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The electric part of the curvature elasticity of a membrane and its relation to flexoelectricity

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The contribution to the curvature elastic modulae k_c and $\bar{k}_c$ of the spontaneous polarization of the dielectric part of the membrane upon bending and that of the flexoeffect due to the double layers, adjacent to the membrane is calculated. It is shown that there is no simple relation between the flexocoefficient of the membrane and the electrostatic contribution to these modulae.

1. Introduction

The flexoeffect in membranes has been well investigated [1–5]. The flexocoefficient f is the coefficient of proportionality between the potential difference ΔU on both sides of the deformed membrane and (c_1+c_2):

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

where ε_0 is the dielectric constant of vacuum. Here (c_1+c_2) is the doubled mean curvature at a certain point of the deformed membrane (c_1 and c_2 are the main curvatures at that point) and we suppose this curvature does not vary in different points of the membrane. The surface density g_c of the elastic free energy is related to the main curvatures of a symmetric membrane by [6]

$$g_c=\frac{k_c}{2}(c_1+c_2)^2+\bar{k}_c c_1 c_2. \tag{2}$$

Several investigations aimed at describing the effect of flexoelectricity on k_c and $\bar{k}_c$ [4, 7, 8] have been carried out. Without talking explicitly of a flexocoefficient Winterhalter and Helfrich [7] have found a correlation between the surface charge (associated with the flexocoefficient due to the double layers of the membrane) and k_c and $\bar{k}_c$. Pelity and Prost [8] have calculated the electric correction to the elastic modulae of a membrane with two double layers and a given flexocoefficient.

The elastic modulae k_c and $\bar{k}_c$ can be decomposed according to

$$k_c=\Delta k_c^{\mathrm{el}}+k_c^*,$$

$$\bar{k}_c=\Delta \bar{k}_c^{\mathrm{el}}+\bar{k}_c^*,$$

where the electrostatic terms Δk_c^{el} and $\Delta \bar{k}_c^{\mathrm{el}}$ are due to the non-zero charge density throughout the membrane, whereas k_c^* and $\bar{k}_c^*$ are due to the inter- and intramolecular interactions, not having an electrostatic origin (van der Waals forces, exchange

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interactions, etc.). In the present work on the basis of a concrete model of a membrane we calculate precisely the electrostatic terms Δk_c^{el} and $\Delta \bar{k}_c^{\mathrm{el}}$. Our results show that there is not an exact relation between the flexocoefficient of the membrane and the electrostatic terms of the elastic modulae.

2. The model

We suppose that the membrane consists of a dielectric layer with constant dielectric permittivity ε and thickness d, comprising the non-polar chains of the lipid molecules and eventually a part of the polar heads, where the electrolyte cannot penetrate, and two adjacent double layers, built from the surface charge on the dielectric borders and the respective counterion diffuse layers in the electrolyte. We consider the case of high charge concentration, when the Debye–Hückel approximation can be used. In this work we deal only with symmetric membranes (with zero spontaneous curvature). Since we are interested in the curvature elastic modulae k_c and $\bar{k}_c$ we consider only two deformations—cylindrical and spherical. In both cases the curvature of the midsurface, dividing the dielectric layer into two layers with thickness $d/2$ are measured. This surface does not change its area in the process of deformation. A frame of reference xyz with an origin O that lies on the midsurface and with a z axis that is perpendicular to the midsurface (before and after the deformation) is introduced. Later on, all the quantities are considered in this frame of reference at $x=0$ and $y=0$. Because only flat, cylindrical and spherical deformations are considered all the vectorial quantities have directions along the z axis.

In an earlier work [3] it was shown that there are two types of elastic modulae, corresponding to the cases of permitted or forbidden charge exchange between the electrolyte on both sides of the membrane. First we consider the case of forbidden charge exchange. Charge exchange is forbidden if there is no electric link between the two electrolyte media and each of the monolayers is neutral. When it is permitted $\Delta U=0$. If the dielectric layer is an ideal insulator charge exchange is forbidden; this is the case we begin with. The results for permitted charge exchange will be presented in the discussion. In further considerations the discrete character of the charges will not be taken into account.

We suppose, that the dielectric layer in its undeformed state is characterized by a certain initial polarization $\mathbf{p}(z, c_1=0, c_2=0)=\mathbf{p}_0(z)$. Since we consider a symmetric membrane:

$$\mathbf{p}_0(z)=-\mathbf{p}_0(-z). \tag{3}$$

Let n_1 and n_2 be the number of lipid molecules in the first and the second monolayer per unit area of the midsurface of the curved bilayer. Let $2n_0$ be the number of molecules per unit area of the flat bilayer. Following Helfrich [6], we introduce the flip-flop coefficient

$$x=(n_2-n_1)/2n_0.$$

Decomposing x in a series with respect to the curvatures c_1 and c_2 we obtain that $x=\alpha(c_1+c_2)+o(c_1^2, c_2^2, c_1c_2)$. The coefficients in front of the second order curvature are equal to zero because of the membrane symmetry; the third and the higher order terms do not influence the calculated quantities. The case of blocked flip-flop corresponds to $\alpha=0$ and the case of free flip-flop to $\alpha=\alpha_0$. α_0 can be determined either experimentaly or theoretically after considering all the inter- and intramolecular interactions, which is not the aim of the present work and so it will be assumed to be a given parameter. The results for blocked, and free flip-flop will be obtained by the substitution $\alpha=0$ and $\alpha=\alpha_0$ respectively.

Upon deformation the polarization $\mathbf{p}_0(z)$ changes. Its second order approximation with respect to the curvature can be written as

$$\mathbf{p}(z, c_1, c_2, \alpha) = \mathbf{p}_0(z) + \gamma_1(z, \alpha)(c_1 + c_2) + \gamma_2(z, \alpha)(c_1 + c_2)^2 + \gamma_3(z, \alpha)c_1c_2. \tag{4}$$

Membrane symmetry can be expressed by

$$\mathbf{p}(z, c_1, c_2, \alpha) = -\mathbf{p}(-z, -c_1, -c_2, \alpha). \tag{5}$$

Consequently:

$$\left.\begin{aligned} \gamma_1(z, \alpha) &= \gamma_1(-z, \alpha), \\ \gamma_2(z, \alpha) &= -\gamma_2(-z, \alpha), \\ \gamma_3(z, \alpha) &= -\gamma_3(-z, \alpha). \end{aligned}\right\} \tag{6}$$

The over-all electric field in the dielectric layer is given by

$$\mathbf{E}(z, c_1, c_2, \alpha) = -\frac{\mathbf{p}(z, c_1, c_2, \alpha)}{\varepsilon}. \tag{7}$$

From now on we will consider the projections of these vectors on the z axis of the defined frame of reference. Because of the membrane symmetry in the undeformed state the electric charge surface densities on both dielectric borders are equal and will be denoted by σ_0.

The flexocoefficient f can be presented as a sum of two terms, f_{diel}, which is due to the dielectric medium and f_{dl}, which is due to the electric double layers:

$$f = f_{\text{diel}} + f_{\text{dl}}. \tag{8}$$

As shown in a previous work [5] (see the Appendix)

$$f_{\text{dl}}(\alpha) = \frac{\varepsilon_0 \sigma_0}{\varepsilon_w \kappa}(d - 2\alpha + 1/\kappa), \tag{9}$$

where ε_w is the dielectric constant of the electrolyte solution and κ is the reciprocal value of the Debye length. Using equations (1) and (4) we find

$$f_{\text{diel}}(\alpha) = \frac{\varepsilon_0}{\varepsilon} \int_{-d/2}^{d/2} \gamma_1(z, \alpha)\, dz, \tag{10}$$

where ε is the constant of the dielectric medium. The flexocoefficients are defined when $(c_1 + c_2)$ is constant [3]. If this is not fulfilled the potential difference ΔU will depend on the average value of $(c_1 + c_2)$ over the whole membrane [3]. The problem is further complicated when the gradients of the curvature are essential. This case requires a separate treatment, including gradient flexocoefficients. They will not be considered here, because they do not affect the values of k_c and $\bar{k}_c$.

3. Surface density of the electrostatic free energy of a flat membrane

This energy is a sum of the electrostatic energy of the dielectric layer and of the energy of the two double layers. The surface density of the energy of the dielectric medium g_0^{diel} is given by

$$g_0^{\text{diel}} = \int_{-d/2}^{d/2} \frac{[p_0(z)]^2}{2\varepsilon} dz. \tag{11}$$

The free energy of the two double layers per unit membrane surface g_0^{dl} is

$$g_0^{\mathrm{dl}}=2\int_0^{\sigma_0} U(\sigma)\,d\sigma=\frac{\sigma_0^2}{\varepsilon_w \kappa}, \tag{12}$$

where $U(\sigma)$ is the potential on the charged dielectric surface with surface charge density σ if the potential far from the membrane $U(\infty)=0$. The overall surface density of the free electrostatic energy is given by $g_0^{\mathrm{el}}=g_0^{\mathrm{diel}}+g_0^{\mathrm{dl}}$.

4. Surface density of the electrostatic free energy of a cylindrically deformed membrane

R is the radius of the midsurface of the cylindrically deformed membrane and $c=1/R$ is its curvature. In this case the polarization of the dielectric medium is

$$p_{\mathrm{cyl}}(z,c,\alpha)=p_0(z)+\gamma_1(z,\alpha)c+\gamma_2(z,\alpha)c^2. \tag{13}$$

The electrostatic energy of the dielectric per unit area of the neutral membrane surface $g_{\mathrm{cyl}}^{\mathrm{diel}}$ is

$$\begin{aligned} g_{\mathrm{cyl}}^{\mathrm{diel}}(c,\alpha)&=\frac{1}{2\varepsilon}\int_{-d/2}^{d/2} p_{\mathrm{cyl}}^2(z,c,\alpha)\left(\frac{R+z}{R}\right)dz \\ &=\frac{1}{2\varepsilon}\int_{-d/2}^{d/2} \{p_0^2(z)+c^2[2p_0(z)\gamma_1(z,\alpha)z+\gamma_1^2(z,\alpha)+2p_0(z)\gamma_2(z,\alpha)]\}\,dz. \end{aligned} \tag{14}$$

For a cylindrical deformation the surface charge densities on the inner (towards the axis of the cylinder) and on the outer border of the dielectric medium are given by

$$\left.\begin{aligned} \sigma_{\mathrm{cyl}}^{\mathrm{in}}(\alpha)&=\sigma_0\frac{1-\alpha c}{1-dc/2}=\sigma_0\left(1+\left(\frac{d}{2}-\alpha\right)c+\left(\frac{d^2}{4}-\frac{\alpha d}{2}\right)c^2\right) \\ &\text{and} \\ \sigma_{\mathrm{cyl}}^{\mathrm{out}}(\alpha)&=\sigma_0\frac{1+\alpha c}{1+dc/2}=\sigma_0\left(1-\left(\frac{d}{2}-\alpha\right)c+\left(\frac{d^2}{4}-\frac{\alpha d}{2}\right)c^2\right). \end{aligned}\right\} \tag{15}$$

Here the dependence of $\sigma_{cyl}^{\mathrm{in}}$ and $\sigma_{cyl}^{\mathrm{out}}$ on the change in the adsorption/desorption rate upon deformation is not taken into account [5]. In the present work we examine the case when the charge per molecule does not change upon deformation.

For $r\leqslant R_1$ the potential $U_{\mathrm{cyl}}^{\mathrm{in}}(r)$ with respect to the potential of the axis of the deformation is

$$U_{\mathrm{cyl}}^{\mathrm{in}}(r,\alpha)=\frac{\sigma_{\mathrm{cyl}}^{\mathrm{in}}(I_0(\kappa r)-1)}{\varepsilon_w \kappa I_1(\kappa R_1)} \tag{16}$$

and for $r\geqslant R_2$ the potential $U_{\mathrm{cyl}}^{\mathrm{out}}(r)$ with respect to the potential at $(r=\infty)$

$$U_{\mathrm{cyl}}^{\mathrm{out}}(r,\alpha)=\frac{\sigma_{\mathrm{cyl}}^{\mathrm{out}}\mathrm{K}_0(\kappa r)}{\varepsilon_w \kappa \mathrm{K}_1(\kappa R_2)}, \tag{17}$$

where r is the radial coordinate, measured from the axis of the deformation, I_i and K_i are ith order modified Bessel functions. The free electrostatic energy of the outer and the inner double layers per unit area of the dielectric border $g_{\mathrm{cyl}}^{\mathrm{out}}$ and $g_{\mathrm{cyl}}^{\mathrm{in}}$ are calculated by analogy to equations (12) as

$$\begin{aligned} g_{\mathrm{cyl}}^{\mathrm{in}}(\alpha) &= \frac{1}{2} U_{\mathrm{cyl}}^{\mathrm{in}}(R_1)\sigma_{\mathrm{cyl}}^{\mathrm{in}} = \frac{1}{2} \frac{(\sigma_{\mathrm{cyl}}^{\mathrm{in}})^2 (I_0 \kappa R_1) - 1)}{\varepsilon_w \kappa I_1(\kappa R_1)} \\ &= \frac{1}{2} \frac{(\sigma_{\mathrm{cyl}}^{\mathrm{in}})^2}{\varepsilon_w \kappa} \left(1 + \frac{1}{2\kappa} c + \left(\frac{d}{4\kappa} + \frac{3}{8\kappa^2}\right) c^2\right), \end{aligned} \tag{18}$$

$$\begin{aligned} g_{\mathrm{cyl}}^{\mathrm{out}}(\alpha) &= \frac{1}{2} U_{\mathrm{cyl}}^{\mathrm{out}}(R_2)\sigma_{\mathrm{cyl}}^{\mathrm{out}} = \frac{1}{2} \frac{(\sigma_{\mathrm{cyl}}^{\mathrm{out}})^2 \mathrm{K}_0(\kappa R_2)}{\varepsilon_w \kappa \mathrm{K}_1(\kappa R_2)} \\ &= \frac{1}{2} \frac{(\sigma_{\mathrm{cyl}}^{\mathrm{out}})^2)}{\varepsilon_w \kappa} \left(1 - \frac{1}{2\kappa} c + \left(\frac{d}{4\kappa} + \frac{3}{8\kappa^2}\right) c^2\right). \end{aligned} \tag{19}$$

The free energy of the double layers per unit area of the midsurface is given by

$$\begin{aligned} g_{\mathrm{cyl}}^{\mathrm{dl}}(c, \alpha) &= g_{\mathrm{cyl}}^{\mathrm{in}}\left(1 - \frac{cd}{2}\right) + g_{\mathrm{cyl}}^{\mathrm{out}}\left(1 + \frac{cd}{2}\right) \\ &= \frac{\sigma_0^2}{\varepsilon_w \kappa}\left[1 + \left(\frac{3}{8\kappa^2} + \alpha^2 + \frac{d^2}{4} - \alpha d + \frac{d}{2\kappa} - \frac{\alpha}{\kappa}\right) c^2\right]. \end{aligned} \tag{20}$$

The overall free energy of the electrostactic field per unit area of the midsurface $g_{\mathrm{cyl}}^{\mathrm{el}}$ is the sum of equations (14) and (20). The change of the free energy on deformation is

$$\Delta g_{\mathrm{cyl}}^{\mathrm{el}} = g_{\mathrm{cyl}}^{\mathrm{el}}(c) - g_0^{\mathrm{el}}.$$

But $\Delta g_{\mathrm{cyl}}^{\mathrm{el}}$ can be expressed by the correction Δk_c^{el} to the elastic modulus, which is due to the electrostatic interactions as $\Delta g_{\mathrm{cyl}}^{\mathrm{el}} = \frac{1}{2} \Delta k_c^{\mathrm{el}} c^2$. Thus we find

$$\Delta k_c^{\mathrm{el}} = \Delta k_c^{\mathrm{diel}} + \Delta k_c^{\mathrm{dl}},$$

where

$$\left.\begin{aligned} \Delta k_c^{\mathrm{diel}}(\alpha) &= \frac{1}{\varepsilon} \int_{-d/2}^{d/2} [2p_0(z)\gamma_1(z, \alpha)z + \gamma_1^2(z, \alpha) + 2p_0(z)\gamma_2(z, \alpha)]\, dz \\ &\text{and} \\ \Delta k_c^{\mathrm{dl}}(\alpha) &= \frac{\sigma_0^2}{\varepsilon_w \kappa}\left(\frac{3}{4\kappa^2} + 2\alpha^2 + \frac{d^2}{2} - 2\alpha d + \frac{d}{\kappa} - \frac{2\alpha}{\kappa}\right). \end{aligned}\right\} \tag{21}$$

Using equation (9) we have

$$\Delta k_c^{\mathrm{dl}}(\alpha) = \frac{f_{\mathrm{dl}}^2(\varepsilon_w \kappa)}{\varepsilon_0^2 (d - 2\alpha + 1/\kappa)^2}\left(\frac{3}{4\kappa^2} + 2\alpha^2 + \frac{d^2}{2} - 2\alpha d + \frac{d}{\kappa} - \frac{2\alpha}{\kappa}\right). \tag{22}$$

If $p_0 = 0$ and $\gamma_1 =$ constant we find

$$\Delta k_c^{\mathrm{diel}}(\alpha) = \frac{\gamma_1^2(z, \alpha)\, d}{\varepsilon}. \tag{23}$$

When $\gamma_1 =$ constant, equation (10) aquires the form

$$f_{\mathrm{diel}} = \frac{\varepsilon_0 \gamma_1 d}{\varepsilon}; \tag{24}$$

in this case we can write

$$\Delta k_c^{\mathrm{diel}} = \frac{f_{\mathrm{diel}}^2 \varepsilon}{\varepsilon_0^2 d}. \tag{25}$$

5. Surface density of the electrostatic free energy of a spherically deformed membrane

R is the radius of the midsurface of the spherically deformed membrane and $c = 1/R$ is its curvature. In this the polarization of the dielectric medium is

$$p_{\mathrm{sph}}(z, c, \alpha) = p_0(z) + \gamma_1(z, \alpha)2c + (4\gamma_2(z, \alpha) + \gamma_3(z, \alpha))c^2. \tag{26}$$

The respective electrostatic energy per unit area of the neutral membrane surface g^{diel} is

$$\begin{aligned} g_{\mathrm{sph}}^{\mathrm{diel}}(c, \alpha) &= \frac{1}{2\varepsilon} \int_{-d/2}^{d/2} p_{\mathrm{sph}}^2(z, c, \alpha) \left(\frac{(R+z)^2}{R^2} \right) dz \\ &= \frac{1}{2\varepsilon} \int_{-d/2}^{d/2} \{ p_0^2(z) + c^2 [p_0(z) z^2 + 8 p_0(z) \gamma_1(z, \alpha) z + 2 p_0(z)(4\gamma_2(z, \alpha) \\ &\quad + \gamma_3(z, \alpha)) + 4\gamma_1^2(z, \alpha)] \} \, dz. \end{aligned} \tag{27}$$

The surface charge densities on the inner (towards the sphere's centre) and on the outer border of the dielectric medium are

$$\left.\begin{aligned} \sigma_{\mathrm{sph}}^{\mathrm{in}}(\alpha) &= \sigma_0 \frac{1 - 2\alpha c}{1 - dc + d^2 c^2/4} = \sigma_0 \left(1 + (d - 2\alpha)c + \left(\frac{3d^2}{4} - 2\alpha d \right) c^2 \right) \\ &\text{and} \\ \sigma_{\mathrm{sph}}^{\mathrm{out}}(\alpha) &= \sigma_0 \frac{1 + 2\alpha c}{1 + dc + d^2 c^2/4} = \sigma_0 \left(1 + (d - 2\alpha)c + \left(\frac{3d^2}{4} - 2\alpha d \right) c^2 \right). \end{aligned}\right\} \tag{28}$$

The potential distributions inside and outside the membrane, $U_{\mathrm{sph}}^{\mathrm{in}}$ and $U_{\mathrm{sph}}^{\mathrm{out}}$, with respect to the potentials of the centre of the deformation and infinity are

$$U_{\mathrm{sph}}^{\mathrm{in}}(r, \alpha) = \frac{\sigma_{\mathrm{sph}}^{\mathrm{in}}}{\varepsilon_w \cosh(\kappa R_1)} \frac{R_1^2}{(\kappa R_1 - 1)} \left(\frac{\sinh(\kappa r)}{r} - \kappa \right), \tag{29}$$

$$U_{\mathrm{sph}}^{\mathrm{out}}(r, \alpha) = \frac{\sigma_{\mathrm{sph}}^{\mathrm{out}}}{\varepsilon_w} \frac{R_2^2}{\exp(-\kappa R_2)(1 + \kappa R_2)} \frac{\exp(-\kappa r)}{r}, \tag{30}$$

respectively. For the free energy of the double layers $g_{\mathrm{sph}}^{\mathrm{dl}}(c)$ per unit area of the neutral surface we obtain

$$\begin{aligned} g_{\mathrm{sph}}^{\mathrm{dl}}(c, \alpha) &= g_{\mathrm{sph}}^{\mathrm{in}}(\alpha) \left(1 - cd + \frac{c^2 d^2}{4} \right) + g_{\mathrm{sph}}^{\mathrm{out}}(\alpha) \left(1 + cd + \frac{c^2 d^2}{4} \right) \\ &= \frac{\sigma_0^2}{\varepsilon_w \kappa} \left[1 + \left(\frac{1}{\kappa^2} + 4\alpha^2 + \frac{3d^2}{4} - 4\alpha d + \frac{3d}{2\kappa} - \frac{4\alpha}{\kappa} \right) c^2 \right], \end{aligned} \tag{31}$$

where $g^{\text{in}}_{\text{sph}}$ and $g^{\text{out}}_{\text{sph}}$ are the free electrostatic energy for the two monolayers per unit layer of dielectric border,

$$g^{\text{in}}_{\text{sph}}(\alpha)=\frac{1}{2}U^{\text{in}}_{\text{sph}}(R_1)\sigma^{\text{in}}_{\text{sph}}=\frac{1}{2}\frac{(\sigma^{\text{in}}_{\text{sph}})^2}{\varepsilon_w\cosh(\kappa R_1)}\frac{R_1^2}{(\kappa R_1-1)}\left(\frac{\sinh(\kappa r)}{r}-\kappa\right)$$
$$=\frac{1}{2}(\sigma^{\text{in}}_{\text{sph}})^2\varepsilon_w\kappa\left(1+\frac{1}{\kappa}c+\left(\frac{d}{2\kappa}+\frac{1}{\kappa^2}\right)c^2\right), \tag{32}$$

$$g^{\text{out}}_{\text{sph}}(\alpha)=\frac{1}{2}U^{\text{out}}_{\text{sph}}(R_2)\sigma^{\text{out}}_{\text{sph}}=\frac{1}{2}\frac{(\sigma^{\text{out}}_{\text{sph}})^2R_2}{\varepsilon_w(\kappa R_2+1)}$$
$$=\frac{1}{2}\frac{(\sigma^{\text{out}}_{\text{sph}})^2R_2}{\varepsilon_w\kappa}\left(1-\frac{1}{\kappa}c+\left(\frac{d}{2\kappa}+\frac{1}{\kappa^2}\right)c^2\right). \tag{33}$$

The overall change of the free energy of the spherically deformed membrane per unit midsurface $\Delta g^{\text{el}}_{\text{sph}}$ is

$$\Delta g^{\text{el}}_{\text{sph}}(c,\alpha)=(2\Delta k_c+\Delta\bar{k}_c)c^2$$
$$=\frac{1}{2c^2\varepsilon}\int_{-d/2}^{d/2}[p_0(z)z^2+8p_0(z)\gamma_1(z,\alpha)z+2p_0(z)(4\gamma_2(z,\alpha)+\gamma_3(z,\alpha))$$
$$+4\gamma_1^2(z,\alpha)]\,dz+\frac{\sigma_0^2}{\varepsilon_w\kappa}\left(\frac{1}{\kappa^2}+4\alpha^2+\frac{3d^2}{4}-4\alpha d+\frac{3d}{2\kappa}-\frac{4\alpha}{\kappa}\right)c^2. \tag{34}$$

This equation enables us to find the electrostatic correction to the saddle splay deformation modulus $\Delta\bar{k}_c$ (having in mind equation (10))

$$\Delta\bar{k}_c=\Delta\bar{k}_c^{\text{diel}}+\Delta\bar{k}_c^{\text{dl}}$$

where

$$\Delta\bar{k}_c^{\text{diel}}(\alpha)=\frac{1}{2\varepsilon}\int_{-d/2}^{d/2}[p_0(z)z^2+2p_0(z)\gamma_3(z,\alpha)]\,dz$$

and

$$\Delta\bar{k}_c^{\text{dl}}(\alpha)=\frac{f_{\text{dl}}^2\varepsilon_w}{\varepsilon_0^2(d-2\alpha+1/\kappa)^2}\left(-\frac{1}{2\kappa^2}-\frac{d^2}{4}-\frac{d}{2\kappa}\right). \tag{35}$$

If $p_0=0$, then $\Delta\bar{k}_c^{\text{diel}}=0$.

6. Discussion

In the present work on the basis of a definite model we obtain exact results for the electrostatic contributions to the elastic modulae k_c and $\bar{k}_c$ in equations (21) and (35). The formulae presented correspond to the case of forbidden charge exchange between the electrolyte media on both sides of the membrane. Our results for k_c^{dl} and $\bar{k}_c^{\text{dl}}$ may be compared with those of Winterhalter and Helfrich [7]. In their model the sum of the surface charges per unit membrane area is not conserved upon spherical deformation. In our model this conversion is valid. That is why our results for $\bar{k}_c^{\text{dl}}$ differ from those of Winterhalter and Helfrich [7]. For $\alpha=d/2$ our result for Δk_c^{dl} coincides with theirs [7].

Expressions for the flexocoefficient are given by equations (9) and (10). Comparison of this formulae with equations (21) and (35) show that there is not a simple relation between f and k_c and $\bar{k}_c$. If we suppose that the polarization of the dielectric is homogeneous ($\gamma_1 = \text{constant}$) and the initial polarization $p_0 = 0$, Δk_c^{el} can be expressed directly by the two terms of the flexocoefficient (the sum of the right hand of equations (22) and (25)). Even in this case there is not a simple link between the overall flexocoefficient and the elastic modulus of deformation of the membrane.

Recently it was shown [3] that in the experimental investigations of fluctuating vesicles the elastic modulus for free transmembrane charge exchange and free flip-flop k_c^0 is measured. It is equal to

$$k_c^0(\alpha) = k_c(\alpha) - 2f^2(\alpha)\left[\varepsilon_0^2\left(\frac{d}{\varepsilon} + \frac{2/\kappa}{\varepsilon_w}\right)\right]^{-1},$$

where $k_c(\alpha)$ is the elastic modulus for forbidden transmembrane charge exchange. For egg yolk lecithin it is measured to be of the order of 10^{-19} J. The expression

$$(\Delta k_c^0(\alpha))^{\text{el}} = \Delta k_c^{\text{el}}(\alpha) - 2f^2(\alpha)\left[\varepsilon_0^2\left(\frac{d}{\varepsilon} + \frac{2/\kappa}{\varepsilon_w}\right)\right]^{-1}$$

is obtained on the basis of the proposed model electrostatic contribution to the elastic deformation modulus for permitted charge exchange between the two electrolyte media. For $p_0(z) = 0$, $\gamma_1 = \text{constant}$ and $\sigma_0 = 0$ it is

$$(\Delta k_c^0(\alpha))^{\text{el}} = \frac{f_{\text{diel}}^2(\alpha)\varepsilon}{\varepsilon_0^2 d} - 2f^2(\alpha)\left[\varepsilon_0^2\left(\frac{d}{\varepsilon} + \frac{2/\kappa}{\varepsilon_w}\right)\right]^{-1}.$$

We note that this result differs from that of Peity and Prost [8].

Now let us make some estimations of the calculated quantities. For $d \propto 30$ Å, $1/\kappa \propto 10$ Å, $\alpha \propto d/2$ and $\sigma_0 \propto 0{\cdot}1$ C/m^2 we find $\Delta k_c^{\text{dl}} \propto 10^{-19}$ J. The value of Δk_c^{diel} depends crucially on the value of f_{diel}; it is $\propto 10^{-18}$ J for $f_{\text{diel}} \propto 10^{-19}$ C and $\propto 10^{-20}$ J for $f_{\text{diel}} \propto 10^{-20}$ C. The term

$$2f^2\left[\varepsilon_0^2\left(\frac{d}{\varepsilon} + \frac{2/\kappa}{\varepsilon_w}\right)\right]^{-1},$$

which takes in the determination of k_c^0 depends in the same way on the overall flexocoefficient of the membrane.

The aim of this work is to calculate precisely the electrostatic parts of the bending elasticity of the membrane. Many of the introduced parameters are not measured yet, but we need to know all of them to make correct estimations.

One evident condition for the stability of a tension free membrane is that k_c^0 is positive. Our calculations show that there are values of the model's parameters for which Δk_c^{el} (and moreover $(\Delta k_c^0)^{\text{el}}$) can take negative values. If in spite of this the membrane is stable this means that either the membrane exists in some rippled state when the higher order curvature elasticity should be taken into account, or the contribution of the forces, not having an electrostatic origin is positive and greater in magnitude than that of the electrostatic forces.

Appendix

Here we derive formula (9) for the flexocoefficient d_{dl} due to the double layers of the membrane. Formally we can consider that in the model of the membrane, described here, the dielectric part is replaced by vacuum. We investigate the case of forbidden charge exchange between the two sides of the membrane. This means that for each double layer the surface charge is equal in value and opposite in sign to the sum of the charges in the diffusive layer.

To find the potential difference due to the double layers across the spherically deformed membrane we solve the Poisson equation $\nabla^2 U = -\rho/\varepsilon_w$ in the Debye–Hückel approximation for the inner and the outer electrolyte media:

$$\nabla^2 U = \kappa^2 U,$$

$$\kappa^2 = \frac{2n_0 e^2}{\varepsilon\varepsilon_0 kT},$$

where ∇^2 is the laplacian, κ is the reciprocal value of the Debye length, n_0 is the concentration of one type of ions in the electrolyte far from the membrane surface, and ε_w is the dielectric constant of the solution. The potential distribution across the membrane due to the electric double layers is given by the expression

$$U(r) = \begin{cases} \dfrac{\sigma_1 R_1^2}{\varepsilon_w \operatorname{ch}(\kappa R_1 - 1)} \dfrac{\operatorname{sh}(\kappa r)}{r} + \dfrac{\sigma_2 R_2}{\varepsilon_w(\kappa R_2 + 1)} - \dfrac{\sigma_1 R_1 \operatorname{th}(\kappa R_1)}{\varepsilon_w(\kappa R_1 - 1)}, & r < R_1, \\ \dfrac{\sigma_2 R_2}{\varepsilon_w(\kappa R_2 + 1)}, & R_1 < r < R_2, \\ \dfrac{\sigma_2 R_2^2}{\varepsilon_w(\kappa R_2 + 1)} \dfrac{\exp[-\kappa(r - R_2)]}{r}, & r < R_2, \end{cases}$$

where $R_1 = R - d/2$ and $R_2 = R + d/2$ are the radii of the inner and the outer vacuum layer surfaces, R is the radius of curvature of the midplane of the vacuum layer, d is the thickness of this layer, r is the current coordinate, σ_1 and σ_2 are the surface charge densities of its inner and outer surfaces. This expression assures the potential to vanish at $r = \infty$ and to have a finite value at $r = 0$. The potential jump, created by the deformed membrane, is

$$\Delta U = U(r = \infty) - U(r = 0),$$

$$\Delta U = -2\frac{\sigma_1 \kappa R_1^2}{\varepsilon\varepsilon_0 \operatorname{ch}(\kappa R_1)(\kappa R_1 - 1)} - \frac{\sigma_2 R_2}{\varepsilon\varepsilon_0(\kappa R_2 + 1)} + \frac{\sigma_1 R_1 \operatorname{th}(\kappa R_1)}{\varepsilon\varepsilon_0(\kappa R_1 - 1)}.$$

If we suppose that upon deformation the charge per lipid head does not change (the general case is considered in [5]) we have

$$\sigma_1(\alpha) = \sigma_0(1 + c(d - 2\alpha)),$$

$$\sigma_2(\alpha) = \sigma_0(1 - c(d - 2\alpha)).$$

Then the first order approximation of the potential difference with respect to the curvature is

$$\Delta U(\alpha) = \frac{2\sigma_0 c(d - 2\alpha + 1/\kappa)}{\varepsilon_w \kappa}.$$

According to equation (1) the flexcoefficient f is

$$f(\alpha)=\frac{\varepsilon_0\sigma_0(d-2\alpha+1/\kappa)}{\varepsilon_w\kappa}.$$

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