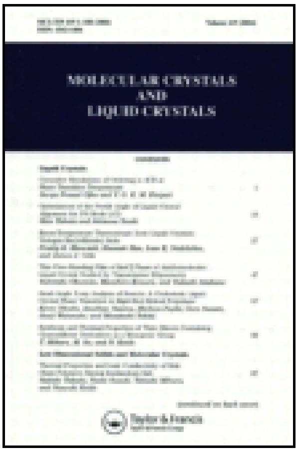

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On the Curvature Elasticity Theory of Fluid Membranes

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On the Curvature Elasticity Theory of Fluid Membranes

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Based on the Oseen-Frank-Nehring-Saupe theory of uniaxial liquid crystals, we give in this report a revised approach that the bending rigidity k, the elastic modulus of Gaussian curvature $\bar{k}$ and the spontaneous curvature c_0 may be expressed in terms of the various elastic constants of liquid crystals by $k = (k_{11} - 2k_{13})d$, $\bar{k} = (2k_{13} - k_{22} - k_{24})d$ and $c_0 = k_{11}s_0/(k_{11} - 2k_{13})d$ respectively, where d is the thickness of the membrane and s_0 is the spontaneous splay of the liquid crystal. With another approach based on the Landau-de Gennes theory we find that k, $\bar{k}$ and c_0 are closely related to the orientational order parameter of the long chains of the molecules in both layers of the bilayer membrane. Comparison of our calculation with experimental results is also discussed.
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Keywords: curvature elasticity, fluid membranes

I. INTRODUCTION

Analogous to the curvature elasticity theory of uniaxial liquid crystals founded by Frank, Helfrich has developed a curvature elasticity theory of fluid membranes (lipid bilayers).[1] In Helfrich's theory, the curvature elastic free energy per unit area of the membrane is given by

$$g = (k/2)(c_1 + c_2 - c_0)^2 + \bar{k}c_1c_2 \tag{1}$$

where c_1 and c_2 are the two principal curvatures of the deformed fluid membrane. The spontaneous curvature c_0 takes care of bilayers with two sides asymmetric or chemically different to each other. The constants k and $\bar{k}$ are the bending rigidity

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and the elastic modulus of Gaussian curvature respectively. Equation (1) is general and complete up to the second order of the curvatures. If the z-axis of the local Cartesian coordinate system is taken along the local normal $\underline{n}$ of the layer, we will have

$$\begin{aligned} c_1 + c_2 &= n_{x,x} + n_{y,y} \\ c_1 c_2 &= n_{x,x} n_{y,y} - n_{x,y} n_{y,x} \end{aligned} \tag{2}$$

where $n_{x,x} = \partial_x n_x$, $n_{x,y} = \partial_y n_x, \cdots$. In this way, the surface density of the curvature elastic free energy may be written as

$$g = (k/2)(n_{x,x} + n_{y,y} - c_0)^2 + \bar{k}(n_{x,x} n_{y,y} - n_{x,y} n_{y,x}) \ . \tag{3}$$

In comparison with the curvature elastic free energy density expression of liquid crystals given by Frank[2]:

$$\begin{aligned} g_{LC} = & \frac{1}{2}[k_{11}(\nabla \cdot \underline{n} - s_0)^2 + k_{22}(\underline{n} \cdot \nabla \times \underline{n} + t_0)^2 + k_{33}(\underline{n} \cdot \nabla \underline{n})^2] \\ & - k_{12}(\nabla \cdot \underline{n})(\underline{n} \cdot \nabla \times \underline{n}) \\ & - \frac{1}{2}(k_{22} + k_{24})[(\nabla \cdot \underline{n})^2 + (\nabla \times \underline{n})^2 - \nabla \underline{n} : \nabla \underline{n}] \end{aligned} \tag{4}$$

we may estimate the values of k and $\bar{k}$ by

$$\begin{aligned} k &= k_{11} d \ , \\ \bar{k} &= -(k_{22} + k_{24}) d \end{aligned} \tag{5}$$

where d is the thickness of the membrane which is of the order of 5×10^{-7} cm. The splay elastic constant k_{11} of liquid crystals is of the order of 10^{-6} dyn.[3] With these values, for the first time, Helfrich estimated that $k = 5 \times 10^{-13}$ erg.[1] This is close to the experimental values 0.9×10^{-12} erg to 2.3×10^{-12} erg measured on lecithin bilayers.[4] Such a good agreement suggests that fluid membranes and liquid crystals are of a great analogy and thus of the similar mathematical formalism. However, the second Equation of Equation (5) may cause some puzzles. The Maier-Saupe model of liquid crystals[5] gives $k_{24} = -3k_{22}/2$ and it leads to $\bar{k} = k_{22}d/2$. For liquid crystals k_{22} is always positive. Thus it suggests that $\bar{k}$ is always positive. However, it is found[6] that for membranes in large amount of water there exist three different equilibrium configurations: a lattice of passages,[7] a single big vesicle, and many small vesicles. The last two configurations correspond to negative values of $\bar{k}$. Therefore, it is necessary to have a close examination to the problem. Here, instead of comparing with the Frank's theory of liquid crystals we shall use the more comprehensive theory developed by Nehring and Saupe[8] for the analogy.

In Frank's theory as well as Helfrich's theory only the first order derivatives of the director n or the surface normal $\underline{n}$ are taken into consideration. However, Nehring and Saupe demonstrated that the second derivatives of $\underline{n}$ must also be considered.[8,9] They showed that, besides the terms given in Equation (4), the elastic free energy density expression has two more terms:

$$\delta g_{LC} = k_{13}\underline{n} \cdot \nabla\nabla \cdot \underline{n} - k_{23}\underline{n} \cdot \nabla(\underline{n} \cdot \nabla \times \underline{n}) \ . \tag{6}$$

Here we are going to examine the terms analogous to k_{13} and k_{23} in the curvature elasticity theory of membrane. In 1978, Mitov argued that, in contrast to the case of nematics, there was no term analogous to k_{13} in the second order elastic free energy of bilayers.[10] In section II we shall show that the consideration of the terms associated with k_{13} and k_{23} will not change the form of the Helfrich free energy Equation (1). However, the bending rigidity k and the Gaussian curvature modulus $\bar{k}$ will now take the forms

$$\begin{aligned} k &= (k_{11} - 2k_{13})d \ , \\ \overline{k} &= (2k_{13} - k_{22} - k_{24})d \ . \end{aligned} \tag{7}$$

We shall also point out the possible mistakes in Mitov's argument.

There are many discussion on the terms associated with k_{13} and k_{24} in the theory of liquid crystals.[11] These terms are difficult to understand. In section III we are going to present a Landau-de Gennes theory[12] for the curvature elasticity of membranes. We find that k_{13}, k_{24} and c_0 are closely related to the orientational order of the long chains of the molecules in the bulk as well as on the two interfaces of the fluid membrane. In particular, the spontaneous curvature c_0 is closely related to the difference of the order parameters on the two side-surfaces of the membrane. It describes the effects of the asymmetry of the membrane or its environment. Section IV compares the present calculation with some known experimental results and suggests some further experiments.

II. OSEEN-FRANK-NEHRING-SAUPE WAY OF APPROACH

Generally, fluid membranes (amphiphilic bilayers) may be idealized as two-dimensional surfaces in an aqueous solution with each membrane being made up of a double layer of long molecules.[13] The long axes (long chains) of the amphiphilic molecules in the membrane are oriented more or less along the direction of the normal of the surfaces. The integrity of the membrane is kept by the interaction between the aqueous solution and the hydrophobic heads as well as the hydrophilic chains of the molecules. At the same time the interaction also maintains the normal orientation of the molecules in the membrane. The fluid membrane may thus be treated as a bending homeotropic liquid crystal cell with uniaxial molecular order. The director $\underline{n}$ of the liquid crystal cell is simply the unit normal vector of the membrane. For simplicity we may take the thickness d of the membrane as uniform.

In order to find the expression of the curvature elastic free energy per unit area of the membrane, let us define the side-surfaces of the imagined "liquid crystal cell" by the vectors $\underline{Y}(u, v)$ and $\underline{Y}(u, v) + d\underline{n}$, where u and v are two real parameters, *i.e.*, material coordinates. To make out calculation be free of coordinates, we use differential geometry formalism and introduce following quantities[14]:

$$\begin{array}{lll} \underline{Y}_i = \partial_i \underline{Y} \ , & \underline{Y}_{ij} = \partial_i \partial_j \underline{Y} \ , & g_{ij} = \underline{Y}_i \cdot \underline{Y}_j \ , \\ g = \det(g_{ij}) \ , & g^{ij} = (g_{ij})^{-1} \ , & L_{ij} = \underline{Y}_{ij} \cdot \underline{n} \ , \\ L = \det(L_{ij}) \ , & L^{ij} = (L_{ij})^{-1} \ , & (i,j = 1,2) \end{array} \tag{8}$$

where $\partial_1 = \partial_u$, $\partial_2 = \partial_v$, and g_{ij} and L_{ij} are associated with the first and the second fundamental forms of the surface $\underline{Y}$ respectively. We shall use the summation convention in our calculation, *i.e.*, repeated indices imply summation over them. For convenience, we call $\underline{Y}$ the inside surface and $\underline{Y} + d\underline{n}$ the outside surface. The outward unit normal vector $\underline{n}$ is then defined by

$$\underline{n} = g^{1/2}(\underline{Y}_1 \times \underline{Y}_2) \ . \tag{9}$$

The two-dimensional gradient operator ∇' on the surface $\underline{Y}$ is defined by[15]:

$$\nabla' = g^{ij}\underline{Y}_i \partial_j \tag{10}$$

and $\underline{n}\partial_n$ is the gradient operator along the direction of $\underline{n}$. The three-dimensional gradient operator ∇ is now given by[15]:

$$\nabla = \nabla' + \underline{n}\partial_n \ . \tag{11}$$

The invariant form of ∇', Equation (10), plays an important role in our calculation. If we denote the mean curvature H and the Gaussian curvature K by

$$\begin{aligned} H &= -\tfrac{1}{2}(c_1 + c_2) = \tfrac{1}{2} g^{ij} L_{ij} \ , \\ K &= c_1 c_2 = L/g \end{aligned} \tag{12}$$

respectively, with Equations (8) and (9) we may easily find that

$$\begin{aligned} \nabla' \cdot \phi \underline{n} = {} & -2H\phi \\ \nabla' \times \underline{F} = {} & g^{-1/2}\{[\partial_1(g_{12}f_1 + g_{22}f_2) - \partial_2(g_{11}f_1 + g_{12}f_2)]\underline{n} \\ & + (f_1 L_{12} + f_2 L_{22})\underline{Y}_1 - (f_1 L_{11} + f_2 L_{21})\underline{Y}_2\} + \nabla' f_3 \times \underline{n} \end{aligned} \tag{13}$$

where $\phi(u, v), f_1(u, v), f_2(u, v), f_3(u, v)$ are scalar functions and $\underline{F} = f_1\underline{Y}_1 + f_2\underline{Y}_2 + f_3\underline{n}$. It follows directly from Equation (13) that

$$\nabla' \cdot \underline{n} = -2H \ , \qquad \nabla' \times \underline{n} = 0 \ . \tag{14}$$

Since the unit outward normal vector $\underline{n}'$ on the outside surface $\underline{Y} + d\underline{n}$ is related to $\underline{n}$ by $\underline{n}' = \underline{n} + O(d^2)$, we may easily show from Equations (8), (9) and (11) that

$$\underline{n} \cdot \nabla \underline{n} = \partial_n \underline{n} = 0 \ . \tag{15}$$

It follows that the three-dimensional divergence and curl of $\underline{n}$ are given by

$$\nabla \cdot \underline{n} = \nabla' \cdot \underline{n} = -2H \ , \qquad \nabla \times \underline{n} = \nabla' \times \underline{n} = 0 \tag{16}$$

respectively. The second condition of Equation (16) is well known for smectics. It leads to

$$\underline{n} \cdot \nabla \times \underline{n} = 0 \ , \qquad (\nabla \underline{n})(\underline{n} \cdot \nabla \times \underline{n}) = 0 \ , \qquad \underline{n} \cdot \nabla(\underline{n} \cdot \nabla \times \underline{n}) = 0 \ . \tag{17}$$

Together with Equations (4) and (6) we see that the elastic constants k_{12} and k_{23} do not enter in the free energy expression of the membranes. Furthermore, Equation (15) shows that the bend elastic constant k_{33} is also ruled out.

However, the term associated with k_{13} in Equation (6) needs further investigation. Since d is very small in comparison with the size of the membrane, we may replace $\partial_n H$ in the expression

$$\underline{n} \cdot \nabla\nabla \cdot \underline{n} = \underline{n} \cdot \nabla(-2H) = -2\partial_n H \tag{18}$$

by

$$\partial_n H = \lim_{d \to 0} (\delta H / d) \tag{19}$$

where $\delta H = H' - H$ is the variation of the mean curvature between the two surfaces $\underline{Y} + d\underline{n}$ and $\underline{Y}$. Using the result $\partial_n H = 2H^2 - K$ recently obtained by Ou-Yang and Helfrich,[16] (cf. Equation (16) of Reference 16) we find that

$$\underline{n} \cdot \nabla\nabla \cdot \underline{n} = 2K - 4H^2 \ . \tag{20}$$

As a direct check, we may consider the case of a sphere with radius r, for which $H = -r^{-1}$ and $K = r^{-2}$. Indeed, here we have that $\partial_n H = \partial_r H = r^{-2} = 2H^2 - K$.

Next let us consider the term $\nabla\underline{n}$: $\nabla\underline{n}$ in Equation (4). With Equations (10), (11) and (15) we have that

$$\nabla\underline{n} : \nabla\underline{n} = \nabla'\underline{n} : \nabla'\underline{n} = g^{ij}\underline{Y}_i\underline{n}_j : g^{kl}\underline{Y}_l\underline{n}_k \ . \tag{21}$$

Use of the Weingarton Equations[14]

$$\underline{n}_i = -L_{im}g^{mn}\underline{Y}_n \tag{22}$$

transforms Equation (21) into

$$\nabla\underline{n} : \nabla\underline{n} = g^{ij}\underline{Y}_i L_{jm} g^{mn}\underline{Y}_n : g^{kl}\underline{Y}_l L_{kp} g^{pq}\underline{Y}_q \ . \tag{23}$$

Using Equations (8) and (12) and the relationships[14]:

$$\begin{aligned} g^{ij}L_{ik}g^{kl} &= 2Hg^{jl} - KL^{jl} \\ L_{ij}g^{ik}L_{kl} &= 2HL_{jl} - Kg_{jl} \end{aligned} \tag{24}$$

we find that Equation (23) reduces simply to be

$$\nabla\underline{n} : \nabla\underline{n} = 4H^2 - 2K \ . \tag{25}$$

In order to find the final expression for the curvature free energy per unit area of the membrane, we use the following approximation:

$$\begin{aligned} F &= \int (g_{LC} + \delta g_{LC})dV \\ &= d\oint (g_{LC} + \delta G_{LC})dA \ , \end{aligned} \tag{26}$$

where dV is the volume element of the bulk between the two sides of the membrane and dA is the area element of $\underline{Y}$ surface. Since the thickness d of the membrane is about twice the length of the amphiphilic molecule and is negligible in comparison with the linear size of the membrane, Equation (26) is a good approximation. With Equations (4), (7), (16), (17), (19) and (20) we have

$$\begin{aligned} F = \ & d\oint[\frac{1}{2}(k_{11} - 2k_{13})(2H)^2 + (2k_{13} - k_{22} - k_{24})K \\ & +2k_{11}s_0H + \frac{1}{2}k_{11}s_0^2]dA \ . \end{aligned} \tag{27}$$

On the other hand, Helfrich's theory gives

$$\begin{aligned} F &= \oint g dA \\ &= \oint[\frac{1}{2}k(2H + c_0)^2 + \bar{k}K]dA \ . \end{aligned} \tag{28}$$

The two forms of F differ by a trivial constant. Comparison of Equations (27) and (28) gives not only Equation (7) but also an expression for the spontaneous curvature:

$$c_0 = k_{11}s_0/d(k_{11} - 2k_{13}) \ . \tag{29}$$

Frank interpreted s_0 as the spontaneous splay of the liquid crystal.[2] One feature of our calculation is that k_{13} enters both in the expression of k and of $\bar{k}$. This result differs from the argument given by Mitov.[10] Mitov concluded that, in contrast to the case of nematics, there was no term related to k_{13} in the second order elastic free energy of bilayer. Mitov gave no details in his paper and we have no way to check his conclusion. We guess, it was possible, that Mitov misused the two-dimensional gradient operator ∇' in the place of the three-dimensional operator ∇, particularly in Equation (18). That would arrive his conclusion.

III. LANDAU-DE GENNES WAY OF APPROACH

For the free energy density of liquid crystals, term

$$k_{13}\underline{n} \cdot \nabla\nabla \cdot \underline{n} \tag{30}$$

was first introduced phenomenologically by Oseen around 1930.[17] Then, it was disregarded for almost forty years. Not until 1971, Nehring and Saupe rediscovered this term.[8] In fact this term is difficult to handle and poses somewhat as a long lasting problem. So far the magnitude and even the sign of k_{13} are still unknown. A basic difficulty in studying k_{13} comes from the fact that, in the free energy expression, this term may be replaced by an alternating form

$$k_{13}\nabla \cdot (\underline{n}\nabla \cdot \underline{n}) \tag{31}$$

with the part $k_{13}\ (\nabla \cdot \underline{n})^2$ being absorbed in the splay free energy density term. In the form of Equation (31), apparently, k_{13} contributes only to a part of the surface energy of the sample and cannot be measured experimentally from the equilibrium structure of the bulk liquid crystal. On the other hand, the expressions of k_{13} derived from the molecular approach by Nehring and Saupe[8] and recently by Barbero and Oldano[18] involve too many terms to handle. Thus it is practically almost impossible to solve the problem from the molecular approach either. Here we would like to propose a compromise, *i.e.*, to find an expression of k_{13} by using the Landau-de Gennes way of approach.[19]

In order to obtain a quantitative theory of the phase transitions of the second kind, Landau introduced the order parameter S of a system and expanded the free energy density of the system in a power series of the order parameter. It was de Gennes who generalized Landau theory to uniaxial liquid crystal systems. For a uniaxial liquid crystal system, the order parameter $S(\underline{r})$ at the point $\underline{r}$ may be defined as

$$S(\underline{r}) = < P_2(\cos\theta) > \qquad (32)$$

where P_2 is simply the Legendre polynomial of second degree and θ is the angle between the long axis of the molecule and the local director $\underline{n}(\underline{r})$ at the point $\underline{r}$. However, de Gennes' generalized order parameter $S_{\alpha\beta}$ is a symmetric traceless tensor of second rank, *i.e.*,

$$S_{\alpha\beta} = S(\underline{r})[n_\alpha(\underline{r})n_\beta(r) - \delta_{\alpha\beta}/3] \qquad (33)$$

where α, β = 1, 2, 3 denote the components along the three orthogonal axes of the Cartesian coordinate system and $\delta_{\alpha\beta} = 1$ for $\alpha = \beta$ and zero otherwise. Up to terms of the order $O(S^2)$, the most general form of the inhomogeneous part of the free energy density g_{LC} is

$$g_{LC} = \frac{1}{2}L_1(\nabla_\alpha S_{\beta\gamma})(\nabla_\alpha S_{\beta\gamma}) + \frac{1}{2}L_2(\nabla_\alpha S_{\alpha\gamma})(\nabla_\beta S_{\beta\gamma}) \ , \qquad (34)$$

where L_1 and L_2 may be referred to as elastic constants and as a good first approximation they may be considered as constants.

Substituting Equation (33) into Equation (34) we find that

$$\begin{aligned} g_{LC} = \ & \frac{1}{3}(L_1 + \frac{1}{6}L_2)(\nabla S)^2 + \frac{1}{6}L_2(\underline{n}\cdot\nabla S)^2 \\ & + \frac{1}{3}L_2 S[2(\nabla\cdot\underline{n})(\underline{n}\cdot\nabla S) + (\underline{n}\times\nabla\times\underline{n})\cdot\nabla S] \\ & + S^2[L_1\nabla\underline{n} : \nabla\underline{n} + \frac{1}{2}L_2(\nabla\cdot\underline{n})^2 + \frac{1}{2}L_2(\underline{n}\cdot\nabla\underline{n})^2] \ . \end{aligned} \qquad (35)$$

In case where S is a constant, Equation (35) reduces to the free energy density expression given by Frank-Nehring-Saupe with the surface energy contribution terms being neglected and

$$\begin{aligned} k_{11} &= k_{33} = 2S^2(L_1 + L_2/2) \ , \\ k_{22} &= 2S^2 L_1 \ . \end{aligned} \qquad (36)$$

Then the elastic constants k_{12}, k_{13}, k_{23}, the spontaneous splay constant s_0, and the spontaneous twist constant t_0 now equal to zero. Therefore, in case of constant S, the Landau-de Gennes free energy density expression is only qualitatively correct for the nematic phase.

Fluid membrane is curved surfaces for which both the surface normal $\underline{n}$ and the order parameter S are functions of the space coordinate $\underline{r}$. Making use of Equations (15), (16) and (25) we see that the last term on the right-hand side of Equation (35) may be written as

$$g_n = S^2[4(L_1 + L_2/2)H^2 - 2L_1 K] \ . \qquad (37)$$

The other terms in Equation (35) are directly related to ∇S. For asymmetric bilayers we could make a simple assumption that

$$S(\underline{r}) = S(u, v, z) = \begin{cases} S_0 & \text{for} \quad d/2 \le z \le d \\ S_i & \text{for} \quad 0 \le z < d/2 \end{cases} \tag{38}$$

where the constants S_0 and S_i are simply the orientational order parameters of the molecules in the two monolayers of the bilayer respectively. Here, in Equation (38), the z-axis of the local Cartesian coordinate system coincides with the local normal $\underline{n}$. With Equation (15) we have

$$\begin{aligned} \nabla S(\underline{r}) = & \ (\nabla' + \underline{n}\partial_z)S \\ = & \ (S_0 - S_i)\underline{n}\delta(z - d/2) \end{aligned} \tag{39}$$

where $\delta(z - d/2)$ is the Dirac delta function. The curvature elastic free energy per unit area of the bilayer G is simply

$$G = \int_0^d g_{LC} dz \ . \tag{40}$$

The first two terms of Equation (35), which are proportional to the square of ∇S, lead to a trivial constant in the integration and can be neglected. The contribution from the third term of Equation (35), which is proportional to ∇S^2, is equal to

$$\begin{aligned} G_1 = & \ (L_2/3) \int_0^d 2(-2H)(S_0 - S_i)S\delta(z - d/2)dz \\ = & \ (2L_2/3)(S_i^2 - S_0^2)H(d/2) \end{aligned} \tag{41}$$

where we have used Equations (16) and (17). Since $\partial_n H = 2H^2 - K$, we have

$$H(d/2) - H = d(2H^2 - K)/2 + O(d^2) \ . \tag{42}$$

It follows

$$G_1 = (2L_2/3)(S_i^2 - S_0^2)[H + d(2H^2 - K)/2] + O(d^2) \ . \tag{43}$$

Similarly the contribution G_2 to G from the last term of Equation (35)is

$$\begin{aligned} G_2 = & \int_0^d g_n dz \\ = & \ (d/2)(S_i^2 + S_0^2)[4(L_1 + L_2/2)H^2 - 2L_1 K] + O(d^2) \ . \end{aligned} \tag{44}$$

Thus we have

$$\begin{aligned} G = &\ G_1 + G_2 \\ = &\ 2kH^2 + \bar{k}K + 2kc_0H \end{aligned} \tag{45}$$

where

$$\begin{aligned} k &= d[S_i^2(L_1 + 5L_2/6) + S_0^2(L_1 + L_2/6)] \ , \\ \bar{k} &= -d[S_i^2(L_1 + L_2/3) + S_0^2(L_1 - L_2/3)] \ , \\ c_0 &= (S_i^2 - S_0^2)L_2/3k \ . \end{aligned} \tag{46}$$

Apart from a trivial constant, Equation (45) is exactly the Helfrich expression Equation (1).

Comparison of Equation (46) with Equations (7) and (36) while replacing $2S^2$ by $S_i^2 + S_0^2$ we find that the Oseen-Frank-Nehring-Saupe elastic constants are given by

$$\begin{aligned} k_{11} = k_{33} &= (S_i^2 + S_0^2)(L_1 + L_2/2) \ , \\ k_{22} &= (S_i^2 + S_0^2)L_1 \ , \\ k_{13} &= -(S_i^2 - S_0^2)L_2/6 \ , \\ k_{24} &= 0 \ . \end{aligned} \tag{47}$$

In case of symmetric bilayers where $S_i = S_0$, and G_1, k_{13} and c_0 all vanish. This confirms that the spontaneous curvature c_0 and the surface contribution elastic constant k_{13} are directly related to the asymmetry property of the membrane.

IV. DISCUSSION

Since k_{13} varies with boundary distortions of directors near the surfaces of the fluid membrane,[18] consequently, as shown in Equations (7) and (29), k, $\bar{k}$ and c_0 are not constants anymore. As one examines Equation (46), he would see that the order parameters S_i and S_0 depend not only upon the polar properties of the membrane molecules but also upon the forces on both sides of the boundary surfaces of the membrane. Helfrich's theory has predicted that the spontaneous curvature c_0 is not a constant. Here, for the first time, we have shown k and $\bar{k}$ are not constants too, and maybe change with two sides in chemical.

The bending rigidity k of lecithin bilayers has been studied in a number of laboratories. The experimental value of k is determined from the measured mean square amplitude of the shape fluctuations. Both the Helfrich group and the Webb group[4] use tubular vesicles in their experiments. The value of k obtained by both groups ranges from 0.9×10^{-12} erg to 2.3×10^{-12} erg. All these experimental values are higher than 0.5×10^{-12} erg as predicted by Helfrich's theory. In the present calculation the calculated value of k from Equation (7) would be higher than 0.5×10^{-12} erg if k_{13} is negative, which is in better agreement with the available experimental values.

Ou-Yang and Helfrich[16] have shown that the necessary condition for a fluctuating circular cylindrical vesicle of radius ρ_0 to be stable is

$$c_0\rho_0 \geq 1 \ . \tag{48}$$

In connection with Equations (46) and (47), for cylindrical vesicles, we have certainly $k_{13} < 0$. This fact suggests, at least qualitatively, the present calculation is in good agreement with the experimental observations. In checking on our calculation, future experiments on the determination of the dependency of k and $\bar{k}$ on the chemical agents around the two sides of the membrane would be very helpful.

Obviously, two monolayer order parameters S_i and S_0 used in section III is a simple assumption. In general, it may need more terms in the expansion of the Landau-de Gennes free energy. For example we may take

$$S(\underline{r}) = \begin{cases} S_0 & \text{for} \quad z \geq d/2 \\ S_m & \text{for} \quad -d/2 < z < d/2 \\ S_i & \text{for} \quad z \leq -d/2 \ . \end{cases} \tag{49}$$

In this case we will find that

$$\begin{aligned} k &= 2S_m^2 d[(L_1 + L_2) + AL] \ , \\ \bar{k} &= -2S_m^2 d[L_1 + AL] \ , \\ c_0 &= 2S_m(S_i - S_0)L_2/3k \end{aligned} \tag{50}$$

where

$$A = (2/3)[1 - (S_0 + S_i)/2S_m] \ . \tag{51}$$

Thus S_m, S_i and S_0 describe the orientational order of the bulk and the orientational order of the two sides of the membrane respectively. And the spontaneous curvature c_0 remains to describe the asymmetry property of the membrane. Further study on this model is still in progress.

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