

Chiral symmetry breaking in three-dimensional smectic-*C* liquid-crystal domains

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We report an observation of a unique type of spontaneous chiral symmetry breaking in three-dimensional domains of a smectic-*C* material consisting of achiral molecules. The observed helical structure clearly demonstrates the effect of an elastic coupling between the bend and the twist distortions in the \mathbf{c} field. The sign and the magnitude of the coupling coefficient are determined experimentally. We also demonstrate that an external chiral bias field favors domains of one handedness. [S1063-651X(97)50411-9]

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The phenomenon of spontaneous chiral symmetry breaking has been known since the time of Louis Pasteur. In recent years there have been many investigations on this phenomenon in sodium chlorate crystals [1,2], drops of nematic and smectic-*C* liquid crystals [3,4] and in two-dimensional systems [5] such as free standing smectic-*C* films [6], hexatic liquid crystal films [7], and Langmuir monolayers with tilt order [8,9]. In this letter we report the first observation of a unique type of chiral symmetry breaking in 3D domains of a smectic-*C* liquid crystal consisting of achiral molecules. The special feature of this symmetry breaking is that it depends crucially on the symmetries of the smectic-*C* phase, in particular its translational order. We also propose a mechanism for the symmetry breaking and demonstrate the effect of an external bias field.

Smectic liquid crystals have a layered structure with 1D periodicity along the layer normal and liquidlike order within the layers [10]. In the smectic-*C* (Sm-*C*) phase the direction of average orientation of the rodlike molecules, described by a unit vector $\hat{\mathbf{n}}$ known as the Frank director, is tilted by an equilibrium angle θ_0 with respect to the unit layer normal $\hat{\mathbf{N}}$. Though $\hat{\mathbf{n}}$ is an apolar vector, its projection \mathbf{c} on the plane of the layers is polar.

Our experiments were performed on a binary mixture of the achiral compounds *p*-heptyloxy benzylidene *p*-heptylaniline (7O.7) and 2-cyano-4-heptylphenyl-4'-pentyl-4-biphenyl carboxylate (7CN5) obtained from Merck. 7CN5 has the following phase sequence as a function of temperature (in °C): crystal (Cr) $\xrightarrow{45.5}$ nematic(N) $\xrightarrow{102}$ isotropic (I). The nematic phase of 7CN5 has a strong skewed cybotactic [10] (Sm-*C*-like) order and supercools down to room temperature. The second component, 7O.7, shows a variety of phases including the Sm-*C* phase in the following sequence: Cr $\xrightarrow{33}$ Sm-*G* $\xrightarrow{55}$ Sm-*B* $\xrightarrow{69}$ Sm-*C* $\xrightarrow{72}$ Sm-*A* $\xrightarrow{83.7}$ N $\xrightarrow{84}$ I. Mixtures of these two compounds in a certain composition range show a first-order N-Sm-*C* transition. All experiments reported here were conducted on a mixture with 31.7 wt % of 7CN5. The N-Sm-*C* coexistence range for this

composition was found to be more than 5 °C. The sample cell was constructed using electrically conducting glass plates pretreated for planar alignment of $\hat{\mathbf{n}}$. The cell thickness was fixed at 35 μm using Mylar spacers. Observations were made through a Leitz polarizing microscope.

On cooling the sample from the nematic phase, Sm-*C* domains nucleate and grow in the bulk of the sample. These domains have a strikingly different shape and optical texture compared to the well known broken focal-conic domains (*bâtonnets*) formed by most Sm-*C* materials [11]. As the temperature is lowered, the domains grow rapidly along the nematic alignment direction. The growth in the perpendicular plane is extremely slow. Thus the domains form highly elongated rodlike structures. Domains with very different lengths have roughly the same width. If the temperature is held constant in the coexistence range, the domains attain their equilibrium shape shown in Fig. 1. Between crossed polarizers it is seen that a helical band consisting of a few dark and bright stripes wraps around each of these domains. The bands terminate at the tips of the domains. The handedness of the helices can be determined by adjusting the focus of the microscope. Roughly equal numbers of both left-handed and right-handed helices are seen. The pitch of the helix depends only on the radius of the domain and decreases

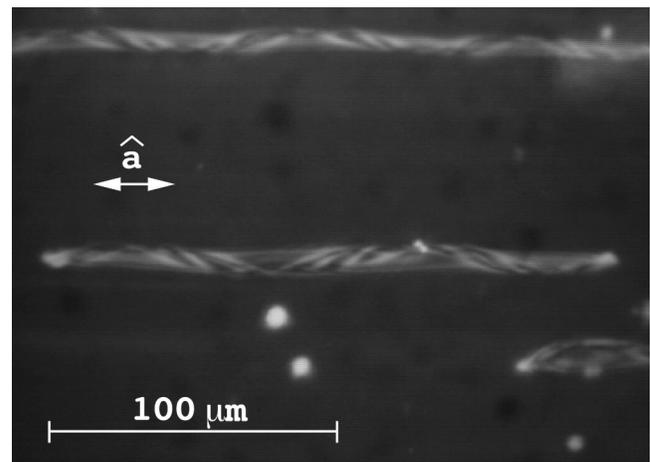


FIG. 1. Micrograph of the Sm-*C* domains in equilibrium with the surrounding nematic. Each domain has a helical band that runs from tip to tip. The polarizer is set along the nematic alignment direction $\hat{\mathbf{a}}$, and the analyzer is crossed.

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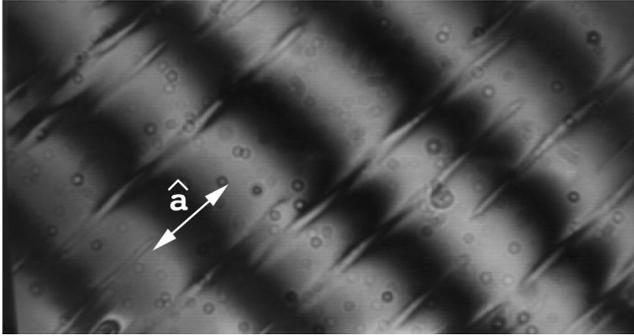


FIG. 2. Fringes of equal path difference obtained by introducing a tilting compensator. The rodlike domains are oriented along \hat{a} which is at 45° with respect to the crossed polarizers. Notice that the path difference starts reducing close to the domains and is a minimum at the interface.

towards the tips. Typically, the pitch is $\sim 95 \mu\text{m}$ near the center where the rod diameter is $\sim 10 \mu\text{m}$. When the temperature is lowered further, the domains merge and also touch the glass walls of the cell. When the entire sample is transformed to the Sm-C phase, two types of broad, uniform regions are seen. Adjacent strips have \hat{n} tilted with opposite signs with respect to the surface alignment direction \hat{a} and are separated by straight, sharp walls. On slowly heating the sample from this state we recover the rodlike domains with the helical bands. The structure can be distorted by applying a high-frequency (30 KHz) ac electric field. When the field is switched off, the structure relaxes back to the original configuration. The last two observations imply that these domains are equilibrium structures. The x-ray diffraction pattern from an oriented sample shows that the layers are perpendicular to the long axes of the rods. The tilt angle θ_0 is about 25° when the Sm-C domains form and increases as the temperature is lowered. In order to determine the structure within the layers we studied the variation of the optical path difference across the domains using a tilting compensator. The path difference decreases as the Sm-C domain is approached, reaches a minimum at the interface, then increases to a maximum value at the center of the helical band (Fig. 2).

Based on these experiments we propose the structure shown in Fig. 3 for the Sm-C domains. On the surface of the domains the local Frank director lies in the tangent plane and is tilted by an angle equal to the Sm-C tilt angle with respect to the cylinder axis. Within each layer the \mathbf{c} field follows circles of different radii; all the circles pass through the point defect S lying on the surface [Fig. 3(a)]. This \mathbf{c} field configuration within each layer resembles the pattern seen by Langer and Sethna in 2D Sm-I domains of a *chiral* compound and can be considered as part of a +2 disclination [13]. The 3D domain can be visualized as a stack of these layers such that the locus of S describes a helical line that wraps around the cylinder as shown in Fig. 3(b).

Clearly, these Sm-C domains break the chiral symmetry. Since this symmetry breaking is spontaneous, both right-handed and left-handed structures form with equal probability. In the surrounding nematic the \hat{n} field has a twist distortion. Numerical calculation of the optical transmission coefficient for the structure described above including the distortion in the nematic [12] closely resembles the helical

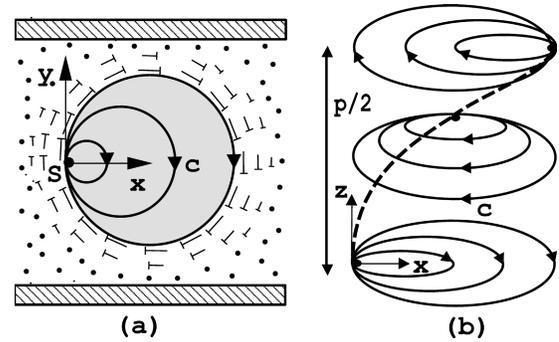


FIG. 3. Schematic diagrams of the proposed structure. (a) The circles represent the \mathbf{c} field within a Sm-C layer (shaded region). The point S is a singularity (which may be expelled from the domain; see text). The nails represent the projection of the \hat{n} field of the nematic around the domain with the heads indicating the end that projects above the plane of the paper. (b) The \mathbf{c} field in a few distant layers within half a pitch p of the structure. The pattern in (a) rotates from layer to layer. The dashed line is the locus of S .

stripe pattern shown in Fig. 1.

We now discuss the alignment of the Frank director at the N-Sm-C interface and make a qualitative comparison of the proposed structure with other contending structures. The N-Sm-C interfacial tension is anisotropic and in the present system has the lowest value for \hat{n} parallel to the interface [12]. This boundary alignment could have been satisfied by a rodlike domain in which the Sm-C layer normal tilts by an angle θ_0 with respect to the domain axis. Though such a structure is free from any elastic distortion in the cylindrical portion, this uniform alignment cannot be continued near the tapering tips of the domain. We do not see this structure in our system. The observed bent \mathbf{c} field configuration near the interface [14,15] and/or (b) an elastic coupling of the \mathbf{c} -field to the concentration gradient in the binary mixture [16]. Even with a bent \mathbf{c} field it is possible to have a concentric \mathbf{c} field configuration with a straight +1 disclination line passing along the axis of the domain. As argued by Langer and Sethna for the 2D case [13], the advantage of the structure shown in Fig. 3(a) is that it can expel the disclination from the cylinder, thereby saving the core energy of the defect. Apart from the above possibilities, the boundary alignment of \hat{n} could also have led to a ‘‘bâtonnet’’ structure that includes a focal-conic domain. Unlike that in Sm-A, the focal-conic structure in Sm-C is ‘‘broken’’ and costs additional energy [17].

The chiral nature of the domains can be understood as follows. With $\hat{n} = \mathbf{c} + \sqrt{(1-c^2)}\hat{N}$ it is easy to see that $\mathbf{c} \times (\nabla \times \mathbf{c}) \neq 0$ implies $\hat{n} \cdot (\nabla \times \hat{n}) \neq 0$. A *bend* in the \mathbf{c} field necessarily generates a *twist* in the \hat{n} field; the curl of \hat{n} has components both in the plane of the layers and along \hat{N} . Thus, a bent \mathbf{c} field removes the \hat{N} - \mathbf{c} mirror plane locally [6]. Since the sign of the bend is the same everywhere inside a domain, the chiral symmetry is broken on a macroscopic scale as well [18].

Using a simple model for the distortions in the \mathbf{c} field we show that with the configuration shown in Fig. 3(a) within each layer, the elastic free energy is indeed minimized for

the twisted structure shown in Fig. 3(b). The physical origin of this effect is the coupling between the *twist* and the *bend* distortions in the \mathbf{c} field.

A complete analysis of the problem involves minimizing the total free energy of the system which includes the interfacial energy apart from the bulk distortion energy of the Sm-C and the surrounding nematic. Such an analysis is not possible analytically. Therefore, in order to understand the mechanism of the symmetry breaking we estimate the bulk elastic free energy for a cylindrical portion of the Sm-C domain and the surrounding nematic separately (we assume that the surface alignment at the N -Sm-C interface is fixed). In what follows we ignore changes in the magnitude of \mathbf{c} and the layer spacing since the relevant elastic energy cost is very much larger compared to that for producing curvature of the \mathbf{c} field. We also assume the layers to be flat in the domain. The bulk elastic free energy density of Sm-C [19] after integrating out the concentration field can then be written as

$$f_e = \frac{K_s}{2} (\nabla \cdot \hat{\mathbf{c}})^2 + \frac{K_t}{2} (\hat{\mathbf{c}} \cdot \nabla \times \hat{\mathbf{c}})^2 + \frac{K_b}{2} (\hat{\mathbf{N}} \cdot \nabla \times \hat{\mathbf{c}})^2 + K_c (\hat{\mathbf{N}} \cdot \nabla \times \hat{\mathbf{c}}) (\hat{\mathbf{c}} \cdot \nabla \times \hat{\mathbf{c}}), \quad (1)$$

where $\hat{\mathbf{c}} \equiv (\cos\phi, \sin\phi, 0)$ and K_s , K_t , and K_b are the elastic constants (renormalized by the concentration field) associated with splay, twist, and bend deformations in the \mathbf{c} field, respectively. The bare elastic constants can be estimated from those for the nematic by taking the tilt angle dependence into account [10]. The last term in Eq. (1) couples the bend to the twist in the \mathbf{c} field. This term is allowed because the Sm-C is invariant under the simultaneous transformations $\hat{\mathbf{N}} \rightarrow -\hat{\mathbf{N}}$ and $\mathbf{c} \rightarrow -\mathbf{c}$. That is, this term is a result of the combination of the layered structure and the tilt order in the Sm-C phase.

For simplicity we put $K_s = K_b = K$. With this approximation the elastic free energy density (1) can be reduced to the form

$$f_e = \frac{K}{2} [(\nabla_x \phi)^2 + (\nabla_y \phi)^2] + \frac{K_t}{2} (\nabla_z \phi)^2 - K_c [(\nabla_x \phi) \cos\phi + (\nabla_y \phi) \sin\phi] (\nabla_z \phi). \quad (2)$$

The thermodynamic stability of the Sm-C phase demands that $K - (K_c^2/K_t) > 0$.

In order to estimate the elastic free energy for the cylinder we model the \mathbf{c} field shown in Fig. 3(b) as

$$\phi = 2 \arctan \left[\frac{y + R \sin(qz)}{x - R \{1 - \cos(qz)\}} \right] - qz \pm \frac{\pi}{2}, \quad (3)$$

where R is the radius of the domain, $2\pi/q$ is the pitch of the helix and a negative(positive) sign of the $\pi/2$ term leads to a clockwise(counterclockwise) rotation of the \mathbf{c} field [Fig. 3(a) corresponds to the negative sign]. The handedness of the

helix depends on the sign of q [Fig. 3(b) corresponds to negative q]. We show below that with the configuration given by Eq. (3) the elastic free energy has a minimum for a nonzero q although Eq. (3) is a solution to the Euler-Lagrange equation obtained from Eq. (2) only for $q=0$. In each layer Eq. (3) models the topological part of the distortion, which can be considered as a part of a $+2$ disclination [20]. The approximation (3) to the solution is very reasonable as the lateral shift of the singular point S between neighboring layers qRd is much smaller than the core radius r_c (~ 100 Å) of the disclination line and the layer spacing d (~ 30 Å). The bulk elastic free energy per unit length of the cylinder is

$$\frac{F_e}{L} \simeq 2\pi K \ln\left(\frac{R}{r_c}\right) \mp 2\pi K_c R q \left[\ln\left(\frac{R}{r_c}\right) - \frac{1}{2} \right] + \pi K_t R^2 q^2 \left[\ln\left(\frac{R}{r_c}\right) - 1 \right], \quad (4)$$

where terms of order r_c/R and higher have been ignored. Equation (4) has a minimum for

$$q_m = \pm \frac{K_c}{K_t R} \left[\frac{\ln(R/r_c) - 1/2}{\ln(R/r_c) - 1} \right], \quad (5)$$

where the signs on the right-hand side of Eq. (5) correspond to those of the $\pi/2$ term in Eq. (3). It is clear that a nonzero K_c implies an elastic free energy minimum for a nonzero value of q .

Using the experimental values for the radius of the domain and the pitch of the helical band we estimate the magnitude of the ratio K_c/K_t to be roughly 0.3. From Eqs. (3) and (5) it follows that for a given sign of the bend in the \mathbf{c} field the sign of q_m is determined by that of K_c . For $K_c > 0$ the disclination line has the same sense of winding as the $\hat{\mathbf{n}}$ field on the surface of the domain, and for $K_c < 0$ the two have opposite senses. The sign of K_c was experimentally determined as explained below.

It can be seen from Fig. 3(a) that the handedness of the twist distortion produced in the nematic surrounding the domains depends on the sense of rotation of the \mathbf{c} field. At the N -Sm-C interface $\hat{\mathbf{n}}$ makes an angle θ_0 with the cylinder axis. If we assume that this angle goes to zero over a distance $R_0 \sim$ half the cell thickness, the nematic distortion energy per unit length of the cylinder is

$$\frac{F_{e(n)}}{L} \simeq K_n \theta_0^2 \left[\frac{R^2}{(R_0^2 - R^2)} \right], \quad (6)$$

where K_n is the Frank elastic constant of the nematic.

An interesting consequence of the distortion in the nematic is that it can be exploited to select the chirality of the Sm-C domains. To demonstrate this a sample cell was constructed using glass plates that were pretreated to get a twist distortion in the nematic (twisted-nematic cell). In such a cell domains with opposite senses of rotation of their \mathbf{c} fields

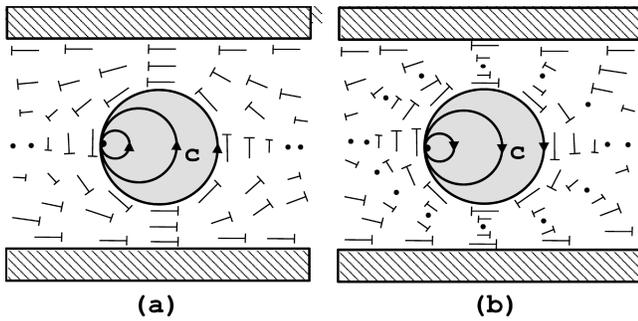


FIG. 4. Schematic representation of the distortion produced in the nematic by domains with opposite \mathbf{c} fields in a twisted-nematic cell. The nails have the same meaning as in Fig. 3. As the distortion in the nematic is much smaller in (a) as compared to that in (b), the former type of Sm-C domain is favored.

produce very different distortions in the surrounding nematic (Fig. 4). The difference in the distortion energy of the nematic between the two types of \mathbf{c} fields favors the formation of domains with a particular chirality. In the experiments an

imposed twist of 15° in a $14\text{-}\mu\text{m}$ -thick cell produced a yield of about 90% of one type of domains. This simple experiment also reveals the sense of rotation of the \mathbf{c} field in the predominant type of domains. The helical band was found to have the same sense of rotation as the \mathbf{c} field in each domain. Thus K_c is positive for this system.

A detailed analysis of the domain shape is not within the scope of this letter. However, a crude calculation of the equilibrium shape, taking into account the anisotropic interfacial tension of the Sm-C and the distortion free energy of the nematic shows that the total energy is minimized for highly anisotropic shapes with an aspect ratio which increases rapidly with the volume of the Sm-C domains [12].

In conclusion, we have demonstrated the phenomenon of spontaneous chiral symmetry breaking in three-dimensional Sm-C domains of a two-component system made of achiral molecules. The symmetry breaking is induced by a specific interfacial alignment of the molecules and the nature of elasticity of layered systems with a tilt order. The coexistence of two anisotropic fluids makes it possible to produce chiral discrimination of the domains by a weak external bias.

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 [15] The orientational order parameter Q can be expected to vary sharply over a coherence length ξ (typically a few molecular lengths) at the N-Sm-C interface. This gives rise to an order-electric polarization $|\mathbf{P}_0| \sim e(\delta Q)/\xi$, where e is the relevant coupling coefficient, and an electric field $\mathbf{E} = (4\pi/\epsilon)\mathbf{P}_0$ normal

- to the interface, where ϵ is the appropriate dielectric constant. The bend distortion in the \mathbf{c} field generates a flexoelectric polarization $|\mathbf{P}_f| \sim e/R$, where R is the radius of the cylinder and for simplicity we have used the same coefficient e . If the mutual orientation between \mathbf{E} and \mathbf{P}_f is favorable, the gain in energy per unit length of the cylinder $\sim (e/R)(e\delta Q/\xi)(4\pi/\epsilon)2\pi R\xi$. The bend distortion costs an energy per unit length $\sim K\pi\ln(R/r_c)$, where K is an elastic constant and r_c the core radius. Using the values (in cgs units) $e \sim 5 \times 10^{-4}$, $\delta Q \sim 0.1$, $\epsilon \sim 5$, and $K \sim 3 \times 10^{-8}$, there is a net gain in energy up to $R \sim 1 \mu\text{m}$ if the \mathbf{c} field has a bend distortion.
- [16] In the two-component system the gradient of the concentration χ across the interface can be large. This can favor a bent \mathbf{c} field configuration at the surface. The surfacelike term $\kappa \int dV \nabla \cdot [\mathbf{c} \times (\nabla \chi \times \mathbf{c})] = \kappa \int dS \cdot [\mathbf{c} \times (\nabla \chi \times \mathbf{c})]$ in the elastic free energy is of particular interest. A negative value for κ encourages the bent \mathbf{c} field configuration at the N-Sm-C boundary. Note that $\nabla \chi$ can also contribute to \mathbf{P}_0 discussed in Ref. [15].
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