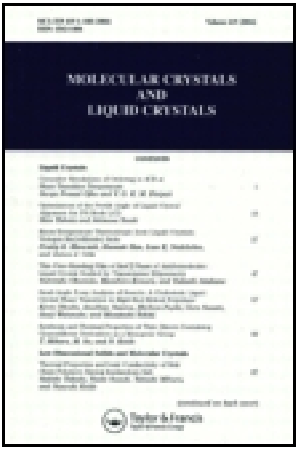
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Periodic Structures in Induced Films of Tilted Smectics

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Surface freezing commonly induces smectic films at the free surface of isotropic droplets close to the isotropic to smectic transition. In the case of films of tilted smectics they generally exhibit stable stripes between crossed polarizers. We show that these stripes correspond to an in-plane continuous rotation of the director, equivalent to a set of parallel disclination walls and which is different from the frequently reported 1D array of defects. On cooling down the isotropic droplet, the disclination walls are observed to form as early as the first smectic layer, one after the other one, from the edge of the film. Then, on decreasing temperature again, the number of the smectic layers increases in the film. During this process the number of disclination walls is kept constant due to anchoring effects onto the borders of the film. We perform such observations on two different non-chiral compounds leading respectively to smectic C_A (or smectic O) and smectic C films. This allows us to exclude chirality effects in the physical mechanism for the disclination walls formation.

Keywords: Periodic structures; Stripe state; Disclination walls; Smectic C and Smectic C_A films; Polar nematic

SMECTIC C_A FILM

In liquid crystals, unlike the other materials, we generally observe a higher ordered phase at the air-liquid crystal interface, induced by surface tension [1]. Therefore, when we cool down from the isotropic phase, a liquid crystal (LC) droplet of the symmetric mixture of 1-(methyl)-heptyl-terephtalidene-bis-amino-cinnamate (MHTAC) [2], a smectic O or smectic C_A (SmC_A) film appears at its free surface.

The SmC_A phase resembles very much the SmC one with the difference that the tilt of the molecules occurs in alternate directions from one layer to the next one [3] [4]. The particularity of this compound is that it produces rather thick induced films with successive layer-by-layer transitions. Each new smectic layer has a different transition temperature. In this way, by acting on the thermostat, it is possible to control the thickness of the induced film.

The sample and the experimental setup are shown in Fig. 1. Practically, a small quantity of the compound is deposited on a clean glass plate between two evaporated gold electrodes. The whole system is precisely thermostated, and observed between crossed polarizers with an Orthoplan Leica microscope. The surface induced SmC_A film is easily observable under these conditions, because the molecules are tilted and strongly birefringent. As the isotropic droplet completely wets the glass substrate, one can consider the film as perfectly horizontal and flat.

In the case of SmC_A films, the surface electric polarization, which generally exists at the interface between materials and air, is tilted because of the tilt of the molecules. The in-plane component, $\mathbf{P_S}$, of the surface polarization is, for symmetry reasons, oriented along the **c**-director defined as the projection of the average molecular direction onto the film plane. Therefore, by applying an electric field **E** tangentially to the film by means of two evaporated gold electrodes, we orient the whole film except where defects produce strong distortions. Such induced smectic films are interesting because, mechanically, they are free from solid contacts, like suspended films [5]. Moreover, they constitute 2D-model systems of polar nematic LC with a director that is a real vector with a sense defined by $\mathbf{P_S}$.

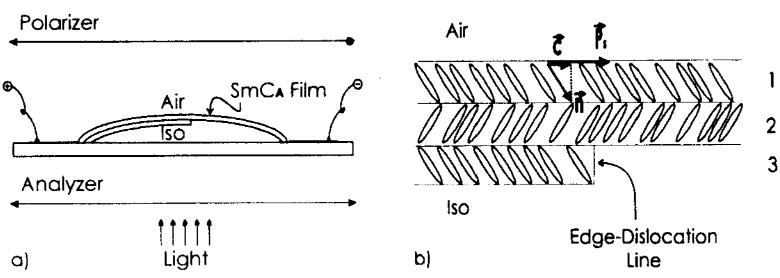

FIG. 1: a) Vertical cross-section of an isotropic LC droplet on which top floats a SmC_A film. The cross-section is perpendicular to a surface edge-dislocation line. The puddle lays on a glass substrate between two gold evaporated electrodes. The whole sample is viewed with an optical microscope between crossed polarizers. b) Herringbone structure of the SmC_A film with the molecules tilted in alternate directions. The vertical component of the electric polarization at the interface with air is not represented.

STABLE PERIODIC ARRAY OF DISCLINATION WALLS

In this paper, we report the formation of a remarkable stable one-dimensional array of 2π-disclination walls, which appears as an array of parallel and linear fringes when observed under polarizing microscope. From the intensity distribution, one can deduce the orientation of the molecules : the **c**-director is parallel to the analyzer-polarizer system where the fringes are dark, and at $\pi/4$ angle with the polarizers where they are clear. In this manner, the **c**-director field is known modulo $\pi/2$. In order to determine it exactly we apply a small electric field **E** tangentially to the film (~ 1 V/mm). The $-\mathbf{E}.\mathbf{P}_S$ coupling tends to orient the smectic film. Observing then the response of the fringes, we can deduce the exact orientation of **c**, defined to be oriented in the same direction as $\mathbf{P}_S$, all along the film. Practically, the best situation is that of fringes parallel to the applied field. The favorable fringes will then widen under the electric field action, whereas the unfavorable one, where $\mathbf{P}_S$ and **E** are roughly opposite, will thin down. Therefore, the **c**-director field can be completely determined everywhere in the film.

By rotating the microscope stage, we can notice that the fringes continuously drift in a direction perpendicular to their length. This reveals that the **c**-director rotates in the film without any discontinuities. In Fig. 2, we show pictures that correspond to four different positions of the microscope stage. It is a bit delicate to perceive the drift of the fringes on the pictures. However, it is easier to observe it directly. More easily, we have also recorded the transverse intensity profile of the fringes and noticed that it does not present any discontinuities. Thus, the observed texture is a one-dimensional array of 2π-walls. Stripe textures have often been reported [6-8]. But our structure is different and it is based on a physical mechanism also completely different. For instance, Maclennan [7] has observed stripes in freely suspended ferroelectric LC films of the chiral mixture ZLI-3654 that correspond to splay domains comprised between defect lines in the first smectic layer. Gorecka and al. have also reported [8] similar textures that they analyzed as an array of defect lines. The stripes observed by Demikhov and Stegemeyer [6] form after the relaxation of a system of point defects and are interpreted in terms of a chirality effect. Clearly the structure reported here is different. First, we do not observe any line defects neither in the first smectic layer nor in the others. Second, all the observations already published were performed on chiral compounds. Clearly, since our compound is a symmetric mixture [2], it does not exhibit ferroelectric properties, and the stripe structure has to be based on a different physical mechanism.

Though our samples have been performed without any particular preparation, we spontaneously and systematically obtain such modulated structures. Experimentally, we deposit some powder of MHTAC on a glass plate that has been carefully cleaned with acetone and ethanol. We then heat up the sample until the crystals melt down in the isotropic phase and form a macroscopic puddle. Next, by slowly cooling down the LC puddle, a few degrees above the bulk transition temperature, we can observe the continuous formation of a first smectic layer. Simultaneously to this first layer transition, we note the appearance of numerous short disclination walls on the freshly constituted film. At the beginning of its formation, the film is restricted to several nucleation domains, which already bear the disclination walls. These domains generally appear near the puddle edge. They correspond to the places of the surface puddle where the isotropic to SmC_A phase transition has already occurred.

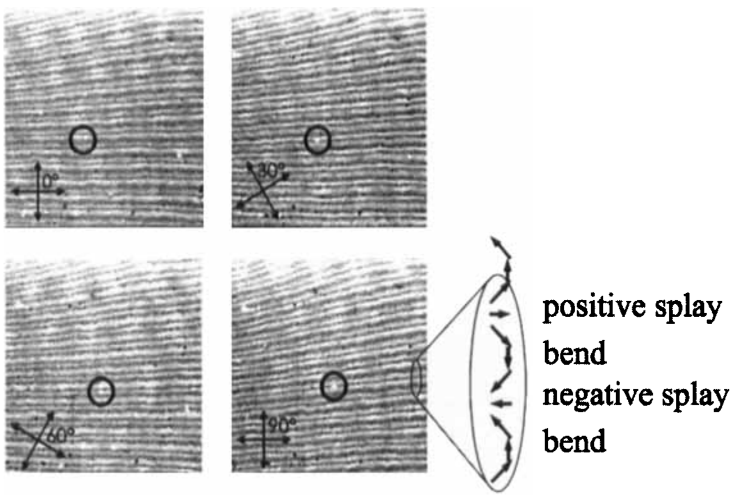

FIG. 2: Array of fringes in a three layers thick SmC_A film of a symmetric mixture of MHTAC. On rotating the polarizers, the fringes continuously drift referred to the bright impurity marked with a circle. We deduce that the c-director rotates in the film as sketched on the right part of the figure.

Then, on decreasing temperature slightly, the nucleation domains grow and quickly collapse to constitute a larger film. As the film keeps on extending, the walls stretch themselves. At the same time, the contrast of the walls increases. This is due to the increase of birefringence, which is consistent with more ordered and increasingly tilted molecules in the film, as the temperature is decreased. So, at the beginning of their formation, the walls are of small length and slightly contrasted. They are, at that moment, locally oriented but they still cannot be considered as forming a periodic array. Then, decreasing temperature again, the walls are observed to get longer and longer as the film increases its area. Nevertheless, the formation process of the walls is still not finished since, in a second step, we observe a longitudinal one-by-one growth of the walls (Fig.3).

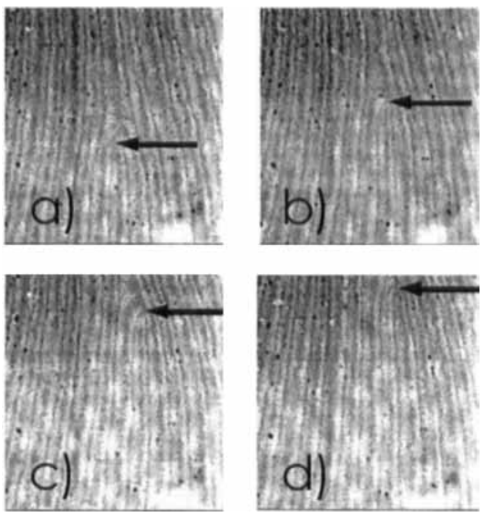

FIG 3: Longitudinal one by one growth of a disclination wall in a 2-layers thick film. The time interval between the photos is about one minute. One can perceive the growth of the wall. Its length is referred to the bright impurity on bottom of each photo. The arrow points to the extremity of the growing 2π-wall.

Thus, the number of walls, and hence their density, is increased. Consequently, they get more and more parallel and the period of array decreases. However, it is to be pointed out that the different stages described above for the formation process of the array of walls are not disconnected. Practically, it is impossible to determine the beginning and the end of each stage because they overlap each other. It is to be noticed also that the formation is spontaneous. This gives the evidence that the observed structure is a *stable state* corresponding to a minimum of free energy, and that its physical mechanism is strong enough to overtake the elastic energy of such a distorted state.

Let us recall that the physical mechanism responsible for the formation of the walls is not based on chirality effects, since the compound is achiral [2]. Therefore, no chirality effect may be invoked to justify the in-plane spontaneous director rotation. We may moreover argue that this structure probably corresponds to a general behavior of tilted smectics since we eventually observed similar structures in SmC induced films of hexadecanoxybenzoïc acid, an achiral compound with a completely symmetric molecule (FIG. 4).

In all our experiments, we have not observed any temperature effects on the structure and on the properties of the walls while keeping the number of layers constant in the film. For example, we have not seen any significant evolution of the period of the array of walls. Even the application of an electric field is not able to change the period of the array and to destroy the structure in any cases in the range of our applied fields ($\leq 100 V.cm^{-1}$).

FIG. 4: Disclination walls in a surface induced smectic C film of Hexadecanoxybenzoïc acid, a non-chiral compound.

Decreasing temperature again from the one-layer state described above, makes the film to form new smectic layers and therefore to thicken up. Under polarizing microscope, the transition front is viewed as an edge-dislocation line passing slowly across the surface of the film. The thickening goes with a discrete increase of the film birefringence. Therefore, the dislocation line cuts the film in two domains of walls with different contrasts. This property permits us to count the number of smectic layers and, hence, to deduce the thickness of the film. On the dislocation line, anchoring conditions exist for the **c**-director [9], which are not strong enough to destroy the orientation modulation. When the film gets thicker, the array of disclination walls thus remains.

Because of the elastic couplings, the molecules of each new layer keep strictly the same orientation as their upper neighbors. We therefore do not observe any superposition of different arrays of fringes. The film, as a whole, constitutes a 2D system. One may also notice that no such modulation of the **c**-director have been observed in bulk samples with achiral compounds. We may therefore suspect that the observed structure is due to surface effects. Consequently, we do not expect, for very thick film, to see any stripe state. Nevertheless, even when the film gets thicker (100 smectic layers) it still exhibits stripes essentially because the walls keep anchored onto the edge of the film. Above a certain film thickness, typically 3 layers, the walls stop forming and some walls even may unhook and withdraw from the film. From these observations, we deduce that, for very thick films, the system is in a *metastable state*: the walls keep trapped because they are anchored on the film edges.

CONCLUSIONS

In summary, we have observed arrays of disclination walls with asymmetric SmC_A films induced at the free surface of LC puddles in the isotropic phase. The formation of these arrays is due to a spontaneous process that gives the evidence for the stability of the structure. This formation occurs in several times. First, the walls spontaneously appear on site as the first layer is formed with a progressive increase of their contrast. Next, they collectively stretch along themselves as the film extends. Finally, they grow one after the other one in a longitudinal way until reaching an equilibrium number of walls. This last stage for the formation process of the walls occurs only in the two first layers and definitely stops when the film gets thicker. It leads finally to an array of fringes, which are the mark of disclination walls, the **c**-director continuously rotating over the film. Then, the system enters a metastable state that is able to trap the distortion in the film.

Chirality effects cannot be evoked to explain this structure since the observations are performed on symmetric mixtures. Moreover, we argue that it is a general behavior of tilted smectics. Indeed, smectic C films of non-chiral compounds lead to the same structure.

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