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Fluctuations in membranes with crystalline and hexatic order

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Résumé. — Nous étudions les effets dûs à la coexistence de l'ordre cristallin (ou hexatique) et des fluctuations thermiques dans les membranes à tension superficielle négligeable. Si la connectivité de l'état cristallin est parfaite, la membrane n'est pas plissée à basse température. Si l'on permet la formation de dislocations, l'écrantage des contraintes élastiques dû au flambage produit une concentration diluée de dislocations libres à toute température non nulle. Si la phase hexatique qui en résulte est stable, la rigidité associée aux corrélations orientationnelles produit une augmentation logarithmique de la rigidité de courbure qui s'oppose à la diminution produite par les fluctuations thermiques que l'on trouve dans les membranes fluides. Il paraît possible d'observer des transitions de plissage à température finie tant dans les membranes cristallines qu'hexatiques.

Abstract. — We study the interplay between crystalline (or hexatic) order and thermal fluctuations in membranes with vanishing surface tension. If the connectivity of the crystalline state is preserved, the membrane remains uncrumpled at low temperatures. When dislocations are allowed, however, screening of elastic stresses by buckling reduces dislocation energies, and promotes dislocation unbinding. When the resulting hexatic phase is stable, the stiffness associated with orientational correlations leads to a logarithmic enhancement of the bending rigidity which counteracts the thermal softening found in fluid surfaces. A finite temperature crumpling transition is predicted for crystalline membranes, and possibly for hexatic membranes as well.

1. Introduction.

The behaviour of lyotropic amphiphiles can be understood on the basis of a phenomenological model [1, 2] of a membrane with small, or vanishing, surface tension. In this model, the membrane is assumed to be a fluid, which means that molecules can flow freely to adapt themselves to a particular membrane configuration. One considers therefore an elastic free energy which only depends on the membrane shape. The dominant contribution to the free energy is the bending elasticity, which depends on the membrane curvature, and violent out-of-plane fluctuations (undulations) take place. On this basis it has been possible to understand a few relevant features of the behavior of vesicles formed by amphiphilic bilayers (such as red blood cells) : in particular the appearance of different shapes [3] and of the flicker phenomenon [4], i.e., the enhanced light scattering due to undulations.

It has been more recently realized [5] that undulations also reduce the effective rigidity of the membrane with respect to its bare (microscopic) value. As a consequence of this effect, which has been confirmed by renormalization group calculations [6, 7], the normals to the membrane are correlated only up to a bending persistence length ξ_b. It was observed in reference [6] that although fluid membranes appear to be at their lower critical dimension, with a phase transition only at $T = 0$, imposition of long-range forces might lead to a finite temperature *crumpling transition*, separating a low temperature, rigid phase ($\xi_b \to \infty$) from a crumpled high temperature one.

Here we argue that the requisite long-range forces in fact appear in membranes with crystalline or hexatic order. Lipid bilayers often exhibit two or more phases [8] and one of them (the L_β phase) is often thought to be associated with in-plane crystalline order. It is therefore interesting to investigate

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the effect of crystalline or hexatic order on undulations and bending elasticity. Additional motivation is provided by the recent observation [9] of hyperswollen lamellar lyotropic liquid crystals with interlamellar separations as large as 6 000 Å. One may speculate on the possibility of obtaining lyotropic analogues of crystalline or hexatic smectic-B phases with similar interlamellar separations. Understanding the behavior of an isolated membrane with in-plane order is a first step towards the treatment of these structures.

Our conclusions may also be applicable to *polymerized* surfactant bilayers [10]. With sufficiently high crosslinking, in-plane fluid phases are no longer possible. Polymerized lipid bilayers provide an experimental realization of *tethered surfaces*, whose high temperature (or low rigidity) crumpled phase has been studied theoretically by Kantor *et al.* [11]. At low temperatures (or high rigidity), we would expect an uncrumpled surface, rather like a single layer of the lyotropic crystalline smectics discussed above.

The results of our investigation can be summarized as follows : in any system with a nonzero in-plane shear modulus, the usual bending energies must be augmented by a phonon-mediated long-range interaction between the Gaussian curvature. In the absence of dislocations, this interaction drastically increases the rigidity, and suppresses crumpling at low temperatures. Screening by curvature fluctuations may cause membranes with thermally activated dislocations to melt the crystal, however. If the film melts into a hexatic phase, there remains a residual logarithmic interaction between the Gaussian curvature. The rigidity in a membrane of size L then takes the form

$$\kappa_{\mathrm{R}} = \kappa - \frac{3\,T}{4\,\pi}\ln\,(L/\xi_{\mathrm{T}}) + \frac{3\,K_{\mathrm{A}}\,k_{\mathrm{B}}\,T}{16\,\pi\kappa}\ln\,(L/\xi_{\mathrm{T}})\,,$$

where ξ_{T} is a translational correlation length. A nonzero hexatic stiffness constant K_{A} tends to counteract the softening of the rigidity found for fluid membranes. Finite temperature crumpling transitions are likely in crystalline membranes, and possibly in hexatic membranes as well.

2. Membranes with crystalline order.

We consider almost planar membranes whose shape can be represented in the Monge form, i.e., by giving the value of the coordinate z as a function of the coordinates $x = x_1$, $y = x_2$:

$$z = f(x_1, x_2)\,, \quad (x_1, x_2) \in S_0\,; \tag{1}$$

where S_0 is the projection of the membrane onto the reference plane (x_1, x_2). If the crystalline order is perfect, there exists a single-valued displacement vector $\mathbf{u} = (u_1, u_2, f)$ from the configuration of minimum energy, which is assumed to lie in the plane (x_1, x_2). The strain tensor u_{ij} is then given by [12]

$$u_{ij} = \frac{1}{2}\,(\partial_i u_j + \partial_j u_i + \partial_i f\;\partial_j f)\,. \tag{2}$$

The elastic-free energy is the sum of the bending free energy F_{b} and the stretching free energy $\tilde{F}_{\mathrm{s}}$. We take for F_{b} Helfrich's expression [2], with zero spontaneous curvature (and we disregard the effects of the Gaussian rigidity). We thus have

$$F_{\mathrm{b}} = \int \mathrm{d}S\left[\frac{1}{2}\,\kappa H^2\right], \tag{3}$$

where dS is the area element of the membrane, H its mean curvature, and κ is the (bare) rigidity. To lowest order in an expansion in f and its derivatives we have

$$F_{\mathrm{b}} = \frac{1}{2}\,\kappa \int \mathrm{d}^2x\,(\nabla^2 f)^2\,, \tag{4}$$

where ∇^2 is the two-dimensional Laplacian, and [12]

$$\tilde{F}_{\mathrm{s}} = \frac{1}{2}\int \mathrm{d}^2x\,(2\,\mu u_{ij}^2 + \lambda u_{kk}^2) \tag{5}$$

where μ and λ are Lamé coefficients. In this approximation the free energy is quadratic in the « phonon » degrees of freedom u_i, which can be then eliminated by a Gaussian integration. This can be efficiently performed by observing that the last term of equation (2) can be written, as can any symmetric, second rank, two-dimensional tensor, in the form [13]

$$\partial_i f\;\partial_j f = \partial_i v_j + \partial_j v_i + P_{ij}^{\mathrm{T}}\,h\,, \tag{6}$$

where v_i is a suitable two-dimensional vector field, h a scalar function, and $P_{ij}^{\mathrm{T}} = (\nabla^2)^{-1}\,\varepsilon_{ik}\,\varepsilon_{jl}\,\partial_k\partial_l$ is the transverse projector. One can then shift u_i by v_i and integrate, finally obtaining an effective free energy which depends only on f:

$$\begin{aligned} F_{\mathrm{eff}} &\equiv F_{\mathrm{b}} + F_{\mathrm{s}} \\ &= \frac{1}{2}\,\kappa \int \mathrm{d}^2x\,(\nabla^2 f)^2 + \\ &\quad + \frac{1}{2}\,K_0 \int \mathrm{d}^2x\left(\frac{1}{2}\,P_{ij}^{\mathrm{T}}\partial_i f\;\partial_j f\right)^2, \end{aligned} \tag{7}$$

where

$$K_0 = \frac{4\,\mu\,(\mu + \lambda)}{2\,\mu + \lambda}\,. \tag{8}$$

Note that the Gaussian curvature S is related to the quantity appearing in equation (7) by :

$$S(\mathbf{x}) = -\,\nabla^2\left(\frac{1}{2}\,P_{ij}^{\mathrm{T}}\,\partial_i f\;\partial_j f\right) = \det\,(\partial_i\partial_j f)\,. \tag{9}$$

Equation (7) exhibits the free energy as a sum of a bending energy, quadratic in f, and a quartic stretching energy F_s. The stretching energy can be rewritten using (9) as

$$F_s = \frac{K_0}{16\,\pi} \int d^2x_a \times$$
$$\times \int d^2x_b\, G(\mathbf{x}_a - \mathbf{x}_b)\, S(\mathbf{x}_a)\, S(\mathbf{x}_b) \quad (10a)$$

where the curvature Green's function $G(x)$ is given by

$$G(x) \approx x^2 \ln (x/a) \quad (10b)$$

for large x, where a is the lattice spacing. Equation (10) exhibits explicitly a phonon-mediated interaction between distant Gaussian curvatures. Comparison of the two terms in equation (7) suggests that the stretching energy in a membrane of size L will become important whenever

$$\langle f^2 \rangle \approx \frac{k_B\, T}{\pi \kappa} L^2 \gtrsim (\kappa / K_0\, a^2)\, a^2 . \quad (11)$$

Taking $K_0\, a^2 \approx 16\, \pi k_B\, T_m$, where T_m is the Kosterlitz-Thouless melting temperature of a flat membrane [14], (assumed to be of order room temperature, 300 K) and [2] $\kappa \approx 10^{-12}$ erg, we find that stretching becomes important whenever $L \gtrsim 6\,a$. Undulations with nonzero Gaussian curvature will therefore be suppressed in crystalline membranes, although one-dimensional fluctuations (whose Gaussian curvature vanishes) are still possible.

Additional insight is provided by studying the renormalized bending constant $\kappa_R(\mathbf{q})$, defined by

$$k_B\, T/\kappa_R(\mathbf{q}) \equiv q^4 \langle |\hat{f}(\mathbf{q})|^2 \rangle , \quad (12)$$

where $\hat{f}(\mathbf{q})$ is the Fourier transform of $f(\mathbf{x})$, and the average is carried out in an ensemble specified by F_{eff}. To lowest order in K_0 we find that

$$\kappa_R(\mathbf{q}) = \kappa + K_0\, k_B\, T \times$$
$$\times \int \frac{d^2k}{(2\,\pi)^2} \frac{[\hat{q}_i\, P_{ij}(\mathbf{k})\, \hat{q}_j]^2}{\kappa\, |\mathbf{k} + \mathbf{q}|^4} , \quad (13a)$$

where $\hat{\mathbf{q}}$ is a unit vector and $P_{ij}(\mathbf{k}) = \delta_{ij} - k_i\, k_j / k^2$. The integral diverges like q^{-2} for small q, showing that the stretching energy drastically increases the effective bending rigidity at long wavelengths. This increase dominates the logarithmic softening of the rigidity due to short wavelength undulations found in reference [6]. A simple self-consistent theory which replaces κ by $\kappa_R(\mathbf{k} + \mathbf{q})$ in the integrand of (13) and *assumes* no significant renormalization of K_0 gives [15]

$$\kappa_R(q) \sim \sqrt{k_B\, T K_0}\, q^{-1} . \quad (13b)$$

To see that (13b) implies long-range order in the normals, note first that the Monge form for the normal is

$$\hat{\mathbf{m}} = (-\,\partial_1 f, -\,\partial_2 f, 1) / \sqrt{1 + |\nabla f|^2} .$$

It follows that the tipping angle of θ of the normal relative to the $\hat{\mathbf{x}}_3$ axis is given by

$$\hat{\mathbf{m}} \cdot \hat{\mathbf{x}}_3 = \cos \theta = 1 / \sqrt{1 + |\nabla f|^2} . \quad (14a)$$

To lowest order in f and θ, we have $\langle \hat{\mathbf{m}} \cdot \hat{\mathbf{x}}_3 \rangle \approx 1 - 1/2 \langle \theta^2 \rangle$, where [16]

$$\langle \theta^2(x) \rangle \approx \langle |\nabla f(x)|^2 \rangle$$
$$= k_B\, T \int \frac{d^2q}{(2\,\pi)^2} \frac{1}{\kappa_R(q)\, q^2} . \quad (14b)$$

Although the integral (14b) is expected to diverge for *fluid* membranes [16, 6, 7], indicating the absence of long-range order in the normals, it remains finite when we use the estimate (13b) appropriate for crystalline or tethered surfaces. It follows that $\langle \theta^2 \rangle$ becomes arbitrarily small at low temperatures, so that $\langle \hat{\mathbf{m}} \cdot \hat{\mathbf{x}}_3 \rangle \approx 1$ in this limit, *i.e., there is long-range order in the normals.* The flat low temperature phase predicted by this argument presumably has finite elastic constants, consistent with the assumption of no significant renormalization of K_0.

3. Screening of dislocations due to buckling.

The above analysis assumes a single-valued displacement field, and neglects topological defects like disclinations and dislocations. Although such defects are impossible in the tethered surfaces of reference [11], they can, of course, be quite relevant in unpolymerized lipid bilayers. In a flat membrane of radius R, an isolated disclination has an in-plane elastic energy of order $K_0\, s^2\, R^2 \ln (R/a)$, where s is the disclination charge, while a dislocation has an energy of order $K_0\, b^2 \ln (R/a)$, where b is the Burger's vector [14]. These estimates must be modified, however, if the membrane is allowed the buckle into the third dimension, and trade stretching energy for bending energy [17].

Consider first a wedge disclination with angular deficit or « charge » s located at the origin. Far from the origin, it becomes preferable for the surface to buckle out of the plane and assume the form $f(r, \theta) = r\Phi(\theta)$ where r and θ are polar coordinates in the reference plane S_0. This form guarantees that the Gaussian curvature vanishes, and hence that there will be no contribution from the nonlinear stretching energy displayed in equation (7) (note that the radius of curvature in the radial direction is infinite). The surface assumes a conical shape for $s > 0$, and a hyperbolic one for $s < 0$. Although the basic equations are nonlinear and difficult to solve [12], it is not hard to show that for small s,

$$f(\mathbf{r}, \theta) \approx \begin{cases} -\sqrt{s/\pi r}\,, & s > 0 \\ \sqrt{\dfrac{2|s|}{3\pi}}\, r \cos 2\theta\,, & s < 0\,. \end{cases} \tag{15}$$

In all cases $\nabla^2 f \propto 1/r$, and the bending energy in equation (7) diverges logarithmically, $F_{\mathrm{eff}} \sim \kappa \ln (R/a)$. The disclination energy still diverges with system size, but it has been reduced considerably by the buckling process.

Because a dislocation can be regarded as a tightly bound pair of oppositely charged disclinations [14], one might expect the disclination strain fields to cancel at large distances, leading to a finite dislocation energy [18]. Although this may indeed be the case, the nonlinear « screening » of a dislocation stress field due to buckling is actually quite subtle. To see this, consider an edge dislocation with Burger's vector b at the origin. We assume a membrane composed of cylindrical objects (e.g., lipids), so that the Burger's vector b is less than the membrane thickness d. Studies of dislocations inserted into slabs of foam rubber suggest that it may be possible to approximate a buckled surface with the factorized form $f(r, \theta) \approx a(r) \cos (\theta)$, at least for small r. For $b \lesssim d$ we can neglect in-plane displacements, and determine $a(r)$ by integrating the displacement field around a loop of radius r,

$$\begin{aligned} \oint \mathrm{d}u &\approx \oint \left\{ \sqrt{1 + \frac{1}{r^2}\left(\frac{\mathrm{d}f}{\mathrm{d}\theta}\right)^2} - 1 \right\} r \,\mathrm{d}\theta \\ &\approx \frac{1}{2r} \int_0^{2\pi} \left(\frac{\mathrm{d}f}{\mathrm{d}\theta}\right)^2 \mathrm{d}\theta \equiv b\,. \end{aligned} \tag{16}$$

This condition leads to a surface of the form

$$f(r, \theta) \approx \left(\sqrt{\frac{2br}{\pi}}\right) \cos \theta\,. \tag{17}$$

A surface displacement which increases like $\sqrt{r}$ ultimately leads to large energies, however. The Gaussian curvature associated with equation (17) is everywhere nonzero, so we must consider both the bending and stretching energies embodied in equation (7). The bending energy in a thin annulus of radius r is of order $R_{\mathrm{bend}} \sim 1/2 (\kappa/r^4) \langle f^2 \rangle_\theta$, while the stretching energy is $E_{\mathrm{stretch}} \sim 1/2 (K_0/r^4) \langle f^4 \rangle_\theta$, where $\langle\ \rangle_\theta$ denotes an angular average. Using (17), we see that the stretching energy exceeds the bending when $r \gtrsim \kappa/K_0\, b$, and diverges logarithmically when integrated over r.

We have reason to doubt the validity of equation (17) for large r, however : by inserting a dislocation into a stiff piece of paper (where stretching is essentially impossible), it is easy to create a buckled surface with *zero* stretching energy. For purposes of estimating the bending energy, we note that the resulting surface has the approximate form, $f(r, \theta) \simeq b (r/b)^{\sin^2 \theta}\, \Psi(\theta)$, where the Burger's vector is in the direction $\theta = \pi/2$. The periodic function $\Psi(\theta)$ is symmetric about $\theta = 0$, has a single minimum at $\theta = 0$ $[\Psi(\theta) \simeq -\sqrt{2}/2]$, and a single maximum at $\theta = \pi$ $[\Psi(\pi) = +\sqrt{2}/2]$. It passes through zero at $\theta \simeq \pm \pi/6$. Note that $f(r, \theta)$ rises linearly with r for $\theta = \pm \pi/2$, and is independent of r for $\theta = 0$ and $\theta = \pi$. Because $\langle f(r, \theta) \rangle_\theta$ increases (up to logarithmic corrections) like $r^{1/2}$, this form leads to a finite bending energy. Although the rough form given above suffices for evaluating the bending energy, the stretching energy is more subtle, due to the transverse projection operator in equation (7). Fortunately, we know that the stretching energy for the true surface vanishes identically. More precise numerical studies of the energies of buckled dislocation are currently in progress.

Assuming that the dislocation energy is indeed finite, we can use a more quantitative calculation of Mitchell and Head, who estimate an upper bound for the radius R_{c} at which a flat dislocated plate becomes unstable with respect to buckling [19]. Adapting their results to lipid films, we find

$$R_{\mathrm{c}} \lesssim 120 \frac{\kappa}{K_0\, b}\,. \tag{18}$$

Estimating K_0 as in section 2 and setting $b = a$, we have $R_{\mathrm{c}} \lesssim 2.4 (\kappa/k_{\mathrm{B}} T_{\mathrm{m}})\, a$, which means (for $\kappa \sim 10^{-12}$ erg and $k_{\mathrm{B}} T_{\mathrm{m}} \sim 300$ K) $R_{\mathrm{c}} \lesssim 60\, a$. For separations R larger than R_{c}, dislocation-dislocation interactions will be well screened. Free dislocations will then appear with a density

$$n_{\mathrm{D}} \simeq a^{-2} \exp(-E_{\mathrm{c}}/k_{\mathrm{B}} T)\,,$$

where E_{c} is their effect core energy. We estimate E_{c} to be of the order of half the energy of a dislocation pair separated by the distance R_{c} :

$$2 E_{\mathrm{c}} \simeq \frac{K_0}{4\pi} b^2 \ln (R_{\mathrm{c}}/a)\,. \tag{19}$$

The typical separation ξ_{T} among dislocations is related to n_{D} by $n_{\mathrm{D}} \approx \xi_{\mathrm{T}}^{-2}$. We obtain therefore (setting $b = a$) :

$$\xi_{\mathrm{T}} \simeq a \left(\frac{R_{\mathrm{c}}}{a}\right)^{K_0 a^2/16 \pi k_{\mathrm{B}} T}\,. \tag{20}$$

For a membrane with local crystalline order, the exponent is always larger than unity [14], so ξ_{T} always exceeds R_{c}. The quantity ξ_{T} is a translational correlation length for crystalline order : membranes with local crystalline order will appear fluid on scales larger than ξ_{T}.

Although we find the arguments given above for a finite dislocation energy convincing, we cannot rigorously rule out a dislocation energy which grows with system size. The worse possibility is that the dislocation energy still diverges logarithmically, but with a smaller coefficient due to the buckling. In this case, we would expect a substantial reduction in the dislocation unbinding temperature, so that membranes with $T_m \approx 300$ K when flat would be melted at room temperature.

4. Effects of hexatic order.

Fluids with a finite density of free dislocations often display the residual bond-orientational order of the hexatic phase [14]. Although disclinations (which now interact logarithmically) can unbind to form a conventional isotropic liquid, this is unlikely when the translational correlation length is large, as indicated by the estimates of section 3. Disclinations can lower their energy somewhat by buckling, but we have seen that a logarithmically divergent bending energy remains. It seems quite probable that many membranes which are crystalline when confined to a plane will become hexatic at sufficiently long length scales when allowed to fluctuate into the third dimension.

To construct a continuum elastic theory of hexatic membranes, recall that hexatics are characterized by long-range correlations in the bond directions, which may be identified by a unit vector field $\mathbf{n}$. It is reasonable to assume that the state of lowest elastic energy would correspond to the situation in which the direction of the bond at a point $\mathbf{r} + \mathrm{d}\mathbf{r}$ can be obtained from that at $\mathbf{r}$ by parallel transport of the vector $\mathbf{n}$ along the infinitesimal path connecting the two points. The curvature of the membrane introduces a frustration, since if a vector undergoes parallel transport along a path bounding a small region of area Σ centred at a point $\mathbf{r}$ with Gaussian curvature $S(\mathbf{r})$, it is not mapped on itself, but comes back rotated by an angle $S(\mathbf{r})\,\Sigma$. Therefore, it will not be possible in general to find a vector field $\mathbf{n}$ which is mapped on itself by parallel transport. We can now introduce the angle θ between the vector $\mathbf{n}$ and the first axis of a local reference frame $\{\mathbf{e}_1, \mathbf{e}_2\}$. It is shown in the Appendix that the elastic free energy associated with the hexatic order can then be written, to lowest order in f and its gradients, as

$$F^{\mathrm{H}} = \frac{1}{2} K_{\mathrm{A}} \int \mathrm{d}^2x \, [\nabla\theta + \mathbf{A}]^2 , \qquad (21\mathrm{a})$$

where K_{A} is the hexatic stiffness constant, and the « vector potential » $\mathbf{A}$, expressing the frustration, is given by :

$$A_i = \frac{1}{2} \varepsilon_{ik} \, \partial_k (P^{\mathrm{T}}_{lm} \, \partial_l f \, \partial_m f) . \qquad (21\mathrm{b})$$

This expression corresponds to the requirement that

$$(\nabla \times \mathbf{A}) \cdot \hat{\mathbf{x}}_3 = \varepsilon_{ij} \, \partial_i A_j = S(r) . \qquad (22)$$

The stiffness K_{A} is expected to be of order $E_{\mathrm{C}}(\xi_{\mathrm{T}}/a)^2$, where E_{C} is a dislocation core energy [14].

If we neglect unbound disclinations, $\theta(x, y)$ is single-valued and we can integrate it out to obtain

$$\begin{aligned} F^{\mathrm{H}}_{\mathrm{eff}} &\equiv F_{\mathrm{b}} + F^{\mathrm{H}}_{\mathrm{s}} \\ &= \frac{1}{2} \kappa \int \mathrm{d}^2x (\nabla^2 f)^2 + \\ &\quad + \frac{1}{2} K_{\mathrm{A}} \int \mathrm{d}^2x \left[\frac{1}{2} \partial_k P^{\mathrm{T}}_{ij} (\partial_i f \, \partial_j f) \right]^2 . \end{aligned} \qquad (23)$$

Just as for crystalline membranes, we can reexpress the contribution of (23) due to the rigidity of bond-orientational order in terms of the Gaussian curvature. We now find

$$\begin{aligned} F^{\mathrm{H}}_{\mathrm{s}} = \frac{K_{\mathrm{A}}}{4\pi} \int \mathrm{d}^2x_{\mathrm{a}} \, \times \\ \times \int \mathrm{d}^2x_{\mathrm{b}} \ln (|\mathbf{x}_{\mathrm{a}} - \mathbf{x}_{\mathrm{b}}|/\xi_{\mathrm{T}}) \, S(\mathbf{x}_{\mathrm{a}}) \, S(\mathbf{x}_{\mathrm{b}}) . \end{aligned} \qquad (24)$$

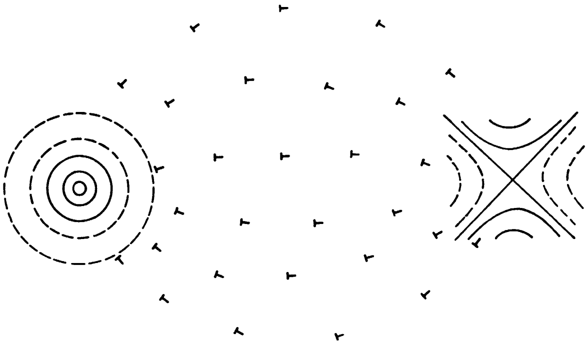

Fig. 1. — Schematic representation of the screening of curvature fluctuations by unbound dislocations. Contours of constant surface displacement f are shown : solid lines lie above the plane of the paper, and dashed lines are below.

As indicated schematically in figure 1, the $x^2 \ln (x/a)$ interaction between distant Gaussian curvatures in crystalline membranes has been screened down to a simple logarithm by the gas of unbound dislocations. The translational correlation length appears in the argument of the logarithm because this plays the role of a microscopic length in the hexatic phase [14].

To lowest order in the hexatic stiffness K_{A}, the renormalized bending constant is now

$$\kappa_{\mathrm{R}}(\mathbf{q}) = \kappa + K_{\mathrm{A}} k_{\mathrm{B}} T \int \frac{\mathrm{d}^2\mathbf{k}}{(2\pi)^2} \frac{k^2 [q_i P_{ij}(\mathbf{k}) q_j]^2}{\kappa |\mathbf{k} + \mathbf{q}|^4} . \qquad (25)$$

This expression is similar to equation (13) but the integral is now only logarithmically divergent and yields a *positive* contribution to the effective rigidity at small q :

$$\delta \kappa = K_{\mathrm{A}} \frac{3\, k_{\mathrm{B}}\, T}{16\, \pi \kappa} \left|\ln (q \xi_{\mathrm{T}})\right| \,. \qquad (26)$$

The stiffening of the bending rigidity exhibited in equation (25) can be contrasted with its softening due to undulations, given e.g. in reference [6] by

$$\delta \kappa' = \frac{-\,3\, k_{\mathrm{B}}\, T}{4\, \pi} \left|\ln (q \xi_{\mathrm{T}})\right| \,. \qquad (27)$$

Taking $q \sim L^{-1}$ we recover the formula quoted in section 1. A self-consistent theory which replaces κ by $\kappa_{\mathrm{R}}(\mathbf{k} + \mathbf{q})$ in the denominator of (25) now gives

$$\kappa_{\mathrm{R}}(q) \sim \sqrt{K_{\mathrm{A}}\, k_{\mathrm{B}}\, T}\, \ln^{1/2} (1/q \xi_{\mathrm{T}}) \,. \qquad (28)$$

Long-range order in the normals survives, but just barely, when this result is inserted into equation (14b). The resummation which leads to this result neglects (possibly important) effects of undulations, however.

A complete understanding of hexatic membranes requires a renormalization group scheme which encompasses both the curvature nonlinearities considered in references [5] and [6] and the nonlinearities embodied in equation (23). Although we have not implemented such a program, it seems possible that a low temperature, infinite rigidity fixed point characterized by becomes stable. At sufficiently high temperatures (even if disclinations do not unbind first), we expect that the thermal softening of undulations will dominate their stiffening due to the hexatic order, and a crumpling transition will result.

This situation is reminiscent of perturbative calculations of the effects of Coulomb interactions among electrons in two-dimensional Anderson localization [20]. In the absence of interactions the trivial fixed point corresponding to the metallic phase is marginally unstable, and all states are localized. For a system with time-reversal invariance and spin conservation, the Coulomb interaction favours the formation of extended states. An attempt to renormalize the theory reveals a runaway Coulomb coupling constant [21]. The final behaviour of the system has not yet been fully elucidated, although a discontinuous transition has been suggested. One can expect similar difficulties if one tries to renormalize hexatic membranes.

5. Discussion.

We hope to have demonstrated that fluctuations in crystalline and hexatic membranes differ markedly from their fluid counterparts and lead to effects which are interesting in their own right. Many open questions remain. Although equation (13b) is a plausible guess, we are unsure of the exact form for the elasticity theory of a low temperature uncrumpled crystalline membrane when stretching energies are taken into account. The nature of the crumpling transition with decreasing bending rigidity (assuming it does not occur at $\kappa = 0$!) is a mystery. To insure that initially crystalline membranes do not melt it would be very interesting to form lyotropic smectics from lipid molecules like those discussed in reference [10], and then polymerize them. A subsequent increase in water content would presumably force the bilayers apart and could, under some circumstances, trigger a crumpling transition. When the layers of a crystalline, but unpolymerized lyotropic smectic are forced apart, one might expect them to melt, due to dislocation buckling.

We have already emphasized the challenging problem of setting up a renormalization group to explore the crumpling transition suggested here for hexatic membranes. It would be interesting to study further the hexatic elasticity theory skecthed in section 3. Although the lipids in red blood cells are usually assumed to be isotropic 2d liquids, mechanical measurements seem to require a small, but nonzero shear modulus [22]. Perhaps some of these mechanical properties could be accounted for by postulating hexatic, rather than fluid, order within the membrane.

When this work had been completed, we received a preprint by S. Ami and H. Kleinert [23] on the « Renormalization of Curvature Elastic Constants for Elastic and Fluid Membranes ». These authors conclude that crystalline order has *no* effect on the bending rigidity κ. We disagree with this conclusion, which appears to be due to be due to the neglect of the coupling between stretching and bending deformation embodied in equations (2) and (5).

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Appendix.

We sketch here the derivation of equations (21) and (22). It is convenient to introduce general curvilinear coordinates σ^i $(i = 1, 2)$ and the metric structure defined by the metric tensor

$$g_{ij} = \partial_i \mathbf{r} \cdot \partial_j \mathbf{r} \,. \tag{A.1}$$

Hexatic order is characterized by long-range correlations in bond directions, which may be identified in turn by means of a vector field n^i satisfying

$$g_{ij}\, n^i\, n^j = 1 \,. \tag{A.2}$$

The elastic free energy per unit area associated with hexatic order is assumed to be proportional to the square of the covariant derivative of n^i :

$$\mathcal{F}_{\mathrm{H}} = \frac{1}{2} K_{\mathrm{A}}\, \nabla_i n^j\, \nabla^i n_j \,. \tag{A.3}$$

The covariant derivative is defined by means of the connection associated to the metric g_{ij}.

It is possible to introduce a local orthonormal reference frame e^i_α $(\alpha = 1, 2)$ satisfying :

$$g_{ij}\, e^i_\alpha\, e^j_\beta = \delta_{\alpha\beta} \,. \tag{A.4}$$

We can now introduce the components $n_{(\alpha)}$ of n^i by means of :

$$n_{(\alpha)} = n^i\, e_{\alpha i} \,. \tag{A.5}$$

Because of equations (A.2)-(A.4) we have :

$$n_{(1)} = \cos\theta \;;\quad n_{(2)} = \sin\theta \,. \tag{A.6}$$

It is possible to express n^i in terms of the $n_{(\alpha)}$ by means of :

$$n^i = \sum_\alpha n_{(\alpha)}\, e^i_\alpha \,. \tag{A.7}$$

On the other hand, we have [24]

$$\nabla_i n^j = \sum_\alpha \left[\partial_i n_{(\alpha)} + \sum_\beta \omega_{i\alpha\beta}\, n_{(\beta)} \right] e^j_\alpha \,, \tag{A.8}$$

where the connection $\omega_{i\alpha\beta}$ is antisymmetric with respect to the indices α and β. Since these indices only assume two values, it is possible to write :

$$\omega_{i\alpha\beta} = \varepsilon_{\alpha\beta}\, A_i \,, \tag{A.9}$$

where A_i is a suitable covector field. Because of equation (A.6) we also have :

$$\partial_i n_{(\alpha)} = \sum_\beta \varepsilon_{\alpha\beta}\, n_{(\beta)}\, \partial_i \theta \,. \tag{A.10}$$

Hence

$$\nabla_i n^j = \sum_{\alpha\beta} \varepsilon_{\alpha\beta}\, e^j_\alpha\, n_{(\beta)} [\partial_i \theta + A_i] \,, \tag{A.11}$$

and, by exploiting equations (A.4), (A.6), it follows that

$$\nabla_i n^j\, \nabla^i n_j = (\partial_i \theta + A_i)(\partial^i \theta + A^i) \,. \tag{A.12}$$

To complete the derivation, we relate A_i to the Gaussian curvature. We have :

$$[\nabla_i, \nabla_j]\, e^k_\alpha = -\, R^k_{lij}\, e^l_\alpha \,, \tag{A.13}$$

where R^k_{lij} is the Riemann curvature tensor. Hence, by (A.8), we have :

$$-\, R^k_{lij}\, e^l_\alpha = \sum_\beta (\nabla_i A_j - \nabla_j A_i)\, \varepsilon_{\alpha\beta}\, e^k_\beta \,, \tag{A.14}$$

and we may as well take simple partial derivatives within the brackets. The scalar curvature R is given by :

$$\begin{aligned} R = R^i_{lij}\, g^{jl} &= \sum_\alpha R^i_{lij}\, e^l_\alpha\, e^j_\alpha \\ &= -\sum_{\alpha\beta} (\partial_i A_j - \partial_j A_i)\, \varepsilon_{\alpha\beta}\, e^i_\beta\, e^j_\alpha \,. \end{aligned} \tag{A.15}$$

Specializing to Euclidean coordinates it is easy to see that

$$\gamma^{ij} = \sum_{\alpha\beta} \varepsilon_{\alpha\beta}\, e^i_\alpha\, e^j_\beta = \varepsilon^{ij} \,, \tag{A.16}$$

where ε^{ij} is the antisymmetric symbol. In general coordinates, therefore

$$\gamma^{ij} = \varepsilon^{ij} / \sqrt{g} \,, \tag{A.17}$$

where $g = \det(g_{ij})$. We have therefore :

$$\partial_i A_j - \partial_j A_i = -\frac{1}{2} R \sqrt{g}\, \varepsilon_{ij} = -\, S \sqrt{g}\, \varepsilon_{ij} \,, \tag{A.18}$$

which corresponds to equation (22b). Equations (21) are obtained from these by going over the Monge form and neglecting terms of higher order in ∇f.

Note added in proof: The renormalization of hexatic membranes turns out to be simpler and more interesting than expected in the present paper (F. David, E. Guitter and L. Peliti, unpublished). The hexatic stiffness constant K_{A} undergoes but a finite renormalization. It is then possible to perform the renormalization of the rigidity exactly as far as its K_{A} dependence is concerned. One then identifies an infrared stable fixed point with $\kappa \sim K_{\mathrm{A}}$ which governs the long distance behaviour of the membrane : it corresponds to a state in which the membrane is self-similarly crumpled, with exponents which depend on K_{A}. The study of this phase is in progress.

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