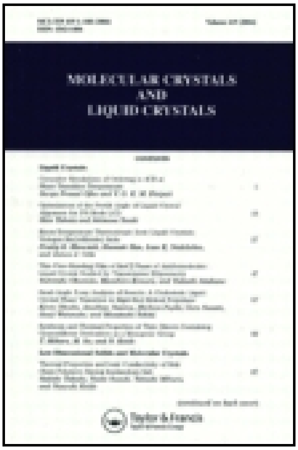

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On the Effects of a Nematic Phase Confined to a Membrane

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On the Effects of a Nematic Phase Confined to a Membrane

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We review and discuss some recent theoretical predictions concerning the effects of surfactants with nematogen polar heads, or anisotropic inclusions, in bilayer membranes.

Keywords: membrane; inclusion; nematic; defect

INTRODUCTION

Membranes are single lamellae of lyotropic smectics, made of amphiphilic molecules that self-assemble into bilayers when dissolved into water or brine[1]. The aliphatic chains of the molecules form an oily sheet that is shielded from contact with water, on both sides, by the polar heads of the molecules. The latter form a two-dimensional (2D) isotropic fluid at the chain–water interface.

Some biological membranes contain a high fraction of *dimeric* phospholipids having a double polar head and four aliphatic chains. In the 2D interfacial fluid of head groups, they behave like rods and might develop a *nematic* order, or a nematic susceptibility. Recently, dimeric surfactants that self-assemble into bilayers have been synthesized[2]. There are several indications that the bilayers they form possess an in-plane nematic order[3]. In this paper, we review and discuss some consequences of the presence of a 2D nematic order in bilayer membranes.

ANISOTROPIC MEMBRANE INCLUSIONS

We shall first consider the case of individual anisotropic inclusions embedded in a bilayer[4]. Membranes have a vanishing surface tension and their elasticity is governed by curvature terms. At every point, a surface has two principal curvatures, c_1 and c_2, along two orthogonal axes. The curvature tensor has the form

$$\mathbf{K} = \begin{pmatrix} c_1 & 0 \\ 0 & c_2 \end{pmatrix} \qquad (1)$$

in the basis of the principal axes. The curvature energy per unit surface of a symmetric membrane, involving all quadratic terms that satisfy rotational symmetry,

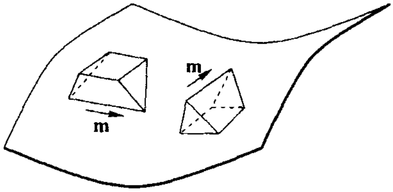

FIGURE 1 Sketch of two identical but reversed anisotropic inclusions shaped as wedges. Orienting at right angle, both match the curvature of a membrane shaped as a saddle.

can be written as[5]

$$F = \frac{1}{2}\kappa\,(c_1 + c_2)^2 + \bar{\kappa}\,c_1\,c_2\,, \tag{2}$$

with κ the bending rigidity and $\bar{\kappa}$ the Gaussian rigidity.

There exist membrane inclusions, e.g., proteins, that span the whole bilayer. Such inclusions will in general break the up-down symmetry of the membrane, and its rotational in-plane symmetry. The former effect arises for instance if the inclusion has a conical shape, and the latter if the cone angle is modulated along the perimeter of the inclusion. Let $\mathbf{m}$ be a unit vector specifying the in-plane orientation of the inclusion. To lowest order, the coupling between the inclusions and the membrane curvature has the form[4]

$$f_c = (a\,\mathbf{I} + b\,\mathbf{m}\otimes\mathbf{m}) : \mathbf{K}\,, \tag{3}$$

where $\mathbf{I}$ is the identity tensor, $(\mathbf{m}\otimes\mathbf{m})_{ij} = m_i\,m_j$, and, generically, $\mathbf{U}:\mathbf{V} = U_{ij}V_{ij}$, summation on repeated indices being understood. Calling θ the angle between $\mathbf{m}$ and the principal axis with curvature c_1, we can rewrite this coupling as $f_c = a'\,(c_1 + c_2) + b'\,(c_1 - c_2)\cos 2\theta$, with $a' = a + b/2$ and $b' = b/2$. Minimizing f_c with respect to the orientation θ yields $f_c^* = a'(c_1 + c_2) - |b'|\,|c_1 - c_2|$. The inclusions are then oriented along the principal axes of curvature (Fig. 1).

Reversing one inclusion up-side down changes the signs of a and b. Hence, for a membrane containing a surface density n of inclusions randomly pointing downwards or upwards, the first term in f_c^* is averaged to zero, while the second term yields a contribution to the energy per unit surface equal to $F_c = -\,n|b'|\,|c_1 - c_2|$. This term, combined with Eq. (2), forces an *anisotropic* spontaneous curvature of the membrane ($c_1 \neq c_2$), i.e., saddle-like or cylindrical shapes.

When $b\,|c_1 - c_2| < T$, where T is the temperature in energy units, orientational fluctuations destroy the alignment of the inclusions along the principal axes of curvature. The reasoning yielding the above expression of F_c is thus only valid when $|c_1 - c_2| > c^*$, with $c^* \approx T/b$. Otherwise, there is only a renormalization of the elastic constants, κ being reduced and $\bar{\kappa}$ increased[4].

For large inclusions (integral proteins), elastic models taking into account the tilt deformation of the bilayer around the inclusion indicate $c^* \approx 1000\,\text{Å}^{-1}$ [4].

Direct calculations of membrane mediated interactions show that anisotropic inclusions of the size of the membrane thickness effectively orient one-another at separations less that 10 times their size[6].

When $n \gtrsim (\kappa/T)\, c^{*2}$, flat membranes undergo an instability in the form of a periodic modulation creating local saddles ("egg-carton"), and spherical vesicles turn into long tubules of radius $\approx 1/c^*$ [4]. Inside the tubule membrane, all the inclusions pointing upwards are oriented in the same direction (either along the axis of the tube or normal to it) and all the inclusions pointing downwards are oriented in the opposite direction. We are therefore in the presence of two para-nematic phases with orthogonal directors. The membrane curvature plays the role of the external field that induces the para-nematic phase.

PARA-NEMATIC BILAYERS

For small inclusions, such as dimeric surfactants, c^* is expected to be microscopic. In this case, we do not expect more than a renormalization of the elastic constants. However, in a membrane made of surfactants with elongated polar heads, one must take into account the possibility of collective nematic effects:

Let us first assume that the anisotropic interactions between the surfactant heads yield a large nematic susceptibility, but not a true nematic phase. The situation is reminiscent of a liquid crystal's isotropic phase in the vicinity of a nematic transition. Applying a strong external field yields a para-nematic phase with a large order-parameter[7]. Here, the situation is particularly interesting since the "external" field is actually the membrane curvature, which is an internal parameter controlled by the global energy of the system.

In bilayer membranes, the two fluids of polar heads are well separated by the aliphatic medium. One must therefore consider *two* tensorial nematic order parameters: $\mathbf{Q}^+$ for the upper and $\mathbf{Q}^-$ for the lower monolayer. Neglecting for the moment the coupling $\mathbf{Q}^+ : \mathbf{Q}^-$ between them and all gradient terms, the nematic energy per unit surface can be written as

$$F_{\rm N} = \frac{1}{2} A \left(|\mathbf{Q}^+|^2 + |\mathbf{Q}^-|^2 \right) + B \left(\mathbf{Q}^+ - \mathbf{Q}^- \right) : \mathbf{K} \,, \qquad (4)$$

where $|\mathbf{Q}^\pm|^2 = Q^\pm_{ij} Q^+_{ij}$. We assume $A > 0$, in order for the minimum energy to correspond to the isotropic phase; the sign of B is arbitrary. In this continuous model, B plays the same role as the coupling b previously introduced.

Minimizing (4) with respect to the nematic tensors yields $\mathbf{Q}^\pm = \mp(B/A)\tilde{\mathbf{K}}$, with $\tilde{\mathbf{K}}$ the traceless part of the curvature tensor, which is proportional to $c_1 - c_2$. The nematic directors of the upper and lower monolayers are therefore aligned along the principal axes of curvature, and they are perpendicular to one another. We are in the presence of an *anti-nematic* order, by analogy with antiferromagnetism.

The free energy (4) can be considered as an effective Hamiltonian. Integrating

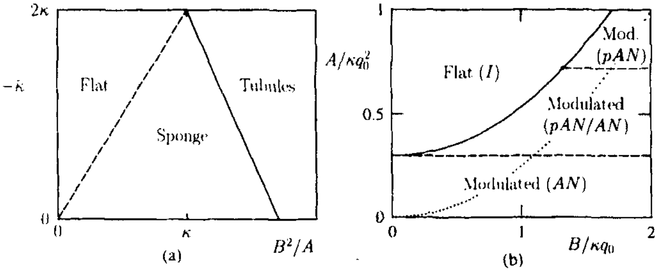

FIGURE 2 (a) Phase diagram of unframed para-nematic membranes. (b) Phase diagram of a framed para-nematic membrane. q_0^{-1} is a length comparable to the bilayer thickness. Full (resp. dashed) lines indicate first-order (resp. second-order) transitions. Dotted line: virtual second-order transition.

out the thermal fluctuations of $\mathbf{Q}^+$ and $\mathbf{Q}^-$ yields the following renormalizations:

$$\delta\kappa = -\frac{B^2}{A} \quad \text{and} \quad \delta\bar{\kappa} = +\frac{2B^2}{A}. \tag{5}$$

Taking into account the coupling between the two nematic order parameters merely adds a constant to A[8]. The reduction of κ produces curvature instabilities when $\kappa < 0$. This occurs for $A \to 0$, i.e., in the vicinity of the nematic transition. The renormalization of the Gaussian modulus can drive $\bar{\kappa}$ positive, which favors the formation of saddles.

The corresponding membrane instabilities can be studied by adding to F the nematic energy F_N taken at its minimum value. To avoid divergences, it is necessary to include fourth-order terms in F_N. One obtains a fourth order effective curvature elasticity, which allows to compare the relative stability of various structures, such as flat membranes, spherical vesicles, tubular vesicles and sponge phases[8]. The resulting phase diagram is shown in Fig. 2(a). As the nematic transition is approached, or B increased, the flat membrane undergoes first a transition to a sponge, then to a tubules phase.

Membranes attached to a frame or spread over a hole cannot form such phases. They may however undulate in order to create a large number of local saddles ("egg-cartons"). Assuming a first-order nematic transition and 1D modulations to simplify, the membrane structure can be determined by including sixth-order terms in F_N and solving numerically for the order-parameter profile[8]. The corresponding phase diagram is shown in Fig. 2(b). Increasing B or approaching the nematic transition drives the modulation instability. The membrane is either anti-nematic (AN) or para-anti-nematic (pAN), according to the value of the order parameter. In the modulated pAN/AN phase, there are regions of high and low order parameter values separated by line boundaries. The modulation wavevector is mesoscopic when the nematic transition is weakly first order, and diverges at the second-order transition.

Freeze-fracture electron micrographs of cell membranes of ***Streptomyces hygroscopicus***[9], which contain 40% weight fraction of cardiolipins (a "nematogen" di-phospholipid with a double elongated polar head to which are attached four aliphatic chains) show "egg-cartons" with a period in the range 200–750 Å. Hexagonal and 1D modulations reminiscent of tubular vesicles have also been reported in similar experimental conditions. Our model is consistent with these observations, in which the wide range of observed wavevectors suggests a critical effect.

NEMATIC BILAYERS

Let us now assume that a fully-developed nematic order is present in both the 2D fluids of polar heads of both monolayers,

$$\mathbf{Q}^{\pm} = S\,(2\mathbf{n}^{\pm} \otimes \mathbf{n}^{\pm} - \mathbf{I}) \;, \tag{6}$$

where $\mathbf{n}^{+}$ and $\mathbf{n}^{-}$ are the directors of the upper and lower monolayer, respectively, and S is constant and identical in both monolayers.

Mesoscopic Tubules

The two nematic monolayers being individually asymmetric, their curvature energy, $F^{\pm}$, must include a ***linear*** term in the curvature tensor. Since the two monolayer have opposite curvatures, we are led to

$$F^{\pm} = \frac{\kappa}{4}\,(c_1 + c_2)^2 + \frac{\bar{\kappa}}{2}\,c_1\,c_2 \pm \mathbf{\Gamma}^{\pm} : \mathbf{K}\,. \tag{7}$$

For the sake of simplicity, the anisotropy in the elastic constants has been neglected. The tensors $\mathbf{\Gamma}^{+}$ and $\mathbf{\Gamma}^{-}$ must be constructed from the symmetry elements of each monolayer, i.e., the identity tensor and the nematic tensors $\mathbf{Q}^{\pm}$:

$$\mathbf{\Gamma}^{\pm} = \alpha\,\mathbf{I} + \beta\,S\,(2\mathbf{n}^{\pm} \otimes \mathbf{n}^{\pm} - \mathbf{I}) \;. \tag{8}$$

The constants α and β can be determined from the two spontaneous curvatures of a monolayer with saturated order ($S = 1$) and uniform director. We denote by $c_{\|}$ (resp. $c_{\perp}$) the spontaneous curvature in the direction parallel (resp. perpendicular) to the director. Assuming for instance the director $\mathbf{n}^{+}$ parallel to the principal axis with curvature c_1, we have $F^{+} = \frac{1}{4}\kappa\,(c_1 + c_2)^2 + \frac{1}{2}\bar{\kappa}\,c_1\,c_2 + \alpha\,(c_1 + c_2) + \beta\,(c_1 - c_2)$. Minimizing this expression with respect to $c_1\,(\equiv c_{\|})$ and $c_2(\equiv c_{\perp})$ yields

$$\alpha = -\frac{2\kappa + \bar{\kappa}}{4}\left(c_{\|} + c_{\perp}\right) , \quad \text{and} \quad \beta = -\frac{\bar{\kappa}}{4}\left(c_{\|} - c_{\perp}\right) . \tag{9}$$

The total curvature energy of the whole bilayer is $F = F^{+} + F^{-}$, i.e.,

$$F = \frac{\kappa}{2}\,(c_1 + c_2)^2 + \bar{\kappa}\,c_1 c_2 + 2\beta\,S\,(\mathbf{n}^{+}\otimes\mathbf{n}^{+} - \mathbf{n}^{-}\otimes\mathbf{n}^{-}) : \mathbf{K}\,. \tag{10}$$

A coupling term, $(-)\frac{1}{2}\lambda S^2(\mathbf{n}^+\cdot\mathbf{n}^-)^2$, can be added to (10). The linear curvature term is larger and most effective when the two directors are orthogonal, which competes against the coupling when $\lambda > 0$.

Let us consider a *tubule*, i.e., a closed membrane curved as a cylinder, having $\mathbf{n}^+$ parallel and $\mathbf{n}^-$ perpendicular to the tube axis. Setting $c_1 = 1/R$ and $c_2 = 0$, we obtain $F_{\text{tub}} = \kappa/(2R^2) - 2\beta S/R$. Minimizing with respect to R yields the equilibrium tube radius

$$R_{\text{tub}} = \frac{2\kappa}{\bar{\kappa}}\,\frac{1}{S(c_\perp - c_\parallel)}\,. \tag{11}$$

In the experiment of Ref. 2, bilayers made of pure *dimeric* quaternary ammonium surfactants with rather long chains (typically C_{18}) were shown to systematically form very long bilayer tubules. The tube radiuses were of order a few 1000 Å, since they could be seen by video-enhanced optical microscopy. Let us estimate the tube radius from Eq. (11) for such dimeric surfactants. Since the latter form membranes and not micelles, we expect their spontaneous curvature to be significantly larger than the monolayer thickness[1], say $100\,\text{Å}^{-1}$. The spontaneous curvatures $c_\parallel$ and $c_\perp$, which mainly result from packing constraints[1] should not be very different, since the chains are quite long. Hence, it seems reasonable to assume, e.g., $c_\perp \simeq 120\,\text{Å}^{-1}$ and $c_\parallel \simeq 100\,\text{Å}^{-1}$. With $2\kappa/\bar{\kappa}$ of order unity, and, e.g., $S \simeq 0.3$, we obtain $R_{\text{tub}} \approx 2000\,\text{Å}$.

For the tubule to be stable with respect to the flat membrane, the energy per unit surface $|F^*_{\text{tube}}|$ must overcome the energy $\frac{1}{2}\lambda S^2$ for orienting the directors perpendicular. With $F^*_{\text{tube}} = -2\beta^2 S^2/\kappa$, this requires $\lambda < \lambda_c \equiv 4\beta^2/\kappa$. With the estimated values of $c_\parallel$ and $c_\perp$, and assuming the membrane elastic constants to be of order $10\,k_BT$, we obtain $\lambda_c \approx 10^{-5}\,\text{J}\,\text{m}^{-2}$.

Since there is usually very little interpenetration between the chains of the two monolayers, the coupling λ can be estimated from anisotropic van der Waals interactions. Summing parwise interactions yields $\lambda \simeq A_a\ell^2/(2\pi d^4)$, where ℓ is the linear size of the head-group, d the membrane thickness, and A_a is the anisotropic Hamaker constant. Since Hamaker constants for interactions across a hydrocarbonic medium are of order T[1], we take $A_a \simeq 0.1\,T$. Hence, with $d \simeq 40\,\text{Å}$ and $\ell \simeq 10\,\text{Å}$ we find $\lambda \simeq 2\times10^{-7}\,\text{Jm}^{-2}$. Thus, $\lambda \ll \lambda_c$, which is consistent with the fact that tubules are more stable than flat membranes.

Bi-defects of Flat Nematic Bilayers

Nematic bilayers exhibit disclination defects with very peculiar features, due to the coupling between the two monolayers[10]. For simplicity, we shall restrict our attention to *planar* bilayers, which could be produced by osmotically blowing up the tubes, or by patch-clamping techniques.

Within the one Frank constant approximation, the nematic free energy of the flat bilayer can be written as

$$F = \frac{1}{2}\int d^2r\left\{K\left|\nabla\mathbf{n}^+\right|^2 + K\left|\nabla\mathbf{n}^-\right|^2 - \lambda\left(\mathbf{n}^+\cdot\mathbf{n}^-\right)^2\right\}, \tag{12}$$

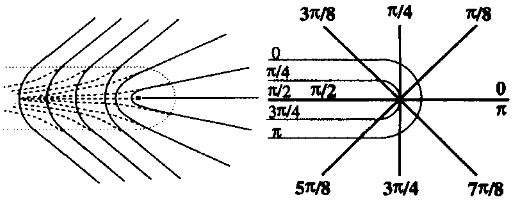

FIGURE 3 (a) Field lines of a $[\frac{1}{2}, 0]$ bi-defect. The textures of the two monolayers coincide outside the wall. (b) Level lines in the free and field- nematics spaces.

where $|\nabla \mathbf{n}^{\pm}|^2 = \partial_i n_j^{\pm} \partial_i n_j^{\pm}$. We assume $\lambda > 0$, however this is no restriction here since redefining $\mathbf{n}^+$ by a $\pi/2$ rotation effectively changes the sign of the interaction term. Let $\theta^{\pm}$ be the polar angle of $\mathbf{n}^{\pm}$ relative to an arbitrary direction. Setting $\theta^{\pm} = \frac{1}{2}(\phi \pm \psi)$ yields

$$F = \frac{1}{2} \int d^2r \, \frac{K}{2} (\nabla \phi)^2 + \frac{1}{2} \int d^2r \, \frac{K}{2} \left\{ (\nabla \psi)^2 + \xi^{-2} \sin^2 \psi \right\}, \tag{13}$$

with $\xi^2 = K/(2\lambda)$. The nematic bilayer is thus equivalent to the superposition of two non-interacting nematics: a free nematic (described by ϕ) and a nematic subject to a *uniform* field (described by ψ). The length ξ is the analog of a magnetic coherence length.

The physics of defects in both the free and the field-nematic is well known. In the latter, defects emit walls of thickness $\approx \xi$ crossing which the director turns by $\pm\pi$. From the above decomposition, we deduce that the textures generated by a defect of strength p present only on the upper monolayer are given by $\theta^{\pm} = \frac{1}{2}(\theta_0(p) \pm \theta_\lambda(p))$, where $\theta_0(p)$ describes the texture of a defect of strength p in a free nematic and $\theta_\lambda(p)$ that in a nematic under field. Figure 3(a) shows the director textures in the real space for $p = \frac{1}{2}$. The full (resp. dashed) lines are the field lines of the upper (resp. lower) monolayer; the dotted line indicate a wall boundary. Figure. 3(b) shows the corresponding textures in the space of the free and field-nematics. The bold lines are the level lines of the free nematic, and the thin ones those of the field nematic.

More generally, one must consider pairs of associated defects in the two monolayer, i.e, *bi-defects*. A $[p, q]$ bi-defect is the physical superposition in the bilayer of a defect with a strength p in the upper monolayer and a defect with a strength q in the lower one; it is equivalent to a pair of defects of strength $p + q$ in the free nematic and of strength $p - q$ in the nematic under field.

Both the texture and the energy of a $[p, q]$ bi-defect follow from simple algebra, according to the previous decomposition. One can show that a $[1, 0]$ and a $[0, 1]$ bi-defect attract each other, with an interaction energy linear for separations larger than ξ, and roughly quadratic for separations less that ξ[10]. The linear interaction comes from the fact that the two bi-defects emit walls (due to the component under field) which recombine, generating a line tension. When the two bi-defects sit on top of each other, their textures match, optimizing both the elastic and the interaction energy. A $[1,0]$ and a $[0,-1]$ bi-defect repel each other up to a separation of order ξ; then their interaction depends in a non trivial way on the walls they generate, which cannot recombine[10].

Bi-defects produce walls that reach the boundary of the sample when $p \neq q$: the textures of the two monolayers are identical outside the walls and different in their interior. The number of wall emitted by a $[p,q]$ bi-defect is $N = 2|p-q|$. The wall thickness can be determined from the value $\lambda \simeq 2 \times 10^{-7}\,\mathrm{Jm}^{-2}$ estimated previously. Taking, e.g., $K \simeq 3T$ in a nematically ordered phase, we obtain $\xi = K^{1/2}/(2\lambda)^{1/2} \simeq 1500\,\text{Å}$. The wall thickness, which is actually $\simeq 5\xi$, should be in the μm range and thus directly observable by optical methods.

PERSPECTIVES

There is no experimental proof yet of the existence of nematic bilayers; however the tubules of dimeric surfactants[2] and the "egg-cartons" of cardiolipin-rich membranes[9] strongly suggest their existence. The anti-nematic orientational order of the polar heads in such systems should however be investigated directly: either by RMN of X-ray studies. Other types of dimeric surfactants forming bilayers could be synthesized, and, more generally, n-meric surfactants with a rodlike polar head. Membranes containing n-meric surfactants should exhibit an enlargement of the sponge phase region, transitions from spherical to tubular vesicles, and undulation instabilities.

The peculiar bi-defects of nematic bilayers could be observed in single flat nematic membranes, using monolayer imaging techniques. Langmuir monolayers of n-meric surfactants spread on water or oil could also be investigated. Compressing a monolayer on water until it overlaps might produce a bilayer and a convenient way to investigate the physics of bi-defects.

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