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Diffusion Constant of a Polymer Chain in Biomembranes

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Abstract. — The diffusion constant of a polymer chain moving in a biomembrane is calculated within a two-dimensional hydrodynamical model coupled to an ambient fluid through the momentum dissipation mechanism. The obtained diffusion constant depends on the polymer size logarithmically and algebraically for the weak and strong coupling limits, respectively.

In a simple model of the diffusion of macromolecules such as proteins made of polymer chains in a biomembrane, a lipid bilayer can be regarded as an infinitely thin sheet of viscous fluid. These macromolecules move laterally in the fluid sheet as Brownian particles due to the forces exerted by the surrounding lipid molecules. In general, Brownian motion is uniquely characterized by a diffusion constant D which is connected with the friction coefficient ζ through the well-known Einstein relation $D = k_B T / \zeta$ (k_B is the Boltzmann constant and T the temperature). As given by the Stokes formula, ζ in a three-dimensional viscous fluid can be obtained from a hydrodynamical argument [1].

However, in a two-dimensional fluid, such as the problem of a flow passing an infinitely long moving cylinder, the hydrodynamics is not very simple. Once we neglect the convective acceleration term in the Navier-Stokes equation, we face the Stokes paradox; the fluid which follows the moving cylinder cannot be at rest at large distances from the cylinder [1]. Even if the convective acceleration term is partly included in the Oseen approximation, we are confronted with the breakdown of the linear relation between the velocity of the cylinder and the drag force acting on it [2].

Actually, the Stokes paradox does not exist in real biomembranes. This is because a lipid bilayer is not an isolated fluid but it is surrounded by adjacent water. Hence the total momentum of the two-dimensional fluid membrane is *not* a conserved quantity and it leaks into the surrounding water being a three-dimensional fluid. Saffman and Delbrück discussed the motion of a cylinder of finite thickness in a membrane in the limit of large membrane viscosity

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by a singular perturbation technique [3,4] They predicted that the translational diffusion constant of the cylinder depends logarithmically on its radius (see later Eq. (12) and Ref. [5] for further arguments). The momentum transfer from the polar heads of the lipid molecules to the water molecules would be purely of molecular nature. Although it is unclear whether such a momentum leakage mechanism can be described by the hydrodynamic boundary condition at the lipid-water interface, the crucial point is the fact that the momentum in the membrane dissipates.

On the basis of these considerations, Izuyama and coworkers proposed a simplified version of the two-dimensional hydrodynamical model [6-9]. In their model, the momentum leak is simply represented by a phenomenological relaxation parameter Γ which should be inversely proportional to the coupling strength between the membrane and the outer fluid. The linearized hydrodynamic equations representing the total momentum decay are [8,9]

$$\rho \frac{\partial \mathbf{v}(\mathbf{r}, t)}{\partial t} - \eta \nabla^2 \mathbf{v}(\mathbf{r}, t) + \text{grad } p(\mathbf{r}, t) + \Gamma \mathbf{v}(\mathbf{r}, t) = \mathbf{F}(\mathbf{r}, t), \quad (1)$$

and the incompressibility condition $\text{div } \mathbf{v}(\mathbf{r}, t) = 0$. In the above, $\mathbf{v}(\mathbf{r}, t)$ and $p(\mathbf{r}, t)$ are the velocity and pressure at space point \mathbf{r} at time t , the constants ρ and η are the density and dynamic viscosity of the lipid membrane, respectively. $\mathbf{F}(\mathbf{r}, t)$ represents any external force acting on the membrane, including Brownian forces. (Notice that both ∇^2 and grad are two-dimensional operators) If we start from this model, the outer fluid can be excluded from our consideration. Physically speaking, the term $\Gamma \mathbf{v}$ in equation (1) introduces the screening effect of the hydrodynamic interaction characterized by the screening length

$$\xi = (\eta/\Gamma)^{1/2}, \quad (2)$$

and hence equation (1) is free from the Stokes paradox. The same equation as equation (1) was also proposed for a membrane associated with a rigid substrate [10] The corresponding experiment has been done by the same group [11].

Brownian dynamics of polymer chains in a *pure* two-dimensional system was previously discussed by Muthukumar [12]. He showed that the mean square displacement of a *monomer* obeys the diffusive law and the square of the hydrodynamic screening length decays exponentially at very high polymer concentrations. In this article, we comment that the screening effect does exist in real biomembranes even for the dilute polymer limit because of the above reasons. We shall also give an explicit form of the diffusion constant of a single *polymer* chain using equation (1) and discuss its polymer size dependence.

The conformation of a single chain is represented by the set of $(N + 1)$ position vectors $\{\mathbf{R}_n\} \equiv (\mathbf{R}_0, \dots, \mathbf{R}_N)$. Following the book by Doi and Edwards [13], we assume that the typical hydrodynamic disturbances in the membrane relax much faster than the chain conformation. Within the preaveraging approximation, the equilibrium value of the mobility matrix is expressed as $\langle \mathbf{H}_{nm} \rangle = h(n - m)\mathbf{I}$, where $\langle \cdot \rangle$ denotes the average over the equilibrium distribution function, \mathbf{I} is the unit tensor ($I_{\alpha\beta} = \delta_{\alpha\beta}$) and

$$\begin{aligned} h(n - m) &= \\ &= \left\langle \int \frac{d^2k}{(2\pi)^2} \frac{\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}}{\eta(k^2 + \xi^{-2})} \exp\{i\mathbf{k} \cdot [\mathbf{R}_n - \mathbf{R}_m]\} \right\rangle \end{aligned} \quad (3)$$

$$\begin{aligned} &= \frac{1}{4\pi\eta} \int_0^\infty dk \frac{k}{k^2 + \xi^{-2}} \exp[-b^2 k^2 |n - m|/4] \\ &= \frac{-1}{8\pi\eta} \exp\left(\frac{b^2 |n - m|}{4\xi^2}\right) \text{Ei}\left(-\frac{b^2 |n - m|}{4\xi^2}\right). \end{aligned} \quad (4)$$

In the above, $\hat{\mathbf{k}}$ is a unit vector parallel to \mathbf{k} , b is the effective bond length and $\text{Ei}(-z)$ is the exponential integral function defined by

$$\text{Ei}(-z) = - \int_z^\infty dt \frac{e^{-t}}{t}. \quad (5)$$

In calculating equation (4), we have assumed that the distribution of $\mathbf{r}_{nm} = \mathbf{R}_n - \mathbf{R}_m$ is Gaussian. For $\xi \rightarrow \infty$, equation (4) diverges as expected.

Then the diffusion constant of a polymer chain can be simply calculated as

$$\begin{aligned} \frac{D_p}{k_B T} &= \frac{1}{\zeta} = \frac{1}{N^2} \int_0^N dn \int_0^N dm h(n-m) \\ &= \frac{1}{4\pi\eta} \frac{1}{x^4} [(1+x^2)(2 \log x + \gamma) - x^2 - \exp(x^2)\text{Ei}(-x^2)], \end{aligned} \quad (6)$$

where $x \equiv (b^2 N / 4\xi^2)^{1/2} \equiv R_p / \xi$ (R_p being the Gaussian polymer size) and γ is Euler's constant $\gamma = 0.5772 \dots$. This is the main result of this paper. Although the excluded volume effect was taken into account in reference [12], we have not considered this problem here for the sake of simplicity, the main results would not be changed as far as results are presented in terms of the polymer size R_p .

In the weak coupling limit ($x \ll 1$), where the rate of momentum dissipation to the surrounding medium is small, the diffusion constant equation (6) reduces to

$$\frac{D_p}{k_B T} \approx \frac{1}{4\pi\eta} \left(\log \frac{\xi}{R_p} + \frac{3}{4} - \frac{\gamma}{2} \right). \quad (7)$$

In this limit, D_p depends only weakly (logarithmically) on the polymer size. In the strong coupling limit ($x \gg 1$), on the other hand, the momentum dissipates rapidly from the membrane to the surrounding medium and equation (6) gives

$$\frac{D_p}{k_B T} \approx \frac{1}{4\pi\eta} \left(\frac{\xi}{R_p} \right)^2, \quad (8)$$

neglecting a logarithmic correction. In contrast to the weak coupling limit, D_p depends now strongly (algebraically) on R_p .

These results should be compared with the translational diffusion constant of a cylinder (radius R_c) moving in a two-dimensional fluid with momentum decay. According to the calculations in References [8-10], the result is given as

$$\frac{D_c}{k_B T} = \frac{1}{4\pi\eta} \left(\frac{y^2}{4} + \frac{yK_1(y)}{K_0(y)} \right)^{-1}, \quad (9)$$

where $y = R_c / \xi$, $K_0(z)$ and $K_1(z)$ are the modified Bessel functions of the second kind of order zero and one, respectively. In the weak coupling limit ($y \ll 1$), equation (9) becomes

$$\frac{D_c}{k_B T} \approx \frac{1}{4\pi\eta} \left(\log \frac{2\xi}{R_c} - \gamma \right), \quad (10)$$

whereas in the strong coupling limit ($y \gg 1$) one finds

$$\frac{D_c}{k_B T} \approx \frac{1}{\pi\eta} \left(\frac{\xi}{R_c} \right)^2. \quad (11)$$

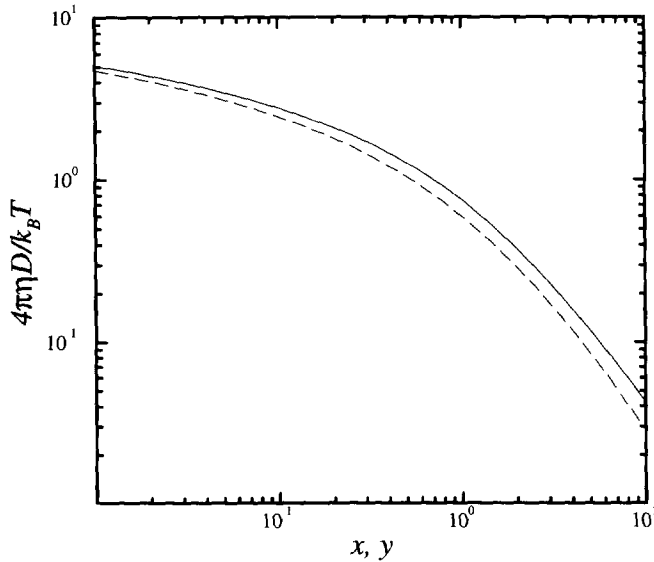


Fig. 1. — Plot of the dimensionless diffusion constants $4\pi\eta D_p/k_B T$ (solid curve) and $4\pi\eta D_c/k_B T$ (dashed curve) versus $x = R_p/\xi$ and $y = R_c/\xi$, respectively.

The dimensionless diffusion constants $4\pi\eta D_p/k_B T$ (Eq. (6)) and $4\pi\eta D_c/k_B T$ (Eq. (9)) are plotted in Figure 1 versus $x = R_p/\xi$ and $y = R_c/\xi$, respectively.

Saffman and Delbrück considered a system where a membrane of dynamic viscosity η and thickness h is surrounded by a three-dimensional fluid which has lower dynamic viscosity η' satisfying $\eta' \ll \eta$ [3]. It can be shown that their result for the diffusion constant of a cylinder

$$\frac{D_c}{k_B T} = \frac{1}{4\pi\eta h} \left(\log \frac{h\eta}{R_c\eta'} - \gamma \right), \quad (12)$$

coincides with equation (10) by putting

$$\Gamma = \eta \left(\frac{2\eta'}{h\eta} \right)^2, \quad (13)$$

apart from h in the denominator of equation (12). By inserting typical values for membranes immersed in water, $\eta \simeq 1$ P, $\eta' \simeq 0.01$ P, $h \simeq 5$ nm and $R_c \simeq 2$ nm, one can estimate $y = 2R_c\eta'/h\eta \simeq 10^{-2}$, which is quite small supporting the assumption $y \ll 1$. However, this does not guarantee the weak coupling condition in actual biomembranes, since the momentum leak arises from molecular processes in the strongly coupled head group and water molecules.

Finally by noticing that \hat{r}_{nm} is independent of $|\mathbf{r}_{nm}|$ in equation (3), $h(n-m)$ can be also written as

$$h(n-m) = \frac{1}{4\pi\eta} \langle K_0(|\mathbf{R}_n - \mathbf{R}_m|/\xi) \rangle. \quad (14)$$

Then the diffusion constant is expressed as

$$\frac{D_p}{k_B T} = \frac{1}{4\pi\eta} \int_0^N \frac{dn}{N} \int_0^N \frac{dm}{N} \langle K_0(|\mathbf{R}_n - \mathbf{R}_m|/\xi) \rangle, \quad (15)$$

which corresponds to the two-dimensional analog of the Kirkwood formula [13]. This expression is rigorous and leads to the same result as equation (6) after evaluating the average.

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