t-t')^\alpha$, Γ denotes the Gamma–Euler function. Eq. (10) can be transformed into the form in which the Riemann–Liouville fractional time derivative of the $1-\alpha$ order occurs on the right–hand side of the equation; this form is most often used in the description of classical subdiffusion[4,6]. Using the formula[35]

$$\mathcal{L}^{-1}\left[s^\nu \mathrm{e}^{-as^\beta}\right] \equiv f_{\nu,\beta}(t;a) = \frac{1}{t^{\nu+1}}\sum_{k=0}^{\infty}\frac{1}{k!\Gamma(-k\beta-\nu)}\left(-\frac{a}{t^\beta}\right)^k \ , \tag{11}$$

we get

$$P(x,t;x_0) = \frac{1}{2\sqrt{D}} f_{\alpha/2-1,\alpha/2}\left(t;\frac{|x-x_0|}{\sqrt{D}}\right) \ . \tag{12}$$

Eq. (12) gives $\left\langle (\Delta x)^2(t)\right\rangle = 2Dt^\alpha/\Gamma(1+\alpha)$. The function f is related to the H–Fox function

$$f_{\nu,\beta}(t;a) = \beta^{-1}a^{-(1+\nu)/\beta}H^{10}_{11}\left(\frac{a^{1/\beta}}{t}\left|\begin{array}{cc} 1 & 1 \\ (1+\nu)/\beta & 1/\beta\end{array}\right.\right) \ , \tag{13}$$

and to the W Wright function, $f_{\nu,\beta}(t;a) = W(-a/t^\beta;-\beta,-\nu)/t^{\nu+1}$.

For slow subdiffusion we assume that $v(s)$ is a slowly varying function[9]. The slow subdiffusion equation depends on the detailed form of $v(s)$. Below we assume

$$v(s) = \frac{1}{\ln^r(1/s)} \ , \ r>0, \tag{14}$$

$0<s<1$. Due to the relation[36]

$$\mathcal{L}^{-1}\left[\frac{1}{s\,\ln^\beta s}\right] = \frac{\mu(t,\beta-1)}{\Gamma(\beta)}, \tag{15}$$

$\beta > 0$, where

$$\mu(t,\beta) = \int_0^\infty d\zeta\,\frac{t^\zeta \zeta^\beta}{\Gamma(1+\zeta)} \tag{16}$$

is the Volterra–type function[37], we get

$$\frac{1}{\Gamma(r)}\int_0^t \mu(t-t',r-1)\frac{\partial P(x,t';x_0)}{\partial t'}dt' = D\frac{\partial^2 P(x,t;x_0)}{\partial x^2} \ . \tag{17}$$

To calculate the inverse Laplace transform of fundamental solutions over the long time limit we use the following strong Tauberian theorem[5]: *If $\phi(t)\geq 0$, $\phi(t)$ is ultimately monotonic like $t\longrightarrow\infty$, $\mathcal{R}$ is slowly–varying and $0<\rho<\infty$, then each of the relations*

$$\hat{\phi}(s) \approx \frac{\mathcal{R}(s)}{s^\rho} \tag{18}$$

as $s\longrightarrow 0$ and

$$\phi(t) \approx \frac{\mathcal{R}(1/t)}{\Gamma(\rho)t^{1-\rho}} \tag{19}$$

as $t \longrightarrow \infty$ implies the other. A slowly varying function $\mathcal{R}$ is defined here by means of the following condition $\mathcal{R}(as)/\mathcal{R}(s) \to 1$ when $s \to 0^+$ for any $a > 0$. In the long time limit $t \gg 1$ we have

$$P(x,t;x_0) = \frac{1}{2\sqrt{D\,\ln^r t}}\,\mathrm{e}^{-\frac{|x-x_0|}{\sqrt{D\,\ln^r t}}}, \tag{20}$$

and $\left\langle (\Delta x)^2(t) \right\rangle = 2D\,\ln^r t$.

Plots of the fundamental solutions (9), (12), and (20) are presented in Fig. 1 . The most focused around the maximum located at $x = 0$ are the fundamental solutions to slow subdiffusion equation for the small values of the parameter r. Fundamental solutions obtained for $r < 1$ are not shown in the plot due to their considerable height and very low variance.

3 | DISCRETE MODEL OF SUBDIFFUSION

We consider random walk of a particle in a one-dimensional homogeneous system in which the time n and the position of the particle m are discrete. In the simplest model, the particle's jump can be made only to adjacent positions with probability equals $1/2$. This process can be described by the following difference equation

$$P_{n+1}(m;m_0) = \frac{1}{2}P_n(m-1;m_0) + \frac{1}{2}P_n(m+1;m_0)\;, \tag{21}$$

where $P_n(m;m_0)$ is a probability that the particle is in the position m after n steps, m_0 is the initial particle's position, $P_0(m;m_0) = \delta_{m,m_0}$.

We move from discrete to continuous variables in two steps. In the first step, we move from discrete to continuous time using the equation

$$P(m,t;m_0) = \sum_{n=0}^{\infty} P_n(m,m_0)\Phi_n(t)\;, \tag{22}$$

where $\Phi_n(t)$ is the probability that the particle takes n steps over a time interval $[0,t]$. This probability is described by the equation

$$\Phi_n(t) = \Psi_n(t')U(t-t_n)\;, \tag{23}$$

where ω is the probability density of waiting time for the particle's jump, $\Psi_n(t')$ is the probability of making n jumps in the time interval $[0,t']$ with the last jump being made exactly at time t', $\Psi_n(t') = \int_0^t \Psi_{n-1}(t')\omega(t-t')dt'$ for $n > 1$, $\Psi_1(t') = \omega(t')$, $U(t-t') = 1 - \int_0^{t-t'} \omega(t'')dt''$ is the probability that the particle does not jump in the time interval $[t-t',t]$. Due to the formulas $\mathcal{L}\left[\int_0^t f(t')g(t-t')dt'\right] = \hat{f}(s)\hat{g}(s)$ and $\mathcal{L}[1] = 1/s$ we get $\hat{\Phi}_n(s) = \hat{\omega}^n(s)(1-\hat{\omega}(s))/s$. In further considerations we use the generating function of the difference equation defined as

$$S(m,z;m_0) = \sum_{n=0}^{\infty} z^n P_n(m;m_0)\;. \tag{24}$$

The above equations provide[7]

$$\hat{P}(m,s;m_0) = \frac{1-\hat{\omega}(s)}{s} S\left(m,\hat{\omega}(s);m_0\right)\;. \tag{25}$$

In the next step, we use the following equations to move from discrete to continuous spatial variable

$$x = \epsilon m\;,\; x_0 = \epsilon m_0\;,\; P(x,t;x_0) = \frac{P(m,t;m_0)}{\epsilon}\;, \tag{26}$$

where ϵ is the distance between adjacent positions. The parameter ϵ can be interpreted as a mean value of the length of a single particle jump, which is very small but non–zero. The frequency of jumps between adjacent points, and thus the waiting time of the particle for a jump, depends on the distance between the discrete points. As shown in[32], there is

$$\hat{\omega}(s) = \frac{1}{1+\frac{\epsilon^2 v(s)}{2D}}\;, \tag{27}$$

where the diffusion coefficient D is independent of ϵ. Due to the normalization condition $\hat{\omega}(0) = 1$, the function v fulfils the condition $v(s) \to 0$ when $s \to 0$.

The generating function of Eq. (21) reads

$$S(m,z;m_0)=\frac{[\eta(z)]^{|m-m_0|}}{\sqrt{1-z^2}},\tag{28}$$

where $\eta(z)=(1-\sqrt{1-z^2})/z$. From Eqs. (22)–(28) we get Eq. (7) in the limit of small ϵ. The Laplace transform of the diffusion equation Eq. (5) can also be derived from Eq. (21). From Eqs. (21), (24), and (25) we get

$$\frac{1}{z}\left[S(m,z;m_0)-P_0(m;m_0)\right]=\frac{1}{2}S(m-1,z;m_0)+\frac{1}{2}S(m+1,z;m_0)\,.\tag{29}$$

Subtracting $S(m,z;m_0)$ from both sides of (29) and using Eqs. (25) and (27) we get Eq. (5) in the limit of small ϵ.

4 | DISCRETE MODEL OF SUBDIFFUSION IN A SYSTEM WITH A THIN MEMBRANE

Let a thin membrane be placed in a discrete system between points N and $N+1$. A particle that tries to jump through the membrane can do it with a probability $1-q$ or can be stopped by the membrane with a probability q, see Fig. 2 . This process is described by the following difference equations

$$P_{A,n+1}(m;m_0)=\frac{1}{2}P_{A,n}(m-1;m_0)+\frac{1}{2}P_{A,n}(m+1;m_0),\ m\le N-1,\tag{30}$$

$$P_{A,n+1}(N;m_0)=\frac{1}{2}P_{A,n}(N-1;m_0)+\frac{1-q}{2}P_{B,n}(N+1;m_0)+\frac{q}{2}P_{A,n}(N;m_0),\tag{31}$$

$$P_{B,n+1}(N+1;m_0)=\frac{1-q}{2}P_{A,n}(N;m_0)+\frac{1}{2}P_{B,n}(N+2;m_0)+\frac{q}{2}P_{B,n}(N+1;m_0),\tag{32}$$

$$P_{B,n+1}(m;m_0)=\frac{1}{2}P_{B,n}(m-1;m_0)+\frac{1}{2}P_{B,n}(m+1;m_0),\ m\ge N+2,\tag{33}$$

where the index A means that the point m is located in the region $A=(-\infty,N]$ and B means that the position of the point is in the region $B=[N+1,\infty)$.

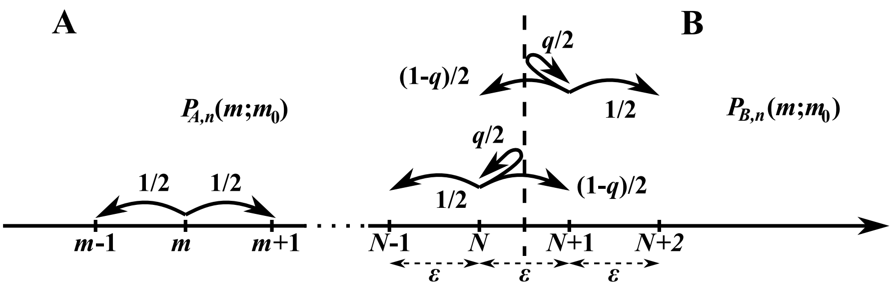

FIGURE 2 Random walk of a particle in a discrete system with a thin partially permeable wall located between N and $N+1$ site, q is the probability of stopping the particle by the wall.

We assume that $m_0\le N$, the initial conditions are

$$P_{A,0}(m;m_0)=\delta_{m,m_0}\,,P_{B,0}(m;m_0)=0.\tag{34}$$

The generating functions are defined separately for the regions A and B

$$S_i(m,z;m_0)=\sum_{n=0}^{\infty}z^nP_{i,n}(m,m_0)\,,\tag{35}$$

$i=A,B$. After calculations we get

$$S_A(m,z;m_0)=\frac{[\eta(z)]^{|m-m_0|}}{\sqrt{1-z^2}}+\Lambda_A(z)\frac{[\eta(z)]^{2N-m-m_0}}{\sqrt{1-z^2}}\,,\tag{36}$$

$$S_B(m,z;m_0)=\frac{[\eta(z)]^{m-m_0-1}}{\sqrt{1-z^2}}\Lambda_B(z)\,, \tag{37}$$

where $\Lambda_A(z)=[(1/\eta(z)-q)(q-\eta(z))+(1-q)^2]/[(1/\eta(z)-q)^2-(1-q)^2]$ and $\Lambda_B(z)=(1-q)(1/\eta(z)-\eta(z))/[(1/\eta(z)-q)^2-(1-q)^2]$. The Laplace transforms of fundamental solutions in the regions $i=A,B$ are calculated by means of the equation

$$\hat{P}_i(m,s;m_0)=\frac{1-\hat{\omega}(s)}{s}S_i\left(m,\hat{\omega}(s);m_0\right)\ . \tag{38}$$

The membrane permeability coefficient should be redefined in a continuous system. The reason for this is that the mean number of particle steps over time interval $[0,t]$ between adjacent positions n increases to infinity when $\epsilon\to 0$, according to the formula $\langle n(t)\rangle=\hat{\omega}(s)/[s(1-\hat{\omega}(s))]\sim 1/\epsilon^2$. However, a particle that tries to jump through a partially permeable membrane any number of times in any short time interval will do it with a probability equals 1. In such a case, the membrane loses its selective property. In order to avoid this 'non-physical effect', we assume that the probability of the particle jumping through the membrane depends on ϵ. Thus, we take the substitution $q\to\tilde{q}(\epsilon)$ in Eqs. (36) and (37). It has been shown[32] that the membrane permeability coefficient γ defined in the continuous system as

$$1-\tilde{q}(\epsilon)=\frac{\epsilon}{\gamma} \tag{39}$$

ensures that the probability of the particle jumping through the membrane does not depend on ϵ.

From Eqs. (34)–(38) we get in the limit of small ϵ

$$\hat{P}_A(x,s;x_0)=\frac{\sqrt{\upsilon(s)}}{2s\sqrt{D}}\left(\mathrm{e}^{-|x-x_0|\sqrt{\frac{\upsilon(s)}{D}}}+\frac{\gamma\sqrt{\frac{\upsilon(s)}{D}}}{2+\gamma\sqrt{\frac{\upsilon(s)}{D}}}\mathrm{e}^{-(2x_N-x-x_0)\sqrt{\frac{\upsilon(s)}{D}}}\right), \tag{40}$$

$$\hat{P}_B(x,s;x_0)=\frac{\sqrt{\upsilon(s)}}{s\sqrt{D}}\left(\frac{1}{2+\gamma\sqrt{\frac{\upsilon(s)}{D}}}\right)\mathrm{e}^{-(x-x_0)\sqrt{\frac{\upsilon(s)}{D}}}, \tag{41}$$

where $x_N=N\epsilon$. The Laplace transforms of probability fluxes in the regions $i=A,B$ are defined as

$$\hat{J}_i(x,s;x_0)=-D\frac{s}{\upsilon(s)}\frac{\partial\hat{P}_i(x,s;x_0)}{\partial x}. \tag{42}$$

Combining the values of functions $\hat{P}_A$, $\hat{P}_B$, $\hat{J}_A$, and $\hat{J}_B$ calculated for $x=x_N$ from Eqs. (40)–(42), we get the following boundary conditions at a thin membrane given in terms of the Laplace transforms

$$\hat{J}_A(x_N^-,s;x_0)=\hat{J}_B(x_N^+,s;x_0)\,, \tag{43}$$

which provides

$$\left.\frac{\partial\hat{P}_A(x,s;x_0)}{\partial x}\right|_{x=x_N^-}=\left.\frac{\partial\hat{P}_B(x,s;x_0)}{\partial x}\right|_{x=x_N^+}, \tag{44}$$

and

$$\hat{P}_A(x_N^-,s;x_0)=\left(1+\gamma\sqrt{\frac{\upsilon(s)}{D}}\right)\hat{P}_B(x_N^+,s;x_0). \tag{45}$$

In the time domain the boundary conditions are

$$\left.\frac{\partial P_A(x,t;x_0)}{\partial x}\right|_{x=x_N^-}=\left.\frac{\partial P_B(x,t;x_0)}{\partial x}\right|_{x=x_N^+}, \tag{46}$$

$$P_A(x_N^-,t;x_0)=P_B(x_N^+,t;x_0)+\frac{\gamma}{\sqrt{D}}\int_0^t G(t-t')P_B(x_N^+,t';x_0)dt', \tag{47}$$

where $G(t)=\mathcal{L}^{-1}[\sqrt{\upsilon(s)}]$. The boundary condition (46) shows that the flux is continuous at the membrane. This is an expected result, because we consider the process in which a particle cannot be retained inside the membrane. The interpretation of boundary condition (47) is that the difference in probability of finding the particle on the membrane surfaces is expressed by the integral operator with a kernel G which depends on a type of diffusion. In the following, we find the boundary conditions for different types of diffusion.

5 | FUNDAMENTAL SOLUTIONS IN A MEMBRANE SYSTEM AND THE BOUNDARY CONDITIONS FOR NORMAL DIFFUSION AND SUBDIFFUSION

Below there are presented the fundamental solutions obtained from the Laplace transforms (40) and (41). We also present the boundary condition at a thin membrane that complements the condition of the diffusion flux continuity (46).

For normal diffusion we get

$$\begin{aligned} P_A(x,t;x_0) = {} & \frac{1}{2\sqrt{\pi D t}}\, \mathrm{e}^{-\frac{(x-x_0)^2}{4Dt}} + \frac{1}{2\sqrt{\pi D t}}\, \mathrm{e}^{-\frac{(2x_N-x-x_0)^2}{4Dt}} \\ & - \frac{1}{\gamma}\, \mathrm{e}^{\frac{2}{\gamma}(2x_N-x-x_0)+\frac{4}{\gamma^2}Dt}\, \mathrm{erfc}\left(\frac{2x_N-x-x_0}{2\sqrt{Dt}}+\frac{2}{\gamma}\sqrt{Dt}\right), \end{aligned} \tag{48}$$

$$P_B(x,t;x_0) = \frac{1}{\gamma}\, \mathrm{e}^{\frac{2}{\gamma}(x-x_0)+\frac{4}{\gamma^2}Dt}\, \mathrm{erfc}\left(\frac{x-x_0}{2\sqrt{Dt}}+\frac{2}{\gamma}\sqrt{Dt}\right), \tag{49}$$

where $\mathrm{erfc}(u) = (2/\sqrt{\pi})\int_u^\infty d\xi\ \mathrm{e}^{-\xi^2}$ is the complementary error function. The boundary condition contains the Riemann–Liouville fractional time derivative of the order $1/2$ and reads

$$P_A(x_N^-,t;x_0) = \left(1+\frac{\gamma}{\sqrt{D}}\frac{\partial^{1/2}}{\partial t^{1/2}}\right)P_B(x_N^+,t;x_0)\,, \tag{50}$$

where the Riemann–Liouville fractional derivative is defined for $0<\beta<1$ as

$$\frac{d^\beta f(t)}{dt^\beta} = \frac{1}{\Gamma(1-\beta)}\frac{d}{dt}\int_0^t dt'(t-t')^{-\beta} f(t'). \tag{51}$$

For classical subdiffusion, from Eqs. (11), (40), (41) with $v(s)=s^\alpha$, $0<\alpha<1$, and using the relation $1/(2+\gamma\sqrt{s^\alpha/D}) = (1/2)\sum_{n=0}^\infty(-\gamma\sqrt{s^\alpha}/(2\sqrt{D}))^n$, we obtain

$$\begin{aligned} P_A(x,t;x_0) = {} & \frac{1}{2\sqrt{D}} f_{\alpha/2-1,\alpha/2}\left(t;\frac{|x-x_0|}{\sqrt{D}}\right) \\ & + \frac{1}{2\sqrt{D}}\sum_{n=0}^\infty(-1)^n\left(\frac{\gamma}{2\sqrt{D}}\right)^{n+1} f_{\alpha(1+n/2)-1,\alpha/2}\left(t;\frac{2x_N-x-x_0}{\sqrt{D}}\right), \end{aligned} \tag{52}$$

$$P_B(x,t;x_0) = \frac{1}{2\sqrt{D}}\sum_{n=0}^\infty\left(-\frac{\gamma}{2\sqrt{D}}\right)^n f_{\alpha((1+n)/2)-1,\alpha/2}\left(t;\frac{x-x_0}{\sqrt{D}}\right). \tag{53}$$

The boundary condition is

$$P_A(x_N^-,t;x_0) = \left(1+\frac{\gamma}{\sqrt{D}}\frac{\partial^{\alpha/2}}{\partial t^{\alpha/2}}\right)P_B(x_N^+,t;x_0)\,. \tag{54}$$

For slow subdiffusion $v(s)$ is a slowly varying function when $s\to 0$. In the limit of long time we use the strong Tauberian theorem to calculate the inverse Laplace transform. We obtain

$$P_A(x,t;x_0) = \frac{\sqrt{v(1/t)}}{2\sqrt{D}}\left(\mathrm{e}^{-|x-x_0|\sqrt{\frac{v(1/t)}{D}}} + \frac{\gamma\sqrt{\frac{v(1/t)}{D}}}{2+\gamma\sqrt{\frac{v(1/t)}{D}}}\mathrm{e}^{-(2x_N-x-x_0)\sqrt{\frac{v(1/t)}{D}}}\right), \tag{55}$$

$$P_B(x,t;x_0) = \frac{\sqrt{v(1/t)}}{\sqrt{D}}\left(\frac{1}{2+\gamma\sqrt{\frac{v(1/t)}{D}}}\right)\ \mathrm{e}^{-(x-x_0)\sqrt{\frac{v(1/t)}{D}}}\,. \tag{56}$$

Plots of the functions (55) and (56) obtained for $v(1/t) = 1/\ln^r t$ in the long time limit $t \gg 1$ are presented in Fig. 3 . From Eqs. (14), (15), (16), and (45), using the formulas $\mathcal{L}^{-1}[s\hat{f}(s)] = df(t)/dt + f(0)$, $d\mu(t,\beta)/dt = \mu(t,\beta+1)/t$, and $\mu(0,\beta) = 0$, we get the following boundary condition at a thin membrane

$$P_A(x_N^-, t; x_0) = P_B(x_N^+, t; x_0) + \frac{\gamma}{\sqrt{D}\Gamma(r/2)} \int_0^t \frac{\mu(t-t'; r/2)}{t-t'} P_B(x_N^+, t'; x_0) dt'. \tag{57}$$

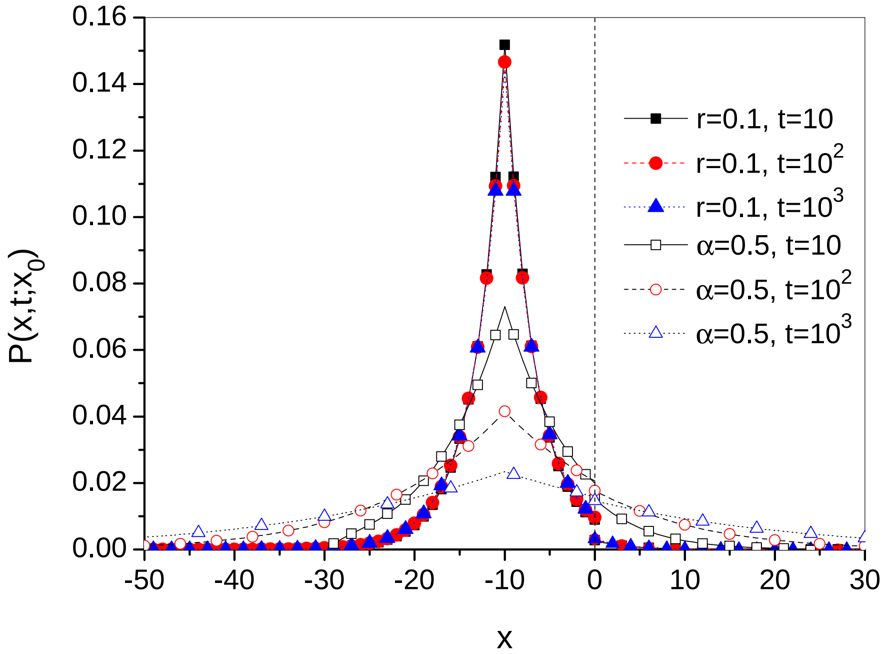

FIGURE 3 Plots of functions Eqs. (52), (53), (55), and (56) for parameters and times given in the legend, here $x_0 = -10$, $x_N = 0$, $\gamma = 2$, and $D = 10$.

The plots showing the time evolution of the functions (52) and (53) for classical subdiffusion with $\alpha = 0.5$ and the functions (55) and (56) for slow subdiffusion with $r = 0.1$ are presented in Fig. 3 . The function for slow subdiffusion changes very little over a fairly long time interval, while the functions for classical subdiffusion change relatively quickly, although subdiffusion with $\alpha = 0.5$ is a very slow process compared to normal diffusion.

6 | FINAL REMARKS

We have shown the model from which both subdiffusion equations and boundary conditions at a thin membrane can be derived. The main issue considered in this paper is whether the boundary conditions depend on the type of diffusion. We have argued that such a relationship exists. Below we present the additional argument that boundary conditions should take into account the type of diffusion. Let us consider the boundary condition commonly used in a system with normal diffusion, namely Eq. (46) and

$$J_B(x_N^+,t;x_0)=\lambda\left[P_A(x_N^-,t;x_0)-P_B(x_N^+,t;x_0)\right]\ , \tag{58}$$

the parameter λ controls the membrane permeability. The Laplace transforms of fundamental solutions to Eq. (5) with boundary conditions (46), (58), and $P_A(-\infty,t;x_0)=P_B(\infty,t;x_0)=0$ for $x_0<x_N$ are

$$\hat{P}_A(x,s;x_0)=\frac{1}{2s}\sqrt{\frac{\upsilon(s)}{D}}\left[\mathrm{e}^{-|x-x_0|\sqrt{\frac{\upsilon(s)}{D}}}+(1-\Xi(s))\mathrm{e}^{-(2x_N-x-x_0)\sqrt{\frac{\upsilon(s)}{D}}}\right]\ , \tag{59}$$

$$\hat{P}_B(x,s;x_0)=\frac{\Xi(s)}{2s}\sqrt{\frac{\upsilon(s)}{D}}\ \mathrm{e}^{-(2x_N-x-x_0)\sqrt{\frac{\upsilon(s)}{D}}}\ , \tag{60}$$

where $\Xi(s)=2/(s\sqrt{D/\lambda\upsilon(s)}+2)$. The functions Eqs. (59) and (60) coincide with Eqs. (40) and (41), respectively, only when $\upsilon(s)=s$ and $\lambda=D/\gamma$. Thus, the boundary condition Eq. (58) is equivalent to boundary condition derived in this paper for the case of normal diffusion only. The above example shows that the boundary condition (58) cannot be applied in the cases of classical or slow subdiffusion unless the diffusion process in the membrane system meets the assumptions of the model, Sec. 4.

The boundary conditions have been derived for the probabilities P_A and P_B. However, if diffusing particles move independently of each other, then the concentration of the particles C can be calculated by means of the formula

$$C(x,t)=\int_{-\infty}^{\infty}P(x,t;x_0)C(x_0,0)dx_0, \tag{61}$$

where $C(x_0,0)$ is the initial concentration. Due to Eq. (61), under the assumption presented above, the boundary conditions, as well as the diffusion equations, are valid also for particle concentration for any initial condition, see the discussion in [32].

The question arises whether the model presented in this paper is universal. In our opinion, this question should remain open, although the following facts prove the model usefulness: (1) the model has a simple physical interpretation, (2) the model provides equations of different types of diffusion that can also be derived from the other models such as the CTRW model [4,6], (3) the boundary condition derived from this model for normal diffusion (50) has been confirmed empirically [38], (4) the boundary condition for classical subdiffusion (54) have provided solutions to the subdiffusion equation that coincide with the empirical results describing the release of antibiotics from the gel medium through a partially permeable membrane [30]. However, regardless of the above arguments, the following conclusion seems to be universal: *the boundary conditions at the membrane should take into account the selective properties of the membrane as well as the type of diffusion in the system.*

References

1. Gardiner CW. *Handbook of stochastic methods for physics, chemistry and the natural sciences*. Berlin:Springer;2004.
2. Risken H. *The Fokker–Planck equation. Methods of solution and applications*. Berlin:Springer;1989.
3. van Kampen NG. *Stochastic processes in physics and chemistry*. Amsterdam:North–Holland;1992.
4. Metzler R, Klafter J. The random walks' guide to anomalous diffusion: a fractional dynamics approach. *Phys Rep*. 2000;339:1-77.
5. Hughes DD. *Random walk and random environments. Vol I, Random walks*. Oxford:Clarendon;1995.
6. Klafter J, Sokolov I. *First steps in random walks. From tools to applications* (Oxford UP, 2011).
7. Montroll EW, Weiss HG. Random walk on lattices. II. *J Math Phys*. 1965;6:167-181.
8. Chechkin AV, Kantz H, Metzler R. Ageing effects in ultraslow continuous time random walk. *Eur Phys J B*. 2017;90:205-1-205-12.
9. Denisov IS, Kantz H. Continuous-time random walk with a superheavy-tailed distribution of waiting times. *Phys Rev E*. 2011;83:041132-1-041132-7.

10. Kosztołowicz T, Dworecki K, Mrówczyński S. How to measure subdiffusion parameters. *Phys Rev Lett*. 2005;94:170602-1-170602-4.

11. Brenner T, Matsukawa S. Anomalous diffusion of poly(ethylene oxide) in agarose gels. *Int J Biol Macromolecules*. 2016;92:1151-1154.

12. Metzler R, Klafter J. The restaurant at the end of the random walk: recent developments in the description of anomalous transport by fractional dynamics. *J Phys A*. 2004;37:R161-R208.

13. Metzler R, Jeon JH, Cherstvy AG. Non-brownian diffusion in lipid membranes: Experiments and simulations. *Bioch Biophys Acta*. 2016;1858:2451-2467.

14. Jeon JH, Javanainen M, Martinez-Seara H, Metzler R, Vattulainen I. Protein crowding in lipid bilayers gives rise to non-Gaussian anomalous lateral diffusion of phospholipids and proteins. *Phys Rev E*. 2016;6:021006-1-021006-17.

15. Banks DS, Fradin C. Anomalous diffusion of proteins due to molecular crowding. *Biophys J*. 2005;89:2960-2971.

16. Xiao F, Hrabe J, Hrabetova S. Anomalous extracellular diffusion in rat cerebellum. Biophys J. 2015;108:2384-2395.

17. Cherstvy AG, Thapa S, Wagner CE, Metzler R. Non-Gaussian, non-ergodic, and non-Fickian diffusion of tracers in mucin hydrogels. *Soft Matter*. 2019;15:2526-2551.

18. Kosztołowicz T. Model of anomalous diffusion-absorption process in a system consisting of two different media separated by a thin membrane. *Phys Rev E*. 2019;99:022127-1-022127-16.

19. Sanders LP, Lomholt MA, Lizana L, Fogelmark K, Metzler R, Ambjörnsson T. Severe slowing-down and universality of the dynamics in disordered interacting many-body systems: ageing and ultraslow diffusion. *New J Phys*. 2014;16:113050-1-113050-14.

20. van Kampen NG, Oppenheim I. Expansion of the Master equation for one-dimensional random walk with boundary. *J Math Phys*. 1972;13:842–849.

21. Lomholt MA, Zaid IM, Metzler R. Subdiffusion and weak ergodicity breaking in the presence of reactive boundary. *Phys Rev Lett*. 2007;98:200603-1-200603-4.

22. Zaid IM, Lomholt MA, Metzler R. How subdiffusion changes the kinetics of binding to a surface. *Biophys J*. 2009;97:710–721.

23. Goychuk I, Hänggi P. Fractional diffusion modeling of ion channel gating. *Phys Rev E* 2004;70:051915-1-051915-9.

24. Korabel N, Barkai E. Boundary conditions of normal and anomalous diffusion from thermal equilibrium *Phys Rev E*. 2011;83:051113-1-051113-7.

25. Grebenkov DS. Subdiffusion in a bounded domain with a partially absorbing-reflecting boundary. *Phys Rev E*. 2010;81:021128-1-021128-13.

26. Feller W. Diffusion processes in one dimension. *Trans Amer Math Soc*. 1954;77:1-31.

27. Bobrowski A. *Convergence of one–parameter operator semigroups in models of mathematical biology and elsewhere*. Cambridge:UP;2016.

28. Yano K. Extension of diffusion processes on intervals and Feller's boundary conditions. *Osaka J Math*. 2014;51:375-404.

29. Chandrasekhar S. Stochastic problems in physics and astronomy. *Rev Mod Phys*. 1943;15:1-89.

30. Kosztołowicz T. Subdiffusion in a system consisting of two different media separated by a thin membrane. *Int J Heat Mass Transf*. 2017;111:1322–1333.

31. Kosztołowicz T. Subdiffusion-absorption process in a system consisting of two different media. *J Chem Phys*. 2017;146:084114-1-084114-7.

32. Kosztołowicz T. Random walk model of subdiffusion in a system with a thin membrane. *Phys Rev E*. 2015;91:022102-1-022102-9.

33. Kosztołowicz T. Subdiffusive random walk in a membrane system: the generalized method of images approach. *J Stat Mech*. 2015;P10021:1-19.

34. Kosztołowicz T, Lewandowska KD, Klinkosz T. How to identify absorption in a subdiffusive medium. *Math Model Nat Phenom*. 2017;12:118-129.

35. Kosztołowicz T. From the solutions of diffusion equation to the solutions of subdiffusive one. *J Phys A: Math Gen*. 2004;37:10779–10789.

36. Oberhettinger F, Badii F. *Tables of Laplace Transforms*. Berlin:Springer;1973.

37. Garrappa R, Mainardi F. On Volterra functions and Ramanujan integrals. *Analysis*. 2015;36:89-105.

38. Kosztołowicz T, Wąsik S, Lewandowska KD. How to determine a boundary condition for diffusion at a thin membrane from experimental data. *Phys Rev E*. 2017;96:010101(R)-1-010101(R)-4.

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