Bi-defects of Nematic Surfactant Bilayers

J.-B. Fournier and L. Peliti

Laboratoire de Physico-Chimie Théorique, E. S. P. C. I., 10 rue Vauquelin, F-75231 Paris Cédex 05, France

(March 24, 2022)

We consider the effects of the coupling between the orientational order of the two monolayers in flat nematic bilayers. We show that the presence of a topological defect on one bilayer generates a nontrivial orientational texture on both monolayers. Therefore, one cannot consider isolated defects on one monolayer, but rather associated pairs of defects on either monolayer, which we call bi-defects. Bi-defects generally produce walls, such that the textures of the two monolayers are identical outside the walls, and different in their interior. We suggest some experimental conditions in which these structures could be observed.

87.22.Bt, 61.30.Gd, 61.30.Jf

Nematic liquid crystals are fluid phases possessing a long-range orientational order [1]. Ordinary nematics, in the three-dimensional (3D) space, consist of rodlike molecules orienting parallel to some unit vector \( \mathbf{n} \), called the “director”. Since nematics bear no polar order, \( \mathbf{n} \) and \(-\mathbf{n}\) represent the same orientational state. Nematics exhibit striking (line or point) topological defects [1,2]. The orientational order is continuous outside the defect, but exhibits on it a singularity which cannot be removed by continuous deformations.

Although several almost 2D nematic systems have been investigated, like thin nematic cells [3] and wetting layers [4], there are few examples of real 2D nematics, e.g., rods suspended on the surface of aqueous solutions [5]. (Actually, 2D systems can only exhibit quasi-long-range order, but this distinction is blurred for usual system sizes.) Very recently, it has been shown that amphiphilic bilayers made of dimeric surfactants (gemini) spontaneously form very long tubes of mesoscopic radius [6]: this conformation can be theoretically explained by introducing a coupling between the surface curvature and one Frank monolayer nematic orders [7]. A number of independent arguments support the existence of nematic order in these membranes [8].

In this Letter, we investigate the behavior of disclination defects in such nematic bilayers. For simplicity, we restrict our attention to planar bilayers, which could be produced by osmotically blowing up the tubes, or by patch-clamping techniques. We find radically new features due to the coupling of the orientational order between the two monolayers. Even if a disclination is present on only one layer, the coupling generates a nontrivial texture on the opposite one: this texture must be considered as a “defect” even in the absence of a singularity. We are thus led to consider pairs of associated defects on the bilayers, one of which can be virtual (of zero strength). We call these structures bi-defects.

We show that the two interacting nematic monolayers can be mapped on two independent, “virtual”, 2D nematic monolayers, one subject to an external orienting field and the other free. In the former, defects generate orientational walls [1], i.e., ribbons where the director turns by \( \pi \) on a finite length. Consequently, bi-defects generally produce walls that reach the boundary of the sample: the textures of the two monolayers are identical outside the walls and different in their interior. The bi-defect energy is dominated by the walls, and scales therefore linearly with the sample size (rather than logarithmically).

We denote by \( \mathbf{m} \) and \( \mathbf{n} \) the directors of the upper and lower monolayer, respectively. Within the one Frank constant approximation, the nematic free energy of the bilayer can be written as

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

where, e.g., \( |\nabla \mathbf{n}|^2 = \partial_i n_j \partial_i n_j \) and summation on repeated indices is understood. To be definite, we suppose \( \lambda > 0 \). This is no restriction, since there is always the freedom to redefine \( \mathbf{n} \) by a \( \pi/2 \) rotation, which effectively changes the sign if the interaction term in Eq. (1). Let us call \( \theta_+ \) (resp. \( \theta_- \)) the polar angle of \( \mathbf{m} \) (resp. \( \mathbf{n} \)) relative to an arbitrary direction. Setting \( \theta_\pm = \frac{1}{2}(\phi \pm \psi) \), we obtain (up to an irrelevant additive constant) \( F = \frac{1}{2}(F_0 + F_\lambda) \), with

\[
F_0 = \int d^2r \frac{K}{2} (\nabla \phi)^2; \tag{2a}
\]

\[
F_\lambda = \int d^2r \left\{ \frac{K}{2} (\nabla \psi)^2 + \lambda \sin^2 \psi \right\}. \tag{2b}
\]

Equation (2a) describes a free nematic, while Eq. (2b) describes a nematic subject to a uniform field directed along the \( \psi = 0 \) axis [11]. The Euler-Lagrange equation deriving from (2b) is a sine-Gordon equation:

\[
\xi^2 \nabla^2 (2\psi) = \sin(2\psi), \tag{3}
\]

where \( \xi^2 = K/(2\lambda) \). The length \( \xi \) is the analog of the magnetic coherence length of ordinary nematics [1]. The corresponding equation for \( \phi \) is simply \( \nabla^2 \phi = 0 \).
A topological defect of strength \( p \), located at the origin, is described in polar coordinates by solutions of the Euler-Lagrange equations of the form

\[
\phi(r, \theta) = p \theta + \phi_c(r, \theta),
\]

(4)

(or the analog for \( \psi \)), where \( p \) is a half-integer, and \( \phi_c(r, \theta) \) is a continuous function. Indeed, the director turns by \( 2\pi p \) in any circuit around the origin. In the nematic under field, minimization of the energy requires that \( \psi = k \pi \) (where \( k \) is an integer) over most of the sample. Therefore, all nonuniformity is confined within “soliton” walls of thickness \( \approx 5\xi \), crossing which \( \psi \) rotates by \( \pm \pi \).

Thus, a defect of strength \( p \) radiates a “star” of \( 2|p| \) walls. Within a region of size \( \sim \xi \) around the defect the texture is similar to that without field.

In mean field, the energy of a defect of strength \( p \) in a free nematic is equal to \( \pi Kp \ln(L/a) \), where \( L \) is the linear size of the sample and \( a \) the radius of a core inside which the nematic order is destroyed. The interaction energy of two defects of strength \( p_1 \) and \( p_2 \) is given by \(-2\pi Kp_1p_2/\ln(d/a)\), where \( d \) is the distance between the defects.

For the nematic under field, the defect energy is dominated by the energy of the walls, which is equal to \( 2K/\xi \) per unit length.

Since Eq. (4) is linear in the defect strength, a bi-defect \([p, q]\), i.e., the superposition of a defect with a strength \( p \) in the upper monolayer and a strength \( q \) in the lower one, is equivalent to a pair of defects of strength \( p + q \) in the free nematic (described by \( \phi \)) and of strength \( p - q \) in the nematic under field (described by \( \psi \)):

\[
\begin{pmatrix} p \\ q \end{pmatrix} = \begin{pmatrix} p + q \\ p - q \end{pmatrix}.
\]

(5)

We call \( p + q \) the free strength and \( p - q \) the field strength of the bi-defect. It follows from our decomposition that a bi-defect of free strength \( \ell \) and field strength \( m \) obeys the relations

\[
\theta_\pm \left( \begin{pmatrix} \ell \\ m \end{pmatrix} \right) = \frac{1}{2} (\theta_0(\ell) \pm \theta_\lambda(m)),
\]

(6a)

and

\[
F \left( \begin{pmatrix} \ell \\ m \end{pmatrix} \right) = \frac{1}{2} (F_0(\ell) + F_\lambda(m)).
\]

(6b)

In this equation, \( \theta_0(\ell) \) is the texture of a defect of strength \( \ell \) in a free nematic, \( \theta_\lambda(m) \) the texture of a defect of strength \( m \) in a nematic under field, and \( F_0(\ell), F_\lambda(m) \) the corresponding energies. In particular, \( \theta_-([p, 0]) = \theta_-([p, p]) = \frac{1}{2} (\theta_0(p) - \theta_\lambda(p)) \), and therefore there is a nontrivial texture even in the lower monolayer of a \([p, 0]\) bi-defect, where there is no singularity.

By applying these rules, one can build up the textures corresponding to different bi-defects. Figure 2(a) shows the texture of a \([1, 0]\) bi-defect. The full (resp. dashed) lines are the field lines of the upper (resp. lower) monolayer, and the wall boundary is indicated by the dotted line. The corresponding \( \{1, \frac{1}{2}\} \) texture is shown in Fig. 2(b): the bold lines are the level lines for the free nematic, and the thin ones for the field nematic. Figure 2 shows the analog texture for a \([1, 0]\) bi-defect.

In crossing a wall, both \( \theta_+ \) and \( \theta_- \) turn by \( \pm \pi/2 \). The actual thickness of the walls is \( \approx 5\xi \), as one finds by integrating Eq. (4). Besides, the walls probably have a persistence length \( \xi_p \) which is several times their thickness. Since they are interfaces in two dimensions, they fluctuate widely: their lateral excursion \( \Delta u \) over a length \( L \) is given by

\[
\Delta u \approx \left( \frac{T}{2\pi^2 K} \right)^{1/2} \xi L^{1/2},
\]

(7)

where \( T \) is the temperature, measured in energy units. They perform therefore a random walk, but their angular fluctuation \( \Delta \alpha \approx (T/4K)^{1/2}(\xi/\xi_p)^{1/2} \) is small, since we expect \( K \) to be of order a few \( T \) in a nematically ordered phase. The fluctuations of the wall decrease the effective line tension by a negligible amount.

The walls issuing from bi-defects can recombine. Since a defect of strength \( \ell \) under field generates \( 2|\ell| \) walls, a \([p, q]\) bi-defect generates

\[
n = 2|p - q|
\]

(8)
walls. Now, if there are two bi-defects, of strengths \( [p, q] \) & \([p', q'] \) respectively, the total field strength equals \( p - q + p' - q' \) and the number of walls that reach infinity is then \( 2|p - q + p' - q'| \). If this number is smaller than \( 2|p - q| + 2|p' - q'| \), some walls must recombine. This happens if \( (p - q)(p' - q') < 0 \). Therefore, we can assign an arrow to each wall, pointing outward from the bi-defect if \( (p - q) > 0 \) and toward it otherwise: walls with matching arrows can recombine. We show in Fig. 3(a) the field lines of a bi-defect pair \([1, 0] \) & \([0, 1] \). The two pairs of walls combine, connecting the two bi-defects, as shown in Fig. 3(b).

The interaction energy of a \([1, 0] \) & \([0, 1] \) bi-defect pair, equivalent to a \([1 & 1, 1 & -1] \) system, can be estimated using Eq. (10). The first contribution, \( \frac{1}{2} F_0 \), is one half of the energy of a pair of defects of strength 1 in a free nematic, i.e., \(-\pi K \ln(d/a)\), where \( d \) is the distance between the defects. The second contribution, \( \frac{1}{2} F_\lambda \), is one half of the energy of the texture under field of a pair of defects of strength 1 and \(-1\). When \( d \gg \xi \) it is dominated by the two walls which connect the defects, and is therefore \( \approx 4K(d/\xi) \). When \( d \ll \xi \) we can distinguish a region of size \( \approx \xi \) where the texture is similar to that without field, and an exterior region where \( \psi \) is exponentially close to \( k\pi \). The corresponding energy \( \frac{1}{2} F_\lambda \) contains two contributions: the elastic energy \( \pi K \ln(d/a) \) and the potential energy, which is estimated by integrating \( \frac{1}{2} \lambda \sin^2 \psi \) for the free texture on a disk of radius \( \approx \xi \). One obtains \( \frac{1}{2} K(d/\xi)^2 \ln(\xi/d) + \frac{1}{2} \). Summing up \( \frac{1}{2} F_0 \) and \( \frac{1}{2} F_\lambda \) we obtain

\[
F_{\text{int}} \simeq \begin{cases} 
\frac{\pi K d^2}{4 \xi^2} \left[ \frac{1}{2} \ln \frac{\xi}{d} \right], & \text{for } d \ll \xi; \\
4K \frac{d}{\xi}, & \text{for } d \gg \xi.
\end{cases}
\]  

(9)

The two bi-defects are therefore attracted by a force which is almost constant at large separation, and vanishes roughly linearly with \( d \) when \( d \ll \xi \). Indeed, when the two bi-defects sit on top of each other, they form a \([1, 1] \) bi-defect which optimizes both the coupling and the elastic energies.

A \([1, 0] \) & \([0, -1] \) bi-defect pair, equivalent to a \([1 & -1, 1 & 1] \) system, generates two walls which wander to the boundary of the sample. The elastic energy, calculated as previously, is given by

\[
F_{\text{int}} \simeq \begin{cases} 
-\frac{\pi K d^2}{48 \xi^2}, & \text{for } d \ll \xi; \\
\pi K \ln \frac{d}{a} + F_{\text{walls}}, & \text{for } d \gg \xi.
\end{cases}
\]  

(10)

The energy in the first line is simply the integral of the \( \frac{1}{2} \lambda \sin^2 \psi \) term. (The free and field elastic energies compensate as previously.) There is also a contribution due to the walls, but it does not depend on \( d \). The first term in the second line represents the logarithmic attraction of the defects in the free nematic. \( F_{\text{walls}} \) is the contribution from the walls of the nematic under field. It will depend in general on the way the walls reach the sample boundary. Let us consider, e.g., the case in which the sample is a ribbon of width \( 2L \), with the two bi-defects in the middle, each sending a wall to the opposite sides of the ribbon. Each wall of length \( L \) wanders within a rectangular region of width \( \Delta u \) given by Eq. (10). Thus, if \( d \gg \Delta u \), \( F_{\text{walls}} \) is independent of \( d \), whereas, if \( d \ll \Delta u \), there is a Helfrich-like repulsion between the walls:

\[
F_{\text{walls}} \approx \frac{T^2 \xi L}{K d^2}.
\]  

(11)

Therefore the interaction is repulsive for \( d \ll \xi \), and is otherwise a combination of repulsive and attractive forces, which identify an equilibrium distance

\[
d_{eq} \approx \frac{T}{K} (\xi L)^{1/2}.
\]  

(12)

Let us now consider a collection of bi-defects \([p_i, q_i] \) placed in a region of size \( R \) inside a sample of size \( L \gg R \). Since the total field strength is given by \( \sum_i p_i - \sum_i q_i \), there are

\[
N = 2 \left| \sum_i p_i - \sum_i q_i \right|.
\]  

(13)

walls going to the boundary. Since the total number of walls issuing from the defects is \( 2 \sum_i |p_i - q_i| \), there are

\[
M = \left| \sum_i p_i - \sum_i q_i \right|.
\]  

(14)

walls linking two bi-defects, that remain confined within \( R \). Therefore the dominant energy, which arises from the walls, scales as

\[
F \approx N K \frac{L}{\xi} + M K \frac{R}{\xi}.
\]  

(15)
In order to minimize its energy, the system will first attempt to bring \( N \) to zero, e.g., by nucleating defects on the boundary, so as to equalize the total strengths of the defects in the upper and lower monolayer. The following step will be to bring together bi-defects having field strengths of opposite sign, in order to reduce to \( \approx \xi \) the total wall length. The bi-defects can then recombine.

In unconstrained membranes, there are numerous and subtle effects of the coupling between in-plane order and curvature (see, e.g., [12, 13]). Here, in addition, the coupling between the nematic directors, \( \mathbf{m} \) and \( \mathbf{n} \), and the curvature tensor \( \mathbf{K} \), of the form

\[
\mathbf{K} : (\mathbf{m} \otimes \mathbf{m} - \mathbf{n} \otimes \mathbf{n})
\]

produces interesting but complicated effects, which are out of the scope of this paper. In particular, shape fluctuations introduce an effective long-range coupling between director gradients [14]. On the other hand, the nematic tends to bend the membrane along its principal axes [7]. Therefore the texture around a nematic bi-defect will deform the membrane, and the membrane shape will react on the texture in a nontrivial way.

The wall thickness can be estimated by assuming that the \( \lambda \) term in Eq. (1) arises from anisotropic van der Waals interactions: \( \lambda \approx A_\lambda \ell^2/(2\pi d^4) \), where \( \ell \) is the linear size of the headgroup, \( d \) the membrane thickness, and \( A_\lambda \) is the anisotropic Hamaker constant. Since Hamaker constants for interactions across a hydrocarbonic medium are of order \( \xi \) [15], we take \( A_\lambda \approx 0 \). Hence, with \( d \approx 40 \text{ Å} \), we find \( \lambda \approx 2 \times 10^{-7} \text{ Jm}^{-2} \). Taking, e.g., \( K \approx 3 \text{ Jm}^{-2} \), we obtain \( \xi = K^{1/2}/(2\lambda)^{1/2} \approx 1500 \text{ Å} \). The wall thickness, which is of the order of \( 5\xi \), should be in the \( \mu \text{m} \) range.

One way to produce flat nematic bilayers would be either to deposit the membrane on a water-air interface, or to compress a Langmuir monolayer of gemini until a second layer overlaps the first. Due to the micrometric thickness of the walls, striking defect patterns should be directly observable by optical microscopy.

We thank A. Ajdari, P. Olmsted and D. Wu for useful discussions. LP acknowledges the support of a Chaire Joliot de l’ESPCI.

* Dipartimento di Scienze Fisiche and Unità INFM, Università “Federico II”, Mostra d’Oltremare, Pad. 19, I-80125 Napoli, Italy. Associato INFN, Sezione di Napoli.

[1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Academic, New-York, 1993).

[2] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge U. P., Cambridge (UK), 1995). Chap. 9.

[3] There is a wealth of experiments in thin nematic cells motivated by the development of nematic displays. See, e.g., S. V. Yablonskii et al., JETP Lett. **67**, 409 (1998).