Paired defects of nematic surfactant bilayers

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(Received 18 June 1998)

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 paired defects. Paired 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.
[S1063-651X(98)50512-0]

PACS number(s): 61.30.Gd, 61.30.Jf, 87.22.Bt

Nematic liquid crystals are fluid phases possessing a long-range orientational order [1]. Ordinary nematics in three-dimensional (3D) space consist of rodlike molecules orienting parallel to some unit vector **n**, called the ''director.'' Since nematics bear no polar order, **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 that cannot be removed by continuous deformations.

Although several almost 2D nematic systems have been investigated, such as 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 tubules of mesoscopic radius [6]: this conformation can be theoretically explained by introducing a coupling between the surface curvature and two independent monolayer nematic orders [7]. A number of independent arguments support the existence of nematic order in these membranes [8].

In this Rapid Communication, 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 nematic 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 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 *paired 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* [9], i.e., ribbons where the director turns by π on a finite length. Consequently, paired 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 paired defect energy is dominated by the walls, and therefore scales linearly with the sample size (rather than logarithmically).

We denote by **m** and **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

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

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 **n** by a $\pi/2$ rotation, which effectively changes the sign of the interaction term in Eq. (1). Let us call θ_+ (respectively, θ_-) the polar angle of **m** (respectively, **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 [10]. The Euler-Lagrange equation derived 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 ξ is the analog of the magnetic coherence length of ordinary nematics [1]. The corresponding equation for ϕ is simply $\nabla^2\phi=0$.

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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

$$\phi(r,\theta)=p\ \theta+\phi_c(r,\theta)\,, \tag{4}$$

(or the analog for ψ), where p is a half-integer and $\phi_c(r,\theta)$ is a continuous function. Indeed, the director turns by $2p\pi$ 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 $\simeq 5\xi$, crossing which ψ rotates by $\pm\pi$ [9,1]. Thus, a defect of strength p radiates a ''star'' of $2|p|$ walls. Within a region of size $\approx\xi$ around the defect the texture is similar to that without field.

In a mean field, the energy of a defect of strength p in a free nematic is equal to $\pi K p^2 \ln(L/a)$ [1], where L is the linear size of the sample and a is 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 $-2\pi K p_1 p_2 \ln(d/a)$, where d is the distance between the defects [1]. 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 [1].

Since Eq. (4) is linear in the defect strength, a paired 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 ϕ) and of strength $p-q$ in the nematic under field (described by ψ):

$$\begin{bmatrix} p \\ q \end{bmatrix} = \begin{Bmatrix} p+q \\ p-q \end{Bmatrix}. \tag{5}$$

We call $p+q$ the *free strength* and $p-q$ the *field strength* of the paired defect. It follows from our decomposition that a pair defect of free strength ℓ and field strength m obeys the relations

$$\theta_{\pm}\left(\begin{Bmatrix} \ell \\ m \end{Bmatrix}\right) = \frac{1}{2}[\,\theta_0(\ell) \pm \theta_\lambda(m)\,], \tag{6a}$$

$$F\left(\begin{Bmatrix} \ell \\ m \end{Bmatrix}\right) = \frac{1}{2}[F_0(\ell)+F_\lambda(m)]\,. \tag{6b}$$

In this equation $\theta_0(\ell)$ is the texture of a defect of strength ℓ in a free nematic, $\theta_\lambda(m)$ is the texture of a defect of strength m in a nematic under field, and $F_0(\ell)$, $F_\lambda(m)$ are 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 $[p,0]$ paired defect, where there is no singularity.

By applying these rules, one can build up the textures corresponding to different paired defects. Figure 1(a) shows the texture of a $[\frac{1}{2},0]$ paired defect. The full (respectively, dashed) lines are the field lines [11] of the upper (respectively, lower) monolayer, and the wall boundary is indicated by the dotted line. The corresponding $\{\frac{1}{2},\frac{1}{2}\}$ texture is shown

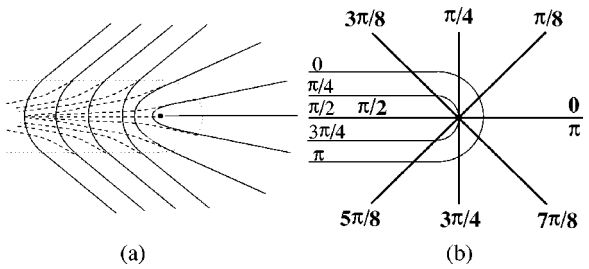

FIG. 1. (a) Field lines of a $[\frac{1}{2},0]$ paired defect. The textures of the two monolayers coincide outside the wall. (b) Level lines of the corresponding $\{\frac{1}{2},\frac{1}{2}\}$ paired defect.

in Fig. 1(b): the bold lines are the level lines for the free nematic and the thin ones are the level lines for the field nematic. Figure 2 shows the analog texture for a $[1,0]$ paired defect.

In crossing a wall, both θ_+ and θ_- turn by $\pm\pi/2$. The actual thickness of the walls is $\simeq 5\,\xi$, as one finds by integrating Eq. (3). Besides, the walls probably have a persistence length ξ_p, which is several times their thickness. Since they are interfaces in two dimensions, they fluctuate widely; their lateral excursion Δu over a length L is given by

$$\Delta u \simeq \left(\frac{T}{2\pi^2 K}\right)^{1/2} (\xi L)^{1/2}, \tag{7}$$

where T is the temperature, measured in energy units. They therefore perform a random walk, but their angular fluctuation $\Delta\alpha \simeq (T/4K)^{1/2}(\xi/\xi_p)^{1/2}$ is small, since we expect K to be of the 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 paired defects can recombine. Since a defect of strength ℓ under field generates $2|\ell|$ walls, a $[p,q]$ paired defect generates

$$n=2|p-q| \tag{8}$$

walls. Now, if there are two paired defects of strengths $[p,q]$ and $[p',q']$, 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

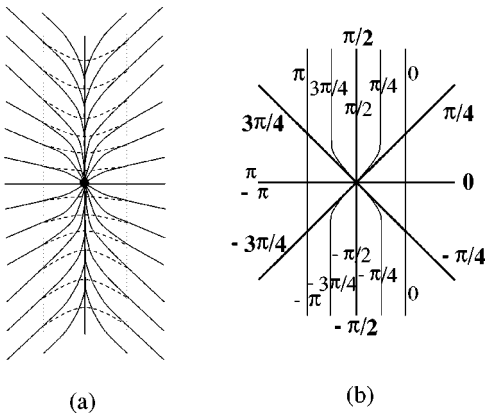

FIG. 2. (a) Field lines of a $[1,0]$ paired defect. (b) Level lines of the corresponding $\{1,1\}$ paired defect.

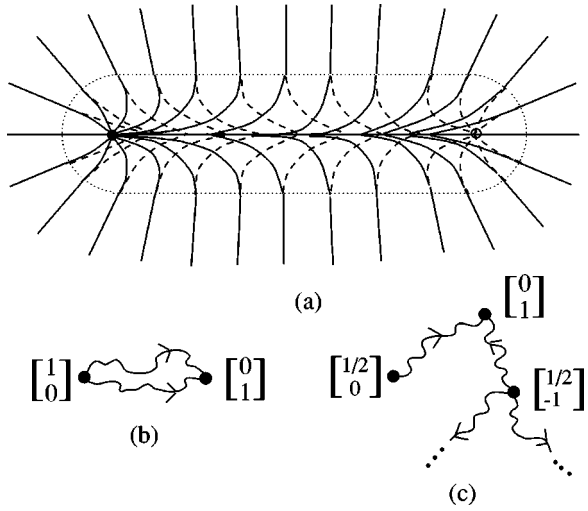

FIG. 3. (a) Field lines of a [1,0] and [0,1] pair of paired defects. (b) Corresponding scheme of the wall connections. (c) Possible wall connections between three paired defects.

if $(p-q)(p'-q')<0$. Therefore, we can assign an arrow to each wall, pointing *outward* from the paired 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 two paired defects [1,0] and [0,1]. The two pairs of walls combine, connecting the two paired defects, as shown in Fig. 3(b).

The interaction energy of a [1,0] and [0,1] pair of paired defects, which is equivalent to a {1 and 1, 1 and -1} system, can be estimated using Eq. (6b). 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 that connect the defects, and is therefore $\simeq 4K(d/\xi)$. 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 ψ is exponentially close to $k\pi$. The corresponding energy (2b) 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 $\frac{\pi}{4}K(d/\xi)^2[\ln(\xi/d)+\frac{1}{2}]$. Summing up $\frac{1}{2}F_0$ and $\frac{1}{2}F_\lambda$ we obtain

$$F_{\rm int} \simeq \begin{cases} \dfrac{\pi}{4}K\dfrac{d^2}{\xi^2}\left[\dfrac{1}{2}+\ln\dfrac{\xi}{d}\right] & \text{for } d \ll \xi \\ 4K\dfrac{d}{\xi} & \text{for } d \gg \xi . \end{cases} \tag{9}$$

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

A [1,0] and [0,-1] pair of paired defects which is equivalent to a {1 and -1, 1 and 1} system, generates two walls that wander to the boundary of the sample. The elastic energy, calculated as previously, is given by

$$F_{\rm int} \simeq \begin{cases} -\dfrac{\pi}{48}K\dfrac{d^2}{\xi^2} & \text{for } d \ll \xi \\ \pi K \ln\dfrac{d}{a} + F_{\rm walls} & \text{for } d \gg \xi . \end{cases} \tag{10}$$

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. $F_{\rm walls}$ 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 paired 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 Δu given by Eq. (7). Thus, if $d > \Delta u$, $F_{\rm walls}$ is independent of d, whereas, if $d < \Delta u$, there is a Helfrich-like repulsion between the walls:

$$F_{\rm walls} \approx \frac{T^2}{K}\frac{\xi L}{d^2}. \tag{11}$$

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

$$d_{\rm eq} \approx \frac{T}{K}(\xi L)^{1/2}. \tag{12}$$

Let us now consider a collection of paired 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 $\Sigma_i p_i - \Sigma_i q_i$, there are

$$N = 2\left|\sum_i p_i - \sum_i q_i\right| \tag{13}$$

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

$$M = \sum_i |p_i - q_i| - \left|\sum_i p_i - \sum_i q_i\right| \tag{14}$$

walls linking two paired defects, which remain confined within R. Therefore, the dominant energy, which arises from the walls, scales as

$$F \approx N K\frac{L}{\xi} + M K\frac{R}{\xi}. \tag{15}$$

In order to minimize its energy, the system will first attempt to bring N to zero, e.g., by nucleating defects on the boundary, in order to equalize the total strengths of the defects in the upper and lower monolayer. The following step will be to bring together paired defects having field strengths of oppo-

site signs, in order to reduce to $\approx \xi$ the total wall length. The paired 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 **m** and **n**, and the curvature tensor **K**, of the form $\mathbf{K}:(\mathbf{m}\otimes\mathbf{m}-\mathbf{n}\otimes\mathbf{n})$ [7], produces interesting but complicated effects, which are outside 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 paired 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 λ term in Eq. (1) arises from anisotropic van der Waals interactions: $\lambda \simeq A_a \ell^2/(2\pi d^4)$, where ℓ is the linear size of the headgroup, d is the membrane thickness, and A_a is the anisotropic Hamaker constant. Since Hamaker constants for interactions across a hydrocarbonic medium are of order T [15], we take $A_a \simeq 0.1T$. Hence, with $d \simeq 40$ Å and $\ell \simeq 10$ Å we find $\lambda \simeq 2\ 10^{-7}$ Jm^{-2}. Taking, e.g., $K \simeq 3T$, we obtain $\xi = K^{1/2}/(2\lambda)^{1/2} \simeq 1500$ Å. The wall thickness, which is of the order of 5ξ, should be in the μm 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. L.P. would like to thank the ESPCI for financial support (Chaire Joliot).

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