Random walk model of subdiffusion - absorption process in a system consisting of two different media separated by a partially permeable wall

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We present a model of the process of diffusion-absorption of a molecule in a system in which a thin partially permeable membrane separates various media. Different types of diffusion can occur in these media: diffusion, sub-diffusion or slow sub-diffusion. The method is based on a simple random walk model in a discrete system with a thin partially permeable wall. Within this method we firstly consider the particle’s random walk in a system with both discrete time and space variables in which a particle can vanish due to absorption with probabilities defined separately for each medium. Then, we move form discrete to continuous variables. We derive the Green’s functions for the system. The Green’s functions are used to derive boundary conditions at the membrane.

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I. INTRODUCTION

In many processes in natural and engineering sciences various kinds of diffusion occur in a system composed of different media separated by a thin membrane. Particles can be also absorbed, with some probability, in the media. There may be a different type of diffusion in each medium. These processes can be described by differential or integral equations. To solve them, boundary conditions at the membrane are needed. These conditions depend on the processes taking place in both media. We add that, until now, various boundary conditions which are not equivalent to one another have been assumed at the membrane, see for example [1–20].

We assume that the system is homogeneous in a plane perpendicular to the $x$ axis, thus the system is effectively one-dimensional. In our consideration, we will show the method of calculating the Green’s functions for a system with a thin membrane. These functions, defined separately for each of the two regions bounded by the membrane, are interpreted as the probability density of finding a diffusing particle at the point $x$ at time $t$. The Green’s function is also defined as the solution to the diffusion equation for the initial condition expressed by the delta-Dirac function. Knowing Green’s function, we can derive the boundary conditions at the membrane. Assuming that diffusing particles move independently of each other, the obtained boundary conditions can be used for any initial concentration.

We start our considerations with the model of random walk in a system in which time and spatial variables are discrete. Then, we move to continuous variables. This method is slightly different from the ‘classical’ Continuous Time Random Walk method [21–26]. Namely, in the CTRW method, the time which is needed to take particle’s next step $\tau$ and the length of the particle’s jump $\epsilon$ are both random variables, while in the method presented in this paper $\tau$ is a random variable only whereas $\epsilon$ is a parameter. The reason for this is that a system of difference equations describing diffusion in a discrete system with thin membrane is solvable; the system of these equations also has a very simple interpretation. Probabilities describing random walk in a discrete system, like the probability of particle’s jump to the other sites, probability of particle’s absorbing and probability of stopping a particle by a membrane should be redefined in a system with continuous variables. One of the main problems is to define the parameters in the system with continuous variables and deriving relations linking these parameters with the probabilities specified in the discrete system.

II. RANDOM WALK IN HOMOGENEOUS SYSTEM

We consider subdiffusion with absorption described by the following difference equation

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

where $P_n(m; m_0)$ is the probability of finding a particle at site $m$ after $n$ steps, $m_0$ denotes the initial position of a particle, $P_0(m; m_0) = \delta_{m_0}$, $R$ is the probability of absorption. In further considerations, we will use the generating function defined as

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

To move from discrete to continuous time we use the standard formula

$$P(m, t; m_0) = \sum_{n=0}^{\infty} P_n(m, m_0) \Phi_n(t)$$
where \( \Phi_n(t) \) is the probability that the particle takes \( n \) steps over a time interval \([0, t]\). The function is the convolution
\[
\Phi_n(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n \omega(t_1) \omega(t_2 - t_1) \ldots \omega(t_n - t_{n-1}) U(t - t_n),
\]
where \( \omega(t) \) is the probability density of time which is needed for the particle to take its next step, \( U(t) = 1 - \int_0^t \omega(t') dt' \) is a probability that the particle has not performed any step over a time interval \([0, t]\). It is convenient to carry out further calculations in terms of the Laplace transform \( \mathcal{L}L \)
\[
\hat{\Phi}_n(s) = \hat{U}(s) \hat{\omega}^n(s),
\]
where
\[
\hat{U}(s) = \frac{1 - \hat{\omega}(s)}{s}.
\]
From Eqs. (3), (5), and (6) we get
\[
\hat{P}(m, s; m_0) = \frac{1 - \hat{\omega}(s)}{s} S(m, \hat{\omega}(s); m_0).
\]

Moving from discrete to continuous space variable we apply the following relations
\[
x = \epsilon m, \quad x_0 = \epsilon m_0,
\]
and
\[
P(x, t; x_0) = \frac{P(m, t; m_0)}{\epsilon}.
\]

The parameter \( \epsilon \) is the distance between neighboring sites, which can be interpreted as a length of a single particle’s jump. In the following we conduct the considerations in the limit of small \( \epsilon \).

Taking into account that \( \hat{\omega}(0) = 1 \) due to the normalization of the function \( \omega(t) \), we assume that for small \( s \) there is
\[
\hat{\omega}(s) = 1 - \mu v(s)
\]

where \( v(s) \) is a function that \( v(s) \to 0 \) when \( s \to 0 \), \( \mu \) is a positive parameter given in the units which provide a dimensionless form of the last term. The choice of the parameter \( \mu \) and function \( v(s) \) is arbitrary. In the following we assume that the parameters occurring in \( v(s) \) are dimensionless or their physical units are the same as the physical unit of \( s \) which is the inverse of the time unit.

### A. Laplace transform of Green’s function

The generating function of Eq. (1) is
\[
S(m, z; m_0) = \frac{[\eta(z)]^{m-m_0}}{\sqrt{(1+zR)^2 - z^2}}.
\]
where
\[
\eta(z) = \frac{1 + zR - \sqrt{(1+zR)^2 - z^2}}{z}.
\]
In the limit of small \( s \) and \( \epsilon \) form Eqs. (5)–(12) we obtain
\[
\hat{P}(x, s; x_0) = \frac{\epsilon v(s)}{2Ds\sqrt{2R + R^2 + \mu(1-2R-2R^2)v(s)}} \left[ \frac{1 + R - \mu R v(s) - \sqrt{2R + R^2 + \mu(1-2R-2R^2)v(s)}}{1 - \mu v(s)} \right]^{1-m_0},
\]

Let us consider the conditions that will ensure that the function Eq. (13) will not be equivalent to the zero function and will take finite values in the limit of small parameter \( \epsilon \). For \( R = 0 \) the above conditions are fulfilled only when \( \epsilon \sim \sqrt{\mu} \). Thus, we define the generalized diffusion coefficient as
\[
D = \frac{\epsilon^2}{2\mu}.
\]

For the case of \( R \neq 0 \) the above condition and Eq. (14) provide \( R \sim \epsilon^2 \), and we suppose that
\[
R = \frac{\kappa^2 \epsilon^2}{2},
\]
where \( \kappa \) is the absorption coefficient defined in the continuous system.

Taking into account the above equations, the Laplace transform of the Green’s function reads in the limit of
small $\epsilon$
\[ \hat{P}(x, s; x_0) = \frac{v(s)}{2Ds\sqrt{\kappa^2 + \frac{v(s)}{D}}} e^{-|x-x_0|\sqrt{\kappa^2 + \frac{v(s)}{D}}}. \] (16)

B. Diffusion equation

We derive the diffusion equation in terms of the Laplace transform starting from Eq. (1). Combining Eqs. (1), (2), and (7) we get
\[ \frac{1}{z} |S(m, z; m_0) - P_0(m; m_0)| = \frac{1}{2} S(m - 1, z; m_0) \] (17)
\[ + \frac{1}{2} S(m + 1, z; m_0) - RS(m - 1, z; m_0). \]
From Eqs. (7)–(17) and the relation $\partial f(x)/\partial x^2 \approx [f(x + \epsilon) + f(x - \epsilon) - 2f(x)]/\epsilon^2$ we obtain
\[ s\hat{P}(x, s; x_0) - P(x, 0; x_0) = \frac{\epsilon^2 s\hat{\omega}(s)}{2(1 - \hat{\omega}(s))} \frac{\partial^2 \hat{P}(x, s; x_0)}{\partial x^2} - \frac{2R}{\epsilon^2} \hat{P}(x, s; x_0). \] (18)

The Green’s function Eq. (16) fulfills Eq. (17) only if
\[ \hat{\omega}(s) = \frac{1}{1 + \frac{\epsilon^2 s\hat{\omega}(s)}{2\epsilon}}. \] (19)
In the limit of small $\epsilon$ Eq. (19) can be approximated as
\[ \hat{\omega}(s) = 1 - \epsilon^2 \frac{v(s)}{2D}. \] (20)
for any positive $s$. This interpretation differs from the interpretation often used in the ‘classical’ Continuous Time Random Walk formalism in which Eq. (19), as well as [20], is supposed to be valid for small $s$ only [21, 26].

Eqs. (18) and (19) provide
\[ \frac{v(s)}{s} \left[ s\hat{P}(x, s; x_0) - P(x, 0; x_0) \right] = D \left[ \frac{\partial^2 \hat{P}(x, s; x_0)}{\partial x^2} - \kappa^2 \hat{P}(x, s; x_0) \right]. \] (21)
The diffusive flux $J$ is defined in terms of the Laplace transform as follows
\[ \hat{J}(x, s; x_0) = -D \frac{s}{v(s)} \frac{\partial \hat{P}(x, s; x_0)}{\partial x}. \] (22)
Combining Eq. (22) with the Laplace transform of the continuity equation, $\frac{\partial \hat{P}}{\partial t} = -\frac{\partial \hat{P}}{\partial x}$, we get Eq. (21) for diffusion without absorption, $\kappa = 0$.

In time domain the general form of the diffusion equation reads
\[ \int_{t_0}^{t} F(t - t') \frac{\partial P(x, t'; x_0)}{\partial t'} dt' = D \left[ \frac{\partial^2 P(x, t; x_0)}{\partial x^2} - \kappa^2 P(x, t; x_0) \right], \] (23)
where
\[ F(t) = \mathcal{L}^{-1} \left[ \frac{v(s)}{s} \right]. \] (24)

C. Normal diffusion, subdiffusion and slow subdiffusion

We define the kind of diffusion by means of fractional moments. The fractional moment of the order $\rho > 0$ is defined as $\langle \tau^\rho \rangle = \int_0^\infty \tau^\rho \omega(\tau) d\tau$. The moment of fractional order $\rho$ can be obtained using the equation $\langle \tau^\rho \rangle = \left( -\frac{1}{\Gamma(\rho)} \right)^n \int_0^\infty s^{n-\rho-1} \hat{\omega}(s) ds$, where $n$ is the smallest natural number such that $n > \rho$. For the moment of natural order $n$ this formula takes the form $\langle \tau^n \rangle = (-1)^n \frac{d^n \hat{\omega}(s)}{ds^n} |_{s=0}$. Normal diffusion is defined as a process in which $\langle \tau \rangle = \int_0^\infty \tau \omega(\tau) d\tau < \infty$, then $v(s) = s$. In the case of ‘classical’ subdiffusion there exists a parameter $\alpha$, $0 < \alpha < 1$, for which $\langle \tau^\rho \rangle = \infty$ for $\rho > \alpha$, and $\langle \tau^\rho \rangle < \infty$ for $\rho \leq \alpha$. In this case $v(s) = s^\alpha$. For slow subdiffusion there is $\langle \tau^\rho \rangle = \infty$ for $\rho > 0$. This condition is fulfilled when $v(s)$ is a slowly varying function [27].

Taking into account the above description and Eqs. (23) and (24) we get the normal diffusion–absorption equation
\[ \frac{\partial P(x, t; x_0)}{\partial t} = D \left[ \frac{\partial^2 P(x, t; x_0)}{\partial x^2} - \kappa^2 P(x, t; x_0) \right], \] (25)
the ‘classical’ subdiffusion–absorption equation
\[ \frac{\partial P(x, t; x_0)}{\partial t} = D \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \left( \frac{\partial^2 P(x, t; x_0)}{\partial x^2} - \kappa^2 P(x, t; x_0) \right), \] (26)
where $0 < \alpha < 1$, where the Riemann–Liouville fractional time derivative is defined for $\beta > 0$ as
\[ \frac{d^\beta f(t)}{dt^\beta} = \frac{1}{\Gamma(n-\beta)} \int_0^t dt'(t - t')^{n-1-\beta} f(t'), \] (27)
the integer number $n$ fulfills the relation $n - 1 < \beta \leq n$. The slow subdiffusion–absorption equation depends on the detailed form of function $v(s)$. For $v(s) = 1/\ln^{-1}(1/s)$, $r > 1$, we get [8]
III. DIFFUSION–ABSORPTION PROCESS IN A SYSTEM IN WHICH THIN MEMBRANE SEPARATES TWO MEDIA

Let the symbol $A$ denotes the region $(-\infty, x_N)$ and the symbol $B$ denotes the region $(x_N, \infty)$, $x_N$ is the position of the partially permeable wall, $x_N = N\epsilon$. The symbols will also be assigned to the $P$ functions defined in these regions.

$$\begin{align*}
A & \quad D_A \quad \varepsilon^2 \quad \rho_{A,n}(m; m_0) \\
B & \quad D_B \quad \varepsilon^2 \quad \rho_{B,n}(m; m_0)
\end{align*}$$

FIG. 1: The discrete thin membrane system with absorption. The more detailed description is in the text.

A particle performs its single jump to the neighboring site only if the particle is not stopped by the wall with a certain probability. The particle which tries to pass through the wall moves from the $N$ to $N+1$ site and can pass the wall with probability $(1-q_1)/2$ or can be stopped by the wall with probability $q_1/2$. When a particle is located at the $N+1$ site, then its jump to the $N$ site can be performed with probability $(1-q_2)/2$. The probability that a particle can be stopped by the wall equals $q_2/2$.

The difference equations describing the random walk in a membrane system with reactions read as follows, see Fig. 1.

$$P_{A,n+1}(m; m_0) = \frac{1}{2} P_{A,n}(m-1; m_0) - R_A P_{A,n}(m; m_0), \quad m \leq N-1,$$

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

$$+ \frac{1-q_2}{2} P_{B,n}(N+1; m_0) + \frac{q_1}{2} P_{A,n}(N; m_0)$$

$$- R_A P_{A,n}(N; m_0),$$

$$P_{B,n+1}(N+1; m_0) = \frac{1-q_2}{2} P_{B,n}(N; m_0)$$

$$+ \frac{1}{2} P_{B,n}(N+2; m_0) + \frac{q_2}{2} P_{B,n}(N+1; m_0)$$

$$- R_B P_{B,n}(N+1; m_0),$$

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

$$+ \frac{1}{2} P_{B,n}(m+1; m_0) - R_B P_{B,n}(m; m_0), \quad m \geq N+2.$$  

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

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

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

$$S_i(m, z; m_0) = \sum_{n=0}^{\infty} z^n P_{i,n}(m, m_0), \quad i = A, B.$$  

we obtain (the details of the calculations are presented in [28])

$$S_A(m, z; m_0) = \frac{[\eta_A(z)]^{m-m_0}}{\sqrt{(1+zR_A)^2 - z^2}}$$

$$+ \Lambda_A(z) \frac{[\eta_A(z)]^{2N-m-m_0}}{\sqrt{(1+zR_A)^2 - z^2}},$$

$$S_B(m, z; m_0) = \frac{[\eta_A(z)]^{N-m_0} [\eta_B(z)]^{m-N-1}}{\sqrt{(1+zR_B)^2 - z^2}} \Lambda_B(z),$$

where

$$\Lambda_A(z) = \frac{(1-q_A)(\eta_B(z)) - \eta_A(z)}{(1-q_A)\eta_A(z) - q_A \eta_B(z)}$$

$$\Lambda_B(z) = \frac{(1-q_A)(\eta_B(z)) - \eta_A(z)}{(1-q_A)\eta_A(z) - q_A \eta_B(z)},$$

$$\eta_i(z) = 1 + \frac{R_i z - \sqrt{(1+R_i z)^2 - z^2}}{z}.$$  

The Laplace transforms of the Green’s functions for continuous time and discrete spatial variable are expressed by the formulae

$$\hat{P}_A(m, s; m_0) = \frac{1 - \hat{\omega}_1(s)}{s} S_A(m, \{\hat{\omega}_1(s), \hat{\omega}_2(s)\}; m_0)$$

$$\hat{P}_B(m, s; m_0) = \frac{1 - \hat{\omega}_1(s)}{s} S_B(m, \{\hat{\omega}_1(s), \hat{\omega}_2(s)\}; m_0)$$

where $\hat{\omega}_1(s) = \frac{1}{1+\sqrt{1+R_1 z}}$. The symbol $\{\hat{\omega}_1(s), \hat{\omega}_2(s)\}$ denotes that both functions $\hat{\omega}_1(s)$ and $\hat{\omega}_2(s)$ are involved into the functions $S_A$ and $S_B$ instead of variable $z$ according to the rules [28, 29].

$$\eta_i(z) \rightarrow \eta_i(\hat{\omega}_1(s)),$$  

$$\sqrt{(1+R_i z)^2 - z^2} \rightarrow \sqrt{(1+R_i \hat{\omega}_1(s))^2 - \hat{\omega}_1^2(s)}.$$  

The above rules were derived using the first passage time distribution $F(N,t;m_0)$ that the particle achieves the point $N$ first time at time $t$ starting from the point $m_0 < N$. Since this distribution is controlled by the function $\eta_1(z)$ only in the discrete system and all steps
are performed in the region $A$, the function $\eta_1$ should depend on the function $\hat{\omega}_1$ only when moving to continuous time. Similarly, the function $\eta_2$ depends on the function $\hat{\omega}_2$ only.

Let’s move to a continuous spatial variable. From Eqs. (10)–(15) and (58)–(63) we get

\begin{equation}
\hat{P}_A(x, s; x_0) = \frac{v_1(s)}{2D_1s\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}} \left[ e^{-|x-x_0|\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}} + \Lambda_A(s)e^{-(2x_N-x_0)\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}/2} \right],
\end{equation}

\begin{equation}
\hat{P}_B(x, s; x_0) = \frac{v_2(s)}{2D_2s\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}} \Lambda_B(s) e^{-(x_N-x_0)\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}} e^{-(x-x_N)\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}/2},
\end{equation}

where

\begin{equation}
\Lambda_A(s) = \frac{(1 - q_1)\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} - (1 - q_2)\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} + \epsilon \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}{(1 - q_2)\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} + (1 - q_1)\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} + \epsilon \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}},
\end{equation}

\begin{equation}
\Lambda_B(s) = \frac{2(1-q_1)\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}{(1 - q_2)\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} + (1 - q_1)\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} + \epsilon \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}. 
\end{equation}

We note that $\Lambda_A(s) + \Lambda_B(s) = 1$.

The Laplace transforms of subdiffusive fluxes are

\begin{equation}
\hat{J}_A(x, s; x_0) = -D_1\frac{s}{v_1(s)} \frac{\partial \hat{P}_A(x, s; x_0)}{\partial x},
\end{equation}

\begin{equation}
\hat{J}_B(x, s; x_0) = -D_2\frac{s}{v_2(s)} \frac{\partial \hat{P}_B(x, s; x_0)}{\partial x}.
\end{equation}

From Eqs. (44)–(49) we obtain

\begin{equation}
\hat{J}_A(x, s; x_0) = \frac{\text{sgn}(x-x_0)}{2} e^{-|x-x_0|\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}} - \frac{\Lambda_A(s)}{2} e^{-(2x_N-x_0)\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}/2},
\end{equation}

\begin{equation}
\hat{J}_B(x, s; x_0) = \frac{\Lambda_B(s)}{2} e^{-(x_N-x_0)\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}} \times e^{-(x-x_N)\sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}/2}.
\end{equation}

From the above equations we get the following boundary conditions at the thin membrane

\begin{equation}
\hat{J}_A(x_N, s; x_0) = \hat{J}_B(x_N, s; x_0),
\end{equation}

\begin{equation}
\frac{D_1}{v_1(s)} \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} \hat{P}_A(x_N, s; x_0) = \frac{D_2}{v_2(s)} \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} \left( 1 + \Lambda_A(s)/\Lambda_B(s) \right) \hat{P}_B(x_N, s; x_0). 
\end{equation}

However, boundary condition Eqs. (53) cannot be applied in a system with continuous variables without defining the membrane permeability coefficients for a continuous system. Let us illustrate this considering diffusion in a system in which a thin symmetrical membrane separates two identical media. In this case there is assumed $q_1 = q_2 \equiv q$, $v_1(s) = v_2(s) \equiv v(s)$, $\kappa_1 = \kappa_2 \equiv \kappa$, and $D_1 = D_2 \equiv D$. Then, we get from Eqs. (40) and (47)

\begin{equation}
\Lambda_A(s) = \frac{\epsilon \sqrt{\kappa^2 + \frac{v(s)}{D}}}{2(1-q) + \epsilon \sqrt{\kappa^2 + \frac{v(s)}{D}}},
\end{equation}

\begin{equation}
\Lambda_B(s) = \frac{2(1-q)}{2(1-q) + \epsilon \sqrt{\kappa^2 + \frac{v(s)}{D}}}. 
\end{equation}

If we assume that the probability of the particle’s passing through a partially permeable membrane $1-q$, $0 < q < 1$, does not depend on the parameter $\epsilon$, then we have $\Lambda_A(s) \to 0$ and $\Lambda_B(s) \to 1$ in the limit of small $\epsilon$. In this case, the Green’s functions Eqs. (44) and (55) take the form of the function for a homogeneous system without a membrane. It means that the membrane does not show its selective properties. The reason for this is as follows. The mean frequency of particle’s jumps between neighboring sites, $\nu(t) = d\langle n(t) \rangle/dt$ where $\langle n(t) \rangle$ is the number of steps over time interval $[0,t]$, is given by the formula $\nu(t) = L^{-1}[2D\dot{\omega}(s)/v^2(s)]$ which provides $\nu(t) \to \infty$ in the limit of small $\epsilon$. Then, the probability that a particle which tries to pass the partially
permeable membrane ‘infinite times’ in every finite time interval passes through the membrane is equal to one. To avoid such a non-physical situation, we use the following procedure when moving to a continuous spatial variable. The permeability properties of membrane are described by the functions $\Lambda_A(s)$ and $\Lambda_B(s)$. These functions should be independent of the parameter $\epsilon$. From Eqs. (40) and (47) it follows that this is possible only if $1 - q \sim \epsilon$. Thus, the parameter $q$ can depend on $\epsilon$. Guided by the result presented above we suppose that

$$1 - q_1 = \frac{\epsilon}{\gamma_1}, \quad 1 - q_2 = \frac{\epsilon}{\gamma_2},$$

(56)

where $\gamma_1$ and $\gamma_2$ are parameters as yet to be determined, $\gamma_1$ and $\gamma_2$ are the membrane permeability coefficients defined for the system with continuous variables. Since $0 \leq q_1, q_2 \leq 1$, we have $\gamma_1, \gamma_2 > 0$. Below we determine values of $\sigma_1$ and $\sigma_2$ for different cases.

For a one-sidedly fully permeable wall the Green’s functions and boundary conditions are given by Eqs. (44)–(47) with $q_1 = 0$ or $q_2 = 0$. When the boundary between media is not an obstacle for the particles we have $q_1 = q_2 = 0$. Below we consider the above mentioned cases. The Green’s functions are still given by Eqs. (44) and (45), but the functions $\Lambda_A(s)$ and $\Lambda_B(s)$ are different for these cases.

A. The case of $q_1 \neq 0$ and $q_2 \neq 0$

For $1 < \sigma_1, \sigma_2$ we get $\Lambda_A(s) = 1$, so we obtain the function for the system with fully reflecting wall. For $\sigma_1, \sigma_2 < 1$ the membrane ‘vanishes’ in the case of the symmetrical system. Thus, we get $\sigma_1 = \sigma_2 = 1$ and

$$1 - q_1 = \frac{\epsilon}{\gamma_1}, \quad 1 - q_2 = \frac{\epsilon}{\gamma_2}.$$  

(57)

Taking into account Eqs. (40), (47) and (57) we have

$$\Lambda_A(s) = \frac{\gamma_1 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} - \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} + \gamma_1 \gamma_2 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}{\gamma_1 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} + \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} + \gamma_1 \gamma_2 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}},$$

(58)

and

$$\Lambda_B(s) = \frac{2 \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}{\gamma_1 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} + \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} + \gamma_1 \gamma_2 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}.$$

(59)

B. The case of $q_1 = 0$ and $q_2 \neq 0$

For $q_2 > 0$ we get $\Lambda_A(s) = -1$ when $\epsilon \to 0$ and we obtain the Green’s function for fully absorbing wall. Thus, we assume $\sigma_2 = 0$ and we obtain

$$\Lambda_A(s) = \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} - \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}},$$

(60)

and

$$\Lambda_B(s) = \frac{2 \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}{\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} + \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} + \gamma_1 \gamma_2 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}.$$

(61)

In this case we have $1 - q_2 = 1/\gamma_2$.

C. The case of $q_1 \neq 0$ and $q_2 = 0$

For $\sigma_1 > 0$ we get $\Lambda_A(s) = 1$ and $\Lambda_B(s) = 0$, which provides the Green’s function for a system with fully reflecting membrane. Thus, we suppose $\sigma_1 = 0$ and

$$\Lambda_A(s) = \frac{\gamma_1 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} - \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}{\gamma_1 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} + \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}},$$

(62)

and

$$\Lambda_B(s) = \frac{2 \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}{\gamma_1 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} + \gamma_2 \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}} + \gamma_1 \gamma_2 \sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}.$$

(63)

In this case we have $1 - q_1 = 1/\gamma_1$.

D. The case of $q_1 = 0$ and $q_2 = 0$

In this case we have

$$\Lambda_A(s) = \frac{\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} - \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}{\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}} + \sqrt{\kappa_2^2 + \frac{v_2(s)}{D_2}}}.$$

(64)
\[ \Lambda_B(s) = \frac{2\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1}}}{\sqrt{\kappa_1^2 + \frac{v_1(s)}{D_1} + \kappa_2^2 + \frac{v_2(s)}{D_2}}} \, . \] (65)

IV. APPLICATIONS OF THE MODEL.
RELEASE OF SUBSTANCE FROM A SUBDIFFUSIVE MEDIUM

We consider the diffusion of the substance from the subdiffusive medium \( A \) in which the diffusing molecules can be absorbed into the medium \( B \) in which normal diffusion occurs. We assume \( \kappa_2 = 0 \) and \( v_2(s) = s \).
The function \( v_1(s) \) determines the type of subdiffusion in the medium \( A \). For 'classical' subdiffusion we assume \( v_1(s) = s^\alpha, \, 0 < \alpha < 1 \), and for slow subdiffusion \( v_1(s) = \xi(1/s) \) where \( \xi \) is a slowly varying function. The example is the system consists of a porous medium and water. The particle can diffuse freely from the porous medium channel into the water, but movement in the opposite direction will be rather difficult. The border between media is fully permeable to particles moving in one direction and partially permeable to particles moving in the opposite direction. Thus, we put \( q_1 = 0 \) and \( q_2 \neq 0 \).

We suppose that at the initial moment there is a homogeneous solution of diffusing substance of concentration \( C_0 \) in the medium \( A \) and there is a pure solvent in the medium \( B \). The initial concentration reads
\[ C(x,0) = \begin{cases} C_0, & x < 0, \\ 0, & x > 0. \end{cases} \] (66)

We are going to determine the temporary evolution of the amount of substance released from the medium \( A \) to the medium \( B \). The concentration of diffusing substance in the region \( B \) can be calculated by means of the following formula
\[ C_B(x,t) = \int_{-\infty}^{x_N} C(x_0,0)P_B(x,t;x_0)dx_0, \] (67)
\( C(x,0) \) is the initial concentration. A temporal evolution of the amount of substance in the region \( B \) reads
\[ W_B(t) = S \int_{x_N}^{\infty} C_B(x,t)dx, \] (68)
where \( S \) is a cross-section area of the system. From Eqs. \( 45, \, 47, \, 61, \) and \( 66 \)–\( 68 \) we get
\[ \hat{W}_B(s) = \frac{SC_0\gamma_2}{\sqrt{D_2s\left(\kappa_1^2 + \frac{v_1(s)}{D_1}\right)\left(\kappa_1^2 + \frac{v_1(s)}{D_1} + \gamma_2 + \frac{v_2(s)}{D_2}\right)}} \] (69)
For \( \kappa_1 \neq 0 \) we get in the limit of small \( s \), which corresponds to the limit of long time,
\[ W_B(t) = \frac{SC_0\gamma_2}{\kappa_1^2\sqrt{\pi D_2t}}. \] (70)

In the system in which there is no absorption, \( \kappa_1 = 0 \), we have
\[ W_B(t) = \frac{SC_0D_1\gamma_2}{\sqrt{\pi D_3}\xi(t)} \] (71)
for slow subdiffusion and
\[ W_B(t) = \frac{SC_0\gamma_2D_1t^{\alpha-1/2}}{\sqrt{D_21(\alpha+1/2)}}, \] (72)
for subdiffusion. To calculate the function Eq. \( 72 \) the following Strong Taubertian Theorem has been used If \( \phi(t) \geq 0, \phi(t) \) is ultimately monotonic like \( t \to \infty, \) \( R \) is slowly-varying at infinity and \( 0 < \rho < \infty \), then each of the relations
\[ \hat{\phi}(s) \approx \frac{R(1/s)}{s^\rho} \] as \( s \to 0 \) and
\[ \phi(t) \approx \frac{R(t)}{\Gamma(p)t^{1-\rho}} \] as \( t \to \infty \) implies the other.

The functions \( 70, \, 71 \) and \( 72 \) are qualitatively different. Their experimental determination can allow to evaluate what type of diffusion process takes place in the subdiffusive medium. This may have practical significance in the case when experimental measurement of particles’ concentration is not possible in the subdiffusive medium.

V. FINAL REMARKS

The most important results presented in this work are:

1. Green’s functions for a system consisting of two media separated by a thin membrane, which is treated as a partially permeable wall, Eqs. \( 44 \) and \( 45 \).
2. boundary conditions at a thin membrane Eqs. \( 52 \) and \( 53 \).

The functions \( \Lambda_A(s) \) and \( \Lambda_B(s) \), which depend on membrane permeability coefficients, are given by Eqs. \( 58 \)–\( 65 \), their detailed form depends on whether the probabilities \( q_1 \) and \( q_2 \) are equal to zero or not. The Green’s functions can be used for systems containing various media in which normal diffusion, sub-diffusion, or slow sub-diffusion can occur. The type of diffusion in each medium determines the appropriate choice of the functions \( v_1(s) \) and \( v_2(s) \) which are described in Sec. IIc.

If the particles move independently of each other and the membrane permeability parameters do not depend on the concentration of the diffusing particles, the boundary conditions at the thin membrane are valid for any initial concentration of particles. This fact can be checked using the integral formula \( C(x,t) = \int P(x,t;x_0)C(x_0,0)dx_0. \)
The above considerations were performed assuming that $x_0 < x_N$. However, when the wall is asymmetrical the boundary condition may depend on which side of the membrane a particle starts its motion. An example is a thin membrane that is completely impenetrable to particles moving in one direction from a region $A$ to a region $B$ and partially permeable when particles move in the opposite direction. Then, for particles initially located in $A$ the boundary condition at the membrane is just as for fully reflecting wall whereas for particles starting form the region $B$ the boundary condition is as for partially absorbing wall. Due to the symmetry arguments, assuming $x_0 > x_N$ we can obtain Green’s functions and boundary conditions making a change $P_A \leftrightarrow P_B$, $\lambda_A(s) \leftrightarrow \lambda_B(s)$, $v_1(s) \leftrightarrow v_2(s)$, $(D_1, \kappa_1) \leftrightarrow (D_2, \kappa_2)$, $(\gamma_1, \gamma_2) \leftrightarrow (\gamma_2, \gamma_1)$, and $(x-x_0, x-x_N, x_0-x_N) \leftrightarrow (x-x, x_N-x, x_N-x_0)$.

The boundary conditions derived in this paper can be used to solve a system of differential equations describing different types of diffusion with absorption in a multilayered system. The solution should be performed in terms of the Laplace transform. Usually, it is difficult to calculate the inverse Laplace transform of the solutions. However, it is often possible to find inverse Laplace transforms over the long time limit, which corresponds to the limit of small parameter $s$.

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