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Effect of flexoelectricity on the curvature elasticity of the membrane

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The contribution of flexoelectricity to the curvature elastic modulus for a symmetric lipid bilayer is calculated. The cases of permitted and forbidden charge exchange between the electrolyte on both sides of the membrane are discussed. On the basis of a simplified model of the lipid bilayer, an estimate of the difference of the moduli corresponding to these two cases is made.

1. Introduction

The influence of the flexoelectric effect on the value of the curvature elastic modulus of a membrane has been investigated in several works [1–3]. In the first of these, assuming that the membrane flexoelectricity is due entirely to dipoles, situated in the dielectric part of the bilayer the flexoelectric effect contribution to the curvature elasticity modulus of the membrane was calculated. Winterhalter and Helfrich [2] solved the same problem for the case when the flexoelectricity is due only to the double layers on both sides of the membrane, without dealing explicitly with a flexocoefficient. Pelity and Prost [3] consider the electric energy of a layer of a bent smectic with a non-zero flexocoefficient.

The aim of the present work is to take into account the influence of the redistribution of the electrolyte charges on the bending elasticity of the lipid bilayer.

2. Definition of the flexocoefficient of a symmetric membrane

According to Petrov [4], who was the first to deal with the flexoelectric effect in membranes, upon deformation the membrane is polarized in the same way as a thin layer of a nematic liquid crystal. He also introduced the flexocoefficient as a phenomenological quantity. This is the coefficient of proportionality between the total curvature of the membrane at a given point and the surface density of the surface polarization at this point [4]. Here we define the flexocoefficient through the measurable potential jump ΔU across the deformed membrane.

Let us consider a real flat symmetric tension free membrane with negligible transverse conductivity. Let the membrane be embedded in an electrolyte, having finite conductivity. We restrict our attention to the deformations of the membrane having the property of not changing the hydrostatic pressure on both sides. The surface inside the membrane, locally retaining its area after this deformation, is called neutral surface. We discuss deformations with the property that at each point of the

neutral surface its total curvature c_{tot} is contant. Here

$$c_{tot} = \tfrac{1}{2}(c_1 + c_2)$$

where

$$c_1 = \frac{1}{R_1} \quad \text{and} \quad c_2 = \frac{1}{R_2},$$

R_1 and R_2 are the radii of the principal curvatures of the neutral surface at this point. The deformations are performed under the condition that there is no exchange of charge between the electrolyte on either side. Upon the deformation of the membrane a potential ΔU across the membrane results which can be written as

$$\Delta U = \frac{f}{\varepsilon_0}(c_1 + c_2). \tag{1}$$

The coefficient f defined in this way is called the flexocoefficient of the membrane. We use the expression $(c_1 + c_2)$ instead of $\frac{1}{2}(c_1 + c_2)$ because of tradition authors dealing with the flexoelectric as well as the elastic properties of the membrane prefer to use this expression). The question arises as to what would happen if $(c_1 + c_2)$ was not a constant over the whole membrane. Then the potential ΔU will depend on the average value of $(c_1 + c_2)$ over the whole membrane, i.e. it will not be a local quantity.

3. Relations between the curvature elastic moduli of the membrane and its flexocoefficient

The expression

$$\mathbf{g}_c = \tfrac{1}{2}k_c(c_1 + c_2 - c_0)^2 + \bar{k}_c c_1 c_2, \tag{2}$$

for the surface density g_c of the elastic energy of curvature was proposed by Helfrich [5] where c_0 is the spontaneous curvature related to the asymmetry of the membrane, k_c and $\bar{k}_c$ are the curvature elastic modulus and the saddle splay curvature elastic modulus, respectively. We deal only with symmetric membranes, i.e. $c_0 = 0$. This expression presupposes that g_c is a local function of c_1 and c_2. We have shown, that if $f \neq 0$, ΔU is not a local function of the curvatures. But g_c is related to ΔU and should not be local. To avoid this difficulty, we consider here the case of a spherical deformation of the membrane, when g_c always exists; Then

$$c_1 = c_2 = c, \tag{3}$$

$$g_c = (2k_c + \bar{k}_c)c^2 \tag{4}$$

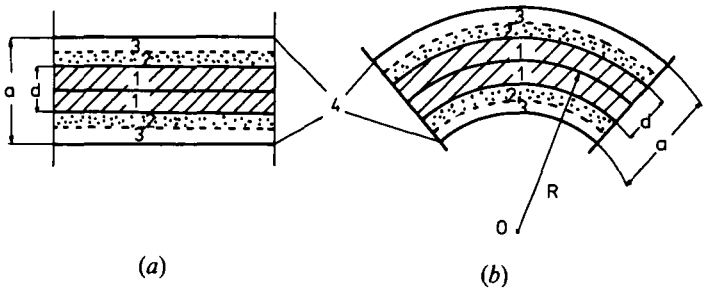
and we define

$$K = 2k_c + \bar{k}_c. \tag{5}$$

The value of K depends on the conditions under which the membrane is deformed:

(*a*) whether the exchange of molecules between the two monolayers comprising the bilayer is permitted or not (free and blocked flip-flop);

(*b*) whether the exchange of charge between the two electrolyte media separated by the membrane is allowed or not. This exchange can be achieved through an outer circuit, connecting the two electrolyte media separated by the membrane or through the membrane itself due to its finite conductivity.



A simple but realistic model of the membrane. It consists of a dielectric layer 1 of thickness d, two double layers 2 and part of the electrolyte adjacent to them 3. The boundaries 4 of the membrane are parallel to the midplane of the dielectric layer at distances $a/2$ from it, far enough from the double layers. *a*, flat membrane; *b*, the same membrane after its spherical deformation with radius of curvature R.

In the present work we try to describe the two cases in (*b*). The results obtained are valid both for free and blocked flip-flop.

The quantities referring to prohibited or allowed exchange of charge between the two electrolyte media separated by the membrane are denoted by the superscripts u and i, respectively. One of the aims of this work is to find a proper expression for the difference $(K^u - K^i)$. In order to do this, we use a simplifed but realistic model of the lipid bilayer (see the figure). We assume that the bilayer consists of a dielectric part having a thickness d and dielectric constant ε_d and adjacent to it regions of the electrolyte, comprising the double layers on both sides of the membrane. The dielectric part includes the hydrophobic chains of the amphiphilic molecules and the part of their hydrophilic heads where the electrolyte cannot penetrate. The neutral surface is assumed to coincide with the middle surface of this dielectric layer. The density of the ions in the electrolyte is assumed to be sufficiently high. In such a case the Debye–Hückel approximation is valid and the potential $U(\mathbf{r})$ satisfies the linearized Poisson–Boltzmann equation in the electrolyte;

$$\nabla^2 U(\mathbf{r}) = \frac{1}{b^2} U(\mathbf{r}), \tag{6}$$

where ∇^2 is the laplacian, $\mathbf{r}$ is the radius vector measured in a frame of reference with an origin coinciding with the centre of the curvature. In addition b is the Debye length of the flat double layer, defined by

$$b = \left(\frac{\varepsilon_e kT}{e^2} \frac{1}{\sum_i n_i z_i 2} \right)^{1/2};$$

here ε_e is the dielectric constant of the electrolyte, n_i is the concentration of the ions of the ith kind and z_i is the valence of the ions of the ith kind. Let $r = |\mathbf{r}|$; it is convenient to introduce a new, auxiliary variable $t = r - R$, where R is the radius of curvature of the neutral surface and t is the distance of the point with a radius vector $\mathbf{r}$ to the neutral surface. Then the electric double layers comprise points with coordinates $|t| > d/2$. If the membrane is spherically deformed when the exchange of charge is forbidden some distribution of the three dimensional density of the electric charge $q^u(t, c)$ will be established. As a result a non-zero transmembrance potential

drop will be formed. If the exchange of electrolyte charge is permitted it must lead to zero equilibrium potential difference between the two regions of the bulk solution separated by the membrane. In this case another distribution $q^i(t, c)$ will appear in the electrolyte where

$$q^i(t, c) = q^u(t, c) + \Delta q(t, c).$$

$\Delta q(t, c)$ will create some contribution $\Delta U'(c)$ to the potential difference across the membrane with the property $\Delta U'(c) = -\Delta U(c)$ where $\Delta U(c)$ corresponds to the case of forbidden exchange of electric charges. When the circuit, connecting the electrolyte on the two sides of the membrane, is turned on, some charge $\sigma(c)$ per unit area of the bilayer will pass through it after the bending and some energy E will be released due to the current associated with this charge. This energy is proportional to the area of the membrane. We denote the surface densities of the energies of curvature of the membrane in the cases of forbidden and permitted exchange of charges by g_c^u and g_c^i, respectively. Then

$$\Delta g_c = g_c^u - g_c^i = (K^u - K^i)c^2, \tag{7}$$

where Δg_c is equal to the thermal energy per unit area of the membrance, released in the outer circuit after turning it on. This energy is equal to $-\frac{1}{2}\sigma\Delta U$. In the proposed model σ is

$$\sigma(c) = -\frac{2f}{(\varepsilon_0 d/\varepsilon_d) + (2\varepsilon_0 b/\varepsilon_e)}\, c. \tag{8}$$

For a membrane with $S = 1$ the thermal energy E, released in the outer circuit is

$$E(c) = \frac{2f^2}{\varepsilon_0[(\varepsilon_0 d/\varepsilon_d) + (2\varepsilon_0 b/\varepsilon_e)]}\, c^2. \tag{9}$$

This quantity is equal to the difference between the energies of bending for forbidden and permitted charge exchange. The value given by equation (9) is always positive. This means that the work of bending for permitted charge exchange is less than the work for forbidden charge exchange. Comparing equations (7) and (9), we conclude that

$$K^u - K^i = \frac{2f^2}{\varepsilon_0[(\varepsilon_0 d/\varepsilon_d) + (2\varepsilon_0 b/\varepsilon_e)]}. \tag{10}$$

The quantity $\bar{k}_c$ must be the same for the two cases in question because at pure saddle splay deformation ($c_1 + c_2 = 0$) ΔU must be zero. Consequently

$$K^u - K^i = 2(k_c^u - k_c^i) \tag{11}$$

and

$$k_c^u - k_c^i = \frac{f^2}{\varepsilon_0[(\varepsilon_0 d/\varepsilon_d) + (2\varepsilon_0 b/\varepsilon_e)]}. \tag{12}$$

4. Discussion

Equation (12) shows that the bending modulus when charge exchange occurs is less in comparison with the binding modulus for forbidden charge exchange. Such a result is quite natural because the possibility of transmembrane redistribution of

electrolyte charge gives an additional degree of freedom to the system comprising the membrane with its two adjacent electrical double layers. After membrane bending this degree of freedom allows the relaxation of the energy of the system. Consequently the total thermodynamical work needed to bend the membrane will be less than the work when this degree of freedom does not exist.

One of the most convenient ways to estimate experimentally the bilayer bending modulus is the analysis of thermal fluctuations of the lipid vesicle structure [6]. In the light of the results of the present work the question arises about the type of bending modulus measured in these experiments. The characteristic time of the thermal fluctuations is quite short (some seconds for giant vesicles with diameters of the order of $10\,\mu$m) and the transmembrane redistribution of electrical charge is presumably impossible. At the same time the lateral charge redistribution on one side of the membrane is a very fast process. Such lateral charge redistribution keeps the electrical potential constant along each side of the membrane. The mean value of the potential difference between the electrolytes inside and outside the vesicle must be equal to zero, because the measurement of the amplitudes of the fluctuations is supposed to be made a long time after the formation of the vesicle, when electrical equilibrium is already attained. The fluctuations of the radius of the vesicle are much less than the radius itself. Consequently for each moment of time the averaged value of the curvature over the whole vesicle is constant, equal with precision of higher order to the mean vesicle curvature, and the potential difference between the inner and outer electrolyte of the vesicle does not fluctuate and is equal to zero. As a result the fluctuations of the membrane can be considered locally as fluctuations at condition of zero transmembrane potential. Similar effects have been considered in an earlier work [7]. It has been shown there that for membrane fluctuations of quasispherical lipid vesicles the lateral lipid redistribution effectively replaces the flip-flop exchange between the monolayers. In this way we can conclude that the bending modulus measured in the experiments with fluctuating lipid vesicles corresponds to the case of free transmembrane charge exchange and free flip-flop.

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