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Spontaneous Breaking of Minimal Surface Condition: Labyrinths in Free Standing Smectic Films

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We present a study of thin free standing films made of intercalated smectic-*C* liquid crystal in which, upon lowering the temperature, the minimal surface area condition is broken. A periodic modulation of the film thickness is obtained and a labyrinth structure of crests and valleys is formed. Thickness variation is coupled to the spatial variation of the molecular orientation. The transition to the labyrinth structure is explained to be driven by the mass density difference between the surface and the bulk layers.

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It is quite often that competing interactions result in the periodic morphology of the system. The common source of such competition in soft matter is the difference in surface and bulk interactions; thus, the periodic morphologies are omnipresent in thin films of liquid crystals (LC), the systems with high ratio of the surface to bulk energy. Different surface effects were proposed to be responsible for the formation of modulated patterns in LC films, e.g., surface polarization [1], chiral symmetry breaking [2], surface elastic energy for thin films with asymmetric boundaries [3], surface chiral energy for chiral materials [4], or surface freezing [5]. Recently, also splay deformation of a local polarization field was suggested to trigger the pattern formation in thin films of bent-core materials [6]. Here we propose a new mechanism for the formation of a modulated pattern in LC film. In the studied system, the molecular reorientation is driven by the change in the film thickness. The thickness instability occurs spontaneously; at a threshold temperature, the film surface starts to undulate, breaking the minimal surface condition. The observed phenomenon is associated to the difference in the mass density at the surface and in the bulk. Although a small difference in the density is probably usual for LC films, the difference becomes particularly pronounced, thus the effect easy to observe, in the intercalated systems in which the surface layers are essentially "half empty." Here we present a study of the intercalated smectic-*C* (Sm-*C*) phase made of molecular dimers with mesogenic cores linked covalently or through the hydrogen bonds. However, the proposed mechanism is general, and it should be valid for any lamellar phase in which the surface density is lower than in the bulk. The effect is also expected for dimers formed by strongly assymetric molecules, e.g., with fluorinated terminal chains or strong longitudinal dipoles. The formation of a periodic pattern was indeed reported for fluorinated compounds [2]; however, it was attributed to chiral symmetry breaking.

The dimeric compounds studied have three-ring mesogenic cores linked through the malonate unit, material **1**, or through the hydrogen bonding of terminal OH groups, material **2** (Fig. 1). According to the x-ray measurements, the molecules arrange in layers, the thickness of one layer being close to half of the dimer length, which is characteristic to the intercalated structures. The optical measurements show that both compounds exhibit narrow temperature range of the smectic-*A* phase and, at lower temperatures, the tilted Sm-*C* phase. The tilt angle in the Sm-*C* phase saturates at ~ 16 deg. No layer thickness anomaly was detected by x-ray method within the temperature range of the Sm-*C* phase or in the surface free samples. In the freely suspended film samples (typically from several to a few hundred smectic layers thick) at a certain temperature T_s ($T_s \sim 85\,°C$ and $\sim 97\,°C$ in materials **1** and **2**, respectively) within the Sm-*C* phase temperature range, the thickness of the film spontaneously modulates and the labyrinth of crests and valleys develops (Fig. 2). The film thickness variation is visible in reflection, as the reflected colors depend strongly on the film thickness. The development of the thickness modulated pattern is particularly striking when thickness islands or the regions near the film meniscus are observed [Fig. 2(a)]; the
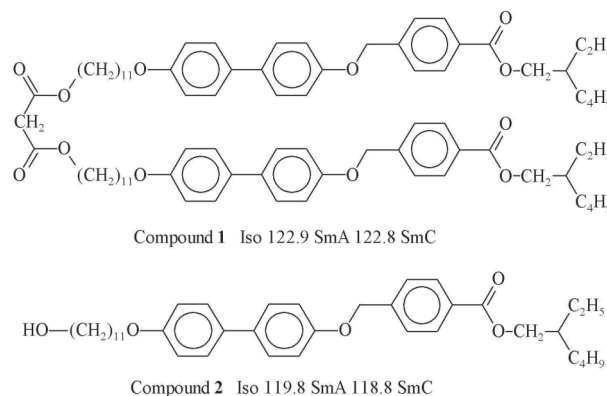

FIG. 1.   Chemical formulas of the studied materials and the phase transition temperatures.
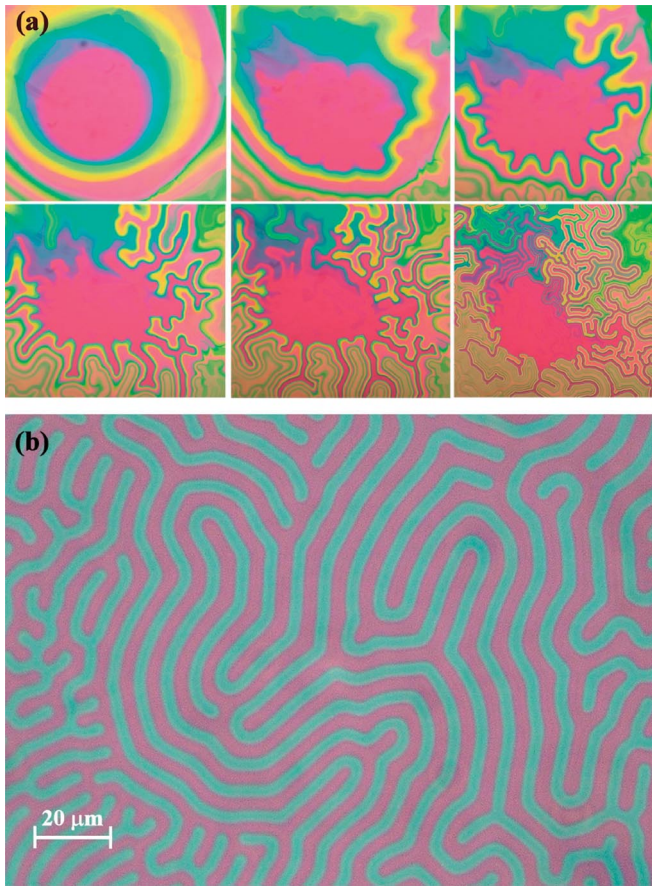
FIG. 2 (color).   Free suspended film of material 2 observed in the reflection mode: (a) film region with strong thickness gradient, the central part is thinner than the outer part. Upon lowering the temperature (from 97.6 to 97.1 °C), the circular edge dislocation lines develop into the labyrinth structure. (b) Enlarged part of the film annealed at $T = 95$ °C.

FIG. 3.   The stripe width (d_S) measured at T_s-2 K as a function of the film thickness (d), fitted to the power low with the exponent $0.6(\pm 0.1)$, which corresponds well to the theoretical prediction. Inset: The stripe width vs temperature for the 260 nm thick film.

boundaries dividing regions of different thickness suddenly start to curve, finally forming a labyrinth structure [Fig. 2(b)]. The texture in film annealed at temperature below T_s for several minutes has a regular pattern with well defined periodicity, from 1 μm (resolution of the microscope) up to 50 μm (Fig. 3). The stripe width increases with increasing temperature and the nucleation of the labyrinth reminds one of a weakly first order phase transition (inset in Fig. 3). Comparing the textures observed in the reflected light and the light transmitted between crossed polarizers, it is found that the film thickness variation is coupled to the spatial variation of the molecular orientation. In the regions with thickness gradient, the **c** vector (projection of the director onto the smectic layer) is uniformly oriented and it is perpendicular to the thickness gradient direction (Fig. 4). In order to determine unambiguously the **c**-vector field corresponding to the observed pattern, a few additional experiments were made. The first order retardation plate (λ plate) that adds a fixed optical path difference to the transmitted light was inserted be-
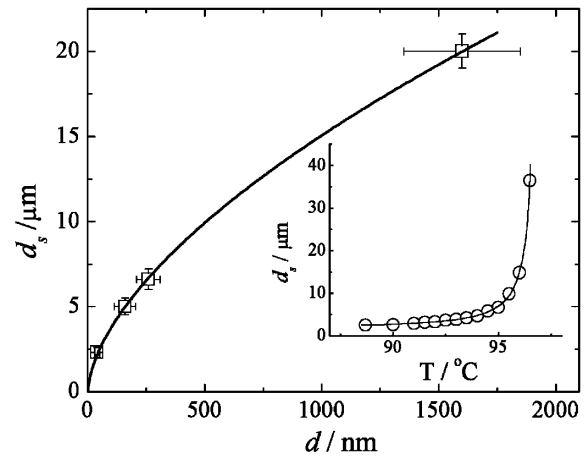
tween the sample and the polarizer, oriented at 45 degrees from the polarizer axis. The onset of colors shows that, within each broad stripe, the **c** vector is oriented along the stripe, and, in regions between the stripes, the orientation is perpendicular to the stripe (Fig. 5). Tilting the sample (imposing the oblique light incidence) along the stripes shows that, in the neighboring broad stripes, the **c** vector has the opposite direction (Fig. 6), while tilting the sample in the direction perpendicular to the stripes shows that, in the narrow regions between the broad stripes, the **c**-vector direction is identical. Thus, it was concluded that the **c** vector rotates by π between the stripes. The rotation is not uniform in space, the broad stripes with nearly uniformly oriented **c** vector are connected by narrow regions over which the **c** vector rotates (π walls), and rotations in the negative and the positive sense interchange between the
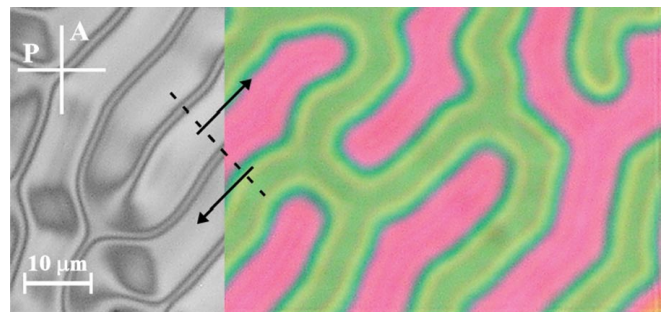

FIG. 4 (color).   Freely suspended film of material 2 at $T = 96$ °C. Left: Observation between crossed polarizers in transmission mode. Right: Observation without polarizers in reflection mode; variation of color pink/green corresponds to thickness variation 520/440 nm. The regions with uniformly oriented **c** vector (arrows) correspond to the film thickness gradient (dotted line), and the orientation of the **c** vector is perpendicular the direction of the thickness gradient.
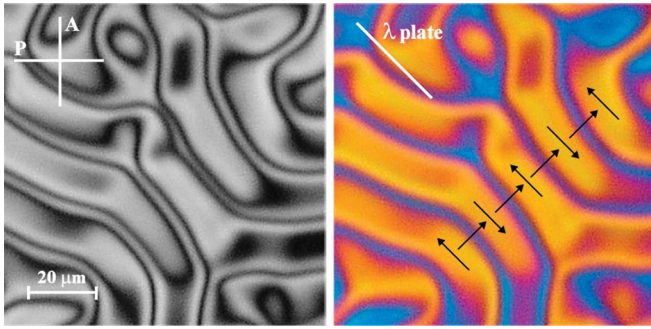
FIG. 5 (color).   Stripe texture observed in the freely suspended film of material **1**, at $T = 80$ °C, between crossed polarizers (left), and with the λ plate inserted between the sample and the polarizer (right). Arrows indicate the direction of the **c** vector. Insertion of the λ plate parallel/perpendicular to the **c** vector increases/decreases the birefringence and thus shifts the birefringence colors to blue/yellow.

neighboring stripes (Fig. 5). The π walls are located at the crests and the valleys of the film surface (Fig. 7). The modulated structure is observed in thin and in very thick films alike. The stripe width and the π-wall width depend on the thickness of the film. The transition to the labyrinth structure is observed also in films that have almost uniform thickness above the transition temperature.

Since the effect is observed for the intercalated smectic phase, we suggest that it is driven by the mass density difference in the surface and the bulk layers. In order to decrease the intermolecular distances and, thus, increase the density of the surface layers, which are "half empty," the molecules increase the tilt in the layer or the layers tilt. Because of the entropic effects, the reduction of density is possible only at a sufficiently low temperature, and, for dimers, the tilt of the layers is energetically more favorable than the tilt of one-half of a dimer. In a uniform thickness
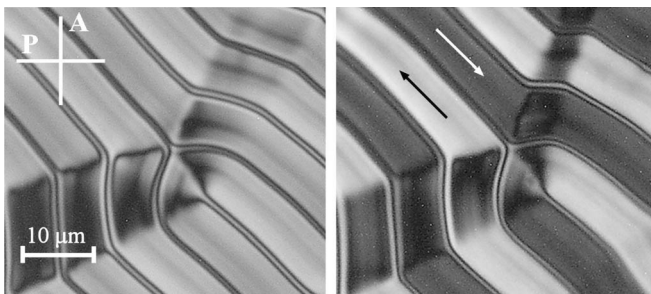

FIG. 6.   Stripe pattern in the freely suspended film of material 2 at $T = 96$ °C, observed between crossed polarizes for normal light incidence (left) and for oblique light incidence (right). The oblique light incidence is obtained by tilting the film in the direction parallel to the stripes; this changes the orientation of the optical indicatrix in respect to the light propagation direction. The observed increase/decrease of birefringence indicates that the tilt direction alternates between stripes. Arrows show the **c**-vector direction.

film, one possibility to reduce the volume of the surface layer is the undulation of the whole film; however, undulation of the bulk layers should be extremely expensive in the intercalated system. Another possibility is to undulate only the surface layer, keeping the bulk layers flat, which leads to the modulation of the film thickness. This scenario involves formation of edge defects close to the film surface (Fig. 7). The position of the edge defects depends on the ratio between the surface tension ($\gamma \sim 10^{-2}$ J/m^2) and the bulk elasticity, which is determined by the smectic layer compressibility constant ($B \sim 10^6$ J/m^3) and the elastic constant for the layer bending (K). If $\gamma < \sqrt{KB}$, dislocation is attracted to the surface [7,8]. In ordinary smectics $K \sim 10^{-12}$ J/m, so the ratio $\gamma/\sqrt{KB} > 1$ and edge defects are repelled from the surface [7,9]. However, in the intercalated structure, K should be larger (strong interlayer interactions) and γ smaller (low mass density in the surface layer) than in ordinary smectic, so it might be expected that edge defects are attracted to the surface. In films with a thickness island, the regions where the surface is inclined (sloped) already exist above the few edge dislocations. If, at a certain temperature, the system reduces the free energy by enlarging the sloped regions more than it pays for the elongation of the edge dislocation lines associated with increasing the sloped areas, surfaces start to deform; this leads to the transition between the uniform and the modulated structure. Deformation of the film surface requires the
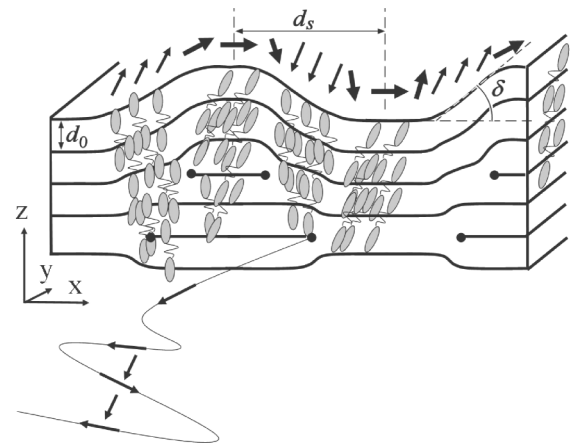

FIG. 7.   Schematic drawing of the few surface layers in modulated film of the Sm-C phase. The change of the film thickness without bending of bulk layers requires the edge dislocations being close to the film surface. In the slope area, additional tilt of the molecules is allowed in the surface layer. Energy of elastic deformation is minimal if, around each dislocation defect, the director is tilted along the defect line (y direction), and the **c** vector (arrows) is uniform through the film thickness. Below the critical temperature, the edge dislocation lines curve, giving rise to the stripe/labyrinth texture. The **c** vector remains along the defect line and has to rotate by π between the neighboring edge dislocation lines. Rotation of the **c** vector in the π-wall region is indicated by thick arrows, d_s is the stripe width, d_0 is the smectic layer thickness, and δ is the surface inclination angle.

flow of the material, which in liquid crystals is the easiest in the direction of the **c** vector [10]. The elastic deformation across the edge dislocation defect in the Sm-C phase is the lowest if the **c** vector is tilted along the defect line [11] (y direction in Fig. 7). Thus, the flow is tangential to the dislocation line. This enhances the dislocation line curvature inhomogeneity and finally creates the labyrinth pattern in the film [Fig. 2(a)]. The initially approximately straight edge dislocation line begins to curl, but the **c** vector remains along the line. As a result, the **c** vector has to rotate by π between the neighboring edge dislocation lines, and the π walls are formed (Fig. 7).

The transition to the labyrinth structure occurs when the energy associated with the formation (or elongation) of the edge defects and the π walls is compensated by the reduction of the surface energy. The contribution (F_S) to the surface energy per unit length of a stripe that privileges a finite tilt δ_0 of the surface layers is assumed to be: $F_S = \frac{1}{2}W_S[1 - (\delta^2/\delta_0^2)]^2 d_S$, where $W_S = W_S(T)$ is the surface strength which increases with lowering temperature, δ is the tilt of the surface layers, and d_S is the stripe width. In a uniform film ($\delta = 0$), the surface energy is $F_S^u = W_S d_S/2$. The energy per unit length of one edge defect is [12] $F_{\text{edge}} = \sqrt{KB}d_0^2/(2r_c) + E_c$, where d_0 is the smectic layer thickness, r_c is the cutoff radius ($r_c \approx d_0$), and E_c is the core energy of the dislocation and cannot be calculated from continuum theories. The energy of the π wall (F_π) is the energy associated with the nematic-type splay of the **c** director. Assuming that the characteristic length for the splay is the stripe width (d_S), the energy of the π wall per unit length of the stripe is $F_\pi = K\pi^2 d/(2d_S)$, where d is film thickness and the splay elastic constant is assumed equal the layer compressibility constant. The energy per unit length of the stripe is $F = F_\pi + F_{\text{edge}}N + F_S$, where the number of edge defects $N = \delta d_S/d_0$ is given by the modulation depth δd_S. Minimizing the energy F with respect to the stripe width and the layer tilt, assuming $\delta \approx \delta_0$, and neglecting E_c, one finds: $\delta = \delta_0 - \delta_0^2\sqrt{KB}/(8W_S)$ and $d_S = \sqrt{K\pi^2 d/[\sqrt{KB}\delta + W_S(1 - \delta^2/\delta_0^2)^2]}$.

Theoretical square root dependence seems to fit experimental d_s vs film thickness data (Fig. 3). For the film thickness $d = 500$ nm and the surface tilt equal to the experimentally observed equilibrium tilt $\delta_0 = 0.5$ deg,

one finds $d_S \sim 3$ μm, which is of the observed order of magnitude (Fig. 3), about 1/3 of measured value. The modulated structure is stable when $F \leq F_s^u$. The critical magnitude of the surface energy W_S is, thus, determined by the condition $F = W_S(T_S)d_S/2$ from which it follows $W_S(T_S) \approx 2\sqrt{KB}\delta_0$.

To conclude, we have presented a system in which the minimal surface condition is broken. Since in the intercalated smectic films made of dimeric molecules the surface layer is half empty and, thus, energetically costly, the surface effect dominates over the bulk effect when temperature is low enough. In order to reduce the intermolecular distance at the surface, the surface layer undulates. This is achieved by a periodic modulation of the film thickness which leads to the formation of the labyrinth structure.

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