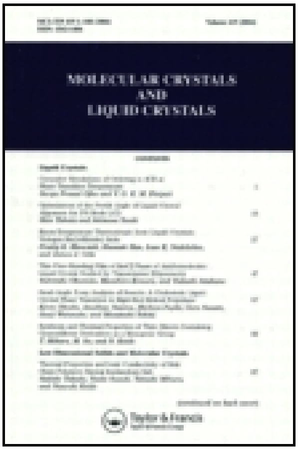

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Latest Theoretical and Experimental Investigations of the Flexoeffect in Membranes

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LATEST THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF THE FLEXOEFFECT IN MEMBRANES

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Abstract A new definition is given of the flexocoefficient of a symmetrical membrane. This quantity is expressed through the distribution of the charges along the thickness of the membrane. A relation is found between the value of the flexocoefficient and the difference between the curvature elasticity moduli at forbidden and permitted exchange of charges on both sides of the membrane. Results of experiments are presented for the influence of adsorbed ions on the value and the sign of the flexocoefficient.

INTRODUCTION

According to Petrov[1] when the membrane is deformed, it is polarized similarly to a thin layer of nematic liquid crystal. The same author introduced also the phenomenological quantity flexocoefficient. 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. The surface polarization of a given element of the membrane is a vector sum of all the dipoles in a volume including the real thickness of the membrane around this element. This idea was developed in a series of works recently reviewed[2]. For such a definition of the flexocoefficient there is no simple relation between its value and the potential jump on both sides of the membrane. On Figure 1 an illustration is given of the situation when at a deformation (e.g. spherical) of a piece of a membrane at a blocked flip-flop and constant dipole moment per head the sum of all the dipoles is zero while the potential jump across the membrane is not zero.

Starting from the idea described, a definition was given[3] connecting the flexocoefficient with the measurable potential jump after the membrane deformation. Based on this definition a relation was

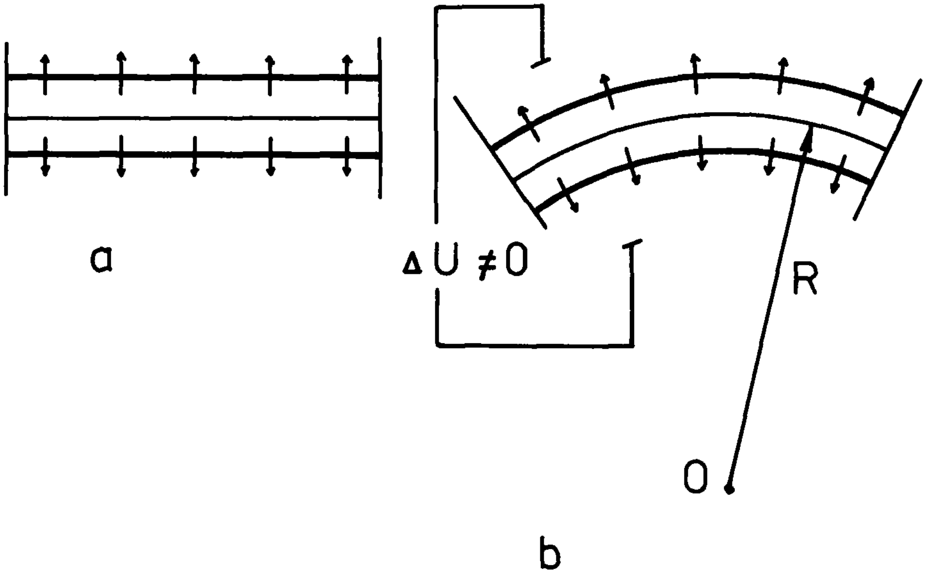

FIGURE 1 Schematic representation of the dipoles of the membrane before the deformation (a) and after the deformation (b) for the case of blocked flip-flop and independent of the curvature dipole per molecule. The sum of all dipoles is zero after the deformation but potential jump ΔU arises across the membrane.

found between the flexocoefficient and the distribution of the charges along the thickness of the membrane[4] as well as the value of the flexocoefficient and the difference between the curvature elasticity moduli at forbidden and permitted exchange of charges on both sides of the membrane.[3] Results of experiments are presented for the influence of adsorbed ions on the value and the sign of the flexocoefficient.[5] These results are compared with the theoretical predictions.

DEFINITION OF THE FLEXOCOEFFICIENT OF A SYMMETRICAL MEMBRANE

Let a real flat symmetrical membrane be given with zero tension, negligible transversal conductivity, area S and embeded in an electrolyte, having finite conductivity. We curve the membrane without changing the hydrostatic pressures on both of its sides. The surface inside the membrane, locally, keeping its area after this deformation, is called neutral surface. We consider deformations with the property that in each point of the neutral surface its total area c_{tot} is constant. Here $c_{tot}=\frac{1}{2}(c_1+c_2)$ where $c_1=\frac{1}{R_1}$ and $c_2=\frac{1}{R_2}$ and R_1 and R_2 are the radii of the principal curvatures of the neutral surface in this point. One deformation of this kind is the spherical deformation. If the contrary is not mentioned explicitly, in what follows spherically deformed membranes will be considered with $c_1=c_2=c$ (Figure 2). Let on both sides of the membrane at a distance far enough from it two electrodes E_1 and E_2 are situated. We will assume that the curvature of the membrane is positive if the center O of the curvature is to the side of the electrode E_1 and negative otherwise. The voltmeter V measures the potential of the electrode E_2 with respect to the potential of E_1. A circuit parallel to the voltmeter is connected consisting of an ampere-

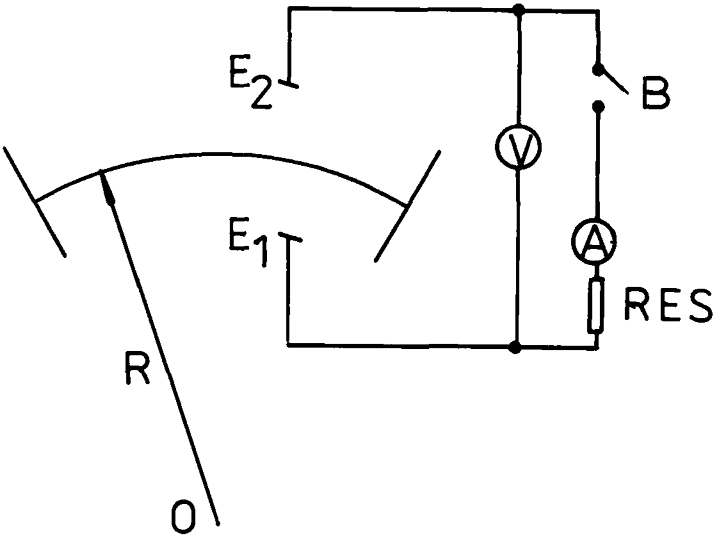

FIGURE 2 Principal set-up for the determination of the flexo-coefficient. Two electrodes are placed on both sides of the membrane at a distance far enough from it. The voltmeter V measures the potential of the electrode E_2 with respect to the potential of the electrode E_1. The curvature elastic moduli of the membrane are different for the cases of turned on and turned off switch B. If the membrane is curved at turned off B the energy released on the resistance RES and the total charge passing through the amperemeter after turning on B depend only on the curvature c of the membrane. c=1/R where R is the radius of the spherically curved membrane.

meter A, a switch B and a resistor RES. When B is turned on, the potentials of E_1 and E_2 become equal. Let the potentials of E_1 and E_2 be equal when the membrane is flat and let B be turned off. After the spherical deformation of the membrane the potential ΔU of E_2 with respect to this of E_1 can be presented as follows:

$$\Delta U = \frac{f}{\varepsilon_o} 2c \tag{1a}$$

where ε_o is the dielectric permitivity of the vacuum, and f is the defined by us flexocoefficient. In the more general case when $c_1 \neq c_2$ but c_1+c_2=const for all the deformed membrane, (1a) is transformed:

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

We use the expression c_1+c_2 instead of $\frac{1}{2}(c_1+c_2)$ because of tradition (the authors dealing with the flexoelectric as well as with the elastic properties of the membrane prefer to use this expression). If the membrane is infinitely thin, then the expression p:

$$p = f(c_1+c_2) \tag{2}$$

should give the polarization per unit area of this two-dimensional surface. A question arises what should happen if c_1+c_2 is not a constant over the surface of the deformed membrane. Then the potential ΔU will depend on the averaged value of this quantity on the whole surface of the membrane, i.e. it will not be a local quantity.

EXPRESSING THE FLEXOCOEFFICIENT THROUGH THE DISTRIBUTION OF THE CHARGE ALONG THE THICKNESS OF THE MEMBRANE

Expressing of this kind was done recently by Derzhanski.[4]

We deal again with a spherically deformed membrane. Boundaries of the membrane are supposed to be two surfaces parallel to the neutral one, situated on its two sides at distances a/2 from it. Here "a" is chosen large enough so that out of the boundaries the electrolyte is electrically, chemically, and mechanically homogeneous and isotropic.

Let R be the radius of curvature of the membrane and O the center of its curvature. We choose a frame of reference XYZ with an origin O. Because of the spherical symmetry, all the related to the membrane quantities will depend only on the modulus r of the the radius-vector $\vec{r}$ and on the curvature c=1/R of the membrane. Let q(r,c) be the three-dimensional density of the free charges inside the membrane, and $\vec{E}(\vec{r},c)$ the electric field there. $\vec{E}(\vec{r},c)$ can be presented as $E(r,c)\frac{\vec{r}}{r}$. The quantities q(r,c) and E(r,c) are different from zero if $R-\frac{a}{2}<r<R+\frac{a}{2}$. It is clear that the potential difference across the membrane ΔU is equal to:

$$\Delta U(c) = U(R + \frac{a}{2}) - U(R - \frac{a}{2}) \tag{3}$$

From the condition that the membrane is electrically neutral it follows that:

$$\int_{R-\frac{a}{2}}^{R+\frac{a}{2}} q(r,c)r^2dr = 0 \tag{4}$$

Using the Gauss theorem, we obtain for the electric field E(r,c) in our spherically symmetrical system the expression:

$$E(r,c) = \frac{1}{\varepsilon(r,c)r^2}\int_{R-\frac{a}{2}}^{r}(r')^2q(r',c)dr' \tag{5}$$

where ε(r,c) is the dielectric permitivity in the respective points of the membrane. In the last formula we change the variables:

$$t = r-R \tag{6}$$

The quantity t is the distance of the respective point to the neutral surface. Then

$$E(t,c) = \frac{1}{\varepsilon(t,c)(t+R)^2}\int_{-\frac{a}{2}}^{t}(t'+R)^2q(t',c)dt \tag{7}$$

The potential difference ΔU is equal to:

$$\Delta U(c) = -\int_{-\frac{a}{2}}^{\frac{a}{2}} E(t,c)dt = -\int_{-\frac{a}{2}}^{\frac{a}{2}} \frac{1}{\varepsilon(t,c)(R+t)^2}\left(\int_{-\frac{a}{2}}^{t} (t'+R)^2 q(t',c)dt'\right)dt \quad (8)$$

We introduce the function $Z(t,c)$:

$$Z(t,c) = \int_0^t \frac{R^2 dt'}{\varepsilon(t',c)(R+t')^2} \quad (9)$$

We note that the differential $dZ = \frac{R^2 dt}{\varepsilon(t,c)(R+t)^2}$ of this function is the capacitance of a layer with thickness dt at a distance t from the neutral surface. Then from (4), (8), and (9):

$$\Delta U(c) = \int_{-\frac{a}{2}}^{\frac{a}{2}} \frac{(t+R)^2}{R^2} q(t,c)Z(t,c)dt = \int_{-\frac{a}{2}}^{\frac{a}{2}} (1+ct)^2 q(t,c)Z(t,c)dt \quad (10)$$

Expanding $\Delta U(c)$ in a series in c, using that $\Delta U(0)=0$ and keeping only the first order term with respect to c, we obtain:

$$\Delta U(c) = c\,\frac{\partial}{\partial c}\left(\int_{-\frac{a}{2}}^{\frac{a}{2}} (1+tc)^2 q(t,c)Z(t,c)dt\right) \quad (11)$$

If ε=const in the area where $E \neq 0$, the expression (11) can be simplified:

$$\Delta U(c) = -c\,\frac{1}{\varepsilon}\frac{\partial}{\partial c}\left(\int_{-\frac{a}{2}}^{\frac{a}{2}} t q(t,c)dt\right) \quad (12)$$

Comparing (11) and (12) with (1a), we obtain:

$$f = \frac{\varepsilon_o}{2\varepsilon}\frac{\partial}{\partial c}\left(\int_{-\frac{a}{2}}^{\frac{a}{2}}(1+tc)^2 q(t,c)Z(t,c)dt\right) \tag{13a}$$

When ε=const inside the membrane, the value of the flexocoefficient $f^{\varepsilon=\mathrm{const}}$ is:

$$f^{\varepsilon=\mathrm{const}} = -\frac{\varepsilon_o}{2\varepsilon}\frac{\partial}{\partial c}\left(\int_{-\frac{a}{2}}^{\frac{a}{2}} tq(t,c)dt\right) \tag{13b}$$

We introduce the function $q^{tot}(t,c)=q(t,c)-\mathrm{div}(\vec{P})$, where $\vec{P}(\vec{r},c)=(\varepsilon-\varepsilon_o)E(t,c)\frac{\vec{r}}{r}$. Then the following expression is valid for the general case:

$$f = -\frac{1}{2}\frac{\partial}{\partial c}\left(\int_{-\frac{a}{2}}^{\frac{a}{2}} tq^{tot}(t,c)dt\right) \tag{13c}$$

Remember that in formulae (13) $q(t,c)$ and $q^{tot}(t,c)$ are the distributions of the respective charges in the spherically deformed membrane.

The expressions (13) give the principal possibility for the flexocoefficient to be calculated for the cases of free as well as of a blocked flip-flop. The distribution $q(t,c)$ can be obtained for the particular cases of dipoles or quadrupoles concentrated on some layers (e.g. connected with parts of the polar heads or the hydrophobic chains of the lipid molecules building up the bilayers), for the case of double layers, etc.

FLEXOCOEFFICIENT AND CURVATURE ELASTICITY MODULI OF THE MEMBRANE

According to Helfrich[6] the elastic energy per unit area of the curved membrane g_c is:

$$g_c = \frac{1}{2}k_c(c_1 + c_2 - c_o)^2 + \bar{k}_c c_1 c_2 \tag{14}$$

where c_1 and c_2 are defined above, c_o is the the spontaneous curvature of the membrane (it is equal to zero for the symmetrical membranes considered) and k_c and $\bar{k}_c$ are the curvature elastic modulus and the saddle splay curvature elastic modulus respectively. A formula of the kind (14) implies that g_c is a local function of the deformations. This assumption is not always correct. As it was already shown, if the membrane has different from zero flexocoefficient, the potential jump across it (and the related with this jump energy of the electric field) depends on the value of the total curvature averaged over the whole membrane and g_c cannot be a local function. To avoid this difficulty, we deal again with spherically curved membranes. For this case:

$$g_c = (2k_c + \bar{k}_c)c^2 \tag{15}$$

We denote:

$$K = 2k_c + \bar{k}_c \tag{16}$$

The constant K has different values for the cases of permitted or forbidden exchange of charges between the electrolyte on both sides of the membrane (i.e. the state of the switch B on Figure 2) at the time when the membrane is deformed. In the first case we denote the modulus with an upper index "i", K^i, and in the second case with an upper index "u", K^u. Following the previously developed method[3], we calculate the difference K^u-K^i. Let a membrane with an area S=1 is curved at turned off switch B (Figure 2). After the switching on B, some current will be registered by the amperemeter and some energy E will be released on the resistance RES. E does not depend on the value of RES and is equal to:

$$E = (K^u-K^i)c^2 \tag{17}$$

To carry out the calculation, we use one simplified but realistic model of the lipid bilayer (Figure 3). We assume that it consists of a dielectric layer with thickness d and dielectric permitivity ε_d and of adjacent to it areas of the electrolyte with dielectric permitivity ε_e, including the double layers on the two sides of the membrane. The dielectric layer spans the hydrophobic chains and the part of the hydrophilic heads, where electrolyte cannot penetrate. The midplane of the dielectric layer is assumed to be the neutral surface of the membrane. The density of the ions in the electrolyte is assumed to be high enough. In such a case the Debye-Huckel approximation is valid and the potential $U(\vec{r})$ satisfies the linearized Poisson-Boltzmann equation in the electrolyte:

$$\nabla^2 U(\vec{r}) = \frac{1}{b^2} U(\vec{r}) \tag{18}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{19}$$

and

$$b = \frac{\varepsilon_e kT}{e^2}\left[\frac{1}{\sum\limits_i n_i z_i^2}\right]^{\frac{1}{2}} \tag{20}$$

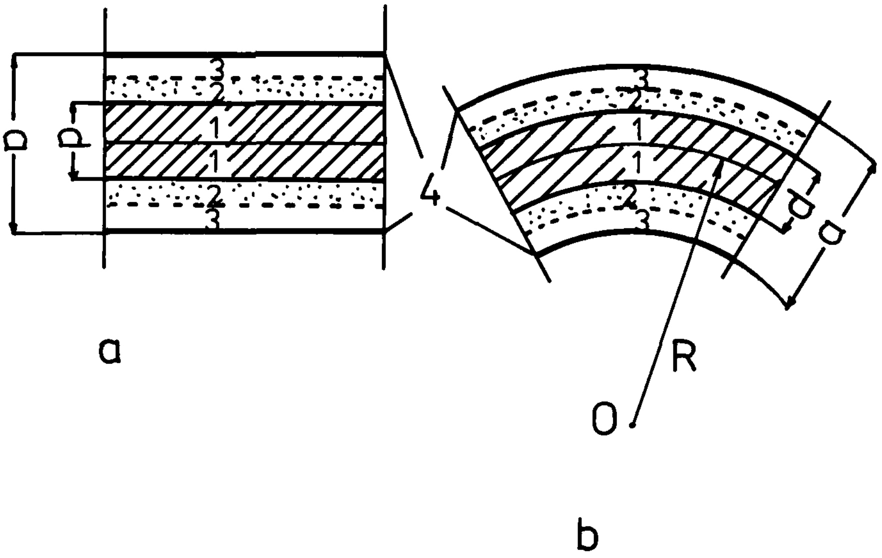

FIGURE 3 A simple but realistic model of the membrane. It consists of: dielectric layer 1 of thickness d, two double layers 2 and part of the electrolyte adjacent to them 3.The boundaries 4 of the membrane are parallel to the midplane of the dielectric layer at distances a/2 from it, far enough from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

The following symbols are used in (20): b - the Debye length of the flat double layer; ε_e - dielectric permitivity of the electrolyte; k - Boltzmann constant; T - absolute temperature; e - charge of the electron; n_i - concentration of the ions of the i-th kind in the electrolyte; z_i - valence of the ions of the i-th kind.

In the dielectric the potential U satisfies the Maxwell equation:

$$\nabla^2 U(\vec{r}) = -\frac{q(\vec{r})}{\varepsilon(\vec{r})} \qquad (21)$$

If the membrane is deformed at forbidden exchange of charges between the two moieties of the electrolyte some distribution $q^u(t,c)$ will be established where t and c are the introduced by us variables. After turning on the switch B (Figure 2) another distribution $q^i(t,c)$ will appear, where $q^i(t,c)=q^u(t,c)+\Delta q(t,c)$. $\Delta q(t,c)$ is different from zero if $|t|>\frac{d}{2}$. Only $\Delta q(t,c)$ creates some potential difference $\Delta U'(c)$ with the property $\Delta U'(c)=-\Delta U(c)$ with $\Delta U(c)$ from (1a). On the base of the model proposed the charge σ can be calculated that will pass through the amperemeter after turning on B and the thermal energy E released on the resistance RES (17). They are:

$$\sigma = -\frac{2f}{\frac{\varepsilon_o d}{\varepsilon_d} + \frac{2\varepsilon_o b}{\varepsilon_e}}.c \qquad (22)$$

$$E = \frac{2f^2}{\varepsilon_o(\frac{\varepsilon_o d}{\varepsilon_d} + \frac{2\varepsilon_o b}{\varepsilon_e})}.c^2 \qquad (23)$$

Comparing (17) and (23):

$$K^u - K^i = \frac{2f^2}{\varepsilon_o(\frac{\varepsilon_o d}{\varepsilon_d} + \frac{2\varepsilon_o b}{\varepsilon_e})}.c^2 \qquad (24)$$

The quantity $\bar{k}_c$ must be the same for the cases when the exchange of charges is permitted or forbidden because at pure saddle splay deformation with $c_1+c_2=0$ the quantity ΔU from (1b) is equal to zero. Consequently:

$$K^u - K^i = 2(k_c^u - k_c^i) \tag{25}$$

and

$$k_c^u - k_c^i = \frac{f^2}{\varepsilon_o\left(\frac{\varepsilon_o d}{\varepsilon_d} + \frac{2\varepsilon_o b}{\varepsilon_e}\right)} . c^2 \tag{26}$$

The result (26) can be used for some estimations of the maximal value of the flexocoefficient[3] at free flip-flop. They are based on the experimentally measured value of k_c^i of the order of 10^{-12}erg. In such a case the following inequality should be valid:

$$|f| < 10^{-19}\mathrm{C}. \tag{27}$$

RESULTS OF SOME NEW EXPERIMENTS FOR THE INVESTIGATION OF THE INFLUENCE OF THE ADSORBED IONS ON THE MAGNITUDE AND THE SIGN OF THE FLEXO-COEFFICIENT

With the help of our new definition of the flexocoefficient one obtaines the influence of the double layers on the values of f. For the case of blocked flip-flop and constant electric charge Ω_o per molecule of the lipid it is:

$$f = \frac{1}{A}\Omega_o b(d - b) \tag{28}$$

where A is the area per molecule in the flat bilayer. All the other quantities in (28) were defined in the previous section. The expression (28) differs from the one obtained earlier[5] because of the difference of the definitions used. Experiments[5] were carried out for the determination of f based on the measurement of flexoelectric responce (i.e. the appearing potential difference across the membrane) when oscillating pressure is applied, forcing the membrane to oscillate, too. Membranes of egg yolk lecithin were prepared in aqueous solution with uranyl acetate having a concentration of 1, 3, 5, and 10 mM/l and in aqueous solution without any uranyl acetate. In the absence of the uranyl acetate the value measured of the flexocoefficient was positive and equal to:

$$f = (5.3 \pm 1.1)10^{-18}\ C \qquad (29)$$

The value of f for the concentrations used of the uranyl acetate was negative and in the range:

$$f = -\ (24 \div 40)10^{-18}\ C \qquad (30)$$

The conditions of the experiment suggest that this is a flexocoefficient at blocked flip-flop, when the relation (28) should be valid. But the theoretical predictions are not in accord with the experimental results. It is expected that the positive UO_2^{2+} ions should be adsorbed on the surface of the membrane. With $d \sim 25$ Å and $b \sim 10$ Å the positive charge of these adsorbed ions is expected to shift f towards the positive values. The absolute values of this shift calculated from (28) are one to two orders of magnitude lower than the measured ones. The discrepancy between the theory and the experiment is for the moment an open question.

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