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Subdiffusion in a system with thin membranes

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We study both theoretically and experimentally a process of subdiffusion in a system with two thin membranes. The theoretical model uses Green's functions obtained for the membrane system by means of the generalized method of images. These Green's functions are combinations of the fundamental solutions to a fractional subdiffusion equation describing subdiffusion in a homogenous, unbounded system. Using Green's functions we find analytical formulas describing the time evolution of concentration profiles and the time evolution of the amount of substance that remains in the region between the membranes. The concentration profiles fulfill a new boundary condition at the membrane, in which the membrane permeability is assumed to change over time according to the special formula presented in the paper. These concentration profiles fulfill a standard subdiffusion equation with fractional Riemann-Liouville time derivative only approximately, but they coincide very well with the experimental data. Fitting the theoretical functions in with the experimental results, we also estimate the subdiffusion coefficient of polyethylene glycol 2000 in agarose hydrogel.

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I. INTRODUCTION

Subdiffusion qualitatively differs from normal diffusion. It occurs in a medium where the mobility of particles is strongly hindered due to the internal structure of the medium as, for example, in porous media or gels [1–4]. Subdiffusion is characterized by the relation where the mean square displacement of a Brownian particle is a power function of time [1],

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

where D_α is a subdiffusion coefficient measured in the units of $\mathrm{m}^2/\mathrm{s}^\alpha$ and α is a subdiffusion parameter which obeys $0 < \alpha < 1$ (for normal diffusion there being $\alpha = 1$). We should add here that relation (1) is treated as the definition of the parameters α and D_α, but it is not always used as the definition of anomalous or normal diffusion (see the discussion presented in [5]).

Subdiffusion in membrane systems occurs in such fields as biophysics or technical sciences [6–9]. Membranes define the geometry of the system, which is convenient for experimental study of anomalous or normal diffusion, including experimental measurement of the parameters α and D_α. We mention here the measurement of the time evolution of near-membrane layers in a system with one thin membrane [3] and the time evolution of an amount of substance released from a thick membrane [10]. An application to a two-membrane system extends the possibilities of such measurements. The crucial role in modeling subdiffusion in a membrane system involves the boundary conditions at the membrane (usually treated as a partially absorbing or partially permeable wall); these boundary conditions are not determined in a unique way. Various boundary conditions at a partially permeable wall for subdiffusive systems have recently been considered [11–16]. In the papers in [17] the generalized method of images was used in order to construct Green's functions for membrane systems for normal diffusion. These Green's functions were then used to determine the boundary conditions at a thin membrane (the theory of this method will be presented in Sec. III). We considered this under the assumption that membrane permeability does not change over time. In our paper we adopt this method to subdiffusive systems, taking into account that membrane permeability can change over time. We mention here that the procedure in which the stochastic arguments at first provide Green's functions, from which boundary conditions were derived, was used by Chandrasekhar in order to discern boundary conditions at a reflecting wall and an absorbing one [18].

In this paper we will present a model of subdiffusion in a system with two thin membranes in which the membranes' permeability changes over time according to a special formula. We will find analytical formulas describing the time evolution of the concentration profiles obtained within a *single-membrane approximation of a multimembrane system* and the time evolution of an amount of the substance remaining in the region bounded by the membranes. The theoretical functions fulfill new boundary conditions at the thin membranes which—as far as we know—have not yet been considered. The theoretical concentration profiles will be compared with the experimental ones. Experimental investigations concern a system with two artificial thin membranes in which at the initial moment its middle part is filled with a homogeneous solution and the external parts contain a pure solvent; for technical reasons the concentration profiles are measured in the middle part only. We will show that theoretical results agree to a good extent with experimental data. We will also estimate the subdiffusion coefficient of polyethylene glycol 2000 in agarose hydrogel by matching the theoretical functions with the experimental results.

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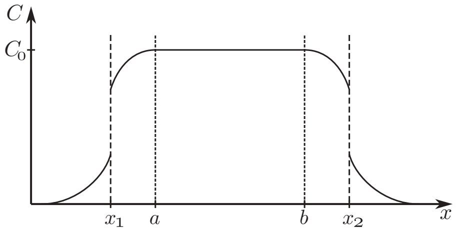

FIG. 1. Schematic view of the system under consideration. The concentration in the interval (a,b) is equal to the initial concentration C_0.

II. THE SYSTEM

The system under consideration consists of three homogeneous parts which are separated from each other by two thin partially permeable membranes located at x_1 and x_2 (see Figs. 1 and 2); the membranes are treated here as infinitely thin partially permeable walls. In each part there are the same subdiffusion parameter α and subdiffusion coefficient D_α. In the following these parts will be denoted as 1 for $x < x_1$, M for $x_1 < x < x_2$, and 2 for $x > x_2$. The system is assumed to be homogeneous in a plane perpendicular to the x axis, which is perpendicular to the membrane surfaces. Thus, the system is effectively one-dimensional. We study the system in which the concentration $C(x,t)$ of a transported substance at the initial moment is

$$C(x,0) = \begin{cases} 0, & x < x_1, \\ C_0, & x_1 < x < x_2, \\ 0, & x > x_2. \end{cases} \tag{2}$$

The method of experimental measurements of concentration profiles will be presented in Sec. V. Guided by the experimental results we adopt the following assumption which facilitates the problem: when $t \ll t_g$, where t_g is the average time when a particle passes the distance between the thin membranes, the solutions to an equation describing subdiffusion in near-membrane regions can be obtained in the same way as for the system with one membrane. The motivation for this assumption is that, for a sufficiently small time, a particle localized in the vicinity of the membrane "does not feel" the presence of the other membrane. According to the above assumption, the concentration in the middle part of the system changes only in relatively small near-membrane intervals, (x_1,a) and (b,x_2) shown in Fig. 1. Points a and b play only auxiliary and illustrative roles in our consideration and we do not consider their exact localization, which actually changes over time. The concentration for $x \in (a,b)$ remains unchanged: $C_M(x,t) = C_0$. The parameter t_g can be estimated from relation (1) in which we identify $d^2 = (x_2 - x_1)^2$ with $\langle \Delta x^2(t) \rangle$, which gives $t_g = (d^2\Gamma(1+\alpha)/2D_\alpha)^{1/\alpha}$. We will solve a diffusion or subdiffusion equation for a system with plural membranes by dividing this system up into subsystems, each of which has one membrane. This procedure we shall name the *single-membrane approximation of a multimembrane system*.

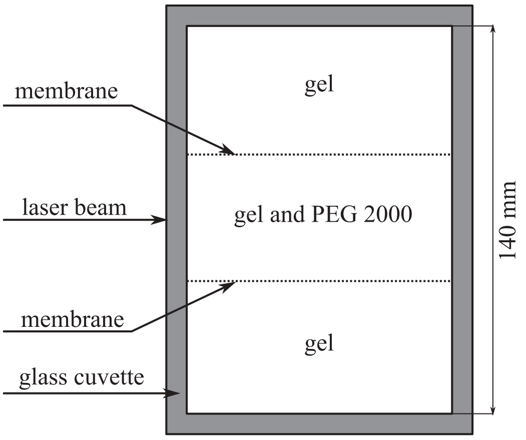

FIG. 2. Scheme of the experimental setup. (See the text for a more detailed description.)

III. FRACTIONAL MODEL

An equation which describes subdiffusion and is well justified through physics is one with a Reimmann-Liouville fractional time derivative [1,19],

$$\frac{\partial C(x,t)}{\partial t} = D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2 C(x,t)}{\partial x^2}. \tag{3}$$

This equation is derived by means of continuous-time random-walk formalism under the assumption that the particles move independently of each another and the system is homogeneous. Within this formalism one obtains a probability density (Green's function) $G(x,t;x_0)$ of finding a single particle at the point x at time t under the condition that the particle is located at x_0 at the initial moment; the Green's function provides Eq. (3). Next, using the following integral formula:

$$C(x,t) = \int_{-\infty}^{\infty} C(x_0,0) G(x,t;x_0) dx_0, \tag{4}$$

one can find that the concentration C fulfils Eq. (3).

The Green's function (GF) is usually defined as a solution to an appropriate differential equation with the initial condition $G(x,0;x_0) = \delta(x - x_0)$ (where δ denotes the Dirac delta function) and boundary conditions characteristic for the system. When the particles are transported independently and all of them start their movement at x_0 at the initial moment $t = 0$, the Green's function can be interpreted as a concentration of the particles normalized to one (i.e., divided by the number of particles).

To find Green's functions for all regions (see Fig. 1) one needs six boundary conditions, two of which require the disappearance of Green's functions at $\pm\infty$:

$$G_1(-\infty,t;x_0) = 0, \quad G_2(\infty,t;x_0) = 0, \tag{5}$$

and two others demand the continuity of the fluxes at the membrane surfaces:

$$J_1(x_1^-,t;x_0) = J_M(x_1^+,t;x_0), \tag{6}$$

$$J_M(x_2^-,t;x_0) = J_2(x_2^+,t;x_0), \tag{7}$$

where the subdiffusion flux is given by the formula

$$J_i(x,t;x_0) = -D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial G_i(x,t;x_0)}{\partial x}, \tag{8}$$

$i = 1,M,2$. The problem consists of determining the missing boundary conditions at the membranes. According to the assumptions presented in Sec. II we assume that, for $t \ll t_g$, the concentration in the interval $(-\infty,a)$ is determined by the particles which are located at the initial moment quite far from the membrane located at x_2. Thus, in order to calculate the concentration profiles in this region, the Green's function for the system with one membrane located at x_1 can be used. A similar assumption can be made in order to calculate the concentration in the interval (b,∞).

There are two different boundary conditions at a thin membrane which have mainly been used in modeling normal diffusion in a membrane system. In the first boundary condition it is assumed that the flux flowing through the membrane is proportional to the concentration difference between membrane surfaces:

$$J(x_W,t;x_0) = \gamma(G(x_W^-,t;x_0) - G(x_W^+,t;x_0)), \qquad (9)$$

where x_W is a membrane position. For normal diffusion this boundary condition is satisfactorily justified as a generalization of standard Fick's law, $J = -D_1 \partial C/\partial x$. However, due to Eq. (8) such a generalization is not evident in the case of subdiffusion. The second boundary condition is obtained within the generalized method of images [17]. Let us treat the Green's function as a concentration normalized to one, generated by a source of N particles located at x_0 ($N \gg 1$). For the fully impenetrable membrane located at x_W the flux at the membrane is equal to zero: $J(x_W,t;x_0) = 0$. Within the method of images the wall is replaced by an additional source of N particles located symmetrically to point x_0 with respect to the wall (i.e., at the point $2x_W - x_0$). Thus, the Green's function for this system reads $G(x,t;x_0) = G_0(x,t;x_0) + G_0(x,t;2x_W - x_0)$ for $x,x_0 < x_W$, where G_0 denotes the Green's function for the system without a membrane. Due to the symmetry of the sources' locations, the same number of particles flow in the opposite directions through the point $x = x_W$ in any given time interval. Therefore, the flux disappears at the membrane. To achieve the situation where the membrane is partially permeable, the additional source representing the membrane should be weakened by the factor σ and should contain σN particles, $0 \leqslant \sigma \leqslant 1$, which gives for $x,x_0 < x_W$

$$G(x,t;x_0) = G_0(x,t;x_0) + \sigma G_0(x,t;2x_W - x_0). \qquad (10)$$

Let us note that Eq. (10) was derived without any assumption concerning the specific form of the function G_0. For the subdiffusion equation (3) there is

$$G_0(x,t;x_0) = \frac{1}{2\sqrt{D_\alpha}} f_{\alpha/2-1,\alpha/2}\left(t;\frac{|x-x_0|}{\sqrt{D_\alpha}}\right), \qquad (11)$$

where

$$f_{\nu,\rho}(t;a) = \frac{1}{t^{1+\nu}} \sum_{k=0}^{\infty} \frac{1}{k!\,\Gamma(-k\rho-\nu)}\left(-\frac{a}{t^\rho}\right)^k . \qquad (12)$$

The function $f_{\nu,\rho}(t;a)$ can also be expressed in the terms of the Fox H-function [20]. The coefficient σ has a simple stochastic interpretation [17]. Namely, it is the probability of finding a particle in a region of $x < x_W$ in a system with a thin membrane under the condition that the particle would be found at the same time in the region of $x > x_W$ in the analogous system with a removed membrane (here $x_0 < x_W$). So, σ can be interpreted as a "reflection coefficient" and $1-\sigma$ as a "permeable coefficient" of the membrane. Taking into account the boundary condition $J(x_W^-,t;x_0) = J(x_W^+,t;x_0)$ and Eqs. (8) and (10) we obtain for $x > x_W$

$$G(x,t;x_0) = (1-\sigma)G_0(x,t;x_0). \qquad (13)$$

By using (4), it is easy to see that the functions (10) and (13) generate the boundary condition which ensures the constant ratio of the concentration at the membrane surfaces:

$$C(x_W^-,t) = \lambda C(x_W^+,t), \qquad (14)$$

where $\lambda = (1-\sigma)/(1+\sigma)$. We add that condition (14) qualitatively differs from (9) for $0 < \sigma < 1$ because the latter generates solutions whose differences between membrane surfaces reach zero over time. Since real systems are finite, the concentrations in a membrane system balance out after a sufficiently long time, which suggests that boundary condition (14) is incorrect. Let us note that, in deriving (10) and (13), we have assumed that the domain is unrestricted (which, in practice, means that the influence of external walls is negligibly small), so boundary condition (14) can be considered within the single-membrane approximation of a two-membrane system.

However, as we will see in Sec. V, the experimental concentration profiles cannot be described satisfactorily by the theoretical functions derived from Eqs. (4), (10), and (13). Therefore, we need a more general model. The fundamental change is that the permeability coefficient σ might depend on time.

IV. BEYOND THE FRACTIONAL MODEL

Let us assume that the membrane permeability changes over time. Then, guided by Eqs. (10) and (13), we postulate the following Green's functions for $x_0 < x_W$:

$$G(x,t;x_0) = \begin{cases} G_0(x,t;x_0) + \sigma(t)G_0(x,t;2x_W - x_0), & x < x_W, \\ (1-\sigma(t))G_0(x,t;x_0), & x > x_W. \end{cases} \qquad (15)$$

For $x_0 > x_W$ the Green's function is still given by Eq. (15) after replacing the relations $x < x_W \leftrightarrow x > x_W$. From (15) we obtain the following boundary condition at the membrane:

$$G(x_W^-,t;x_0) = \lambda(t)G(x_W^+,t;x_0), \qquad (16)$$

where

$$\lambda(t) = \frac{1-\sigma(t)}{1+\sigma(t)}. \qquad (17)$$

Taking into account Eqs. (4) and (15), we obtain within the single-membrane approximation the following:

$$C_1(x,t) = \frac{C_0\lambda_1(t)}{1+\lambda_1(t)} f_{-1,\gamma/2}\left(t;\frac{x_1-x}{\sqrt{D_\gamma}}\right), \qquad (18)$$

$$C_M(x,t) = \begin{cases} C_0\left[1 - \frac{\lambda_1(t)}{1+\lambda_1(t)} f_{-1,\alpha/2}\left(t; \frac{x-x_1}{\sqrt{D_\alpha}}\right)\right], & x \in (x_1,a), \\ C_0, & x \in (a,b), \\ C_0\left[1 - \frac{\lambda_2(t)}{1+\lambda_2(t)} f_{-1,\alpha/2}\left(t; \frac{x_2-x}{\sqrt{D_\alpha}}\right)\right], & x \in (b,x_2), \end{cases} \tag{19}$$

$$C_2(x,t) = \frac{C_0\lambda_2(t)}{1+\lambda_2(t)} f_{-1,\alpha/2}\left(t; \frac{x-x_2}{\sqrt{D_\alpha}}\right). \tag{20}$$

It is easy to see that the functions (18)–(20) obey the following boundary conditions at the membranes:

$$C_1(x_1^-,t) = \lambda_1(t) C_M(x_1^+,t), \tag{21}$$

$$C_2(x_2^+,t) = \lambda_2(t) C_M(x_2^-,t), \tag{22}$$

as well as (see the Appendix)

$$J_1(x_1^-,t) = J_M(x_1^+,t), \tag{23}$$

$$J_M(x_2^-,t) = J_2(x_2^+,t), \tag{24}$$

where $\lambda_j(t) = [1-\sigma_j(t)]/[1+\sigma_j(t)]$, $j = 1,2$, controls the membranes' permeability, and J_i is the flux generated by concentration C_i according to formula (8). The variation of the membrane permeabilities over time can be explained as the temporary blocking of the membrane channels by the particles which are too numerous in the near-membrane region to pass through the membrane without additional complications. However, the functions (18)–(20) fulfill (3) only approximately. The condition under which the solution of Eq. (3) can be satisfactorily approximated by (18)–(20) reads

$$\frac{\lambda_j'(t)}{1+\lambda_j(t)} \ll \frac{\lambda_j(t)}{t}, \tag{25}$$

where λ_j' denotes the time derivative of λ_j. (See the Appendix for the derivation.)

Until now, the form of the functions $\lambda_1(t)$ and $\lambda_2(t)$ has not yet been assumed. As we will show in the next section, the experimental results are clearly described by the functions (18)–(20) if we assume that

$$\lambda_1(t) = a_1 - b_1 e^{-w_1 t}, \quad \lambda_2(t) = a_2 - b_2 e^{-w_2 t}, \tag{26}$$

where a_1 and a_2 are positive and b_1, b_2, w_1, and w_2 are nonnegative constants. The functions (26) were found by trial and error to match the experimental results. Combining (26) with (25) we obtain the following formula for $j = 1,2$:

$$b_j \omega_j t \ll (a e^{\omega_j t} - b_j)(1 + a_j - b_j e^{-\omega_j t}). \tag{27}$$

The experimentally measured function, which is more frequently used then the concentration profiles, is the time evolution of the amount of substance released from the sample, $R(t)$ [10]. In our system $R(t) = A[\int_{-\infty}^{x_1} C_1(x,t)\,dx + \int_{x_2}^{\infty} C_2(x,t)\,dx]$, where A is the area of the membrane; so, the amount of substance which remains in the sample, $R_M(t)$, is equal to $R_M(t) = A[C_0 d - R(t)]$. After simple calculations from Eqs. (18) and (20) we obtain for a long-time approximation

$$R_M(t) = C_0 A\left[d - \left(\frac{\lambda_1(t)}{1+\lambda_1(t)} + \frac{\lambda_2(t)}{1+\lambda_2(t)}\right)\frac{\sqrt{D_\alpha}\,t^{\alpha/2}}{\Gamma(1+\alpha/2)}\right]. \tag{28}$$

V. EXPERIMENTAL RESULTS

We will apply our theoretical model to describing subdiffusion of PEG2000 in agarose hydrogel. The measurement has been conducted in a membrane system shown in Fig. 2. The membrane system under study is a cell with three glass cuvettes separated by horizontally located membranes. Initially, we fill the lower and upper cuvettes with pure agarose hydrogel (a 2% water solution of agarose) while in the middle cuvette there is the same agarose hydrogel dripped by the solute of the transported substance (PEG2000). Then, the substance diffuses from the middle cuvette to the exterior ones through the membranes. We assume that the subdiffusion parameters α and D_α are the same in each cuvette. This assumption is supported by an experiment which shows that the subdiffusion parameters do not depend on the solute concentration (at least for low concentrations) for some substances transported in agarose hydrogel [3]. Since the concentration gradients are in the vertical direction only, the diffusion is expected to be one-dimensional (along the x axis). The substance concentration is measured by means of laser interferometry [3,21]. The experimental setup was already used to study transport in a system with one thin membrane and it is described in detail in the papers of [21]. Here we only mention that it consists of the cuvette with two thin membranes, the Mach-Zehnder interferometer including the He-Ne laser, a television–charge-coupled device camera, and the computerized data acquisition system. For each measurement we prepared two gel samples: the pure gel 2% $(\%w/v)$ water solution of agarose and the same gel dripped by the solute of PEG2000. The concentration of solutes in the gel was fixed to be $0.0075\ \mathrm{mol/dm^3}$. The agarose gel water solvent was prepared by dissolving agarose powder (Sigma) in $90\,^\circ$C water. All experiments were performed at room temperature [$(22 \pm 0.5)\,^\circ$C]. The agarose gels are assumed to be inert to the solute at our experimental conditions. The polymer membranes (which are 20 μm thick) initially separated the homogenous gel solution in one cuvette from the pure gels in other ones. At the beginning of the experiment the cuvettes were pressed against each other in close contact so that diffusion across the membranes was initiated. For technical reasons the measurement of the concentrations can be performed in only one part of the system.

In Fig. 3 we present the experimentally measured concentrations in the middle part of the system for several times from 0 to 7200 s. The errors of the concentrations are estimated as 7% of its value. The subdiffusion parameter $\alpha = 0.88 \pm 0.02$ was found in another experiment when the time evolution of the near-membrane layer was analyzed by means of the method presented in [22]. The theoretical functions, which are also shown in Fig. 3, are calculated for $C_0 = 0.0075\ \mathrm{mol/dm^3}$, $D_\alpha = (2.43 \pm 0.9) \times 10^{-10}\ \mathrm{m^2/s^{0.88}}$, $\lambda_1(t) = 0.320 - 0.302 e^{-3.024\times 10^{-4} t}$, and $\lambda_2(t) = 0.329-0.305 e^{-3.371\times 10^{-4} t}$, where the coefficients in the exponents are

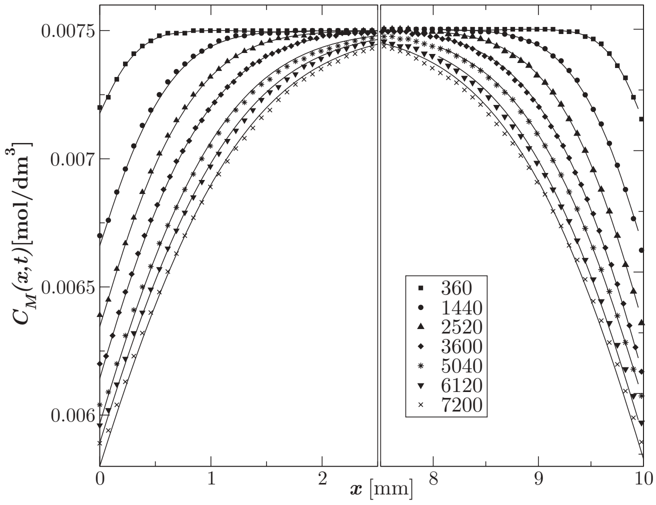

FIG. 3. Concentration profiles for the times (in seconds) given in the legend. The symbols represent the experimental data, and solid lines represent the theoretical functions. For clarity of the plot the error bars and the concentrations in the interval (2.5,7.5) are not shown (since inside this interval the experimental curves contained the constant function $C = C_0$ present for all times).

given in units of s^{-1}. The subdiffusion coefficient D_α, which is assumed to be independent of concentration, was treated as a fit parameter which ensures the best matching of theoretical and experimental results using the least-squares method. The functions $\lambda_1(t)$ and $\lambda_2(t)$ were found in the following manner. For each time the values of λ_1 and λ_2 give the best match of function (19) to the experimental data. Next, the values of λ_1 and λ_2, presented in Fig. 4, were matched to the functions (26).

In Fig. 5 we present the time evolution of the amount of substance which remains in the middle part of the system. The experimental values were calculated for the data given in Fig. 3 by means of numerical integration and the theoretical ones were obtained from Eq. (28) (where, for our experimental setup, $A = 70\ \mathrm{mm}^2$). We observe consistent agreement between the theoretical and experimental functions.

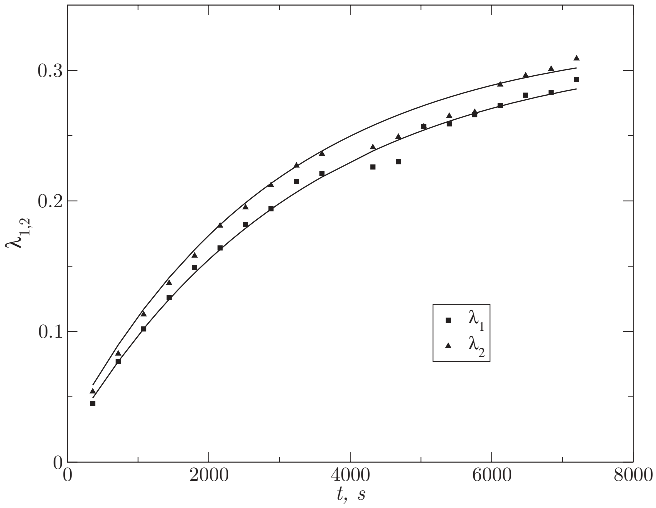

FIG. 4. Time dependence of λ_1 and λ_2 obtained as fit parameters (symbols) and their approximation given by Eq. (26) (solid lines) for the parameters presented in the text.

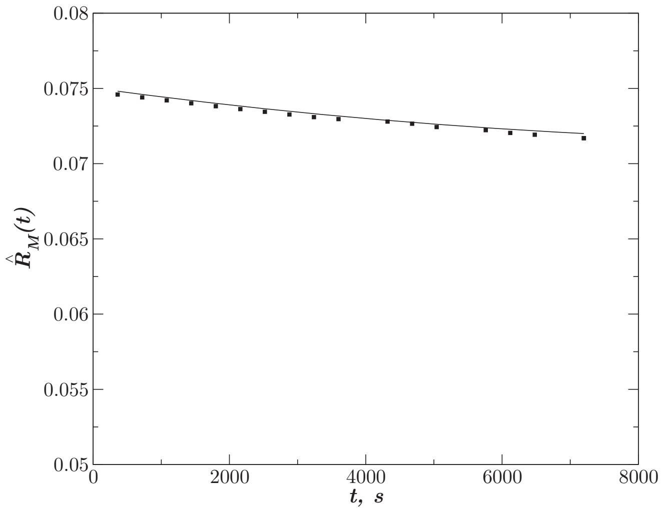

FIG. 5. The amount of substance which remains in the middle part of the system, $\hat{R}_M \equiv R_M(t)/A$, given here in units of mol mm/dm^3. The symbols represent the data obtained from the experiment, and the solid line represents the function (28) for the parameters given in the text. The error bars, which are estimated as 5% of the value of R_M, are not shown in the plot.

VI. FINAL REMARKS

We have proposed a model of subdiffusion in a system with two thin membranes. The model is considered within the approximation in which a two-membrane system is treated as two one-membrane systems, which are considered independent of each other. To find the concentration profiles of transported substance we have used the Green's functions for a one-membrane system. The Green's functions have been constructed by means of the generalized methods of images as combinations of GFs (11) derived from the subdiffusion equation (3) with the fractional Riemann-Liouville time derivative. We have assumed that the membrane permeability coefficients depend on time according to the special formula (26). The theoretical results are in consistent agreement with the experimental ones, which initially confirms the usefulness of the model.

Our analysis allows us to extract the subdiffusion coefficient of the released substance from the experimental data. For PEG2000 transported in 2% agarose hydrogel we find $D_\alpha = (2.43 \pm 0.9) \times 10^{-10}\ \mathrm{m}^2/\mathrm{s}^{0.88}$. Let us note that for sufficiently long times the amount of substance, R, leaving the region between the membranes evolves in time as $R(t) \sim t^{\alpha/2}$ [see (28)]. Thus, measuring the time evolution of R allows us to find the subdiffusion parameter α. We add that the results presented in [3,22] suggest that the subdiffusion parameter α of a water solution of agarose depends on the agarose concentration; namely, for a 1.5% solution of agarose $\alpha = 0.90 \pm 0.02$ [3] whereas for a 2% solution we have $\alpha = 0.88 \pm 0.02$ [22].

It seems that six free parameters—a_1, a_2, b_1, b_2, ω_1, and ω_2 [Eq. (26)]—which control the membrane permeability should be determined during a fitting procedure. Such a large number of parameters which are determined experimentally can be considered as too many to effectively construct a theoretical model. However, within the single-membrane approximation, which we apply in our considerations, the regions (x_1,a) and (b,x_2) are treated separately. This means that the boundary conditions are controlled by the three parameters in each of the regions. Therefore, when we fit theoretical curves to the experimental data we use only three fitting parameters for each region.

The parameters extracted from the experimental data give $t_g \sim 10^6$ s. This confirms that the functions (18)–(20) can be used to model the concentrations for times used in the experiment. When t is of the order of t_g (or larger) λ_1 and λ_2 are almost constants, then the analytical solutions with constant ratio of substance concentrations on both sides of the membrane surface, presented in [23], can be used to describe this process.

The theoretically calculated concentration profiles (18)–(20) fulfill the boundary conditions (21)–(24) but they obey the subdiffusion equation (3) only approximately. The reason is that Eq. (3) is derived by taking into account the movement of a single particle [1], which is extended to the equation describing particle concentrations by means of formula (4). So, the movement of a particle is independent of other particles. The collective effects of the particles' movement cause deviation from the assumptions mentioned above and they also mean that the subdiffusion equation is not exactly fulfilled. We note that saturation occurring at a membrane surface can also cause collective effects in some thin near-membrane layers. Therefore, it is worth considering finding a more relevant equation to describe subdiffusion in this layer. The natural way to do this would be to assume that the subdiffusion coefficient D_α depends on the concentration in the subdiffusion equation, which provides an equation which is very difficult to treat theoretically (see, for example, [24]). Let us note that the equation for which functions (18)–(20) are exact solutions seems to be somewhat unclear and difficult to interpret physically [see Eqs. (A8)–(A12) in the Appendix]. In such a situation, to find the concentration profiles of a subdiffusive substance in a membrane system we can use Eqs. (4), (15), (17), and (26). Despite the difficulties mentioned above we can also use Eq. (3) with the following ansatz: *We solve Eq.* (3) *with the initial condition* (2) *and the boundary ones* (21)–(24) *for* λ_1 *and* λ_2*, which are assumed to be independent of time, and next we replace* λ_1 *and* λ_2 *with* $\lambda_1(t)$ *and* $\lambda_2(t)$ *according to Eq.* (26)*, respectively, in the obtained solutions.* We suppose that Eq. (3) with the ansatz could be useful for modeling subdiffusion in various membrane systems including inhomogeneous ones with both thin and thick membranes.

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APPENDIX

Differentiating (12) term by term and using the formula

$$\frac{d^\gamma}{dt^\gamma}t^\nu = \frac{\Gamma(\nu+1)}{\Gamma(\nu-\gamma+1)}t^{\nu-\gamma}, \tag{A1}$$

we get

$$\frac{\partial}{\partial t}f_{-1,\alpha/2}\left(t;\frac{|x_1-x|}{\sqrt{D_\alpha}}\right) = f_{0,\alpha/2}\left(t;\frac{|x_1-x|}{\sqrt{D_\alpha}}\right), \tag{A2}$$

$$\frac{\partial^{1-\alpha-j}}{\partial t^{1-\alpha-j}}\frac{\partial^2}{\partial^2 x}f_{-1,\alpha/2}\left(t;\frac{|x_1-x|}{\sqrt{D_\alpha}}\right) = \frac{1}{D_\alpha}f_{-j,\alpha/2}\left(t;\frac{|x_1-x|}{\sqrt{D_\alpha}}\right), \tag{A3}$$

$$\frac{\partial^{1-\alpha-j}}{\partial t^{1-\alpha-j}}\frac{\partial}{\partial x}f_{-1,\alpha/2}\left(t;\frac{|x_1-x|}{\sqrt{D_\alpha}}\right) = \frac{\mathrm{sgn}(x_1-x)}{\sqrt{D_\alpha}}f_{-j-\alpha/2,\alpha/2}\left(t;\frac{|x_1-x|}{\sqrt{D_\alpha}}\right). \tag{A4}$$

By using Leibniz's formula for fractional derivatives [25],

$$\frac{d^\alpha f(t)g(t)}{dt^\alpha} = \sum_{j=0}^{\infty}\frac{\Gamma(\alpha+1)}{j!\Gamma(\alpha-j+1)}\frac{d^{\alpha-j}f(t)}{dt^{\alpha-j}}\frac{d^j g(t)}{dt^j}, \tag{A5}$$

the fluxes generated by (18) and (19) [the latest one for $x \in (x_1,a)$] read

$$J_i(x,t) = -C_0\sqrt{D_\alpha}\sum_{j=0}^{\infty}\frac{\Gamma(2-\alpha)}{\Gamma(2-\alpha-j)}f_{-j-\alpha/2,\alpha/2}\times\left(t;\frac{|x_1-x|}{\sqrt{D_\alpha}}\right)\frac{d^j}{dt^j}\frac{\lambda_1(t)}{1+\lambda_1(t)}, \tag{A6}$$

$i = 1,M$, and thus

$$J_1(x_1,t) = J_M(x_1,t). \tag{A7}$$

Substituting (18) into (3) we obtain

$$F_1(x,t) + F_2(x,t) = F_3(x,t) + F_4(x,t), \tag{A8}$$

where

$$F_1(x,t) = C_0\frac{\lambda_1(t)}{1+\lambda_1(t)}\frac{\partial}{\partial t}f_{-1,\alpha/2}\left(t;\frac{|x_1-x|}{\sqrt{D_\alpha}}\right), \tag{A9}$$

$$F_2(x,t) = C_0 f_{-1,\alpha/2}\left(t;\frac{x_1-x}{\sqrt{D_\alpha}}\right)\frac{\partial}{\partial t}\frac{\lambda_1(t)}{1+\lambda_1(t)}, \tag{A10}$$

$$F_3(x,t) = D_\alpha C_0\frac{\lambda_1(t)}{1+\lambda_1(t)}\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}\frac{\partial^2}{\partial x^2}f_{-1,\alpha/2}\left(t;\frac{x_1-x}{\sqrt{D_\alpha}}\right), \tag{A11}$$

$$F_4(x,t) = D_\alpha C_0\sum_{j=1}^{\infty}\frac{\Gamma(2-\alpha)}{\Gamma(2-\alpha-j)}\frac{\partial^{1-\alpha-j}}{\partial t^{1-\alpha-j}}\frac{\partial^2}{\partial x^2}f_{-1,\alpha/2}\times\left(t;\frac{x_1-x}{\sqrt{D_\alpha}}\right)\frac{\partial^j}{\partial t^j}\frac{\lambda_1(t)}{1+\lambda_1(t)}. \tag{A12}$$

Let us note that $F_1 \equiv F_3$ [see (A2) and (A3)] and F_2 and F_4 vanish when λ is independent of time. The function (18) approximately fulfills Eq. (3) if $F_2 \ll F_1$ and $F_4 \ll F_3$. Taking into account the above relations and the leading terms of Eqs. (A2)–(A4) [which correspond to terms of smallest number j in (A5) and k in (12)] we find that above inequalities are fulfilled when relation (25) works.

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