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SUBDIFFUSION IN A MEMBRANE SYSTEM*

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The subdiffusion is defined by the relation $\langle(\Delta x)^2\rangle \sim t^\alpha$ with $\alpha < 1$. We present a new method of calculating the coefficient α, which can be used to obtain it experimentally. The method refers to the time evolution of the thickness of the so-called near-membrane layers.

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1. Introduction

A large number of physical processes display the anomalous diffusion, such as a diffusion in porous media. In one dimension subdiffusion is characterized by a time dependence of mean square displacement, which is of the form

$$\langle(\Delta x)^2\rangle \sim t^\alpha \tag{1}$$

with $0 < \alpha < 1$; for $\alpha = 1$ the process is called normal or Gaussian diffusion [1]. Recently our experimental investigations of the transport of organic substances in the membrane system with gel solvent show some deviation from the results already obtained for the Gaussian diffusion. The strong deviation is observed in time evolution of the thickness of near-membrane layer δ. This layer is defined as a distance from the membrane where the substance concentration drops κ times with respect to the membrane surface. In our previous paper [2] we showed that for Gaussian diffusion the relation takes the following form $\delta \sim t^\gamma$ with $\gamma = 1/2$. The experiment of the gel solvent gives $\gamma < 1/2$. There arises a question: can the coefficient γ be used to identify the anomalous diffusion in the membrane system and is it related with the coefficient α of Eq. (1) which holds for homogeneous media?

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2. Time evolution of near-membrane layers

When the substance diffuses across the membrane into the pure solvent, for the initial concentration

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

the thickness δ of the near-membrane layer is defined as a length over which the concentration decreases κ times,

$$C(\delta,t)=\kappa C(0^+,t) \tag{2}$$

with $\kappa<1$. The concentration profiles can be calculated by the integral formula

$$C(x,t)=\int dx_0 G(x,t;x_0)C(x_0,0)\,. \tag{3}$$

The Green's function $G(x,t;x_0)$ is interpreted as a probability density for finding a particle at location x at time t after a departure from x_0 at the initial moment. From the relations (2) and (3) we deduce that

$$G(\delta,t;x_0)=\kappa G(0^+,t;x_0)\,. \tag{4}$$

To find the time evolution of the near-membrane layer, we use the following relation (for $x>0$ and $x_0<0$)

$$G(x,t,x_0)=\int_0^t dt' J(0^+,t';x_0)G_{\mathrm{Ref}}(x,t-t';0^+)\,, \tag{5}$$

where J is the flux and G_{Ref} denotes the Green's function for the system with fully reflecting wall; $x=0$ is the location of membrane. This function can be easily obtained by means of the method of images [1] as

$$G_{\mathrm{Ref}}(x,t;x_0)=G_0(x,t;x_0)+G_0(-x,t;x_0)\,,$$

where G_0 is the Green's function for the homogeneous system. Using the Laplace transform

$$L\{f(t)\}\equiv\hat{f}(s)=\int_0^\infty dt f(x)\exp(-st)\,,$$

from (4) and (5) we obtain

$$\begin{aligned}\hat{G}(\delta,s;x_0) &= \kappa\hat{G}(0^+,s;x_0)\,,\\ \hat{G}(x,s;x_0) &= \hat{J}(0^+,s;x_0)\hat{G}_{\mathrm{Ref}}(x,s;0^+)\end{aligned}$$

and finally we get

$$\hat{G}_{\mathrm{Ref}}(\delta, s; 0^+) = \kappa \hat{G}_{\mathrm{Ref}}(0^+, s; 0^+)\,. \tag{6}$$

The Laplace transform of the function G_{Ref} is [1]

$$\begin{aligned} \hat{G}_{\mathrm{Ref}}(x, s; x_0) &= \frac{1}{2\sqrt{D_\alpha} s^{1-\frac{\alpha}{2}}} \\ &\times \left[\exp\left(-\frac{|x - x_0| s^{\frac{\alpha}{2}}}{\sqrt{D_\alpha}} \right) + \exp\left(-\frac{|x + x_0| s^{\frac{\alpha}{2}}}{\sqrt{D_\alpha}} \right) \right]. \end{aligned} \tag{7}$$

Using (6) and (7), we find

$$\frac{\delta}{s} = \sqrt{D_\alpha} \ln\left(\frac{2}{\kappa}\right) s^{-(1+\alpha/2)}. \tag{8}$$

The inverse Laplace transform of (8) gives

$$\delta \sim t^\gamma \quad \text{with} \quad \gamma = \frac{\alpha}{2}\,.$$

3. Concluding remarks

The experimental study usually concern the concentration profiles of the transported substances. However, the thickness of the near-membrane layers can be measured much more accurately than the concentration profiles. Thus, the identification of subdiffusion can be performed on the basis of time evolution of near-membrane layers. We show that $\delta \sim At^\gamma$ with $\gamma = 1/2$ for normal diffusion and $\gamma < 1/2$ for subdiffusion. In this way, we propose the method to identify the subdiffusion through the analysis of temporal evolution of the near-membrane layers. The practical examples of calculating the coefficient α from experimental data are presented in the paper [3].

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