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LANDAU THEORY OF THE LAMELLAR-TO-CUBIC PHASE TRANSITION

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Abstract - A Landau theory of the lamellar-to-cubic phase transition of lipid bilayers in water is developed. The preference for the infinite periodic minimal surfaces G, D and P is explained and preliminary criteria for the selection of one of them are given.

I. Introduction

There is wide agreement today that membrane bending elasticity determines among other factors if a given lipid in water displays lamellar, hexagonal, or cubic order. In particular, it is thought to control whether or not a bilayer tends to fuse. Rather early Petrov, Mitov and Derzhanski /1/, using a particular model, showed that negative spontaneous monolayer curvature, i.e. a tendency of the monolayer to be concave towards the water, should give rise to bilayer fusion. The same idea underlies the frustration model of cubic bilayer phases put forward by Charvolin and Sadoc /2/ and the considerations on monolayer bending presented by Anderson, Gruner, and Leibler /3/.

A quantitative analysis of this sort may start from the formula

\[ g_m = \frac{1}{2} \kappa_m (c_1^m + c_2^m)^2 - \kappa_m c_0 (c_1^m + c_2^m) + \tilde{\kappa}_m c_1^m c_2^m \]  

(1)

for the monolayer bending elastic energy per unit area, \( g_m \). Here \( c_1^m \) and \( c_2^m \) are the two principal curvatures, \( c_0 \) the spontaneous curvature, \( \kappa_m \) the bending rigidity and \( \tilde{\kappa}_m \) the elastic modulus of Gaussian curvature, all for the monolayer. The equivalent of (1) for the symmetric bilayer, which by definition has no
spontaneous curvature, may be written as

\[ g = \frac{1}{2} \kappa (c_1 + c_2)^2 + \bar{\kappa} c_1 c_2 \quad (2) \]

The principal curvatures \( c_1 \) and \( c_2 \) refer to the mid-surface of the symmetric bilayer. While the bending rigidity of the bilayer is twice that of the monolayer, i.e. \( \kappa = 2\kappa_m \), its Gaussian modulus depends on the material properties of the monolayer through

\[ \bar{\kappa} = 2(\bar{\kappa}_m - 2\kappa_m c_0 l) \quad (3) \]

Here \( l \) is the distance of the neutral surface of either monolayer from the mid-surface of the bilayer under cylindrical curvature \( /4,5/ \). Accordingly, \( \bar{\kappa} \) is not just twice \( \bar{\kappa}_m \), but contains another term in which the monolayer spontaneous curvature appears with the expected sign. The energy of fusion, may be defined as

\[ \epsilon_{\text{fusion}} = -4\pi \bar{\kappa} \quad (4) \]

This is the bending energy of a connection, also called neck or passage, between bilayers as calculated from (2) if the contribution of the \( \kappa \) term is negligible.

Recently, Gruner et al.\(/6/ \) suggested to treat phase transitions between the lamellar, cubic, and hexagonal phases of lipid/water systems in terms of a Landau theory, with the radius of spontaneous curvature being the control parameter. Anderson et al.\(/3/ \) equated the average of the negative monolayer curvature in the cubic phase \( G \), \( D \) and \( P \) to the monolayer spontaneous curvature, thus relating \( c_0 \) to lattice parameters in a manner similar to Landau theory.

In the following we wish to develop a complete Landau theory, taking all terms up to quartic order in the principal bilayer curvatures. This amounts to a quadratic form in the average Gaussian curvature. We will also propose an explanation why the three most common cubic bilayer phases are those represented by the three well-known infinite periodic minimal surfaces \( G \), \( D \) and \( P \). Finally, we will try to associate the selection by nature among them with simple criteria involving bending energies and membrane interactions.

II. A Landau theory of the cubic bilayer phases

A symmetric bilayer forming a minimal surface satisfies everywhere \( c_1 + c_2 = 0 \). However, the sum of the principal curvatures of the monolayers, \( c_1^m + c_2^m \), is in general negative whenever the neutral surfaces of the monolayers are at a distance \( l > 0 \) from the mid-surface of the bilayer. When \( R \) is the radius of the bilayer principal curvatures, one has \( /3/ \)

\[ c_1^m = \frac{1}{R + l} \]
and
\[ c_2^m = -\frac{1}{R-l} \quad (5) \]
Replacing the principal curvatures by the mean curvature,
\[ H = \frac{1}{2}(c_1 + c_2) \quad (6) \]
and the Gaussian curvature,
\[ K = c_1 c_2 \quad (7) \]
for the bilayer, and analogously for the monolayer, one finds for both monolayers
\[ H_m = \frac{lK}{1+l^2K} \quad (8) \]
and
\[ K_m = \frac{K}{1+l^2K} \quad (9) \]
We also need the area ratio of the monolayer neutral surface \( A_m \) and the bilayer mid-surface \( A \). It may be expressed in differential form by
\[ dA_m = (1+l^2K)dA \quad (10) \]

The neutral surface of a membrane of finite thickness is by definition the surface that does not change its area under bending. The neutral surface, unique only for pure cylindrical bend, is assumed to lie inside the monolayer, which is in accordance with experimental data /7/ and justifies putting \( l > 0 \). Incidentally, for our special case of pure saddle curvature of the bilayer, i.e. \( c_1 + c_2 = 0 \), we could use as an alternative the neutral surface of the other monolayer from a purely formal point of view.\(^1\)

The average energy of the monolayer may now be written as
\[ \langle g_m \rangle_{quadr} = \frac{\int [2\kappa_m H_m^2 - 2\kappa_m c_0 H_m + \overline{\kappa_m K_m}] dA}{\int [1+l^2K_m] dA} \quad (11) \]
if we restrict ourselves to the quadratic form (1) for the monolayer bending elastic energy. Insertion of (8) to (10) and expanding up to order \( K^2 \) transform (11) into
\[ \langle g_m \rangle_{quadr} = (\overline{\kappa_m} - 2\kappa_m c_0 l) \langle K \rangle + 2\kappa_m l^2 \langle K^2 \rangle - (\overline{\kappa_m} - 2\kappa_m c_0 l)l^2 \langle K \rangle^2 \quad (12) \]
\(^1\)We disregard the unlikely possibility that there are no neutral surfaces for pure saddle curvature.
The first term of \( \langle g_m \rangle_{\text{quad}} \) confirms eq. (3) and that a cubic phase may be expected if \( \bar{\kappa} = 2(\bar{\kappa}_m - 2\kappa_m c_0 l) \) is positive. The second term is the bending energy of the symmetric bilayer. The third term, a correction of the first, arises because of (10).

Equation (12) has all the features required to describe a second-order lamellar-to-cubic phase transition. It predicts \( \langle K \rangle = 0 \) for \( \bar{\kappa} < 0 \) and a continuous increase of \( \langle |K| \rangle \) as \( \bar{\kappa} \) passes zero and becomes positive. Although based on the quadratic approximation of monolayer bending energy, \( \langle g_m \rangle_{\text{quad}} \) is quartic in \( \langle |c| \rangle \), i.e. the average principal curvatures of the bilayer. However, there are additional terms of the same order which also contribute. The total average of \( g_m \) up to quadratic order in \( K \) may be written as

\[
\langle g_m \rangle_{\text{total}} = (\bar{\kappa}_m - 2\kappa_m c_0 l) \langle K \rangle + 2\kappa_m l^2 < K^2 > \\
- (\bar{\kappa}_m - 2\kappa_m c_0 l)^2 (\langle K \rangle)^2 \\
+ \bar{\kappa}_m < K^2 > - (\kappa_m c_0 \frac{\partial l}{\partial K} + \frac{\partial (\kappa_m c_0 l)}{\partial K}) < K^2 >
\] (13)

The \( \bar{\kappa}_m \) term has been considered before in connection with a specific microscopic model of the bilayer /8/; it may include a correction of \( \bar{\kappa}_m \) due to an interaction between the monolayers which we do not write separately. The last term is a correction of the second part of the first. It could be expressed by a single material parameter instead of the two derivatives which we choose to separate, perhaps inadmissibly, the effect of \( \partial l/\partial K \) from a pure monolayer part. There are none of the gradient terms in (13) which were introduced by Mitov /9/. The only such term of fourth power in the bilayer principal curvatures is \( \Delta K = \nabla^2 K \). Viewing this as the gradient of a vector, one sees immediately that its surface integral can be converted into a closed line integral. The line integrals around two adjacent patches neutralize each other where they have a common border. Accordingly, all the line integrals cancel out and the surface integral vanishes.

Equation (13) consists of one term proportional to \( \langle K \rangle \) and four terms varying as \( \langle K \rangle^2 \). These quantities could be replaced by \( \langle |c| \rangle \) and \( \langle |c| \rangle^4 \), respectively, to show that \( \langle |c| \rangle \) is indeed the order parameter of an ordinary Landau theory containing a quadratic and a composite quartic term. We refrain from this transformation since unlike its ferromagnetic counterpart the order parameter \( \langle |c| \rangle \) can have only one sign (unless we consider either the positive or the negative principal curvature). For \( -c_0 l << 1 \) one can neglect all contributions to (13) containing \( c_0 \) except for that in the first term. However, the term \( \bar{\kappa}_m K^2 \) which contains a pure monolayer part of fourth order in the monolayer principal curvatures cannot be omitted.
We think that a Landau theory of the lamellar-to-cubic phase transition can be useful for intermediate curvatures. In the first place, they should be weak enough, say $|c| << 1/(\text{bilayer thickness})$, to ensure the irrelevance of terms of higher than quartic order in $<|c|>$. On the other hand, they should not be too weak since the critical point of the theory and a vicinity of it will not be observable for many reasons. The divergence of the lattice parameter when this point is approached seems difficult to achieve experimentally. This is not only a problem of sample size: a more serious obstacle could be the weakening of the restoring forces. Also, the effective bending rigidity of the bilayer may decrease and the number of interspersed vesicles and other defects of the cubic phase increase as the lattice parameter gets larger and larger /10/.

It appears easy to understand why the cubic bilayer phases $G$, $D$ and $P$ are the most commonly observed. Among the large number of infinite periodic minimal surfaces they seem to be those with the smallest relative variation of the saddle curvature /11/. Ideally, the Gaussian curvature $K$ should be everywhere such that $g_{m}$ is minimized. In practice, the Gaussian curvature cannot be uniform on any minimal surface and there must be flatpoints on an infinite periodic minimal surface. This means that one has to settle for the minimum relative variance of $<K>$. We use as a measure of it the ratio $<K^2>/(<K>)^2$ which, starting from unity, increases with the relative variance. Using the ratio to express in (13) $<K^2>$ by $(<K>)^2$, we see that some of the terms gain in strength as the ratio goes up. Provided their sum is positive, as we may assume for reasons of stability, this verifies that the phases with the lowest variation are energetically the most favorable.

The elementary pieces of the minimal surfaces $G$, $D$ and $P$ are related by Bonnet transformations, which implies that both the metric and the Gaussian curvature are the same for all three of them. Accordingly, the ratio $<K^2>/(<K>)^2$ is also the same for the three infinite periodic minimal surfaces. We compute $<K^2>/(<K>)^2 = 100.294 \cdot 1.9188903/(4\pi)^2 = 1.218724$ from the numbers of Anderson et al. /3/. In order to establish criteria predicting which of them should be found in a given system we have to realize that they represent different space groups and structures: The space groups and the numbers of water channels converging in connecting points are $Ia3d$ and 3 for $G$, $Pn3m$ and 4 for $D$, and $I m3 m$ and 6 for $P$, respectively. As a result, the three periodic structures differ slightly at a given $<K>$ in two important quantities, the ratio $V/A^{\frac{2}{3}}$ and $d_{\text{min}}$. Here $A$ is the area of a surface (comprising many unit cells) and $V$ the volume of the three-dimensional structure formed by it. The numbers $V/A^{\frac{2}{3}}$ were calculated some years ago by Schoen /12/. The length $d_{\text{min}}$ is the minimum distance of neighboring parallel sections of the minimal surface. The points whose distances we calculated are indicated in the Poincaré
Figure 1: Poincaré diagram indicating pairs of points (G-G, D-D, P-P) used for calculating the minimum spacings $d_{min}$ of neighboring parallel membrane sections in three-dimensional space.

The two quantities are listed in relative units in the following table:

<table>
<thead>
<tr>
<th></th>
<th>G</th>
<th>D</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V/A^{3/2}$</td>
<td>1.00</td>
<td>1.022</td>
<td>1.07</td>
</tr>
<tr>
<td>$d_{min}$</td>
<td>1.066</td>
<td>1.11</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Inspection suggests that each of the three infinite periodic minimal surfaces can occur, depending on the details of the system: G should be energetically favored if resistance to further bending dominates (as $V/A^{3/2}$ is minimal), D should be favored if intermembrane repulsion dominates (as $d_{min}$ is maximal), and P should appear if membrane attraction dominates (as $d_{min}$ is minimal). On the basis of these criteria we expect only D and P to occur in excess water. Here the surface is free to choose the optimum $<K>$ which is then modified depending on whether the neighboring parallel sections of membrane attract or repel each other. G should be obtained if sufficient water is extracted from D or P since the bending energy diverges for $<|K|> \rightarrow 0$ whereas the energy of repulsion is bounded. Whether D is passed on the way from P to G depends, according to these arguments, on the existence of an interval of $<K>$ where
membrane repulsion is predominant. Such an interval might be the rule since the sequences D-G /13/ and P-D-G /14/ but not P-G have been reported to date. Our criteria are, of course, preliminary and have to be refined, especially by taking the bilayer thickness into account.

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