Ripples in Tilted Bilayers and Lyotropic Smectics

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The elastic theory of tilted lyotropic smectics and single tilted bilayers is extended to include internal twist of the bilayers. The coupling of internal twist to layer curvature offer an explanation for the corrugation or ripples displayed by these structures.

The lyotropic smectic phase[1,2] and single bilayers[3,4] of some lecithins have been found to be corrugated, if the lipid chains are in their "rigid" phase and tilted with respect to the layer normal. In lyotropic smectics corrugation gives rise to a two-dimensional oblique lattice, *i. e.* the phase of the ripples changes as one goes from one layer to the next. The period of the ripples ranges from 85 Å (lyotropic smectic didodecanoyl phosphatidyl choline in its P β' phase[2]) to 400 Å (freeze-etched lamellae of dipalmitoyl phosphatidyl choline[4]).

Tardieu *et al.*[1,2] suggested an alternate accumulation and release of strain as a possible explanation for rippling. In the present note we wish to propose a specific mechanism. A slight "internal twist" within the bilayer should couple to bilayer curvature so that corrugation may lower the total elastic energy of the structure.

The X-ray studies[1,2] of "rigid" chain phases indicate that the essentially straight chains form a two-dimensional hexagonal lattice in the bilayers. We may think of the polar heads of the lecithin molecules as "bridges", each connecting two chains. In the presence of tilt the bridges will have a preferred orientation within the plane of the bilayer. The asymmetry is likely to be associated with an anisotropic spontaneous curvature of the monolayers, *i. e.* an inherent tendency to curve which is different for the two principal directions. In an undeformed bilayer the spontaneous curvatures of the constituent monolayers must, of course, cancel each other. However, if the hydrocarbon chains having normally the same direction in both monolayers are brought slightly out of line (at fixed tilt angle), compensation is no longer complete and the bilayer should display two principal spontaneous curvatures. They will be equal but opposite in sign and at angles of 45° with respect to the chain projection on the layer plane. The deformation may be designated "internal twist". The concept of "spontaneous curvature" has been introduced earlier[5] for lipid bilayers.

We first write down a formula for the elastic energy density G of tilted smectic phases

$$
\begin{aligned}
G = {} & \tfrac{1}{2} A\left(\frac{\partial \Omega_x}{\partial x}\right)^2 + \tfrac{1}{2} A_{12}\left(\frac{\partial \Omega_y}{\partial x}\right)^2 + \tfrac{1}{2} A_{21}\left(\frac{\partial \Omega_x}{\partial y}\right)^2 \\
& + \tfrac{1}{2} B_1\left(\frac{\partial \Omega_z}{\partial x}\right)^2 + \tfrac{1}{2} B_2\left(\frac{\partial \Omega_z}{\partial y}\right)^2 + \tfrac{1}{2} B_3\left(\frac{\partial \Omega_z}{\partial z}\right)^2 \\
& + B_{13}\frac{\partial \Omega_z}{\partial x}\,\frac{\partial \Omega_z}{\partial z} \qquad (1) \\
& + C_1\frac{\partial \Omega_x}{\partial x}\,\frac{\partial \Omega_z}{\partial x} + C_2\frac{\partial \Omega_x}{\partial y}\,\frac{\partial \Omega_z}{\partial y} \\
& + \tfrac{1}{2} B_3'(\Delta\varphi)^2 + B_{13}'\frac{\partial \Omega_z}{\partial x}\,\Delta\varphi + B_{33}'\frac{\partial \Omega_z}{\partial z}\,\Delta\varphi \\
& + C'\frac{\partial \Omega_x}{\partial x}\,\Delta\varphi\,.
\end{aligned}
$$

The terms with unprimed elastic moduli have been introduced before[6,7]. In this local representation Ω denotes the rotation of the whole structure as one proceeds from the point considered. At the origin, where $\Omega = 0$, the z and x axes of the right-handed coordinate system are parallel to the layer normal and to the projection of the chains onto the layer plane, respectively. The terms with primed moduli are new: They take account of internal twist, $\Delta\varphi$ being a measure of the angle between the alcyl chain projections of the monolayers onto the layer plane. Ω_z is an average over both monolayers.

Correspondingly, we may write for the elastic energy g per unit area of a single bilayer

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$$
\begin{aligned}
g = {} & \tfrac{1}{2}\,\alpha\left(\frac{\partial\Omega_x}{\partial x}\right)^2 + \tfrac{1}{2}\,\alpha_{12}\left(\frac{\partial\Omega_y}{\partial x}\right)^2 + \tfrac{1}{2}\,\alpha_{21}\left(\frac{\partial\Omega_x}{\partial y}\right)^2 \\
& + \tfrac{1}{2}\,\beta_1\left(\frac{\partial\Omega_z}{\partial x}\right)^2 + \tfrac{1}{2}\,\beta_2\left(\frac{\partial\Omega_z}{\partial y}\right)^2 \\
& + \gamma_1 \frac{\partial\Omega_x}{\partial x}\frac{\partial\Omega_z}{\partial x} + \gamma_2 \frac{\partial\Omega_x}{\partial y}\frac{\partial\Omega_z}{\partial y} \\
& + \tfrac{1}{2}\,\beta_3'\,(\Delta\varphi)^2 + \beta_{13}'\,\frac{\partial\Omega_z}{\partial\Omega_x}\,\Delta\varphi + \gamma'\,\frac{\partial\Omega_x}{\partial x}\,\Delta\varphi\,,
\end{aligned}
\tag{2}
$$

where all terms containing $\partial\Omega_z/\partial z$ have been dropped. (These terms may also be of minor importance in lyotropic smectics of high water content because of weak interaction between layers.)

The derivative $\partial\Omega_y/\partial y$ does not occur in the two formulas because the layer structure requires $\partial\Omega_x/\partial x + \partial\Omega_y/\partial y = 0$. The product $(\partial\Omega_y/\partial x)$ $(\partial\Omega_x/\partial y)$ is omitted as partial integration gives a contribution to the $(\partial\Omega_x/\partial x)^2$ term besides another contribution whose integral depends only on boundary conditions. Analogously, $(\partial\Omega_x/\partial x)\,(\partial\Omega_z/\partial z)$ can be transformed into $(\partial\Omega_x/\partial z)\,(\partial\Omega_z/\partial x)$ which because of the first factor must be zero for fixed interlayer distance. More generally, Eqns (1) and (2) do not contain any terms taking account of changes of tilt angle and interlayer distance nor linear terms of $\partial\Omega_z/\partial x$, $\partial\Omega_z/\partial z$, $\partial\Omega_x/\partial x$, and $\Delta\varphi$. The second[7] and last of the latter four may lead to a spontaneous twist $\partial\Omega_z/\partial z \neq 0$.

We assume that the moduli in front of all simple squares are positive. Corrugation of initially flat bilayers can come about through the mixed terms. As ripples have not been reported for thermotropic smectics we think that the primed coupling terms are decisive. The mechanism proposed above comes in through C' (γ'). Corrugation must take place whenever there are perturbations $(\Omega_{x0}, \Omega_{y0}, \Delta\varphi_0)$ $\exp(\mathrm{i}\,\boldsymbol{q}\,\boldsymbol{r})$ that reduce the elastic energy in comparison with the flat structure. Whether the system is stable with respect to a perturbation does not depend on the magnitude of the wave vector $\boldsymbol{q}$. For (practically) fixed interlayer distance $\boldsymbol{q}$ must be perpendicular to the layer normal.

Let us consider the special case $A > 0$, $A_{12} = A_{21} > 0$, $B_3' > 0$, $C' \neq 0$, all other moduli negligible. For reasons of symmetry ripple formation is most favored for wave vectors in the x, y plane at angles of ±45° from the x axis. The condition for corrugation is easily found to be

$$(C')^2 > (A + 2\,A_{12})\,B_3' \tag{3}$$

or in the analogous case with single bilayers

$$(\gamma')^2 > (\alpha + 2\,\alpha_{12})\,\beta_3'\,. \tag{4}$$

The infinite growth of both $\boldsymbol{\Omega}_0$ and $\boldsymbol{q}$ may be prevented by the breakdown of continuum elastic theory, at least of the type restricted to quadratic terms. In lyotropic smectics it is also hindered by changes in interlayer distance. One should expect the wavelength of the ripples to be of the order of 2π times molecular length, in agreement with the experimental data. Clearly, our model cannot predict the wave vector and amplitude of corrugation nor the oblique two-dimensional lattice, but it appears to provide a criterion for ripple formation.

The dimensions of B_3' (β_3') and the other primed moduli are erg cm^{-3} (erg · cm^{-2}) and erg cm^{-2} (erg · cm^{-1}), respectively. The modulus B_3' (β_3') multiplied by b^2 and the other primed moduli multiplied by b, where b is the bilayer thickness, could be of the order of the unprimed moduli. Interestingly, bilayers are known[8] to have a thin region of relatively low chain ordering at the interface of the constituent monolayers. As a result, the elastic moduli B_3' and β_3' might be quite small, thus facilitating corrugation.

The polar heads of lecithin molecules contain an optically active carbon atom. The apparent absence of spontaneous twist in the lyotropic tilted smectic phase, as optically found with dipalmitoyl lecithin[9], might be due to corrugation. Another mechanism of locking in parallel the axes of two-dimensional lattices, leaving the layers free to slide past each toher, has been proposed in connection with thermotropic smectic B liquid crystals[7, 10]. Furthermore, one may speculate that the corrugated phase is a solid rather than a liquid crystal.

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