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Confined mobility in biomembranes modeled by early stage Brownian motion

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ABSTRACT

An equation of motion, derived from the fractal analysis of the Brownian particle trajectory, makes it possible to calculate the time dependence of the mean square displacement for early times, before the Einstein formula becomes valid. The diffusion coefficient increases with the distance travelled which can be restricted by the geometrical conditions. The corresponding diffusion coefficient cannot increase further to achieve a value characteristic for unrestricted environment. Explicit formula is derived for confined diffusivity related to the unrestricted one as dependent on the maximum particle mean square displacement possible normalized by the square of its mean free path. The model describes the lipid and protein diffusion in tubular membranes with different radii, originally fitted by the modified Saffman–Delbrück equation, and the lateral mobility of synthetic model peptides for which the diffusion coefficient is inversely proportional to the radius of the diffusing object and to the thickness of the membrane.

1. Introduction

The mobility in biological membranes is described by the Brownian motion although the diffusion coefficient is not determined by the Stokes–Einstein equation. The motion of the nanoparticles in biological systems is usually restricted to bounded domains. Theoretical description of the Brownian motion in biological membranes has been given by Saffman and Delbrück [1], who predicted a logarithmic dependence of the protein diffusion coefficient on the inverse of the size of the protein and on the membrane size if restricted.

The space restriction demands a more detailed analysis of the motion of nanoparticles. At very short times the motion of a Brownian particle is regarded as ballistic whereas for long times the particle starts to behave according to Einstein's theory [2]. At short distances the Einstein formula is still not valid and the mean square displacement of the particle position is lower than would be for fully developed diffusive motion at the same time. The lower mean square displacement corresponds to the lower diffusion coefficient for early stage of Brownian motion. First description of this phenomenon was done by Langevin [3].

A solution to the corresponding equation was given by Uhlenbeck and Ornstein [4] in the form

$$\frac{\langle x^2\rangle}{2Dt} = 1 - \frac{\tau}{t}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \qquad (1)$$

This is a time dependence of the mean square displacement of the particle position in one dimension $\langle x^2\rangle$. The solution contains two parameters which are the diffusion coefficient D and the characteristic time τ, being the momentum relaxation time, is calculated as the particle mean free path in one dimension divided by the corresponding mean velocity of the particle.

$$\tau = \lambda_x / v_{0_x} \qquad (2)$$

Regarding the functional form of the velocity autocorrelation function in respect to the Langevin equation, a fast exponential transition occurs from the ballistic to the diffusive region, in which the time dependence of the mean square displacement scales with the diffusion coefficient and the momentum relaxation time. Instead of an exponential decay, a long-tail proportional to $t^{-3/2}$ is postulated by Vladimirsky and Terletzky [5] and Hinch [6] for Brownian particle. This form of the velocity autocorrelation function has the experimental confirmation given by Kim and Matta [7]. It is also confirmed by the fractal model of the Brownian particle motion discussed in this paper.

A moving particle follows the straight-line segments. At a very short time, when the movement can be considered as ballistic, the particle travels along the same segment with the fractal dimension equal to one. At a very long time the movement can be regarded as Brownian, along a trajectory with the fractal dimension equal to two due to evolution of fractal character of particle trajectory. It

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Nomenclature

a	radius of cylindrical particle (m)	$\langle x^2 \rangle$	mean square displacement of the particle position in one dimension (m^2)
C_V	normalized velocity autocorrelation function (–)	η_b	bulk fluid viscosity (kg m^{-1} s^{-1})
D	diffusion coefficient (m^2/s)	η_m	membrane viscosity (kg m^{-1} s^{-1})
$D_{<x^2>}$	diffusion coefficient in restricted space (m^2/s)	λ_x	particle mean free path in one dimension (m)
h	membrane height (m)	τ	particle momentum relaxation time (s)
t	time (s)		
v_{0_x}	mean velocity of the particle in one direction (m/s)		

seems reasonable to describe the transition between the two using the scale-dependent fractal dimension changing from one for small scale (ballistic) to two for large ones (diffusive), as postulated by Takayasu [8], who considered an isotropic Brownian motion of a particle in three-dimensional space. The scale (s) dependent fractal dimension for a random walk trajectory, given in a general form by Bujan-Nuñez [9], reads

$$D_w(s) = 2 - \frac{1}{1 + s/k\lambda} \tag{3}$$

where k is a proportionality constant, being a fitting parameter, and λ is the particle mean free path. Accordingly, $D_w(s)$ varies between 1 if $s/k\lambda \to 0$ and 2 if $s/k\lambda \to \infty$. The bigger the scale of observation, the random motion is thus more close to the Brownian motion.

The trajectory length depends on the scale of observation according to the fractal formula

$$\frac{d \ln L(s)}{d \ln s} = 1 - D_w(s) \tag{4}$$

Integrating with $D_w(s)$ given by Eq. (3)

$$\int_{L(0)}^{L(r)} \frac{dL}{L} = \int_0^r - \frac{\frac{s}{k\lambda}}{1 + \frac{s}{k\lambda}} \frac{ds}{s} \tag{5}$$

one gets the result described by Gmachowski [10]

$$\frac{r}{L(0)} = \frac{1}{1 + \frac{r}{k\lambda}} \tag{6}$$

$L(0)$ is the trajectory contour length equal to the product of the mean velocity of the particle and time v_0t. Hence

$$\frac{1}{1 + \frac{r}{k\lambda}} = \frac{r}{v_0 t} = \frac{r\tau}{\lambda t} \tag{7}$$

where the mean velocity of the particle is replaced by the mean free path of diffusing particle divided by the characteristic momentum relaxation time

$$v_0 = \lambda/\tau \tag{8}$$

The obtained relation reads

$$\frac{r}{\lambda}\left(k + \frac{r}{\lambda}\right) = k\frac{t}{\tau} \tag{9}$$

Then replacing r by $\sqrt{\langle r^2 \rangle}$, the root of the mean square displacement of the particle position in three dimensions, one gets the formula describing the mean square displacement of the particle position in three dimensions $\langle r^2 \rangle$ as dependent on the number of steps t/τ

$$\frac{\langle r^2 \rangle^{1/2}}{\lambda}\left(k + \frac{\langle r^2 \rangle^{1/2}}{\lambda}\right) = k\frac{t}{\tau} \tag{10}$$

Substituting in Eq. (10)

$$\langle r^2 \rangle = 3\langle x^2 \rangle \tag{11}$$

$$\lambda = \sqrt{3}\lambda_x \tag{12}$$

one gets the formula describing the mean square displacement of the particle position in one dimension $\langle x^2 \rangle$ as dependent on the number of steps t/τ

$$\frac{\langle x^2 \rangle^{1/2}}{\lambda_x}\left(k + \frac{\langle x^2 \rangle^{1/2}}{\lambda_x}\right) = k\frac{t}{\tau} \tag{13}$$

The derived equation describes a smooth crossover from ballistic to diffusive motion of a Brownian particle, which is essential during the initial stage of the particle motion. For very short times the formula takes the form characteristic for ballistic movement

$$\langle x^2 \rangle^{1/2} = \lambda_x \frac{t}{\tau} = v_{0x} t \tag{14}$$

and for very long times

$$\langle x^2 \rangle = k\lambda_x^2 \frac{t}{\tau} = k v_{0x} \lambda_x t \tag{15}$$

Taking the unrestricted diffusion coefficient described by the kinetic theory, as dependent on the Brownian step parameters

$$D = v_{0x}\lambda_x \tag{16}$$

we get the agreement with the Einstein formula $\langle x^2 \rangle = 2Dt$ for the value of the fitting parameter $k = 2$. The final form of Eq. (13) reads

$$\frac{\langle x^2 \rangle^{1/2}}{\lambda_x}\left(2 + \frac{\langle x^2 \rangle^{1/2}}{\lambda_x}\right) = 2\frac{t}{\tau} \tag{17}$$

With Eqs (2) and (16) the formula can be rearranged to the form

$$\frac{\langle x^2 \rangle}{2Dt} + \frac{\langle x^2 \rangle^{1/2}}{v_{0x} t} = 1 \tag{18}$$

or after solving the quadratic Eq. (17)

$$\frac{\langle x^2 \rangle}{2Dt} = 1 - \frac{\sqrt{1 + 2t/\tau} - 1}{t/\tau} \tag{19}$$

The fractal model of the particle motion was utilized to formulate [11] the aerosol collision kernel. The applicability of the model of the ballistic-diffusive transition seems to be much wilder, especially to describe the diffusion in restricted environments.

2. Model of confined Brownian movement

Before formulation of the restricted diffusion problem, let us check the reliability of the derived formulae. Eq. (18), which is the sum of diffusive and ballistic contributions, describes the behavior of a Brownian particle for short ($\langle x^2 \rangle^{1/2} \to v_{0x}t$) and long ($\langle x^2 \rangle \to 2Dt$) times. It clearly indicates that the mean square displacement is less than its value for fully developed diffusive motion ($\langle x^2 \rangle < 2Dt$). Huang et al. [12] investigated the full transition from ballistic to diffusive Brownian motion of small particles in water, observing the behavior of a single particle in an optical trap. Experiments conducted make it possible to verify the model