Subdiffusive random walk in a membrane system: the generalized method of images approach

Tadeusz Kosztołowicz

Institute of Physics, Jan Kochanowski University, ul. Świętokrzyska 15, 25-406 Kielce, Poland
E-mail: tadeusz.kosztolowicz@ujk.edu.pl

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Abstract. Using two random walk models in a system with a thin membrane we find the Green’s functions describing various kinds of diffusion in this system; the membrane is treated here as a thin, partially permeable wall. The models differ in the assumptions concerning how the particle is stopped or reflected by the membrane when the particle’s attempts to pass through it fail. We show that the Green’s functions obtained for both models are equivalent with the exception of the values of these functions at the membranes’ surfaces. As examples we present the Green’s functions for a membrane system in which subdiffusion or slow subdiffusion occurs and we briefly discuss the properties of the functions. We also show that the Green’s functions can be obtained by means of the generalized method of images. Within this method, the Green’s functions appear to be a combination of the Green’s functions derived for a homogeneous system without a membrane by means of the rules presented in this paper. Additionally, the obtained Green’s functions are used to derive a boundary condition at the membrane. It is shown that the condition contains a specific term which can be interpreted as a ‘memory term’ depending on the kind of diffusion occurring in the system which is generated by the membrane.

Keywords: subdiffusion, slow subdiffusion, membrane system, method of images
1. Introduction

Diffusion processes in a membrane system widely occur in biology and engineering sciences (see, for example, [1–3]). In this paper we consider diffusion in a one-dimensional system with a thin membrane. The most commonly used definition of various kinds of diffusion is that this process is the random walk of particles in which

\[ \langle (\Delta x)^2 \rangle \sim f(t), \]  

(1)

where \( \langle (\Delta x)^2 \rangle \) is the mean square displacement of a particle and \( f(t) \) is the function which defines a kind of diffusion. For \( f(t) = t \) we have normal diffusion, for \( f(t) = t^\alpha \), \( 0 < \alpha < 1 \), we have subdiffusion whereas for \( \alpha > 1 \) there is superdiffusion and when \( f(t) \) is a slowly varying function we have slow subdiffusion (which is also called ‘ultraslow diffusion’); ‘slowly varying function’ is defined as a function which \( \frac{f(at)}{f(t)} \to 1 \) for \( t \to \infty \) for any positive \( a \). We add that subdiffusion occurs in media in which the particles’ movement is strongly hindered due to the complex internal structure of the medium, such as, for example, in porous media or gels [4, 5].

Normal diffusion can be interpreted as a particle’s random walk in which both the mean square displacement of a single jump length and the mean frequency of the jumps are finite; this process is the Markov process. It was shown in [6] that there are processes in which the anomalously long waiting time for a particle to take its next...
step is entangled with the anomalously large length of jumps in a particular way that provides \( f(t) = t \). As was concluded in [6] the relation (1) should be supplemented by an appropriate stochastic interpretation of the random walk process in order to define subdiffusion. Such a simple interpretation is given within the continuous time random walk (CTRW) model where the random walk is described by the probability density \( \lambda(\rho) \) of a single jump length \( \rho \) and a probability density \( \omega(\tau) \) of time \( \tau \), which is needed for the particle to take its next step. It is assumed that for normal diffusion both distributions have finite moments of natural order, whereas for subdiffusion the mean value of \( \omega(\tau) \) is infinite and the moments of \( \lambda(\rho) \) are finite. In this paper we base our consideration on the random walk model on a lattice for which \( \lambda \rho \delta \rho \delta \rho = -1 \) (at the vicinity of the membrane the definition of \( \lambda \rho \rho \) is slightly different), \( \epsilon \) is the distance between discrete sites; in this paper \( \delta \) denotes both the Kronecker symbol (for a discrete space variable) or the delta-Dirac function (for a continuous space variable). The kind of diffusion process is defined here by the function \( \omega(\tau) \). Having the results for a system with a discrete spatial variable, we pass into a continuous variable having as the limit \( \epsilon \rightarrow 0 \) and using the formulae presented in this paper.

The movement of a diffusing particle is described by the Green’s function which is interpreted as a probability density, \( P(x; t; x_0) \), of finding a particle at point \( x \) after time \( t \) under the condition that at the initial moment, \( t = 0 \), the particle was at point \( x_0 \). The classical version of the method of images has been used to determine the Green’s function in a system containing a fully reflecting or fully absorbing wall. In this method Green’s function is considered to be the normalized concentration of diffusing particles beginning their movement from the initial point \( x_0 \) at \( t = 0 \). The main idea of this method is to replace the wall by an additional source of particles in such a way that the concentration of particles generated by all particle sources occurring in the system fulfills the boundary condition which is assumed to be at the wall. For a system with a fully reflecting wall the boundary condition at the wall assumes that the diffusive flux vanishes at the wall: \( J(x_N, t; x_0) = 0 \), where \( x_N \) is the position of the wall. The same effect would be achieved if the wall were to be replaced by an additional source of particles located symmetrically to point \( x_0 \) with respect to the wall. For a system with a fully absorbing wall, the boundary condition reads \( P(x_N, t; x_0) = 0 \) thus the additional source located symmetrically to point \( x_0 \) with respect to the wall should be subtracted from the Green’s function representing the particles source located at \( x_0 \). Thus, assuming that \( x_0 < x_N \), the Green’s function for the above-mentioned cases can be written in the following compacted form

\[
P(x; t; x_0) = P_H(x; t; x_0) + \varsigma P_H(x; t; 2x_N - x_0),
\]

where \( \varsigma = 1 \) for a fully reflecting wall and \( \varsigma = -1 \) for a fully absorbing wall; \( P_H \) denotes the Green’s function for a homogeneous system without wall.

The situation is more complicated for a system with a partially permeable thin membrane in which two Green’s functions describing diffusion in both regions located on opposite sides of the membrane are needed. In such a system it is possible to find the Green’s function using a simple random walk model. In this paper we show that the structure of the Green’s functions, obtained for a membrane system, have a specific structure which is more complicated than the one expressed by equation (2) and reads
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\[
P(x, t; x_0) = P_H(x, t; x_0) \pm \left( \kappa_0 P_H(x, t; x_a) + \kappa_G \frac{\partial P_H(x, t; x_0)}{\partial x} \right),
\]

where \( x_a = 2x_N - x_0 \) and the sign \( + \) occurring just before the bracket in the right-hand side of the above equation corresponds to \( x < x_N \), whereas \( x_a = x_0 \) and the sign \( - \) corresponds to \( x > x_N \). We note that the Green’s functions obtained for the membrane system and the function equation (2) have the same property, which is the basis of the method of images: both of them can be expressed by the function \( P_H \). The parameters \( \kappa_0 \) and \( \kappa_G \), described later in this paper, can be calculated by means of phenomenological models of particle transport through a thin membrane or can be treated as parameters ensuring the best fit of theoretical functions to the experimental results.

Until now several boundary conditions, which are not equivalent, have been set at the thin membrane [7–10]. The boundary conditions at the membrane can be derived from the obtained functions. A similar strategy was carried out in Chandrasekhar’s paper [11] in which the Green’s function for the diffusive system with a reflecting or absorbing wall was obtained for the first time and then the boundary condition at the wall was derived.

The aim of this paper is to derive Green’s functions for a system with a thin membrane and to devise a generalized method of images which can be used to derive such Green’s functions. The thin membrane is defined here as a partially permeable wall which is so thin that the particle’s transport inside the membrane is not considered. A particle can pass through the membrane with some probability while it is taking a jump. We use two random walk models which differ in assumptions as to whether the particle is stopped or reflected by the membrane when the particle’s attempt to pass through the membrane fails. The method presented here provides the general form of the Green’s function which is also valid for various kinds of diffusion (normal diffusion, subdiffusion, slow subdiffusion). These Green’s functions can be obtained within the generalized method of images which is discussed in this paper. The generalized method of images is understood here as the method which allows one to find the Green’s function for the system under consideration as a combination of the functions \( P_H \) which represents particles’ sources located at various points. In general, the method of images appears to be a useful tool for the construction of the Green’s functions for more complicated systems such as two-membrane systems. The additional aim of this paper is to check if the Green’s functions obtained for both models are equivalent.

The paper is organized as follows. In section 2 we will present the method of derivation of the Green’s function in a homogeneous system without a membrane. In sections 3 and 4 we will derive the generalized form of the Green’s functions obtained for the model with reflecting membrane (section 3) and for the model with stopped membrane (section 4). In section 5 we will present the generalized method of images which allows us to obtain the Green’s functions derived in sections 3 and 4 in a simpler way. In this section will also be found the generalized form of the boundary conditions for these functions. The forms of Green’s functions for subdiffusion and slow subdiffusion along with the discussion of their properties will be presented in section 6. Section 7 contains final remarks. The details of the calculations of the generating function will be given in the appendix.
2. Random walk model

To find the Green’s function for a system with a thin membrane we use a particle’s random walk model in a system in which the time $n$ and spatial variable $m$ are discrete; after this, we pass from discrete to continuous variables. For normal diffusion and subdiffusion long jumps occur with a low probability, thus we assume that the particle can only jump to its adjacent position. It is not allowed to remain in the current occupied position in the particle after the time at which the jump should be executed unless the particle is stopped by the membrane. After solving these equations (more precisely, after determining the generating function for the equations) one can make the transition from discrete to continuous variables.

In order to illustrate the method we consider diffusion in a homogeneous system. In a system with discrete variables, the particle’s random walk is described by the following difference equation

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

(3)

where $P_n(m; m_0)$ is the probability of finding a particle at site $m$ after step $n$ and $m_0$ is the initial position of the particle

$$P_0(m; m_0) = \delta_{m,m_0}.$$  

(4)

To solve the differential equations we use the generating function which is defined as

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

(5)

In terms of the Laplace transform, $L[f(t)] \equiv \hat{f}(s) = \int_0^\infty e^{-st} f(t) dt$, the general form of the Green’s function for continuous time reads (see, for example, [10])

$$\hat{P}(m, s; m_0) = \frac{1 - \hat{\omega}(s)}{s} S(m, \hat{\omega}(s); m_0),$$

(6)

where $\hat{\omega}(s)$ is the Laplace transform of $\omega(t)$ which is the probability distribution of the time which is needed for the particle to take its next step. From equations (3)–(5) one gets (see [12, 13] and the appendix in this paper)

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

(7)

where

$$\eta(z) = \frac{1 - \sqrt{1 - z^2}}{z}.$$  

(8)

To pass from a discrete to continuous spatial variable we suppose

$$x = em, \quad x_0 = em_0, \quad x_N = eN,$$

(9)
where \( \varepsilon \) denotes the distance between discrete sites. To pass from probability \( \hat{P}(m, s; m_0) \) to spatial probability density \( \hat{P}(x, s; x_0) \) we use the following relation valid for small values of \( \varepsilon \)

\[
P(m, t; m_0) = \varepsilon P(x, t; x_0),
\]

and finally we take limit \( \varepsilon \to 0 \). Further considerations are performed assuming that \( s \) is small, which corresponds to the case of large time due to Tauberian theorems. In practice, the limit of small \( s \) means that only the leading terms with respect to this variable will be present in the Laplace transform of the Green’s function whereas the limit of small \( \varepsilon \) means that this parameter will be absent in this function.

In the continuous time random walk model it is assumed that \( \hat{\omega}(s) \) is considered for small \( s \) [4]. Since, due to the normalized condition, \( \hat{\omega}(0) = 1 \), we suppose that for small \( s \) there is

\[
\hat{\omega}(s) = 1 - \mu v(s),
\]

where \( \mu \) is a parameter defined for each type of diffusion alone; this parameter ensures the dimensionless form of the last term in equation (11). The function \( v(s) \) defines the kind of diffusion and \( v(s) \to 0 \) as \( s \to 0 \). Equations (8) and (11) provide, for small values of \( s \)

\[
\eta(\hat{\omega}(s)) = 1 - \sqrt{2\mu v(s)}.
\]

The generalized diffusion coefficient is defined as

\[
D = \frac{\varepsilon^2}{2\mu}.
\]

From equations (6)–(13) we obtain

\[
\hat{P}_H(x, s; x_0) = \sqrt{\frac{v(s)}{2\sqrt{D} s}} \left( 1 - \frac{v(s)}{\sqrt{D}} \right)^{|x-x_0|}. \tag{14}
\]

Formally, the transition to a continuous variable was obtained by calculating limit \( \varepsilon \to 0 \). However, due to equation (13) this provides \( \mu \to 0 \) which means that \( \omega(t) \) is beyond any physical interpretation. In order to avoid problems of interpretation, we assume that \( \varepsilon \) is finite but small enough so that the following relation is satisfied (see also the discussion presented in [10])

\[
\left( 1 - \frac{v(s)}{\sqrt{D}} \right)^{|x-x_0|} \approx e^{-\frac{|x-x_0|v(s)}{\sqrt{D}}}. \tag{15}
\]

From equations (14) and (15) we have

\[
\hat{P}_H(x, s; x_0) = \frac{\sqrt{v(s)}}{2\sqrt{D} s} e^{-\frac{|x-x_0|v(s)}{\sqrt{D}}}. \tag{16}
\]
3. Random walk model with particle reflection from a membrane

Let us suppose that the thin membrane is located between the \( N \) and the \( N + 1 \) site. We assume that the particle can be reflected from the membrane with probability \( q_1 \) when trying to jump from the \( N \) to the \( N + 1 \) site and with probability \( q_2 \) when trying to jump from the \( N + 1 \) to the \( N \) site (see figure 1); in this paper we assume \( q_1, q_2 \neq 0 \). The difference equations describing this process read

\[
P_{n+1}(N-1; m_0) = \frac{1}{2} P_n(N-2; m_0) + \frac{1 + q_1}{2} P_n(N; m_0),
\]

\[
P_{n+1}(N; m_0) = \frac{1}{2} P_n(N-1; m_0) + \frac{1 - q_2}{2} P_n(N+1; m_0),
\]

\[
P_{n+1}(N+1; m_0) = \frac{1 - q_1}{2} P_n(N; m_0) + \frac{1}{2} P_n(N+2; m_0),
\]

\[
P_{n+1}(N+2; m_0) = \frac{1 + q_2}{2} P_n(N+1; m_0) + \frac{1}{2} P_n(N+3; m_0),
\]

\[
P_{n+1}(m; m_0) = \frac{1}{2} P_n(m-1; m_0) + \frac{1}{2} P_n(m+1; m_0),
\]

\[
m = N - 1, N, N + 1, N + 2,
\]

the initial condition is given by equation (4). Equations (17)–(21) which describe a random walk in a membrane system in which the homogeneity of the system is impaired at a single point, are solvable by means of the generating function method, see [13–15].

In the following, the functions \( S \) and \( P \) will be labeled by the indices \( ij \), which denote the signs of \( m - N \) and \( m_0 - N \), respectively. We consider the case of \( m_0 \leq N \). From equations (4), (5) and (17)–(21) we obtain (the details of the calculation are presented in the appendix)

\[
S_{-m}(m, z; m_0) = \frac{\eta^{m-m_0}}{\sqrt{1 - z^2}} + K_0(z) \frac{\eta^{2N-m-m_0}}{\sqrt{1 - z^2}}, \ m \leq N - 1,
\]
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\[ S_{-\lambda}(N, z; m_0) = K_{1N}(z) \frac{\eta^{N-m_0}}{\sqrt{1-z^2}}, \quad (23) \]

\[ S_{+\lambda}(m, z; m_0) = K_2(z) \frac{\eta^{m-m_0}}{\sqrt{1-z^2}}, \quad m \geq N + 2, \quad (24) \]

\[ S_{+\lambda}(N+1, z; m_0) = K_{2N}(z) \frac{\eta^{N+1-m_0}}{\sqrt{1-z^2}}, \quad (25) \]

where

\[ K_1(z) = \frac{q_1 - q_2 \eta^2(z)}{1 - q_1 q_2 \eta^2(z)}, \quad K_{1N}(z) = \frac{1 - q_2 \eta^2(z)}{1 - q_1 q_2 \eta^2(z)}, \quad (26) \]

\[ K_2(z) = \frac{(1 - q_1)(1 + q_2)}{1 - q_1 q_2 \eta^2(z)}, \quad K_{2N}(z) = \frac{1 - q_1}{1 - q_1 q_2 \eta^2(z)}. \quad (27) \]

Functions (26) and (27) play a key role in the Green’s function for the membrane system, because only these functions depend on the permeability coefficients of the membrane. The main difficulty of finding the Green’s functions for the continuous system is to find a suitable form of functions (26) and (27) for \( \epsilon \rightarrow 0 \). We assume that in this limit the Green’s function must depend on the parameters of membrane permeability.

Similarly to [10], the probabilities characterizing membrane permeability are assumed to be functions of \( \epsilon \); this function for small values of argument \( \epsilon \) reads

\[ q_1(\epsilon) = 1 - \frac{\epsilon^\sigma}{\gamma_1}, \quad q_2(\epsilon) = 1 - \frac{\epsilon^\sigma}{\gamma_2}, \quad (28) \]

\( \gamma_1 \) and \( \gamma_2 \) being the membrane permeability coefficients defined for the continuous system, and \( \sigma \) being the parameter to be determined. The reason for the introduction of these equations is that the frequency of jumps performed by the particle increases to infinity when \( \epsilon \) drops to zero. For a very small value of \( \epsilon \), the frequency takes an ‘anomalously’ large value [10]. A very large number of attempts to pass through the partially permeable membrane made over an arbitrarily small time interval means that the particle passes through the membrane with probability equal to one; then, the membrane loses its selective property.

From equations (12), (13) and (26)–(28) we obtain

\[ K_0(\tilde{\omega}(s)) = \frac{e^{\sigma-1} \left( \frac{1}{\gamma_1} - \frac{1}{\gamma_2} \right) + 2 \sqrt{\frac{\eta(s)}{D}}}{e^{\sigma-1} \left( \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right) + 2 \sqrt{\frac{\eta(s)}{D}}}, \quad (29) \]
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$$K_{1N}(\hat{\omega}(s)) = \frac{\epsilon^{-1} \frac{1}{\gamma_2} + 2 \sqrt{\frac{\nu(s)}{D}}}{\epsilon^{-1} \left( \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right) + 2 \sqrt{\frac{\nu(s)}{D}}}, \quad (30)$$

$$K_2(\hat{\omega}(s)) = \frac{2 \epsilon^{-1} \frac{1}{\gamma_1}}{\epsilon^{-1} \left( \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right) + 2 \sqrt{\frac{\nu(s)}{D}}}, \quad (31)$$

$$K_{2N}(\hat{\omega}(s)) = \frac{\epsilon^{-1} \frac{1}{\gamma_1}}{\epsilon^{-1} \left( \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right) + 2 \sqrt{\frac{\nu(s)}{D}}}. \quad (32)$$

The only possibility is that Green’s functions depend on the parameters of membrane permeability in the limit of small values of $\epsilon$, also for the case of a symmetrical membrane for which $\gamma_1 = \gamma_2$, is $\sigma = 1$. Then, from equations (29)–(32) we get for small values of $s$

$$K_0(\hat{\omega}(s)) = \frac{\gamma_1 - \gamma_2}{\gamma_1 + \gamma_2} + \frac{4 \gamma_2 \gamma_\epsilon \sqrt{\nu(s)}}{(\gamma_1 + \gamma_2) \sqrt{D}}, \quad (33)$$

$$K_{1N}(\hat{\omega}(s)) = \frac{\gamma_1}{\gamma_1 + \gamma_2} + \frac{2 \gamma_2 \gamma_\epsilon \sqrt{\nu(s)}}{(\gamma_1 + \gamma_2) \sqrt{D}}, \quad (34)$$

$$K_2(\hat{\omega}(s)) = \frac{2 \gamma_2}{\gamma_1 + \gamma_2} - \frac{4 \gamma_2 \gamma_\epsilon \sqrt{\nu(s)}}{(\gamma_1 + \gamma_2) \sqrt{D}}, \quad (35)$$

$$K_{2N}(\hat{\omega}(s)) = \frac{\gamma_2}{\gamma_1 + \gamma_2} - \frac{2 \gamma_2 \gamma_\epsilon \sqrt{\nu(s)}}{(\gamma_1 + \gamma_2) \sqrt{D}}, \quad (36)$$

where $\gamma_\epsilon = \frac{\gamma_2}{\gamma_1 + \gamma_2}$.

From equations (6)–(10), (22)–(25) and (33)–(36) we obtain

$$\hat{P}_{\sigma}(x, s; x_0) = \frac{\nu(s)}{2 \sqrt{D} s} \left[ e^{-\frac{|x-x_0| \sqrt{\nu(s)}}{\sqrt{D}}} + K_0(\hat{\omega}(s)) e^{-\frac{(2x_N-x-x_0) \sqrt{\nu(s)}}{2 \sqrt{D}}} \right], \quad (37)$$

for $x < x_N,$

$$\hat{P}_{\sigma}(x_N, s; x_0) = \frac{\sqrt{\nu(s)}}{2 \sqrt{D} s} e^{-\frac{(x_N-x_0) \sqrt{\nu(s)}}{\sqrt{D}}} K_{1N}(\hat{\omega}(s)), \quad (38)$$

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\[ \hat{P}_{+}(x, s; x_0) = \frac{\sqrt{v(s)}}{2\sqrt{D}} K_2(\omega(s)) e^{-\frac{(x-x_0)\sqrt{v(s)}}{\sqrt{D}}}, \quad x > x_N; \]  

\[ \hat{P}_{+}(x_N, s; x_0) = \frac{\sqrt{v(s)}}{2\sqrt{D}} K_{2N}(\omega(s)) e^{-\frac{(x_N-x_0)\sqrt{v(s)}}{\sqrt{D}}}. \]  

It is easy to see that the above Green’s functions lose their continuity at membrane surfaces

\[ \lim_{x \to x_N^-} P_{+}(x, t; x_0) = 2P_{-}(x_N, t; x_0), \]  
\[ \lim_{x \to x_N^+} P_{+}(x, t; x_0) = 2P_{-}(x_N, t; x_0). \]

4. Random walk model with particle stopped by a membrane

In [10] we considered a particle’s random walk model in a system with a thin membrane, in which the particle trying to pass the membrane from the \( N \) to the \( N+1 \) site may be stopped by the membrane with probability \( q_1 \) or pass through the membrane with probability \( 1 - q_1 \). The particle’s halting by the membrane means that the particle does not change its position after its ‘jump’. When the molecule is trying to jump from position \( N+1 \) to \( N \), the probability of the blocking of the particle through the membrane is \( q_2 \), and the probability of passage through the membrane equals \( 1 - q_2 \) (see figure 2). In this case we have the following difference equations

\[ P_{n+1}(N; m_0) = \frac{1}{2} P_n(N-1; m_0) + \frac{1 - q_2}{2} P_n(N+1; m_0) + \frac{q_1}{2} P_n(N; m_0), \]  

\[ P_{n+1}(N+1; m_0) = \frac{1 - q_1}{2} P_n(N; m_0) + \frac{1}{2} P_n(N+2; m_0) + \frac{q_2}{2} P_n(N+1; m_0), \]  

\[ P_{n+1}(m; m_0) = \frac{1}{2} P_n(m-1; m_0) + \frac{1}{2} P_n(m+1; m_0), \quad m \neq N, N+1. \]

In the following, \( \tilde{\gamma}_1 \) and \( \tilde{\gamma}_2 \) denote the permeability coefficients of the stopping membrane, defined for a system with a continuous spatial variable. As shown in [10], the probabilities of passing through the membrane should be chosen as the following functions of \( \epsilon \)

\[ q_1(\epsilon) = 1 - \frac{\epsilon}{\tilde{\gamma}_1}, \quad q_2(\epsilon) = 1 - \frac{\epsilon}{\tilde{\gamma}_2}. \]
Taking into account the generating functions for this system, presented in [10], which, together with equations (12)–(16) provide

\[
\hat{P}_-(x, s; x_0) = \frac{\sqrt{v(s)}}{2\sqrt{D}s} \left[ e^{-\frac{|x-x_0|\sqrt{v(s)}}{\sqrt{D}}} + \Lambda_1(s)e^{\frac{(2x_0-x-x_0)\sqrt{v(s)}}{\sqrt{D}}} \right],
\]

\[
\hat{P}_+(x, s; x_0) = \Lambda_2(s)e^{\frac{(x-x_0)\sqrt{v(s)}}{\sqrt{D}}},
\]

where

\[
\Lambda_1(s) = \frac{\gamma_1 - \gamma_2}{\gamma_1 + \gamma_2} + \frac{2\gamma_2 \gamma_0 \sqrt{v(s)}}{(\gamma_1 + \gamma_2)\sqrt{D}}, \quad \Lambda_2(s) = \frac{2\gamma_2}{\gamma_1 + \gamma_2} - \frac{2\gamma_2 \gamma_0 \sqrt{v(s)}}{(\gamma_1 + \gamma_2)\sqrt{D}},
\]

\[
\tilde{\gamma}_w = \frac{\gamma_0}{\gamma_1 + \gamma_2}.
\]

The Laplace transforms of the Green’s functions equations (47) and (48) coincide with the Laplace transforms of Green’s functions obtained for the system with a reflecting membrane, equations (37) and (39), respectively, if \( \gamma_1 = 1/2 \) and \( \gamma_2 = 1/2 \). In contrast to the Green’s functions presented in section 3, the Green’s functions presented in this section are continuous at the membrane surfaces

\[
\lim_{x \to x_N^-} P_-(x, t; x_0) = P_-(x_N, t; x_0),
\]

\[
\lim_{x \to x_N^-} P_+(x, t; x_0) = P_+(x_N, t; x_0).
\]

5. Generalized method of images

The form of the Green’s functions, (37) and (39), shows that these functions can also be determined using the method of images which is understood here as a replacement of the membrane by the additional source function. Analyzing the structure of the Green’s functions obtained in the previous sections we note that the functions can be expressed by the following equations

\[
P_-(x, t; x_0) = P_H(x, t; x_0) + P_C(x, t; 2x_N - x_0),
\]

\[
P_+(x, t; x_0) = P_H(x, t; x_0) - P_C(x, t; x_0),
\]

where \( P_C \) denotes a ‘compound’ source function. This function has the following structure

\[
P_C(x, t; x_0) = \kappa_0 P_H(x, t; x_0) + \kappa_G P_G(x, t; x_0),
\]

where

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\[ P_G(x, t; x_0) = \left| \frac{d}{dx} P_H(x, t; x_0) \right| \] (55)

is a ‘gradient source function’. Parameters \( \kappa_0 \) and \( \kappa_G \) depend on the membrane permeability coefficients. In general, \( \kappa_0 \) can be interpreted as the relative measure of the asymmetry of the membrane; \( \kappa_0 = 0 \) for the symmetrical membrane. For the system with a reflecting membrane we observe

\[ \kappa_0 = \frac{\gamma_1 - \gamma_2}{\gamma_1 + \gamma_2}, \quad \kappa_G = \frac{4\gamma_1}{(1 + \gamma_1/\gamma_2)^2}. \] (56)

For the system with a stopping membrane, equations (52)–(56) are still valid, with \( \gamma_{1,2} = \tilde{\gamma}_{1,2}/2 \). For the case of a fully reflecting wall we have \( \gamma_1 \rightarrow \infty \), then \( \kappa_0 = 1 \) and \( \kappa_G = 0 \), which means that function \( P_- \) takes the form of function (2) with \( \zeta = 1 \) and \( P_{++} \) being equal to zero. For a partially absorbing wall there is \( \gamma_2 \rightarrow \infty \) and \( 0 < \gamma_1 < \infty \) which gives \( \kappa_0 = -1 \) and \( \kappa_G = 4\gamma_1 \).

The considerations presented in this paper concern the case of \( x_0 < x_N \). In general, the coefficient \( \gamma_1 \) can be defined as a coefficient which controls the membrane permeability when a particle tries to pass through the membrane from a region of the initial particle’s location to the opposite region, and \( \gamma_2 \) is the membrane permeability coefficient when the particle moves in the opposite direction. It is easy to see that the Green’s functions equations (37) and (39) fulfil the following boundary condition at the membrane in terms of the Laplace transform

\[ \hat{P}_-(x_N, s; x_0) = \lambda_1 \hat{P}_{++}(x_N, s; x_0) + \lambda_2 \sqrt{v(s)} \hat{P}_+(x_N, s; x_0), \] (57)

where we have \( \lambda_1 = \frac{\gamma_1}{\gamma_2} \) and \( \lambda_2 = \frac{2\gamma_1}{\sqrt{\beta}} \). This boundary condition is complemented by the condition of flux continuity at the membrane.

For the case of \( x_0 > x_N \), the functions and boundary conditions can be obtained from the functions presented in this paper when, due to symmetry arguments, the following conversion is made: \( \gamma_1 \rightarrow \gamma_2, \gamma_2 \rightarrow \gamma_1 \) (or \( \tilde{\gamma}_1 \rightarrow \tilde{\gamma}_2, \tilde{\gamma}_2 \rightarrow \tilde{\gamma}_1 \)), \( x-x_0 \rightarrow x_0-x, x-x_N \rightarrow x_N-x \) and \( x_N-x_0 \rightarrow x_0-x_N \) which also provide \( \hat{P}_- \rightarrow \hat{P}_{++} \) and \( \hat{P}_{++} \rightarrow \hat{P}_- \).

6. Green’s functions for various models of diffusion

In this section we will consider two special cases of diffusion: subdiffusion for which \( v(s) = s^\alpha, \ 0 < \alpha < 1 \), and slow subdiffusion for which \( v(s) \) is a slowly varying function.

6.1. Subdiffusion

In order to calculate the inverse Laplace transform of Green’s functions we use the formula [16]

\[ \mathcal{L}^{-1}[s^\nu e^{-\lambda x}] = f_{\nu, \beta}(t; a) = \frac{1}{\nu+1} \sum_{k=0}^{\infty} \frac{1}{k!(-k\beta - \nu)} \left( \frac{a}{t^\beta} \right)^k, \] (58)
We add that the function \( f_{\alpha, \beta} \) can be also expressed in terms of the Fox function. Putting \( \beta > a, 0 < \alpha < 1 \), into equations (16) and using the formula (58) we obtain

\[
P_H(x, t; x_0) = \frac{1}{2\sqrt{D_0}} f_{\alpha/2-1, \alpha/2} \left( t; \frac{|x-x_0|}{D} \right). \tag{59}
\]

The Green’s function can be obtained in a similar way from equations (37) and (39) or can be derived by means of the generalized methods of images from equations (52)–(55) and equation (59)

\[
P_{-}(x, t; x_0) = \frac{1}{2\sqrt{D}} f_{\alpha/2-1, \alpha/2} \left( t; \frac{|x-x_0|}{\sqrt{D}} \right) + \frac{\gamma_1 - \gamma_2}{2\sqrt{D}(\gamma_1 + \gamma_2)} f_{\alpha/2-1, \alpha/2} \left( t; \frac{2x_N - x - x_0}{\sqrt{D}} \right) + \frac{2\gamma_2 \gamma_w}{D(\gamma_1 + \gamma_2)} f_{\alpha-1, \alpha/2} \left( t; \frac{2x_N - x - x_0}{\sqrt{D}} \right), \quad x < x_N, \tag{60}
\]

\[
P_{+}(x, t; x_0) = \frac{\gamma_2}{\sqrt{D}(\gamma_1 + \gamma_2)} f_{\alpha/2-1, \alpha/2} \left( t; \frac{x-x_0}{\sqrt{D}} \right) - \frac{2\gamma_2 \gamma_w}{D(\gamma_1 + \gamma_2)} f_{\alpha-1, \alpha/2} \left( t; \frac{x-x_0}{\sqrt{D}} \right), \quad x > x_N. \tag{61}
\]

The inverse Laplace transform of equation (57) provides the boundary condition at the membrane

\[
P_{-}(x_N, t; x_0) = \lambda_1 P_{-}(x_N, t; x_0) + \lambda_2 \frac{\partial^{\alpha/2} P_{+}(x_N, t; x_0)}{\partial t^{\alpha/2}}, \tag{62}
\]

where the Riemann–Liouville fractional derivative is defined as being valid for \( \vartheta > 0 \) (here \( k \) is a natural number which fulfils \( k - 1 \leq \vartheta < k \))

\[
\frac{d^\vartheta f(t)}{dt^\vartheta} = \frac{1}{\Gamma(k-\vartheta)} \frac{d^k}{dt^k} \int_0^t (t-t')^{k-\vartheta-1} f(t')dt'. \tag{63}
\]

The second term on the right-hand side of equation (62) shows that the process of the particle crossing membrane is a long-memory process. The properties of the boundary condition (62) are discussed in detail in [10].

### 6.2. Slow subdiffusion

Slow subdiffusion occurs when we assume that \( v(s) \) is a slowly varying function \([17]\). The considerations presented below will be performed for particular chosen functions

\[
v(s) = \left( \frac{1}{\ln(1/s)} \right)^{-1}, \tag{64}
\]

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\( r > 1, \text{ and} \)

\[
\dot{\omega}(s) = 1 - (\ln \xi)^{-1} v(s), \tag{65}
\]

\( \xi > 0 \) (in this case \( s \) and \( t \) are treated as dimensionless variables). The slow subdiffusion coefficient is defined here as

\[
D = \frac{\epsilon^2}{2(\ln \xi)^{-1}}. \tag{66}
\]

To calculate the inverse Laplace transform of Green’s functions over the long time limit we use the following strong Tauberian theorem (STT) \[18\]: if \( \phi(t) \geq 0, \phi(t) \) is ultimately monotonic like \( t \to \infty \), \( \mathcal{R} \) is slowly varying at infinity and \( 0 < \rho < \infty \), then each of the relations

\[
\hat{\phi}(s) \approx \frac{\mathcal{R}(1/s)}{s^\rho}, \tag{67}
\]

as \( s \to 0 \) and

\[
\phi(t) \approx \frac{\mathcal{R}(t)}{\Gamma(\rho)t^{1-\rho}} \tag{68}
\]

as \( t \to \infty \) implies the other.

Using the STT, from equation (16) we get

\[
P_{\text{H}}(x, t; x_0) = \frac{1}{2\sqrt{D(\ln t)^{-1}}} e^{-\frac{|x-x_0|}{\sqrt{D(\ln t)^{-1}}}}. \tag{69}
\]

It is easy to see that the Green’s functions for the slow subdiffusion process in a system with a thin membrane can be obtained from equations (37) and (39) using the STT as well as by means of the generalized method of images. These functions read

\[
P_{-\ldots}(x, t; x_0) = \frac{\kappa_0}{2\sqrt{D(\ln t)^{-1}}} e^{-\frac{|x-x_0|}{\sqrt{D(\ln t)^{-1}}} + \left[ \frac{\kappa_0}{2\sqrt{D(\ln t)^{-1}}} e^{\frac{(2\ln x-x_0)}{\sqrt{D(\ln t)^{-1}}}} + \frac{\kappa_G}{2D(\ln t)^{-1}} e^{\frac{(2\ln x-x_0)}{\sqrt{D(\ln t)^{-1}}}} \right]}, \tag{70}
\]

\[
P_{+\ldots}(x, t; x_0) = \frac{1 - \kappa_0}{2\sqrt{D(\ln t)^{-1}}} e^{-\frac{(x-x_0)}{\sqrt{D(\ln t)^{-1}}} - \frac{\kappa_G}{2D(\ln t)^{-1}} e^{\frac{(x-x_0)}{\sqrt{D(\ln t)^{-1}}}}}, \tag{71}
\]

coefficients \( \kappa_0 \) and \( \kappa_G \) are defined by equation (56).

Taking the inverse Laplace transform of equation (57), using the formulae \( \mathcal{L}^{-1}[\hat{f}(s)\hat{g}(s)] = \int_0^t f(t - t')g(t')dt' \text{ and } \mathcal{L}^{-1}[\hat{f}(s)] = \frac{df(t)}{dt} + f(0) \) we obtain the boundary condition at the membrane for slow subdiffusion

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\[ P_-(x_N, t; x_0) = \lambda_1 P_-(x_N, t; x_0) + \lambda_2 \frac{d}{dt} \int_0^t F(t - t') P_-(x_N, t'; x_0) dt', \]  
(72)

where

\[ F(t) = \mathcal{L}^{-1} \left[ \frac{\sqrt{v(s)}}{s} \right] \]  
(73)

is the kernel of the integral operator which reaches zero when time continues to infinity. Equations (72) and (73) show that for a slow subdiffusion case the passing of a particle through the membrane can also be treated as a long memory process. For function \( v(s) \) expressed by equation (64) we get [19]

\[ F(t) = \frac{\mu(t, (r - 1)/2)}{\Gamma(r/2)}, \]  
(74)

where \( \mu(t, (r - 1)/2) = \int_0^\infty \frac{\rho^{(r-1)/2}}{\Gamma(1 + \zeta)} d\zeta \) is the Volterra-type function.

Figure 2. System with a stopping membrane; a more detailed description can be found in the text.

The example plots of Green’s functions for subdiffusion and slow subdiffusion are presented in figures 3 and 4. In figure 4 one can observe a characteristic minimum at point \( x_d \) which is located between points \( x_0 \) and \( x_N \). This minimum is observed when function \( P_- \) takes its local maximum at the membrane and then \( \frac{\partial}{\partial x} P_-(x, t; x_0) \bigg|_{x=x_N} \geq 0 \).

This maximum is caused by the fact that the process of the particle passing through the membrane is a long-memory process which vanishes over time. The probability of finding the particle in the vicinity of the membrane is relatively large, especially for a small time; this probability decreases over time. The structure of the boundary condition equation (57) suggests that this effect is stronger when the function \( v(s) \) takes larger values for a small \( s \), i.e. when the diffusion process is slower. Point \( x_d \), which changes its position very slowly, can be calculated from equation \( \frac{\partial}{\partial x} P_-(x, t; x_0) \bigg|_{x=x_d} = 0 \). When \( x_d > x_N \), the minimum vanishes. Using function equation (37) and the formulæ presented above, after simple calculations, we obtain equation \( x_d = x_N - \frac{\sqrt{D}}{2\sqrt{\epsilon(s)}} \ln \sqrt{K_0(\omega(s))} \).

The minimum is observed when \( K_0(\omega(s)) > 1 \). The minimum vanishes for subdiffusion when \( t > \left( \frac{4\gamma_1^2}{D(1-\alpha)} \right)^{1/\alpha} \) and for slow subdiffusion when \( t > e^{(4\gamma_1^2/D)^{1/(1-\alpha)}} \).

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7. Final remarks

In this paper we have considered the two models of subdiffusion in a system with a thin membrane. The differences between the models are related to the assumption concerning the process of the reflection or stopping of a particle by the membrane when an attempt to pass the particle through the membrane fails. In the first model, the particle can be reflected by the membrane with a certain probability, the second model assumes that the particle can be stopped, with a certain probability, at the membrane. These assumptions can be associated with the following physical interpretation. If there is a slight repulsive force, generated by the membrane and acting on the particle, then the model of the reflecting membrane can be used. Otherwise, including the case in which a small attraction of the particle exerted by the membrane is assumed, the stopping membrane model can be used to describe subdiffusion in a membrane system.

The Green’s functions for both models, equations (37) and (39) for the model with a reflecting membrane and equations (47) and (48) for the model with a stopping membrane coincide in region $(-\infty, x_N) \cup (x_N, \infty)$ if $\gamma_1 = \frac{1}{D} / 2$ and $\gamma_2 = \frac{\sigma_2}{D} / 2$, respectively. The quantitative difference between models derived in this paper occurs for the values of the Green’s functions at the membrane surfaces alone. The Green’s functions are discontinuous at the membrane surface for the model with a reflecting membrane and continuous for the model with a stopping membrane.

In order to study diffusion in a membrane system we use the model with both discrete time and space variables, then we transform the Green’s functions to both the continuous variables by means of the formulae presented in this paper. Such a
model seems to be oversimplified. However, for a homogeneous system without a membrane, it provides results which can be derived by means of more ‘realistic’ models of diffusion. Thus, we assume that the model used in this paper provides Green’s functions which are useful in the modeling of various kinds of diffusion in a system with a thin membrane.

The method of images appears to be a useful tool for determining the Green’s functions in a membrane system for a various model of diffusion. It has been shown that the newly generalized method of images presented in this paper for the first time allows us to obtain the Green’s functions for a membrane system for various kinds of diffusion. We hypothesize that this generalized method of images is applicable to other diffusion processes, including superdiffusion and the case in which $P_H$ has no simple stochastic interpretation.

Equation (56) shows the relations between parameters $\kappa_0$ and $\kappa_G$ occurring in the generalized method of images and the parameters $\gamma_1$ and $\gamma_2$ which control the membrane permeability within the model studied in this paper. The parameters $\kappa_0$ and $\kappa_G$ can be calculated by means of phenomenological models of particle transport through a thin membrane. For example, supposing that the probabilities $p_1 = 1 - q_1$ and $p_2 = 1 - q_2$ are known and supposing that $\epsilon = d$, where $d$ is a membrane thickness, from equations (28) (for $\sigma = 1$) and (56) we get $\kappa_0 = \frac{p_2 - p_1}{p_1 + p_2}$ and $\kappa_G = \frac{4p_1d}{(p_1 + p_2)^2}$. As an example we mention here that $q_1$ and $q_2$ can be treated as the Staverman coefficients [20]. The concentration profiles, which depend on the parameters $\kappa_0$ and $\kappa_G$, can be calculated by means of the formula $C(x, t) = \int P(x; t; x_0)C(x_0, 0)dx_0$. Thus, the parameters $\kappa_0$ and $\kappa_G$ can also be treated as parameters ensuring the best fit of theoretical functions to the experimental results.

The Green’s functions obtained in this paper provide a new boundary condition at the membrane. The second term on the right-hand side of equation (57) which
vanishes over a sufficiently long time (see the discussion presented in [10]) represents
the ‘additional’ memory effect created by the membrane. For subdiffusion this term
was discussed in [10]. It has been shown that this term occurs for different kinds of
diffusion.

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Appendix

Using equations (4), (5) and (17)–(21) we obtain

\[
S(m, z; m_0) - \delta_{m, m_0} = \frac{z}{2} S(m - 1, z; m_0) + \frac{z}{2} S(m + 1, z; m_0),
\]

\[m \neq N - 1, N, N + 1, N + 2,\]  \hspace{1cm} (A.1)

\[
S(N - 1, z; m_0) - \delta_{N-1, m_0} = \frac{z}{2} S(N - 2, z; m_0) + \frac{z(1 + q_1)}{2} S(N, z; m_0),
\]

\[A.2\]

\[
S(N, z; m_0) - \delta_{N, m_0} = \frac{z}{2} S(N - 1, z; m_0) + \frac{z(1 - q_2)}{2} S(N + 1, z; m_0),
\]

\[A.3\]

\[
S(N + 1, z; m_0) - \delta_{N+1, m_0} = \frac{z(1 - q_1)}{2} S(N, z; m_0) + \frac{z}{2} S(N + 2, z; m_0),
\]

\[A.4\]

\[
S(N + 2, z; m_0) - \delta_{N+2, m_0} = \frac{z(1 + q_2)}{2} S(N + 1, z; m_0) + \frac{z}{2} S(N + 3, z; m_0).
\]

\[A.5\]

To solve equations (A.1)–(A.5) we use the following generating function with respect
to space variable

\[
G(u, z; m_0) = \sum_{m=-\infty}^{\infty} u^m S(m, z; m_0).
\]

(A.6)

Generating function \( S \) can be obtained by means of the following formula

\[
S(m, z; m_0) = \frac{1}{2\pi i} \oint_{K(0,1)} \frac{G(u, z; m_0)}{u^{m+1}} du,
\]

(A.7)

where integration is carried out along unit circle \( K \) centered at point \( 0 = (0,0) \) in
order to be consistent with the increasing argument of a complex number. From equations (A.1)–(A.6) we obtain

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\[ G(u, z; m_0) = \frac{u^{m_0}}{1 - \frac{z}{2}(u + \frac{1}{u})} + S(N, z; m_0) \frac{zq_1}{2} \left( u^{N-1} - u^{N+1} \right) \]

\[ - S(N+1, z; m_0) \frac{zq_2}{2} \left( u^{N} - u^{N+2} \right) \]

(A.8)

Using the integral formula

\[ \frac{1}{2\pi i} \oint_{K(0,1)} \frac{u^{m_0}}{u^{m+1}} \left[ 1 - \frac{z}{2}(u + \frac{1}{u}) \right] \mathrm{d}u = \frac{\eta^{m-m_0}(z)}{\sqrt{1-z^2}}, \]  

(A.9)

from equations (A.7) and (A.8) we obtain after simple calculations equations (22)–(27).

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