ANOMALOUS DIFFUSION IN A MEMBRANE SYSTEM

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We briefly discuss the physical basis of anomalous diffusion and equations with fractional derivatives, which describe this process. We also present the method of extracting subdiffusion parameters from experimental data.

1. Introduction

Anomalous diffusion is a process in which a mean square displacement, $\langle x^2(t) \rangle$, satisfies the relation [1]

$$\langle x^2(t) \rangle \sim t^\alpha , \qquad (1)$$

where α is an anomalous diffusion parameter. For $0 < \alpha < 1$, we are dealing with subdiffusion; for $\alpha = 1$, we have a situation of normal diffusion, and, for $\alpha > 1$, we encounter superdiffusion. To describe the anomalous diffusion, one usually uses differential equations with derivatives of fractional order [1, 2].

In our paper, we briefly discuss the subdiffusion in a system with a thin membrane, which has been intensively studied experimentally [3–6] (see also [7] and references therein). Subdiffusion is a process which is qualitatively different from normal diffusion. Due to the complex structure of the variuos forms of media, a subdiffusive particle waits an anomalously long time to make its step, and the mean value of this time is infinite. The exact formula for the mean square displacement in one-dimensional system reads [1]

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

for $0 < \alpha < 1$; D_α is the subdiffusion coefficient measured in the units m^2/s^α, and $\Gamma(z)$ denotes the Gamma
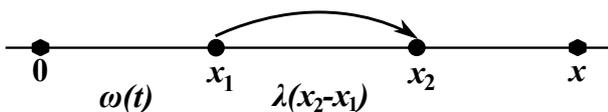
Fig. 1. Schematic representation of a one-dimensional random walk

function. In what follows, we assume that the anomalous diffusion parameters are independent of the time and the space variable.

There is a problem with distinguishing between subdiffusion and normal diffusion with a very small diffusion coefficient. We present a method which allows us to extract the subdiffusion parameters from experimental data. The method utilizes a membrane system where a thin membrane separates a homogeneous solute from a pure solvent at the initial time moment. Since the concentration profiles of the diffusing substance have been experimentally investigated, the subdiffusion parameters α and D_α are treated as the fitting parameters of theoretical functions in relation to the experimental data. However, the concentration profiles are usually measured with relatively large errors, so the obtained values of the parameters are not very accurate. To estimate the parameters with greater precision, the time evolution of the thickness of the so-called near membrane layers is used according to this method [3, 4].

2. Anomalous Diffusion Equations

Let us consider a one-dimensional random walk of a particle (see Fig. 1). By $\omega(t)$, we denote the probability density of waiting time between two successive jumps, and $\lambda(x)$ is the probability density of the jump length.

Within the Continuous Time Random Walk approach, the type of transport process is determined by the functions $\omega(t)$ and $\lambda(x)$ (strictly speaking, by the moments of these functions). There are three main possibilities [1].

– When $\omega(t) \sim e^{-t/\tau}$ and $\lambda(x) \sim e^{-x^2/2\sigma}$, which ensures that $\langle \omega(t) \rangle$ and $\langle \lambda^2(x) \rangle$ are finite, the particle transport constitutes normal diffusion which is described by the equation

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} ,$$

where D is the normal diffusion coefficient. The parameters τ and σ satisfy the relation $D = \sigma/2\tau$.

– When $\omega(t) \sim (1/t)^{1+\alpha}$ for $t \to \infty$ and $\lambda(x) \sim e^{-x^2/2\sigma}$, which ensures that $\langle \omega(t) \rangle = \infty$ and $\langle \lambda^2(x) \rangle$ is finite, then the particle transport process is the subdiffusion which is described by the subdiffusion equation with the fractional time derivative

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

where $\partial^\alpha f(t)/\partial t^\alpha$ denotes the Riemann–Liouville fractional derivative defined for $0 < \alpha < 1$ as [1, 8]

$$\frac{\partial^\alpha f(t)}{\partial t^\alpha} = \frac{1}{\Gamma(1-\alpha)} \frac{\partial}{\partial t} \int\limits_0^t dt' \frac{f(t')}{(t-t')^\alpha} \ .$$

– When $\omega(t) \sim e^{-t/\tau}$ and $\lambda(x) \sim |x|^{-(1+\beta)}$ for $|x| \to \infty$, which ensures that $\langle \omega(t) \rangle$ is finite and $\langle \lambda^2(x) \rangle = \infty$, then the particle transport process is the superdiffusion which is described by the following equation with the Riesz fractional space derivative

$$\frac{\partial C(x,t)}{\partial t} = D_\beta \frac{\partial^\beta C(x,t)}{\partial x^\beta} \ ,$$

where D_β is the superdiffusion coefficient.

3. Subdiffusion in a Membrane System

Let us consider the system where a thin membrane separates a homogeneous solution from a pure solvent (see Fig. 2) (we should mention that such a system has often been used in experimental studies [3–6, 9]). Assuming that the length of the system is very long as compared with the regions in which the concnetration profiles change noticeably with respect to their initial values, we can treat the system as unbounded.

Thus, we choose the initial condition as

$$C(x,0) = \begin{cases} C_0, & x < 0 \ , \\ 0, & x > 0 \ . \end{cases} \qquad (3)$$

We denote the concentration and the flux in the region $x < 0$ as $C_1(x,t)$ and $J_1(x,t)$ and in the region $x > 0$ as $C_2(x,t)$ and $J_2(x,t)$, respectively. The subdiffusion parameters in both parts of the system are α and D_α. To solve the subdiffusion equation, we need four boundary conditions, two of them should be set at the thin membrane. The first boundary condition requires the continuity of the flux at the membrane

$$J_1(0^-, t) = J_2(0^+, t)(\equiv J(0,t)) \ , \qquad (4)$$
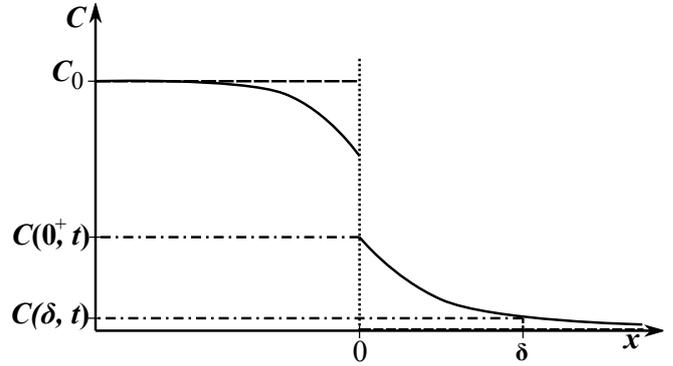
Fig. 2. The schematic view of the system under consideration. The broken line represents the initial concentration, the solid line shows the concentration, and the dotted vertical line indicates the thin membrane

where the subdiffusive flux $J(x,t)$ is given by generalized Fick's law

$$J(x,t) = -D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial C(x,t)}{\partial x} \ . \qquad (5)$$

There is no obvious predetermined choice for the second boundary condition. We will assume that this boundary condition is provided by a linear combination of concentrations and a flux at the membrane

$$b_1 C_1(0^-, t) + b_2 C_2(0^+, t) + b_3 J(0,t) = 0 \ , \qquad (6)$$

where $b_1 b_3 \leq 0$ and $b_2 b_3 \geq 0$. Equations (5) and (6) provide the commonly used membrane boundary conditions at a thin membrane [10, 11]. The physical interpretation has the quotients of the coefficients b_1, b_2 and b_3. When $b_3 \neq 0$, Eq. (6) yields

$$J = \lambda_1 C(0^-, t) - \lambda_2 C(0^+, t) \ ,$$

with $\lambda_1 = -b_1/b_3$ and $\lambda_2 = -b_2/b_3$ being membrane permeability coefficients. For the symmetric membrane ($\lambda_1 = \lambda_2 \equiv \lambda$), we obtain the often used boundary conditions where the flux flowing through the membrane is proportional to the difference of concentrations at the membrane. When $b_3 = 0$, for $b_1 \neq 0$ and $b_2 \neq 0$, we obtain

$$C(0^-, t) = \sigma C(0^+, t) \ ,$$

with $\sigma = -b_2/b_1$ interpreted as the membrane reflection coefficient; this membrane boundary condition can be obtained from the generalized method of images [10]. We note that the cases $b_3 = b_1 = 0$, $b_2 \neq 0$ and $b_3 = b_2 = 0$, $b_1 \neq 0$ correspond to the fully absorbing membrane, whereas $b_1 = 0$, $b_2 \neq 0$, $b_3 \neq 0$ and $b_2 = 0$, $b_1 \neq 0$,
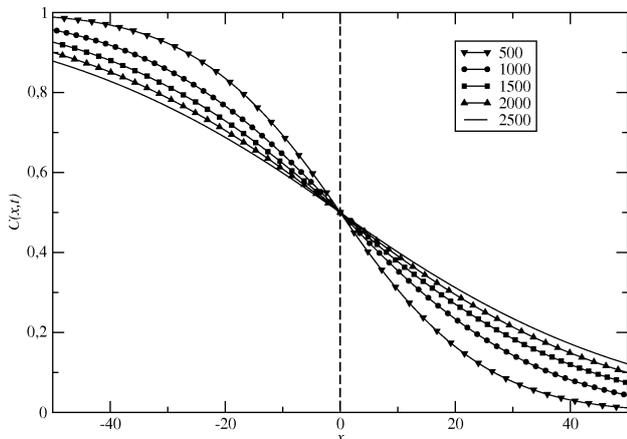
Fig. 3. Concentration profiles for $\alpha = 0.9$, $D_\alpha = 0.5$, $C_0 = 1.0$, $b_1 = -b_2 = 1$, $b_3 = 0$ and for times given in the legend; all quantites are given in arbitraty units

$b_3 \neq 0$ correspond to the partially absorbing membrane. The coefficients λ_1, λ_2 (or λ), and σ are measured experimentally.

Since Eq. (6) is a generalized form of the linear boundary conditions at the membrane, we will use b_1, b_2, and b_3 as the coefficients for the description of the permeability of the membrane. Therefore, the final solutions contain these parameters.

Additional boundary conditions are chosen as

$$C_1(-\infty, t) = C_0 , \qquad C_2(\infty, t) = 0 . \tag{7}$$

The solutions to Eq. (2) with boundary conditions (4), (6), (7) and the initial one (3) are as follows (the procedure we used to solve the equation is based on the Laplace transformation and is presented in [12]).
– For $b_3 = 0$,

$$C_1(x, t) = C_0 \left[1 - \frac{2}{\alpha} \frac{b_1}{b_1 - b_2} \times \right.$$

$$\left. \times H_{1\,1}^{1\,0} \left(\left(\frac{-x}{\sqrt{D_\alpha t^\alpha}} \right)^{2/\alpha} \middle| \begin{array}{cc} 1 & 1 \\ 0 & 2/\alpha \end{array} \right) \right] ,$$

$$C_2(x, t) = \frac{2C_0}{\alpha} \frac{b_1}{b_1 - b_2} H_{1\,1}^{1\,0} \left(\left(\frac{x}{\sqrt{D_\alpha t^\alpha}} \right)^{2/\alpha} \middle| \begin{array}{cc} 1 & 1 \\ 0 & 2/\alpha \end{array} \right) ,$$

where H is the Fox function

$$H_{11}^{10} \left(\frac{a^{1/\beta}}{t} \middle| \begin{array}{cc} 1 & 1 \\ (1+\nu)/\beta & 1/\beta \end{array} \right) =$$

$$= \frac{\beta a^{(1+\nu)/\beta}}{t^{1+\nu}} \sum_{k=0}^{\infty} \frac{1}{k!\Gamma(-k\beta - \nu)} \left(-\frac{a}{t^\beta} \right)^k .$$

– For $b_3 \neq 0$,

$$C_1(x, t) =$$

$$= C_0 \left[1 - \frac{2\eta}{\alpha\sqrt{D_\alpha}} \sum_{n=0}^{\infty} \gamma^n \left(\frac{\sqrt{D_\alpha}}{-x} \right)^{\frac{2}{\alpha}[1 - (\frac{\alpha}{2} - 1)n] - 1} \times \right.$$

$$\left. \times H_{1\,1}^{1\,0} \left(\left(\frac{-x}{\sqrt{D_\alpha t^\alpha}} \right)^{\frac{2}{\alpha}} \middle| \begin{array}{cc} 1 & 1 \\ \frac{2}{\alpha}\left[\left(\frac{\alpha}{2} - 1 \right) n - 1 \right] + 1 & \frac{2}{\alpha} \end{array} \right) \right] ,$$

$$C_2(x, t) =$$

$$= \frac{2C_0\eta}{\alpha\sqrt{D_\alpha}} \sum_{n=0}^{\infty} \gamma^n \left(\frac{\sqrt{D_\alpha}}{x} \right)^{\frac{2}{\alpha}[1 - (\frac{\alpha}{2} - 1)n] - 1} \times$$

$$\times H_{1\,1}^{1\,0} \left(\left(\frac{x}{\sqrt{D_\alpha t^\alpha}} \right)^{\frac{2}{\alpha}} \middle| \begin{array}{cc} 1 & 1 \\ \frac{2}{\alpha}\left[\left(\frac{\alpha}{2} - 1 \right) n - 1 \right] + 1 & \frac{2}{\alpha} \end{array} \right) ,$$

where

$$\eta = -\frac{b_1}{b_3} , \qquad \gamma = \frac{b_1 - b_2}{b_3\sqrt{D_\alpha}} .$$

We note that the parameters η and γ control the membrane permeability. These parameters can be easily expressed by parameters λ_1, λ_2 (or λ), and σ discussed previously.

As an example, the graphs of the solutions of the subdiffusion equation for the system under consideration are presented in Fig. 3.

Applying the Laplace transformation method, it is shown that for the sufficiently long times $t \geq t_g$ (in the commonly used experimental systems $t_g \approx 2$ s), the time evolution of the thickness of near-membrane layers, which is defined as a length at which the concentration drops κ times, $C(\delta(t), t) = \kappa C(0, t)$, (see Fig. 2) is [3, 4]

$$\delta(t) = A(\alpha, D_\alpha, \kappa) t^{\alpha/2} , \tag{8}$$

where

$$A(\alpha, D_\alpha, \kappa) = \sqrt{D_\alpha} \left[\left(H_{1\,1}^{1\,0} \right)^{-1} \left(\frac{\alpha\kappa}{2} \middle| \begin{array}{cc} 1 & 1 \\ 0 & 2/\alpha \end{array} \right) \right]^{\alpha/2} .$$

In this way, the time evolution of near-membrane layers is expressed as a power function with the exponent controlled by the subdiffusion parameter α alone. Comparing the theoretical function (8) with experimental data, we can estimate the subdiffusion parameters α and D_α for the system under study.

4. Conclusions

The method presented above was used to identfy the kind of glucose and sucrose transport in gel (1.5% water solution of agarose), which proved to constitute the subdiffusion with $\alpha = 0.90 \pm 0.01$ and to determine the values of subdiffusion coefficients: $D_{0.90} = (9.8 \pm 1.0) \times 10^{-4}$ mm^2/s$^{0.90}$ for glucose and $D_{0.90} = (6.3 \pm 0.9) \times 10^{-4}$ mm^2/s$^{0.90}$ for sucrose [3, 4].

We note that the power functions, similar to (1), characterize the subdiffusion not only in a membrane system but, among others, the subdiffusive transport in a system with chemical reactions. In this system, the power function describes the time evolution of the reaction front [9, 13].

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АНОМАЛЬНА ДИФУЗІЯ У МЕМБРАННІЙ СИСТЕМІ

Т. Коштолович, К.Д. Левандовська

Р е з ю м е

Стисло обговорено фізичний базис аномальної дифузії і рівняння з дробовими похідними, що описують цей процес. Розвинуто метод виділення субдифузійних параметрів з використанням експериментальних даних.