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LETTER TO THE EDITOR

The hardening transition in swollen lamellar phases

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Abstract. We reanalyse the competition between two leading anharmonic corrections, due to rotational invariance, to the harmonic description of lyotropic smectic liquid crystals. We show that these corrections have an opposite effect on the bending rigidity and imply the existence of a 'hardening' transition in lamellar phases. For swollen lyotropic lamellar phases for which the entropic steric interaction gives the dominant contribution to the compression modulus, this transition can be reached simply by swelling the system and separates a 'soft' phase at small swelling from a 'rigid' phase at large swelling. This could explain the extraordinary stability of hyperswollen lamellar phases and their extremely thin scattering Bragg peaks. Suggestions for experimental observation of this transition are presented.

In fluid membranes, the molecules can freely and rapidly adjust to shape changes of the membrane. In this case, the membrane deformation is described only in terms of a surface tension γ and a bending elastic modulus k_c. γ is often very small and can even vanish (Brochard *et al* 1976) and the membrane shape is uniquely controlled by k_c. Due to the smallness of the bending energy associated with long-wavelength deformations, large transverse thermal fluctuations (undulations) take place. This feature explains, among other properties, the flicker phenomenon of red blood cells (Brochard and Lennon 1975) and the stability of swollen lamellar lyotropic phases (Larche *et al* 1986), and is involved in stability of microemulsions (Safran *et al* 1986, 1987).

Recently, it was recognised (Helfrich 1985, 1987, Peliti and Leibler 1985, Sornette 1985, Foerster 1987) that non-linear coupling between undulation modes, due to rotational invariance, leads to a decrease of the effective bending rigidity of the membrane at large-scale r according to

$$k_c(r) = k_c^0[1 - (\alpha k_B T/4\pi k_c^0)\log(r/a)] \tag{1}$$

where k_c^0 is the microscopic value of the bending rigidity at the microscopic scale $a \simeq 2$ nm and $\alpha = 1$ (Helfrich 1985, 1987, Foerster 1987) or 3 (Peliti and Leibler 1985, Sornette 1985) depending upon the approach. As a consequence, the correlation of the normals $\boldsymbol{n}(\boldsymbol{r})$ to the membrane appears to decrease exponentially, instead of only algebraically, (de Gennes and Taupin 1982) (if one neglects the non-linear coupling) with a typical persistence length

$$\xi_k \simeq a \exp(4\pi k_c^0/\alpha k_B T). \tag{2}$$

Futhermore, two-dimensional membranes in a three-dimensional space appear to be at their lower critical dimension. Correspondingly, suggestions have been made concerning

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the possible existence of a crumpling transition in the presence of *long-range forces* (for example mediated by phonons) between distant parts of the same membrane (Peliti and Leibler 1985, Nelson and Peliti 1987, David *et al* 1987, Kantor and Nelson 1987, David and Guitter 1988). This crumpling transition would separate a 'low-temperature' rigid phase ($\xi_k \to +\infty$) from a 'high-temperature' crumpled phase corresponding to the situation found in the absence of the long-range force.

The purpose of this Letter is to point out that, when a steric constraint hinders the spontaneous single membrane undulations, long-range forces also appear between distant parts of a same *fluid* membrane that are not mediated by phonons but rather by inter-membrane coupling. As a consequence, a second anharmonic correction intrinsic to smectics, and also due to rotational invariance, must be considered, which competes with the non-linear coupling between undulation modes leading to (1). This term has been considered by Grinstein and Pelcovitz (1981, 1982) and leads to a breakdown of the hydrodynamic description of smectics at large scales. We show that these two corrections (the one that appears for isolated membranes and leads to equation (1), and the other that is intrinsic to smectics) have an opposite effect on the bending rigidity and imply the existence of a 'hardening' transition in lamellar phases. For a swollen lyotropic lamellar phase for which the entropic steric interaction gives the dominant contribution to the compression modulus, this transition can be reached simply by swelling the system and separates a 'soft' phase at small swelling from a 'rigid' phase at large swelling. This could explain the extraordinary stability of hyperswollen lamellar phases and their extremely thin scattering Bragg peaks (Larche *et al* 1986).

The harmonic Hamiltonian for a smectic reads (de Gennes 1974)

$$f = \int \mathrm{d}^3x \, [\tfrac{1}{2}(k_c/\langle z\rangle)\nabla^2 u^2 + \tfrac{1}{2}B(\partial u/\partial z)^2] \tag{3}$$

where the operator ∇ is the transverse gradient (i.e. in the plane of the membranes), the z axis is perpendicular to the membranes and $u = z - \langle z\rangle$ denotes the displacement along z of the point (x, y) of the zth membrane.

We now consider the limiting case of an isolated membrane. For a single membrane with vanishing surface tension, the deformation free energy is again given by equation (3) with $B = 0$. Let us define the local normal to the membrane $\boldsymbol{n} = (n_x = -\partial u/\partial x; n_y = -\partial u/\partial y; n_z \simeq 1)$. For small fluctuations $\delta\boldsymbol{n} = (n_x; n_y)$, the orientational fluctuations $\theta^2(r) = \langle|\delta\boldsymbol{n}(r) - \delta\boldsymbol{n}(0)|^2\rangle$ diverge logarithmically; in the harmonic approximation (Parodi 1984) $\theta^2(r) = (k_B T/\pi k_c^0)\log(r/a)$, where r is the distance along the membrane.

Non-linear coupling between undulation modes comes from the requirement that expression (3) (with $B = 0$) should be invariant with respect to global rotations. Such symmetry considerations lead us to replace $\nabla^2 u$ by the complete expression of the mean curvature (Helfrich 1973)

$$c = \mathrm{div}[\nabla u(1 + |\nabla u|^2)^{-1/2}] \simeq \nabla^2 u(1 - \tfrac{1}{2}|\nabla u|^2 + \ldots) + \ldots \tag{4}$$

The anharmonic corrections of (4) lead to the renormalisation of k_c by fluctuations according to (1) (Helfrich 1985, 1987, Peliti and Leibler 1985, Sornette 1985, Foerster 1987). k_c decreases at large scales meaning that it is easier to bend a crumpled surface than a flat one.

We now consider the case of a multilamellar phase, for which $B \neq 0$. This corresponds to length scales that are large compared to the inter-membrane spacing $\langle z\rangle$. The harmonic deformation energy (3) leads to the following form for the orientational fluctuations (Parodi 1984)

$$\theta^2(r) = (k_B T/2\pi k_c^0)(1 + \log(\lambda\langle z\rangle/\pi a^2)] \qquad \text{as } r \to +\infty \tag{5}$$

for a stack of membranes of mean separation $\langle z \rangle$. λ is the so-called penetration length given by $\lambda^2 = k_c/B\langle z \rangle$ where B is the elastic compression modulus of the smectic liquid crystal formed by the stack of lamellae. B takes into account the interactions between adjacent membranes which introduce a macroscopic compression elastic modulus in the direction z normal to the membranes. The fact that $\theta^2(r)$ is finite as $r \to +\infty$ demonstrates that membrane interactions lead to a phase of planar membranes at large scale.

In this case, rotational invariance brings another correction to expression (3). Since a global rotation of the lamellar phase must not change the energy, $\partial u/\partial z$ must be replaced by (de Gennes 1974, Ribotta and Durand 1977, Sornette 1987a, b)

$$\partial u/\partial z \to (\partial u/\partial z - \tfrac{1}{2}|\nabla u|^2). \tag{6}$$

The influence of this anharmonic correction has been discussed in Grinstein and Pelcovitz (1981, 1982) and leads to a renormalisation by fluctuations of both k_c and B, which become size dependent for length scales larger than the inter-membrane spacing $\langle z \rangle$. The effect of the inter-membrane coupling can be heuristically understood as follows. The anharmonic term (6) is such that a tensile stress can be relaxed by membrane undulations. This is at the basis of the so-called undulation instability studied in smectics (Ribotta and Durand 1977, Sornette 1987a, b). In the presence of thermal fluctuations, one therefore expects that B decreases at large scales due to the coupling between tension and undulation (this is indeed found in Grinstein and Pelcovitz (1981, 1982)) and over the same time k_c increases since additional undulation deformations must appear in order to relax a tensile or compressive stress. Note that the results presented in Grinstein and Pelcovitz (1981, 1982) only considered the anharmonic correction (6) and neglected the correction in (4).

We now consider the competition between the two non-linear corrections (4) and (6). It is clear that a consistent treatment of the anharmonic coupling induced from global rotational invariance in lamellar phases must include both correction terms since rotational invariance must apply both at the single membrane scale and as a whole when considering their interactions. Furthermore, both contributions appear in the full non-harmonic Hamiltonian and it turns out that they are of the same order of magnitude, for example in swollen lamellar phases. Within a perturbative treatment, one can add the contribution of each term calculated separately within the field-theoretical renormalisation group of Peliti and Leibler (1985), Sornette (1985) and Grinstein and Pelcovitz (1981, 1982) to obtain the overall effect of both corrections (4) and (6) on the curvature rigidity. This is due to the fact that the two non-linear corrections to the harmonic smectic Hamiltonian appear, to leading order, as additive terms in the writing of the total non-linear smectic Hamiltonian. We thus obtain

$$k_c(r) = k_c^0\{1 + [(B\langle z \rangle^3/64k_c^0)^{1/2} - \alpha](k_B T/4\pi k_c^0)\log(r/a)\}. \tag{7}$$

The term $(B\langle z \rangle^3/64k_c^0)^{1/2}(k_B T/4\pi k_c^0)\log(r/a)$ on the RHS of (7) is obtained simply by linearising equation (3.15) of Grinstein and Pelcovitz (1982). Equation (7) is valid to leading order in $k_B T/4\pi k_c$. It is similar to (1) but with α replaced by

$$\underline{\alpha} = \alpha - (B\langle z \rangle^3/64k_c)^{1/2}. \tag{8}$$

Expression (7) is valid at length scales r larger than $\langle z \rangle$. It shows the influence of the inter-membrane coupling via the term B which may change $\underline{\alpha}$ from a positive to a negative value. This suggests the existence of a 'hardening' transition separating a 'soft' phase at $\underline{\alpha} > 0$ (for which k_c decreases at large scales) from a 'rigid' phase at $\underline{\alpha} < 0$ (for which k_c increases at large scales). This transition is distinct from the crumpling transition

occurring for single membranes since both the 'soft' and 'rigid' phases present quasi-long-range translational order and long-range orientational order with algebraic decay of the density correlation function (with, however, different exponents in the two phases).

Of the two corrections (4) and (6), only (6) couples transverse and normal deformations. Therefore, the anharmonic correction (4) does not enter the renormalisation of B by fluctuations and we may use directly the result of Grinstein and Pelcovitz (1981, 1982), for example at fixed q_z:

$$B(r) = B_0[1 - (\beta^{1/2}/16\pi)(k_B T/k_c)^2 \log(r/a)] \tag{9}$$

which does not exhibit any remarkable behaviour.

An interesting case occurs in swollen lamellar phases where $\langle z \rangle$ becomes much larger than the molecular size $a \simeq 2$ nm. Then, experiments show that, for neutral membranes, the Helfrich steric interaction (Helfrich 1978, Sornette and Ostrowsky 1984, Janke and Kleinert 1987) may become the dominant contribution to the effective inter-membrane interaction leading to a finite value of B. In this case, B is given by (Helfrich 1978, Sornette and Ostrowsky 1984, Janke and Kleinert 1987)

$$B = \beta[(k_B T)^2/k_c]\langle z \rangle^{-3} \tag{10}$$

with β in the range 0.44–1.38 ($\beta = 9\pi^2/64$ in Helfrich 1978). This means that adjacent membranes are coupled only via the excluded volume constraint exerted on long-wavelength undulations. The steric interaction is felt essentially by modes of in-plane wavevector q less than a cut-off $q(z)$ given by (Sornette 1986)

$$q(z)^{-1} \simeq (k_c/k_B T)^{1/2}\langle z \rangle. \tag{11}$$

$q(z)^{-1}$ sets the scale separating two regimes.

Firstly, for modes such that $q > q(z)$, i.e. at scales less than $q(z)^{-1}$, the steric constraint is absent and the constraint modulus $B(q)$ exerted on these modes is vanishingly small. Therefore, the problem is that of *isolated membranes* and the bending modulus $k_c(q)$ should be renormalised by fluctuations according to (1), since the membranes are essentially free and do not feel each other at these scales. At the scale $r \sim q(z)^{-1}$, k_c is reduced to

$$k_c^* = k_c^0\{1 - (\alpha k_B T/4\pi k_c^0) \log[(k_c/k_B T)^{1/2}\langle z \rangle/a]\}. \tag{12}$$

Secondly, at scales larger than $q(z)^{-1} \simeq (k_c/k_B T)^{1/2}\langle z \rangle$, steric interactions between adjacent membranes become important and decrease the amplitude of modes with wavevectors $q < q(z)$. Then, the effect of the competition between the two non-linear corrections (4) and (6) leads to (7) but with a value of the 'bare' bending rigidity changed into k_c^*, since k_c^* sets the scale of the bending rigidity in the absence of steric constraint.

Equation (12) shows that the effective bending rigidity controlling the steric interaction can be significantly smaller than k_c^0 and this leads to an enhanced steric interaction according to (10) (Sornette 1986). Then, the renormalisation of the bending rigidity reads

$$k_c(r) = k_c^*[1 - \underline{\alpha}(k_B T/4\pi k_c^*) \log(q(z)r)]. \tag{13}$$

Due to the particular form of B, $\underline{\alpha}$ takes a simple expression given by

$$\underline{\alpha}(\langle z \rangle) = \alpha - k_B T\beta^{1/2}/8k_c^*(\langle z \rangle) \tag{14}$$

where $\underline{\alpha}$ is defined in (8). Equation (14) is valid at scales $r > q(z)^{-1}$. Note that if one

neglects the z-dependence of k_c^*, $\underline{\alpha}$ is a pure number (Leibler and Lipowsky 1987).

Equation (13) with (14) shows the existence of a 'hardening' transition which occurs at $\underline{\alpha} = 0$, i.e. $k_c^*/k_B T = \beta^{1/2}/8\alpha$. Using expression (14), this occurs for

$$\langle z\rangle_c/a = (k_c^0/k_B T)^{-1/2} \exp\{4\pi[(k_c^0/k_B T) - \beta^{1/2}/8\alpha]/\alpha\}. \tag{15}$$

Let us take a fixed membrane composition such that $k_c^0/k_B T$ is fixed. For $\langle z\rangle < \langle z\rangle_c$, $\underline{\alpha} > 0$ and for $\langle z\rangle > \langle z\rangle_c$, $\underline{\alpha} < 0$. Therefore, by swelling, a lamellar system can cross the transition point and go from a phase in which the membranes are 'soft' (k_c decreases with scale) to a phase where the membranes are 'rigid' (k_c increases with scale). The fact that the 'rigid' phase is reached by swelling could be an important factor alternative to the electrostatic explanation (Larche *et al* 1986, Safinya *et al* 1986) for explaining the observed stability of hyperswollen lamellar phases, which present a stronger smectic order for larger lamellae separation $\langle z\rangle$ (Helfrich 1985, 1987). Precise measurements of k_c^0 are difficult to obtain (Meunier *et al* 1987). Recent work (Larche *et al* 1986, Safinya *et al* 1986) on swollen lamellar phases shows that k_c^0 is in the range of $k_B T$. Taking typically $k_c^0/k_B T \simeq 1$, we find $\langle z\rangle_c/a \simeq 43$ (with $a \simeq 2$ nm, this leads to $\langle z\rangle_c \simeq 86$ nm) which is well in the range explored in recent experiments (Larche *et al* 1986). These numerical estimates are, however, extremely sensitive to the value of $k_c^0/k_B T$.

Note that the hardening transition can also be detected in x-ray, neutron or light-scattering experiments that measure the exponent X_m of the algebraic decay of correlations characteristic of the quasi-long-range translational order in lamellar phases (Callié 1972). This exponent $X_m = k_B T q_m^2/8\pi(k_c B/\langle z\rangle)^{1/2}$ $(m = 1, 2, \ldots)$ can be obtained by analysing the power-law scattering intensity peak $S(q_z) \sim (q_z - q_m)^{-(2 - X_m)}$. Reporting the scale dependence of k_c and B given by (7) and (9) in X_m yields to leading order

$$X_m(r) \simeq X_m^*\{1 + [(\underline{\alpha}/8\pi)(k_B T/k_c^*) + (\beta^{1/2}/32\pi)(k_B T/k_c^*)^2] \log(q(z)r)\} \tag{16}$$

where X_m^* is the unrenormalised correlation exponent. X_m increases or decreases with the transverse scale r according to the sign of $(\underline{\alpha}/8\pi)(k_B T/k_c^*) + (\beta^{1/2}/32\pi)(k_B T/k_c^*)^2$. Considering the second term in $(k_B T/k_c)^2$ as a correction to the first one, the 'hardening' transition should appear in the change of behaviour of X_m at large scales: (i) the 'soft' phase with $\underline{\alpha} > 0$ corresponds to X_m which increases with scale; (ii) the 'rigid' phase with $\underline{\alpha} < 0$ corresponds to X_m which decreases with scale. Suppose that $X_{m=1}^* < 2$ but $X_{m=2}^* \geqslant 2$ so that only the first Bragg peak exists at small swelling. As the lamellar phase is swollen, one eventually crosses the 'hardening' transition and enters into the rigid phase for which $\underline{\alpha} < 0$. Let us take typically $\langle z\rangle \sim q(z)^{-1} \sim 0.1$ μm (for $k_c/k_B T \sim 1$), $r \sim 10$ μm and $\underline{\alpha} \simeq -2$. This yields, using (16), $X_{m=2} \simeq 0.6 X_{m=2}^* \simeq 1.2$ for $X_{m=2}^* \simeq 2$. Thus, the second Bragg peak may appear as the lamellar phase is swollen and undergoes the hardening transition. This prediction is in agreement with the observations of Larche *et al* (1986).

Several regimes for a swollen lyotropic smectic liquid crystal have been discussed, which depend on the relative size of $r_\parallel$ with respect to $q(z)^{-1}$. At scales $r_\parallel > q(z)^{-1}$, the competition between two anharmonic corrections to the smectic free energy shows the existence of a 'hardening' transition for each lamella which can be reached by swelling the system. It separates a 'soft' phase at small swelling from a 'rigid' phase at large swelling. This paradoxical result (one could intuitively expect that larger swelling implies lower order) stems from the fact that a larger swelling implies a smaller effective bending rigidity k_c^* at the crossover scale $q(z)^{-1}$ and therefore a larger stabilising steric interaction. Note that the present analysis relies on perturbative corrections valid rigorously for

large $k_c^0/k_B T$. Our use of these results in the regime $k_c^0/k_B T \sim 1$ can only be taken as an indication of the results of a more general analysis which is unfortunately out of reach of present techniques. An ultimate bound for $k_c^0/k_B T$ is given by the geometrical condition $\langle z \rangle < \xi_k$, for a lamellar phase to be defined. This is verified for $\langle z \rangle_c$ if $k_c^0/k_B T > 0.7$.

These ideas have an interesting theoretical implication for the unbinding transition predicted for lamellar systems and studied recently within functional renormalisation groups (Lipowsky and Leibler 1986, Sornette 1987a, b). Developing a renormalisation scheme placing on the same footing the effect of undulations on the membrane curvature rigidity k_c and on the membrane interactions remains a stimulating challenge for future works.

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