

Subdiffusion–Absorption Process in a System with a Thin Membrane

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Abstract. We study a subdiffusion–absorption process which takes place in a system with a thin membrane. We present the method of deriving the Green’s functions (probability densities) describing the process. Within this method we consider a particle’s random walk in a system with both a discrete time and space variable. Then, we move from a discrete system to a continuous system by means of the procedures which are presented in this paper.

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1. Introduction

Subdiffusion is a random walk process in which the mean square displacement of a random walker $\langle(\Delta x)^2(t)\rangle$, fulfills the relation [1, 2]

$$\langle(\Delta x)^2(t)\rangle = \frac{2D_\alpha t^\alpha}{\Gamma(1 + \alpha)}, \quad (1.1)$$

where α is a subdiffusion parameter ($0 < \alpha < 1$), D_α is a subdiffusion coefficient measured in units m^2/s^α , and Γ denotes the Gamma function. This relation is frequently considered to be a definition of subdiffusion. Subdiffusion occurs in systems in which particle movement is strongly hindered due to a complex structure of a medium such as, for example, gel [3, 4]. The process is more complex when subdiffusion is accompanied by particles absorption in a system with a thin membrane. Such systems may be present in biological and engineering sciences. If absorption is caused by static particles of B type, which are homogeneously placed in a system, then this process can be treated as the reaction of subdiffusive particle A and static particle B , according to the rule $A + B \rightarrow B$.

A subdiffusion–reaction process is often described by means of a differential equation with the Riemann–Liouville fractional time derivative [5–8]

$$\frac{\partial P(x, t; x_0)}{\partial t} = D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \left[\frac{\partial^2 P(x, t; x_0)}{\partial x^2} - \kappa^2 P(x, t; x_0) \right], \quad (1.2)$$

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where $P(x, t; x_0)$ is the probability density of finding particle A , which starts its movement at the initial point x_0 , at a point x , at time t , κ^2 being the reaction rate constant. While the well-known subdiffusion equation without reactions (Eq. (1.2) for $\kappa = 0$) can be derived by means of different random walk models such as, for example, the continuous time random walk model [1, 9] or subordinated model [10]; different models of the subdiffusion–reaction process result in different subdiffusion–reaction equations which frequently have a form different to Eq. (1.2) [11–13]. In this paper we will apply a simple model which results in Eq. (1.2) (see also [14, 15]).

In order to solve Eq. (1.2), two boundary conditions at a membrane should be assumed. The first boundary condition assumes that a subdiffusive flux $J = -D_\alpha (\partial^{1-\alpha}/\partial t^{1-\alpha}) (\partial P(x, t; x_0)/\partial x)$, is continuous. The second boundary condition is not unambiguous. We add that till now different boundary conditions, which are not equivalent, have been considered ([16–18] and the references cited therein).

In this paper we will present a model which allow us to determine the Green’s function for a subdiffusion–absorption process taking place in a membrane system. This method does not consist of solving Eq. (1.2) with any assumed boundary conditions at a membrane but is based on a simple model of a random walk. The model is based on a particle’s random walk model on a discrete lattice. The particle’s random walk is then described by a set of difference equations which can be solved by means of the generating function method. Using the generating function obtained for these equations we pass from discrete to continuous time and space variables by means of the procedure presented in this paper. We add that the random walk model has been used in describing subdiffusion in a membrane systems [16–18] and in subdiffusion–reaction system [14, 15].

In this paper we will take up the following issues. Firstly, we will consider subdiffusion in a system with a thin, partially permeable membrane. The membrane is assumed to be so thin that we do not consider any particle movement inside the membrane and a particle cannot be hidden inside it. Next, we will study a subdiffusion–absorption process in a homogeneous system under the assumption that the probability of reaction does not change over time. Then, we will consider a subdiffusion–absorption process in a system with a thin, partially permeable membrane. In all of these issues, we will start our studies from a system with both discrete time and space variables. In these discrete systems we will ensure that a particle may only change its position between neighbouring sites m at a discrete moment n with a probability equal to $1/2$. At every discrete moment n , the particle has to change its position. The only exception to this rule is when a particle tries to pass a membrane and is stopped by this membrane; the stopped particle returns to its last position. As a result of these studies we will obtain the Green’s functions for discrete variables, which will next be moved to both a continuous time and space variable by means of the rule presented in this paper. At the end, we will obtain the Green’s functions for all issues discussed in this paper. A definite advantage is that we can obtain the Green’s functions and there is no necessity of choosing boundary conditions which are required in order to solve subdiffusion–absorption equations. The other advantage of this method is its relatively simple interpretation of the processes described by these models.

The aim of these studies is twofold. Firstly, we are going to present a method and in particular, a method of moving from discrete to continuous variables. Secondly, using the method presented here we are going to determine the Green’s function for subdiffusion with absorption occurring in a system with a thin, partially permeable membrane.

The organization of this paper is as follows. In Sec. 2 we will present the general assumptions of considered models through an example of subdiffusion in a homogeneous system without any membranes and reactions. In Sec. 3 we will describe an application of the model in the case of a subdiffusion process in a system with a thin, partially permeable membrane, but without any reactions. The main results presented in this section are more widely discussed in [16]. In Sec. 4 we will show an application of the method in the description of subdiffusion with absorption in a system without any membranes. The more detailed considerations concerning the issues described in this section can be found in [14]. In Sec. 5 we will present new results, namely the Green’s function describing subdiffusion with absorption in a system with a thin, partially permeable membrane. In Sec. 6 we will present the final remarks.

2. The random walk model of subdiffusion

Supposing $P_n(m; m_0)$ denotes the probability of finding a particle which has just arrived at site m at the n -th step and m_0 is the initial position of the particle. The random walk is described by the following difference equation

$$P_{n+1}(m; m_0) = \sum_{m'} p_{m,m'} P_n(m'; m_0) , \quad (2.1)$$

where $p_{m,m'}$ is the probability that a particle jumps from site m' directly to site m . The initial condition is $P_0(m; m_0) = \delta_{m,m_0}$. The above equation is usually solved by means of the generating function which is defined as

$$S(m, z; m_0) = \sum_{n=0}^{\infty} z^n P_n(m; m_0) . \quad (2.2)$$

In order to move from a discrete to a continuous time variable we use the relationship

$$P(m, t; m_0) = \sum_{n=0}^{\infty} P_n(m, m_0) \Phi_n(t) , \quad (2.3)$$

where $\Phi_n(t)$ is the probability that a particle takes n jumps over a time interval $(0, t)$. In terms of the Laplace transform, $\mathcal{L}[f(t)] \equiv \hat{f}(s) = \int_0^{\infty} e^{-st} f(t) dt$, function $\Phi_n(t)$ reads [1, 19]

$$\hat{\Phi}_n(s) = \hat{U}(s) [\hat{\omega}(s)]^n , \quad (2.4)$$

where $\hat{\omega}(s)$ is the Laplace transform of a probability density $\omega(t)$, which a particle needs in order to take its next step and

$$\hat{U}(s) = \frac{1 - \hat{\omega}(s)}{s} , \quad (2.5)$$

is the Laplace transform of a probability $U(t) = 1 - \int_0^t \omega(t') dt'$, that a particle does not perform any steps over a time interval $(0, t)$. Combining the Laplace transform of Eq. (2.3) with Eq. (2.4) we obtain

$$\hat{P}(m, s; m_0) = \hat{U}(s) S(m, \hat{\omega}(s); m_0) . \quad (2.6)$$

Over a long time limit we consider

$$\hat{\omega}(s) = 1 - \tau_{\alpha} s^{\alpha} , \quad (2.7)$$

where τ_{α} is a parameter which, together with α , fully characterizes time distribution $\omega(t)$.

In order to move from a discrete space variable to a continuous space variable, we suppose that ϵ denotes the distance between discrete sites and

$$x = \epsilon m , \quad x_0 = \epsilon m_0 . \quad (2.8)$$

The subdiffusion coefficient is defined as

$$D_{\alpha} = \frac{\epsilon^2}{2\tau_{\alpha}} . \quad (2.9)$$

Taking into consideration the relation

$$\frac{P(m, t; m_0)}{\epsilon} \approx P(x, t; x_0) , \quad (2.10)$$

which is valid for small values of ϵ , we move from a discrete to a continuous space variable. We note that, due to Eqs. (2.7) and (2.9), we have

$$\hat{\omega}(s) = 1 - \epsilon^2 \frac{s^{\alpha}}{2D_{\alpha}} . \quad (2.11)$$

When moving from a discrete space variable to a continuous space variable, we use Eqs. (2.11) over the limit of small values of ϵ . However, practically, we assume that ϵ is extremely small, but finite. Otherwise, $\omega(t)$ is beyond any physical interpretation.

We illustrate the determination of the Green's function for the example of a homogeneous system without any reactions. In this case, the random walk is described by the equation

$$P_{n+1}(m; m_0) = \frac{1}{2}P_n(m-1; m_0) + \frac{1}{2}P_n(m+1; m_0), \quad (2.12)$$

for which the generating function reads

$$S(m, z; m_0) = \frac{[\eta(z)]^{|m-m_0|}}{\sqrt{1-z^2}}, \quad (2.13)$$

where

$$\eta(z) = \frac{1 - \sqrt{1-z^2}}{z}. \quad (2.14)$$

For small values of ϵ , we have

$$\eta[\hat{\omega}(s)] = 1 - \epsilon \frac{s^{\alpha/2}}{\sqrt{D_\alpha}}. \quad (2.15)$$

From Eqs. (2.5), (2.6) and (2.13) we obtain

$$\hat{P}(x, s; x_0) = \frac{s^{-1+\alpha/2}}{2\sqrt{D_\alpha}} [\eta(\hat{\omega}(s))]^{\frac{|x-x_0|}{\epsilon}}, \quad (2.16)$$

which, taking into account Eq. (2.15), takes the form over the limit of small values of ϵ

$$\hat{P}(x, s; x_0) = \frac{s^{-1+\alpha/2}}{2\sqrt{D_\alpha}} e^{-\frac{|x-x_0|s^{\alpha/2}}{\sqrt{D_\alpha}}}. \quad (2.17)$$

Applying the following formula [20]

$$\mathcal{L}^{-1} \left[s^\nu e^{-as^\beta} \right] \equiv f_{\nu, \beta}(t; a) = \frac{1}{t^{\nu+1}} \sum_{k=0}^{\infty} \frac{1}{k! \Gamma(-k\beta - \nu)} \left(-\frac{a}{t^\beta} \right)^k, \quad (2.18)$$

where $a, \beta > 0$ (the function $f_{\nu, \beta}$ can be treated as a special example of the Fox function), the inverse Laplace transform of Eq. (2.17) reads

$$P(x, t; x_0) = \frac{1}{2\sqrt{D_\alpha}} f_{\alpha/2-1, \alpha/2} \left(t; \frac{|x-x_0|}{\sqrt{D_\alpha}} \right). \quad (2.19)$$

Function (2.19) is a solution to the subdiffusion equation without any reactions (see, Eq. (1.2) for $\kappa^2 = 0$) for the initial condition $P(x, 0; x_0) = \delta(x - x_0)$.

3. Subdiffusion in a membrane system

A random walk in a system with a thin membrane can be described by the following difference equations

$$P_{n+1}(m; m_0) = \frac{1}{2}P_n(m-1; m_0) + \frac{1}{2}P_n(m+1; m_0), \quad m \neq N, N+1, \quad (3.1)$$

$$P_{n+1}(N; m_0) = \frac{1}{2}P_n(N-1; m_0) + \frac{1-q_2}{2}P_n(N+1; m_0) + \frac{q_1}{2}P_n(N; m_0), \quad (3.2)$$

$$P_{n+1}(N+1; m_0) = \frac{1-q_1}{2}P_n(N; m_0) + \frac{1}{2}P_n(N+2; m_0) + \frac{q_2}{2}P_n(N+1; m_0), \quad (3.3)$$

where q_1 is the probability of stopping a particle when it tries to cross a membrane from the N site to $N + 1$ site and q_2 is the probability of stopping a particle which is moving in the opposite direction. In the following, we assume that $q_1, q_2 \neq 0$.

In the following, generating functions and probabilities will be denoted by means of the subscript ij , where the indices i, j denote the signs $m - N$, $m_0 - N$, respectively. We assume that $m_0 \leq N$. From Eqs. (2.2) and (3.1)–(3.3) we obtain

$$S_{--}(m, z; m_0) = \frac{[\eta(z)]^{|m-m_0|}}{\sqrt{1-z^2}} + \Lambda_{--}(z) \frac{[\eta(z)]^{2N-m-m_0+1}}{\sqrt{1-z^2}}, \quad (3.4)$$

$$S_{+-}(m, z; m_0) = \Lambda_{+-}(z) \frac{[\eta(z)]^{m-m_0}}{\sqrt{1-z^2}}, \quad (3.5)$$

where

$$\Lambda_{--}(z) = \frac{q_1 - q_2 \eta(z)}{1 - (q_1 + q_2 - 1)\eta(z)}, \quad (3.6)$$

$$\Lambda_{+-}(z) = \frac{(1 + \eta(z))(1 - q_1)}{1 - (q_1 + q_2 - 1)\eta(z)}. \quad (3.7)$$

From Eqs. (2.5), (2.6) and (3.4) – (3.7) we obtain

$$\hat{P}_{--}(m, s; m_0) = \frac{1 - \hat{\omega}(s)}{s\sqrt{1 - [\hat{\omega}(s)]^2}} \left[[\eta(\hat{\omega}(s))]^{|m-m_0|} + \Lambda_{--}(\hat{\omega}(s)) [\eta(\hat{\omega}(s))]^{2N-m-m_0+1} \right], \quad (3.8)$$

$$\hat{P}_{+-}(m, s; m_0) = \frac{1 - \hat{\omega}(s)}{s\sqrt{1 - [\hat{\omega}(s)]^2}} \Lambda_{+-}(\hat{\omega}(s)) [\eta(\hat{\omega}(s))]^{|m-m_0|}. \quad (3.9)$$

Let us consider the mean number of a particle's jumps between neighbouring sites over time t , $\langle n(t) \rangle = \sum_{n=0}^{\infty} n \Phi_n(t)$. Taking into account Eqs. (2.4) and (2.5), the Laplace transform of $\langle n(t) \rangle$ reads for small ϵ $\mathcal{L}\{\langle n(t) \rangle\} = 2D_\alpha/\epsilon^2 s^{1+\alpha}$ (see also [21]). The inverse Laplace transform of the above equation reads

$$\langle n(t) \rangle = \frac{2D_\alpha}{\Gamma(1+\alpha)} \frac{t^\alpha}{\epsilon^2}. \quad (3.10)$$

It should be noticed from Eq. (3.10) that for a fixed time t , $\langle n(t) \rangle \rightarrow \infty$ when $\epsilon \rightarrow 0$. This means that the number of a particle's jumps between neighbouring sites can be of an arbitrarily large value if we fix an adequately small value for ϵ . The same situation takes place when we consider a particle's behaviour between the N and $N + 1$ sites. The number of attempts to cross a membrane moves up to ∞ when $\epsilon \rightarrow 0$. Then the probability of passing a thin partially permeable membrane by a particle over any time interval reaches 1. Therefore, the membrane appears to lose its selective properties. In order to avoid this nonphysical situation, we assume that q_1 and q_2 are functions of ϵ and that they fulfil $q_1(0) = q_2(0) = 1$. The calculations presented in [16–18] show that

$$q_1(\epsilon) = 1 - \frac{\epsilon}{\gamma_1}, \quad q_2(\epsilon) = 1 - \frac{\epsilon}{\gamma_2}, \quad (3.11)$$

where γ_1 and γ_2 are membrane reflection coefficients defined for a continuous system. We should add here that the model presented in this paper requires redefining some parameters which, in a discrete model, are interpreted as probabilities. The examples of such parameters are the membrane reflection coefficient (3.11) and the absorption coefficient (4.9) which will be discussed below. In order to interpret coefficients $\gamma_{1,2}$ let us put forward the following considerations. We should add here that from Eqs. (1.1) and (3.10) results $\langle (\Delta x)^2 \rangle = \epsilon^2 \langle n(t) \rangle$. Let t_1 be time for which $\langle n(t_1) \rangle = 1$ (then $\langle (\Delta x)^2 \rangle = \epsilon^2$). Coefficient $1/\gamma_{1,2}$ can be interpreted as the rescaled probability of a particle passing a membrane during one jump, and accordingly reads $1/\gamma_{1,2} = \beta(1 - q_{1,2})$, where scaling parameter β is given by the formula

$\beta = \sqrt{\Gamma(1 + \alpha)/2D_\alpha t_1^\alpha}$. If the values of probabilities $q_{1,2}$ are known (for example, from phenomenological models), we can find the approximate values of parameters $\gamma_{1,2}$ assuming $\epsilon = d$, where d is the thin membrane thickness. Then from (3.11) we obtain $(1/\gamma_{1,2}) \approx (1 - q_{1,2})/d$.

We obtain from Eqs. (2.15), (3.6), (3.7) and (3.11)

$$\Lambda_{--}(\hat{\omega}(s)) = \frac{\frac{1}{\gamma_2} - \frac{1}{\gamma_1} + \frac{s^{\alpha/2}}{\sqrt{D_\alpha}}}{\frac{1}{\gamma_1} + \frac{1}{\gamma_2} + \frac{s^{\alpha/2}}{\sqrt{D_\alpha}}}, \quad (3.12)$$

$$\Lambda_{+-}(\hat{\omega}(s)) = \frac{\frac{2}{\gamma_1}}{\frac{1}{\gamma_1} + \frac{1}{\gamma_2} + \frac{s^{\alpha/2}}{\sqrt{D_\alpha}}}. \quad (3.13)$$

From Eqs. (2.15), (3.8), (3.9), (3.12) and (3.13), we obtain over the limit of small values of ϵ

$$\hat{P}_{--}(x, s; x_0) = \frac{s^{-1+\alpha/2}}{2\sqrt{D_\alpha}} \left[e^{-\frac{|x-x_0|s^{\alpha/2}}{\sqrt{D_\alpha}}} + \Lambda_{--}(\hat{\omega}(s))e^{-\frac{(2x_N-x-x_0)s^{\alpha/2}}{\sqrt{D_\alpha}}} \right], \quad (3.14)$$

$$\hat{P}_{+-}(x, s; x_0) = \frac{s^{-1+\alpha/2}}{2\sqrt{D_\alpha}} \Lambda_{+-}(\hat{\omega}(s))e^{-\frac{(x-x_0)s^{\alpha/2}}{\sqrt{D_\alpha}}}, \quad (3.15)$$

where $x_N = \epsilon N$. Let us note that a calculation of the inverse Laplace transforms of Eqs. (3.14) and (3.15) can prove troublesome on account of the complex form of $\Lambda_{\mp-}(\hat{\omega}(s))$ (see Eqs. (3.12) and (3.13)). Therefore, we conduct a calculations over the limit of small values of s . We obtain over this limit

$$\Lambda_{--}(\hat{\omega}(s)) = \mu_1 + \mu_2 \frac{s^{\alpha/2}}{\sqrt{D_\alpha}}, \quad (3.16)$$

$$\Lambda_{+-}(\hat{\omega}(s)) = 1 - \mu_1 - \mu_2 \frac{s^{\alpha/2}}{\sqrt{D_\alpha}}, \quad (3.17)$$

where

$$\mu_1 = \frac{\gamma_1 - \gamma_2}{\gamma_1 + \gamma_2}, \quad \mu_2 = \frac{\frac{2}{\gamma_1}}{\left(\frac{1}{\gamma_1} + \frac{1}{\gamma_2}\right)^2}. \quad (3.18)$$

The inverse formulae to Eq. (3.18) read $\gamma_1 = 2\mu_2/(1 - \mu_1)^2$, $\gamma_2 = 2\mu_2/(1 - \mu_1^2)$. For inverse Laplace transform of Eqs. (3.14) and (3.15), we obtain, taking into account Eqs. (2.18), (3.16)–(3.17)

$$P_{--}(x, t; x_0) = \frac{1}{2\sqrt{D_\alpha}} \left[f_{\alpha/2-1, \alpha/2} \left(t; \frac{|x-x_0|}{\sqrt{D_\alpha}} \right) + \mu_1 f_{\alpha/2-1, \alpha/2} \left(t; \frac{2x_N-x-x_0}{\sqrt{D_\alpha}} \right) \right] + \frac{\mu_2}{2D_\alpha} f_{\alpha-1, \alpha/2} \left(t; \frac{2x_N-x-x_0}{\sqrt{D_\alpha}} \right), \quad (3.19)$$

$$P_{+-}(x, t; x_0) = \frac{1 - \mu_1}{2\sqrt{D_\alpha}} f_{\alpha/2-1, \alpha/2} \left(t; \frac{x-x_0}{\sqrt{D_\alpha}} \right) - \frac{\mu_2}{2D_\alpha} f_{\alpha-1, \alpha/2} \left(t; \frac{x-x_0}{\sqrt{D_\alpha}} \right). \quad (3.20)$$

The properties of functions (3.19) and (3.20) are discussed in [16].

4. The subdiffusion–absorption process

In this part, we consider a subdiffusion process with absorption. A static particle B may absorb a mobile particle A with some probability, if particles A and B meet. Particles meeting means that particle A is found within the influence area of a particle B . This process can be treated as a reaction of the $A + B \rightarrow B$ type. We assume that particles B are distributed homogeneously throughout a system.

A subdiffusion process described by means of discrete equations, such as Eq. (2.12), can be interpreted as the discretization of a process occurring in a continuous system. Within this interpretation a system is divided into equal cells of a size $(x - \epsilon/2, x + \epsilon/2)$, where $x = \epsilon m$, m is the number of the cell and ϵ is a parameter taking small values. In discrete moments, particles can only jump to neighbouring cells. In such cases $P_n(m; m_0)$ can be interpreted as the probability of finding a particle in a cell of a number m . We assume that particle A can be found at every point of a cell with an equal probability. Now, we will include in this picture processes the possibility of a reaction occurring. Particle A , which has just jumped into a cell can meet particle B , with probability p . Since we do not restrict the number of B particles in one cell to one, but we assume that B particles are distributed homogeneously throughout, probability p depends on the concentration of B particles. Let R be the probability of a reaction occurring while particle A is present in the cell. If a reaction takes place immediately after particle A meets particle B , then $R = p$. If the waiting time for a reaction occurring after particles A and B meet is given by a probability distribution $\phi(t)$, then probability R has a more complicated form. When $\phi(t) = \lambda e^{-\lambda t}$, λ is a positive parameter, then $R = p(1 - \hat{\omega}(\lambda))$ (see discussion in Sec. 5A in [14]). In such a case the generalization of Eq. (2.12) to the random walk process with reactions is

$$P_{n+1}(m; m_0) = \frac{1}{2}P_n(m+1; m_0) + \frac{1}{2}P_n(m-1; m_0) - RP_n(m; m_0). \quad (4.1)$$

The above presented interpretation assumes the homogenization of the probabilities of finding a particle in particular cells and it is in accordance with assumptions on mean field approximation. However, if B particles are mobile, then fluctuations of probability p will occur. This could result in the breaking down of the mean field approximation over a long time limit.

The generating function of Eq. (4.1) reads [14]

$$S(m, z; m_0) = \frac{[\eta_R(z)]^{|m-m_0|}}{\sqrt{(1+zR)^2 - z^2}}, \quad (4.2)$$

where

$$\eta_R(z) = \frac{1+zR - \sqrt{(1+zR)^2 - z^2}}{z}. \quad (4.3)$$

Since the vanishing of a particle caused by the reaction is included in Eq. (4.1), we assume that the particle's jumps are ruled by $\omega(t)$ (as in the random walk considered in Secs. 2 and 3). From Eqs. (2.5), (2.6), (2.11), (4.2) and (4.3), we obtain

$$\hat{P}(m, s; m_0) = \frac{\hat{U}(s)}{\sqrt{[1+R\hat{\omega}(s)]^2 - \hat{\omega}^2(s)}} [\eta_R(\hat{\omega}(s))]^{|m-m_0|}. \quad (4.4)$$

In the following we assume that $R \neq 0$. From Eqs. (2.11) and (4.3), we obtain over a limit of small values of ϵ

$$\eta_R(\hat{\omega}(s)) = a_R - b_R \frac{\epsilon^2}{2D_\alpha} s^\alpha, \quad (4.5)$$

where

$$a_R = 1 + R - \sqrt{2R + R^2}, \quad b_R = \frac{(1+R)}{\sqrt{2R + R^2}} - 1. \quad (4.6)$$

Equations (2.5), (2.8), (2.11) and (4.4)–(4.6) provide

$$\hat{P}(x, s; x_0) = \frac{\epsilon s^{\alpha-1}}{2D_\alpha \sqrt{2R + R^2}} \left(1 + R - \sqrt{2R + R^2}\right)^{\frac{|x-x_0|}{\epsilon}} \left(1 - \frac{\epsilon^2 s^\alpha}{2D_\alpha \sqrt{2R + R^2}}\right)^{\frac{|x-x_0|}{\epsilon}}. \quad (4.7)$$

The only way in order to ensure that function (4.7) has non-zero (and finite) values over a limit of small values of ϵ , is to assume that

$$\frac{\epsilon}{\sqrt{2R + R^2}} \equiv \frac{1}{\kappa} \equiv \text{const.}, \quad (4.8)$$

where κ is a reaction coefficient defined for a continuous system. From Eq. (4.8) we obtain

$$R = \sqrt{1 + \epsilon^2 \kappa^2} - 1. \quad (4.9)$$

From Eq. (4.9) we obtain, over a limit of small values of ϵ ($\epsilon \ll 1/\kappa$)

$$R = \frac{\epsilon^2 \kappa^2}{2}, \quad (4.10)$$

and from Eqs. (4.7) – (4.10):

$$\hat{P}(x, s; x_0) = \frac{s^{\alpha-1}}{2D_\alpha \kappa} e^{-\kappa|x-x_0|} e^{-\frac{|x-x_0|s^\alpha}{2D_\alpha \kappa}}. \quad (4.11)$$

From Eqs. (2.18) and (4.11) we get

$$P(x, t; x_0) = \frac{1}{2D_\alpha \kappa} e^{-\kappa|x-x_0|} f_{\alpha-1, \alpha} \left(t; \frac{|x-x_0|}{2D_\alpha \kappa} \right). \quad (4.12)$$

The Green's function for the problem of subdiffusion with reactions can be found in another way. Namely, we suppose that the probability of the reaction occurring is incorporated into the probability density $\omega_R(t)$, which is now defined as the probability density that the particle takes its jump after time t and continues to exist at this moment. The random walk of the particle is then described as in a system without reactions by Eq. (2.12) and the Laplace transform of the Green's function reads, for a continuous time

$$\hat{P}(m, s; m_0) = \frac{\hat{U}_R(s)}{\sqrt{1 - \hat{\omega}_R^2(s)}} [\eta(\hat{\omega}_R(s))]^{|m-m_0|}. \quad (4.13)$$

The Green's function does not depend on the model that was used in order to derive it, therefore Eqs. (4.4) and (4.13) should provide the same function. We obtain this when the following equations are fulfilled

$$\eta_R(\hat{\omega}(s)) = \eta(\hat{\omega}_R(s)), \quad (4.14)$$

and

$$\frac{\hat{U}_R(s)}{\sqrt{1 - \hat{\omega}_R^2(s)}} = \frac{\hat{U}(s)}{\sqrt{[1 + R\hat{\omega}(s)]^2 - \hat{\omega}^2(s)}}, \quad (4.15)$$

where $\hat{U}_R(s)$ is the Laplace transform of $U_R(t)$ which corresponds to the probability that a particle does not jump over a time interval $(0, t)$ and continues to exist up to time t . Taking into account Eqs. (2.14) and (4.3), the solution to Eq. (4.14) is

$$\hat{\omega}_R(s) = \frac{\hat{\omega}(s)}{1 + R\hat{\omega}(s)}, \quad (4.16)$$

and to Eq. (4.15) reads

$$\hat{U}_R(s) = \hat{U}(s) \frac{1}{1 + R\hat{\omega}(s)}. \quad (4.17)$$

Let us note that from Eqs. (2.5), (2.9), (2.11), (4.16) and (4.17) for small values of ϵ , we get

$$\hat{\omega}_R(s) = 1 - \epsilon^2 \left(\frac{s^\alpha}{2D_\alpha} + \frac{\kappa^2}{2} \right), \quad (4.18)$$

$$\hat{U}_R(s) = \frac{\epsilon^2 s^{\alpha-1}}{2D_\alpha}, \quad (4.19)$$

and taking into account Eqs. (2.14), (4.14), (4.18) and (4.19), we obtain

$$\eta(\hat{\omega}_R(s)) \equiv \eta_R(\hat{\omega}(s)) = 1 - \epsilon \left(\kappa + \frac{s^\alpha}{2D_\alpha \kappa} \right). \quad (4.20)$$

It is straightforward to check that Eqs. (4.13), (4.18), (4.19) and (4.20) provide Eq. (4.11) over a limit of small values of ϵ . In order to obtain the Green's function in a system with reactions, we replace $\hat{\omega}(s)$ with $\hat{\omega}_R(s)$ and $\hat{U}(s)$ with $\hat{U}_R(s)$ according to Eqs. (4.16) and (4.17) in the Laplace transform of the Green's function which has been carried out for a discrete space variable and continuous time in a system without any reactions.

The above considerations have been focused on a homogeneous system but we will show below that the obtained rules are also valid in a system with a thin membrane.

5. The subdiffusion–absorption process in a system with a thin membrane

We assume that subdiffusion occurs in a system with a thin membrane at which a subdiffusive particle A can react with particles B according to the formula $A + B \rightarrow B$. This process is described by the equations

$$P_{n+1}(m; m_0) = \frac{1}{2}P_n(m-1; m_0) + \frac{1}{2}P_n(m+1; m_0) - RP_n(m; m_0), \quad m \neq N, N+1, \quad (5.1)$$

$$P_{n+1}(N; m_0) = \frac{1}{2}P_n(N-1; m_0) + \frac{1-q_2}{2}P_n(N+1; m_0) + \frac{q_1}{2}P_n(N; m_0) - RP_n(N; m_0), \quad (5.2)$$

$$P_{n+1}(N+1; m_0) = \frac{1-q_1}{2}P_n(N; m_0) + \frac{1}{2}P_n(N+2; m_0) + \frac{q_2}{2}P_n(N+1; m_0) - RP_n(N+1; m_0). \quad (5.3)$$

The generating functions for the above equations are

$$S_{--}(m, z; m_0) = \frac{[\eta_R(z)]^{|m-m_0|}}{\sqrt{(1+zR)^2 - z^2}} + \Lambda_{R--}(z) \frac{[\eta_R(z)]^{2N-m-m_0+1}}{\sqrt{(1+zR)^2 - z^2}}, \quad (5.4)$$

$$S_{+-}(m, z; m_0) = \Lambda_{R+-}(z) \frac{[\eta_R(z)]^{m-m_0}}{\sqrt{(1+zR)^2 - z^2}}, \quad (5.5)$$

where

$$\Lambda_{R--}(z) = \frac{q_1 - q_2 \eta_R(z)}{1 - (q_1 + q_2 - 1)\eta_R(z)}, \quad (5.6)$$

$$\Lambda_{R+-}(z) = \frac{(1 + \eta_R(z))(1 - q_1)}{1 - (q_1 + q_2 - 1)\eta_R(z)}. \quad (5.7)$$

Equations (2.5), (2.6) and (5.4) – (5.7) provide the following form of the Laplace transform of the Green's functions

$$\hat{P}_{--}(m, s; m_0) = \frac{\hat{U}(s)}{\sqrt{[(1 + R\hat{\omega}(s))^2 - \hat{\omega}^2(s)]}} \left\{ [\eta_R(\hat{\omega}(s))]^{|m-m_0|} + \Lambda_{R--}(\hat{\omega}(s)) [\eta_R(\hat{\omega}(s))]^{2N-m-m_0+1} \right\}, \quad (5.8)$$

$$\hat{P}_{+-}(m, s; m_0) = \frac{\hat{U}(s)}{\sqrt{[(1 + R\hat{\omega}(s))^2 - \hat{\omega}^2(s)]}} \Lambda_{R+-}(\hat{\omega}(s)) [\eta_R(\hat{\omega}(s))]^{m-m_0}. \quad (5.9)$$

We note that, due to Eq. (4.14), we can observe

$$\Lambda_{\mp-}(\hat{\omega}_R(s)) = \Lambda_{R\mp-}(\hat{\omega}(s)), \quad (5.10)$$

Taking into account Eqs. (2.11), (5.6) and (5.7), $\Lambda_{\mp-}(\hat{\omega}_R(s))$ all read, over the limit of small values of ϵ

$$\Lambda_{--}(\hat{\omega}_R(s)) = \frac{\kappa - \frac{1}{\gamma_1} + \frac{1}{\gamma_2} + \frac{s^\alpha}{2D_\alpha}}{\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2} + \frac{s^\alpha}{2D_\alpha}}, \quad (5.11)$$

$$\Lambda_{+-}(\hat{\omega}_R(s)) = \frac{\frac{2}{\gamma_1}}{\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2} + \frac{s^\alpha}{2D_\alpha}}. \quad (5.12)$$

We show that the two methods of determining the Green's functions for a subdiffusion–absorption process in a homogeneous system which was presented in Sec. 4, can also be applied for a subdiffusion–reaction process in a membrane system. Using Eqs. (4.14) and (4.15) we obtain

$$\hat{P}_{--}(m, s; m_0) = \frac{1 - \hat{\omega}_R(s)}{s\sqrt{1 - [\hat{\omega}_R(s)]^2}} \left\{ [\eta(\hat{\omega}_R(s))]^{|m-m_0|} + \Lambda_{--}(\hat{\omega}_R(s)) [\eta(\hat{\omega}_R(s))]^{2N-m-m_0+1} \right\}, \quad (5.13)$$

$$\hat{P}_{+-}(m, s; m_0) = \frac{1 - \hat{\omega}_R(s)}{s\sqrt{1 - [\hat{\omega}_R(s)]^2}} \Lambda_{+-}(\hat{\omega}_R(s)) [\eta(\hat{\omega}_R(s))]^{|m-m_0|}. \quad (5.14)$$

It can be observed from Eqs. (5.11)–(5.14) that a calculation of the Laplace transforms for these equations is somewhat troublesome. Thus, we conduct further calculations over a limit of small values of s . Equations (5.11) and (5.12) take the form over a limit of small values of s

$$\Lambda_{--}(\hat{\omega}_R(s)) = \frac{\kappa - \frac{1}{\gamma_1} + \frac{1}{\gamma_2}}{\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2}} + \frac{s^\alpha}{2D_\alpha} \frac{\frac{1}{\gamma_2}}{\left(\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2}\right)^2}, \quad (5.15)$$

$$\Lambda_{+-}(\hat{\omega}_R(s)) = \frac{\frac{2}{\gamma_1}}{\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2}} \left[1 - \frac{s^\alpha}{2D_\alpha} \frac{\frac{1}{\gamma_2}}{\left(\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2}\right)^2} \right]. \quad (5.16)$$

We should note here, that Eqs. (5.13) and (5.14) can be obtained from Eqs. (3.8) and (3.9) which have been derived for a system with a thin membrane and without any reaction, by replacing $\hat{\omega}(s)$ with $\hat{\omega}_R(s)$. Thus, the method presented in Sec. 4 can be used in the case of the membrane system.

In order to move from a discrete to continuous space variable we obtain from Eqs. (5.13)–(5.16)

$$\hat{P}_{--}(x, s; x_0) = \frac{s^{-1+\alpha}}{2D_\alpha\kappa} \left[e^{-\kappa|x-x_0|} e^{-\frac{|x-x_0|s^\alpha}{2D_\alpha\kappa}} + \left(\vartheta_1 + \vartheta_2 \frac{s^\alpha}{D_\alpha} \right) e^{-\kappa(2x_N-x-x_0)} e^{-\frac{(2x_N-x-x_0)s^\alpha}{2D_\alpha\kappa}} \right], \quad (5.17)$$

$$\hat{P}_{+-}(x, s; x_0) = \frac{s^{-1+\alpha}}{2D_\alpha\kappa} e^{-\kappa(x-x_0)} e^{-\frac{(x-x_0)s^\alpha}{2D_\alpha\kappa}} \left(1 - \vartheta_1 - \vartheta_2 \frac{s^\alpha}{D_\alpha} \right). \quad (5.18)$$

where

$$\vartheta_1 = \frac{\kappa + \frac{1}{\gamma_1} - \frac{1}{\gamma_2}}{\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2}}, \quad \vartheta_2 = \frac{1}{\gamma_2 \left(\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2}\right)^2}. \quad (5.19)$$

The inverse Laplace transform of Eqs. (5.17) and (5.18), together with Eq. (2.18), provide

$$P_{--}(x, t; x_0) = \frac{1}{2D_\alpha\kappa} \left[e^{-\kappa|x-x_0|} f_{\alpha-1,\alpha} \left(t; \frac{|x-x_0|}{2D_\alpha\kappa} \right) + \vartheta_1 f_{\alpha-1,\alpha} e^{-\kappa(2x_N-x-x_0)} \left(t; \frac{2x_N-x-x_0}{2D_\alpha\kappa} \right) \right] \\ + \frac{\vartheta_2}{2D_\alpha^2\kappa} e^{-\kappa(2x_N-x-x_0)} f_{2\alpha-1,\alpha} \left(t; \frac{2x_N-x-x_0}{2D_\alpha\kappa} \right), \quad (5.20)$$

$$P_{+-}(x, t; x_0) = \frac{1 - \vartheta_1}{2D_\alpha \kappa} e^{-\kappa(x-x_0)} f_{\alpha-1, \alpha} \left(t; \frac{x-x_0}{2D_\alpha \kappa} \right) - \frac{\vartheta_2}{2D_\alpha^2 \kappa} e^{-\kappa(x-x_0)} f_{2\alpha-1, \alpha} \left(t; \frac{x-x_0}{2D_\alpha \kappa} \right). \quad (5.21)$$

We illustrate the Green's functions in Figs. 1 and 2. The values of parameters used in order to draw these figures are $\alpha = 0.9$, $D_\alpha = 0.001$, $t = 10000$, $x_0 = -0.5$, $x_N = 0.0$ and $\gamma_1 = 0.5$ (all quantities are given in arbitrarily chosen units). In Fig. 1 we present the dependence of the Green's functions on parameter γ_2 whereas in Fig. 2 — on parameter κ .

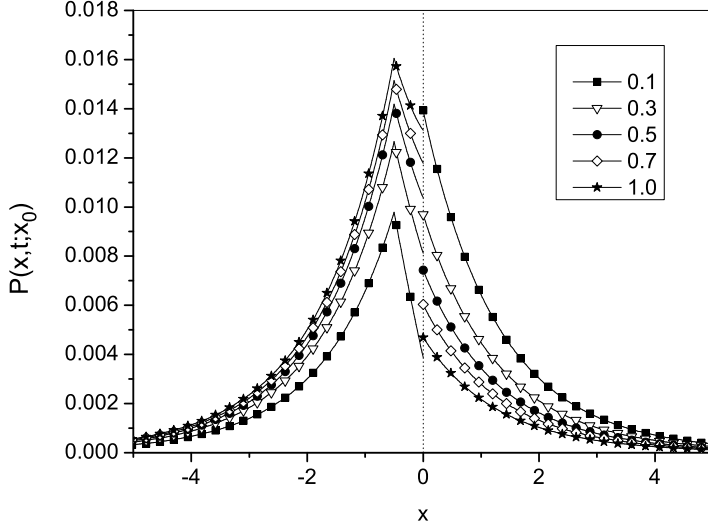


FIGURE 1. The Green's function calculated for different values of γ_2 given in the legend. Here $\kappa = 1.0$.

The addition of a thin membrane into the system causes particles to partially stop and has an influence on the course of absorption and decreases the probability of absorption occurring in the part of the system in which the particle does not start its movement. Below, we will determine the probability of finding a particle in the region $x < x_N$ at time t which is defined as $W_{--}(t; x_0) = \int_{-\infty}^{x_N} P_{--}(x, t; x_0) dx$, and similarly, the probability of finding a particle in the region $x > x_N$, which reads $W_{+-}(t; x_0) = \int_{x_N}^{\infty} P_{+-}(x, t; x_0) dx$. In terms of the Laplace transform, these probabilities are as follows

$$\hat{W}_{--}(s; x_0) = \frac{s^{-1+\alpha}}{2D_\alpha \kappa^2 + s^\alpha} \left[2 + \left(\vartheta_1 - 1 + \frac{\vartheta_2 s^\alpha}{2D_\alpha} \right) e^{-(x_N - x_0) \left(\kappa + \frac{s^\alpha}{2D_\alpha \kappa} \right)} \right], \quad (5.22)$$

$$\hat{W}_{+-}(s; x_0) = \frac{s^{-1+\alpha}}{2D_\alpha \kappa^2 + s^\alpha} \left(-\vartheta_1 + 1 - \frac{\vartheta_2 s^\alpha}{2D_\alpha} \right) e^{-(x_N - x_0) \left(\kappa + \frac{s^\alpha}{2D_\alpha \kappa} \right)}. \quad (5.23)$$

Over the limit of small values of s we obtain

$$\hat{W}_{--}(s; x_0) = \frac{s^{-1+\alpha}}{D_\alpha \kappa^2} \left[1 - \frac{1 - \vartheta_1}{2} e^{-(x_N - x_0) \left(\kappa + \frac{s^\alpha}{2D_\alpha \kappa} \right)} \right], \quad (5.24)$$

$$\hat{W}_{+-}(s; x_0) = \frac{(1 - \vartheta_1) s^{-1+\alpha}}{2D_\alpha \kappa^2} e^{-(x_N - x_0) \left(\kappa + \frac{s^\alpha}{2D_\alpha \kappa} \right)}. \quad (5.25)$$

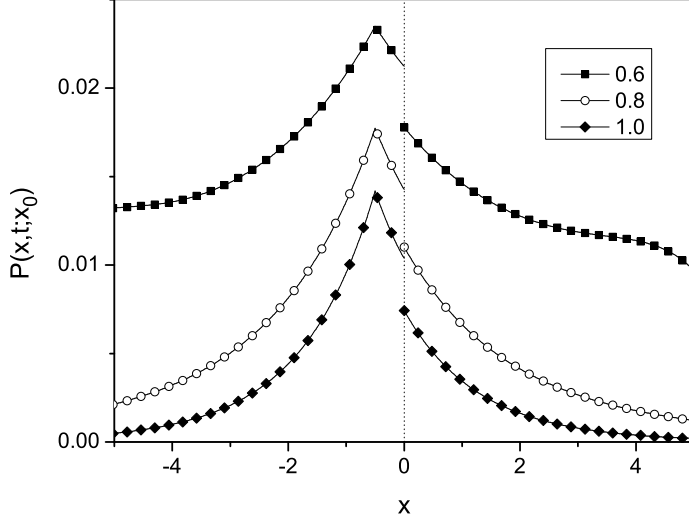


FIGURE 2. The Green's function calculated for different values of κ given in the legend. Here $\gamma_2 = 0.5$.

The inverse Laplace transforms of Eqs. (5.24) and (5.25), are

$$W_{--}(t; x_0) = \frac{1}{D_\alpha \kappa^2} \left[\frac{1}{t^\alpha \Gamma(1-\alpha)} - \frac{1-\vartheta_1}{2} e^{-\kappa(x_N-x_0)} f_{\alpha-1,\alpha} \left(t; \frac{x_N-x_0}{2D_\alpha \kappa} \right) \right], \quad (5.26)$$

$$W_{+-}(t; x_0) = \frac{1-\vartheta_1}{2D_\alpha \kappa^2} e^{-\kappa(x_N-x_0)} f_{\alpha-1,\alpha} \left(t; \frac{x_N-x_0}{2D_\alpha \kappa} \right). \quad (5.27)$$

We note that the total amount of substance which vanishes from a system reads $W(t; x_0) \equiv W_{--}(t; x_0) + W_{+-}(t; x_0) = 1/(D_\alpha \kappa^2 \Gamma(1-\alpha) t^\alpha)$. Since function (2.18) can be approximated as $f_{\nu,\beta}(t; a) \approx 1/(t^{\nu+1} \Gamma(-\nu))$ for $t \gg [a/\Gamma(1-\beta)]^{1/\beta}$ (see Sec. 3 in [18]), from Eqs. (5.26) and (5.27) for $t \gg [(x_N-x_0)/2D_\alpha \kappa \Gamma(1-\alpha)]^{1/\alpha}$ we obtain

$$\frac{W_{--}(t; x_0)}{W_{+-}(t; x_0)} = \gamma_2 \left(\kappa + \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right) e^{\kappa(x_N-x_0)} - 1. \quad (5.28)$$

Therefore, the ratio of the probabilities of finding a particle in region $x < x_N$ and $x > x_N$ is fixed over a long time limit. This ratio is independent of the subdiffusion parameters α and D_α but depends on reflection probabilities γ_1 and γ_2 , reaction coefficient κ , and the distance between the initial position and the membrane position $x_N - x_0$, in accordance with Eq. (5.28).

6. Final remarks

In this paper we present the method of finding the Green's function for a subdiffusive system with a thin, partially permeable membrane, in which a subdiffusive particle A may be absorbed with a certain probability as a result of contact with static particles B . The absorption process can be treated as the reaction $A + B \rightarrow B$. We assume that particles B are homogeneously distributed in the system. Thus, the absorption probability does not depend on a time and space variables.

The essence of this method is its focusing on the subdiffusion–absorption process in a system with both discrete time and space variables in which the process is described through difference equations. These equations are soluble by means of the generating function method. Then we move from discrete variables to continuous variables using the procedures presented in this paper. More particularly, we move from discrete variables to continuous variables in two steps. In the first step, we move from a discrete time variable to a continuous variable. We can do this in two ways which are described in Sec. 5. In the second step, we move from a discrete space variable to a continuous space variable. This move requires an introduction of the parameters which are defined for a continuous system in connection with the parameters which are defined for the discrete system. Within a discrete model, the parameters describing both the selective properties of a thin membrane and the absorption properties of a medium are given as probabilities of the processes occurring. In this paper we also show the relationships between parameters which are defined for a discrete system and a continuous system. These coefficients, for a discrete system, can be determined with phenomenological models. The example is the Staverman coefficient (defined as the ratio of the area of membrane pores to the area of the whole membrane surface [22]), which is interpreted as the probability of a particle crossing a membrane. The specified relationships between discrete probabilities and coefficients defined for a continuous system, are given by Eqs. (3.11) and (4.10). In order to move from a discrete space variable to a continuous variable, a particle’s jump distance has to be defined (in the model presented here, the particle’s jump distance is not a random variable). The thickness of the thin membrane seems to be a natural choice for ϵ .

If absorption accompanies the subdiffusion process, this means that the technical side of calculations becomes more difficult in comparison to a process without any reaction. The studies presented in this paper show that the fundamental solutions (the Green’s functions) obtained for a membrane system without absorption, can be used in the determination of the fundamental solutions of a membrane system with absorption. The models presented here can be useful in describing the various processes occurring in engineering and biology. The example is a filtration process depending on absorption in a filtration medium which is assisted by thin membranes present in the medium. Placing $\alpha = 1$ into the obtained formula, we obtain the description of a normal diffusion process in a membrane system in which absorption takes place.

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