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Thermal instability in lamellar phases of lecithin: a planar undulation model

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Résumé. — En chauffant un échantillon multilamellaire de lécithine d’œuf hydratée, en géométrie planaire (lamelles normales aux plaques), on observe d’abord une instabilité à striation périodique, puis les domaines « en épi ». Nous montrons qu’une contraction normale des lamelles chauffées peut produire une instabilité d’ondulation des lamelles en géométrie planaire comme en géométrie homéotrope. En supposant un ancrage fort des lamelles sur les plaques, l’absence de contrainte sur la surface extérieure des lamelles localise les ondulations près des plaques. La période spatiale et le seuil de ces ondulations sont estimés. L’observation d’échantillons de DLL hydratée, de diverses épaisseurs, nous permet d’identifier les striations périodiques avec cette instabilité d’ondulations localisées.

Abstract. — Under heating, a hydrated egg lecithin multilamellar sample in a planar geometry (lamellae normal to the plates) shows a periodic striation instability, followed at higher heating by the so-called « ear-like » domains. We first demonstrate that a normal lamellae contraction under heating can result into a lamellar undulation instability in a planar sample, as well as in a homeotropic geometry. Assuming a strong anchoring of the lamellae on the plates, with the force free condition on the lamellae outer surface, the undulations are localized close to the plates. The spatial period and the threshold are estimated. Observations of hydrated DLL samples of various thicknesses allow us to identify the periodic striations with this localized undulation instability.

The so-called « ear of wheat-like » domains have been observed [1] in hydrated egg lecithin multilamellar samples subjected to an A.C. electric field. A further study of this phenomenon [2] has demonstrated that : a) the ear-like domains are generated by Joule heating and b) below the threshold for ear-like domains, periodic striations occur above a lower heating threshold of typical temperature jump $\Delta T \sim 1$ °C. To explain this observation we propose in this letter a layer undulation thermal instability analogous to the one currently observed in smectic liquid crystals under dilation [3], or else in heated lamellar lecithin phases [4], but in a different geometry.

Let us first resume the finding of reference 2.

a) At room temperature ($T = 27$ °C) a lamellar phase of hydrated egg lecithin (10 % wt. $\text{H}_2\text{O}$) placed in between two transparent $\text{SnO}_2$ coated parallel electrodes (sample thickness $d \sim 5-50$ µm) takes spontaneously an « homeotropic » alignment, with the layers parallel to
the electrodes. The first effect of a low frequency (1 kHz) A.C. electric field seems to reorient the lamellae perpendicular to the glass plates, i.e. to induce a homeotropic to planar transition. After that, for voltage of about 60 V, most of the effects observed in planar monodomains are just due to Joule heating, from the relatively large A.C. current (10-100 mA/cm² in the aqueous phases) flowing through the sample. This was demonstrated by the observation of a non aqueous lamellar phase prepared with synthetic dilauroyl lecithin (DLL, Fluka) and ethylene glycol: in absence of water, the current through the sample was much lower, and no instability could be induced up to applied voltages \( \sim 175 \) V. On the other hand, by purely heating the sample, instabilities in the form of rows of focal conics, merging into « ear-like » domains under further heating, were observed.

\( b) \) Below the threshold heating for structure disruption by focal conics, at a much lower \( \Delta T \sim 0.5 \) to 1 °C, quasi periodic striations occur. An example of these striation is shown on figure 1, which represents the picture of a thin \( (d = 20 \mu) \) planar monodomain of hydrated DLL (10 % wt. H₂O) at \( T = 27 \) °C, seen between crossed polarizers under a microscope. Picture 1a is more or less uniformly dark, because polarizer and analyser, parallel to the edges, are orientated along the optical eigen-axes of the planar uniaxial texture. More precisely, the lamellae are normal to the plates and parallel to the small side of the picture. This is deduced from the observation of the direction of easy motion of bubbles in the sample. Heating is usually achieved by removing the thermal filter of the microscope. For a temperature increase of \( \Delta T = 1 \) °C (measured by thermocouples inside the sample), one observes (Fig. 1b) the periodic striations as a system of dark lines parallel to the optical axis, separated by brighter lines. The average period (distance between three adjacent lines) varies from 4-7 \( \mu \)m, several times lower than the width of the ear-like domains. This instability is reversible, i.e., it disappears slowly by lowering the temperature. At higher thermal excitation, the periodic striations have an organizing action on the ear-like domains. The focal conics are arranged in rows, with the ellipses in the plane of the sample and the hyperbolae along some of the periodic striations.

Resuming these observations on DLL, we look now at the periodic striations. By rotating slightly the polarizer, we note a lateral shift of the dark lines. As these lines are oriented perpendicular to the lamellae, it is reasonable to think that the periodic striations could be explained by a thermal undulation instability of the lamellae seen from the side. Undulation instability under heating was indeed observed [4] in lamellar lecithin samples with very low water content (2 % wt.) in the homeotropic geometry. The thermal thickness expansion coefficient \( \beta \) of lipid bilayers in egg lecithin is known [5] to be negative: \( \beta = -2 \times 10^{-3}/\text{oC} \). This contraction is one order of magnitude larger than, say, the thermal volume expansion of water \( (0.207 \times 10^{-3}/\text{oC}) \) and is probably related to the increased disorder of lipid chains in the bilayers. When heated between two fixed parallel plates, the lamellae are submitted to a dilative strain. Above the instability threshold, the lamellae undulate to fill better the space. Elastic free energy is now stored also as lamellae curvature energy rather than uniform lamellae dilation. The new point in the present planar geometry is that the lamellae are not parallel, but perpendicular to the fixed boundary plates. Let us show that, provided the lamellae anchoring is strong enough on the electrodes, one can also observe an analogous undulation instability in planar orientation, but localized close to the plates.

Our geometry is described in figure 2. \( z \) is the normal to the lamellae. The plates are parallel to \( y \) (in the plane of the lamellae) and \( z, x \) is the direction of observation. The striations are observed parallel to \( z \), i.e. can be described as an undulation \( u \sim \exp(iqy) \) [\( q//y, u//z \)], where \( u \) is the normal distortion of the lamellae. We call \( B \sim 10^8 \text{ cgs} \) [6] the constant pressure elastic modulus of the 1-dimensional « crystal » of lamellae. Let us call \( K \sim 10^{-6} \text{ cgs} \) the Franck curvature constant of the layers. The quantity \( \lambda = (K/B)^{1/2} \) is the penetration length, of the order of the distance between lamellae. The measured [4] \( \lambda \) is in the range of 100 Å for almost dry samples, and could be a little larger in our case, to account for the higher water content of our samples.
Fig. 1. — Planar texture of hydrated DLL : $d = 20 \, \mu m$, $T = 27 \, ^\circ C$. The lamellae are vertical, parallel to the left side elongated bubble. a) Before heating; b) after heating ($\Delta T \approx 1 \, ^\circ C$), showing periodic striations. The small side of the picture corresponds to $250 \, \mu m$. 
The problem of layer contraction under heating, with fixed boundary plates, is exactly the same as the one of layers with fixed spacing, attached to linearly expanding plates along $z$, which simplifies the notations. We write the elastic free energy of the lamellar system as [7]:

$$ F = \frac{1}{2} \frac{\lambda^2}{\lambda} \left[ \frac{\partial u}{\partial z} - \frac{1}{2} \left( \frac{\partial u}{\partial x} \right)^2 - \frac{1}{2} \left( \frac{\partial u}{\partial y} \right)^2 \right] + \frac{1}{2} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right). $$

The first term represents the layer compression, in presence of a layer tilt. Expanded in $u$, it contains a third order term which will lead to the instability. The last term is the layer curvature contribution. In the linear regime, $u$ obeys the Euler equation:

$$ \frac{1}{\lambda^2} \frac{\partial^2 u}{\partial z^2} - \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) u = 0. $$

We look for a solution $u \sim \exp(iqy) W(x) V(z)$.

This implies the relationship:

$$ \frac{\lambda^2}{V} = \frac{W - 2q^2 W + q^4 W}{W} = \text{const}. $$

The free edges of the layers, in contact with water or some desordered part of the sample, do not transmit uniaxial forces i.e. $\partial u/\partial z = 0$ at these boundaries. Calling $L$ the $z$-extension of the planar monodomain, $V$ must be of the shape

$$ V_n = V_0 n \sin \frac{n\pi}{L} z, \quad (n \text{ odd integer} > 0) $$

writing now $W = \exp(k_n x)$, we find the dispersion relationship: $k_n^2 = q^2 \pm i\pi n/\lambda L$. When the plates expand, we assume that the lamellae stick to the plates and remain parallel to $x, y$ (strong anchoring). To calculate the exact profile $W(x)$, we must Fourier analyse the disturbance $u = \beta \Delta T z$ on the $V_n$. To simplify, we keep only the first term $V_1 = V_0 n \sin \pi z/L$. In the simplest 2-dimensional case ($q = 0$), we get $k = \pm 1/\sqrt{2} \left( \pi/2L \right)^{1/2}$, which shows that the layer disturbance propagates only over a distance $L \sim (L, z)^{1/2}$ from the plates. $L$ is in the range of a few $\mu$m, for typical $L \sim$ a few hundred $\mu$m. In thick samples ($d > 2 L \sim 5 \mu m$), all the bulk is under dilative stress. In thick samples ($d > 2 \ell$), just the two boundary layers close to the plates are under stress (see Fig. 2).

Assume now a small layer undulation $u' \sim \exp(iqy) \exp(kx)$ uniform in $z$. It obeys the free edge condition $\partial u/\partial z = 0$. In absence of dilative stress, one must have $k^2 = q^2$, i.e. a small perturbation of lamellae orientation on the plates is attenuated in the bulk on its wave length. We can now make a simple prediction for the threshold undulation instability.

a) Thin samples ($d < 2 \ell$). There exist a uniform dilation $\partial u/\partial z \sim \beta \Delta T$. The undulation appears when the non linear coupling term between tilt and compression $-1/2 \lambda^2 \partial u/\partial z \left( \partial u/\partial x \right)^2 + \left( \partial^2 u/\partial x^2 \right)^2$ compensates for the additional curvature energy $1/2 \left[ \left( \partial^2 u/\partial x^2 \right)^2 + \left( \partial^2 u/\partial y^2 \right)^2 \right]$, i.e. for:

$$ \beta \Delta T \sim \lambda^2 \left( q^2 + \pi^2 \right). $$
The undulation penetrates all the bulk, to relax all the stresses, as soon as \( q < \pi / d \). At lowest threshold \( q \) can be taken equal to zero, which gives: \( \beta \Delta T \sim \lambda^2 \pi^2 / d^2 \). The appearance of the instability should depend very much on the boundary orientation fluctuations.

b) **Thick samples** (\( d > 2 \lambda \)). \( q \) must be small enough for the undulation to penetrate the stressed boundaries, but large enough to leave the unstressed central part unperturbed — this means \( q \ell \sim 1 \). As \( qd > 1 \), the threshold is defined by: \( \beta \Delta T \sim \frac{\lambda^2 \pi^2}{\lambda L} = \pi^2 \frac{\lambda}{L} \), independent from the thickness \( d \). The undulation instability should appear with a period \( \ell \sim (\lambda L)^{1/2} \). With the previously quoted figures, one expects \( \beta \Delta T \sim 10^{-3} \) for \( L \sim 200 \mu m \) and \( \lambda \sim 100 \AA \), i.e. \( \Delta T \sim 1^\circ C \) for \( |\beta| = 2 \times 10^{-3} / ^\circ C \), and \( \ell \sim 1.5 \mu m \). These figures compare well with the observed data.

Finally, we must expect in absence of undulation a direct non linear effect of the layer tilt in the \( x \) direction, to relax locally the dilative stresses, in the case of thick samples, at the junction between the stressed boundary and the central unstressed region. This could lead to the nucleation of layer dislocations or focal conic lines and could explain the nucleation of the ear-like domains.

To check our model, we have measured the periodic striation threshold in samples of 7% hydrated DLL of various thicknesses corresponding to the case of thick sample. \( \Delta T \) seems to increase with \( d \), from \( \Delta T = 0.75^\circ C \) for \( d = 5 \mu m \) up to \( \Delta T = 1.8^\circ C \) for \( d = 110 \mu m \). However, this increase compares with the large dispersion of threshold determination, which can be as high as 100%. We can consider that the threshold is more or less thickness independent. More accurately, we find that the striation period is equal to \( 6 \pm 1 \mu m \) independent of thickness for \( d \) varying from 5 to 110 \( \mu m \). The lateral extension \( L \) was comparable for these samples, in the range of 200-300 \( \mu m \). In practice, the period is found equal to \( 4 \ell \). These two results on the threshold and the period are in agreement with the prediction of the planar undulation model for thick samples. To be complete, let us mention that the ear-like domain period, observed at higher heating, is practically equal to \( d \) between 110 and 20 \( \mu m \), and slightly larger (16 \( \mu m \)) for the thinner 5 \( \mu m \) sample. The best check of our model, however, is the observation, for \( d = 110 \mu m \), of two sets of striations. The first one is focused just below the upper plate, the other one just above the lower plate. Varying the focus, one sees that two dark lines from the lower striations collapse into one dark line of the upper one and *vice versa*. This can easily be understood: the two layer
undulations close to the plates must be out of phase, to cancel their residual distortion in the unstressed central part of the sample.

In conclusion we have shown that, in presence of a strong anchoring, a planar lamellar system undergoing a heating contraction, can present an undulation instability which relaxes the dilative stresses localized close to the plates. The expected behaviour (threshold, period, localization) of this lamellar undulation instability compares well with our observations on the lamellar hydrated phase of DLL. Further observation of this instability is necessary to check other points of our model, like for instance the strong anchoring hypothesis. We believe however that the observation of this thermal instability can provide useful information on the mechanical properties of lipid lyotropic phases and, possibly, on biological lamellar textures like myelin or chloroplasts.

References