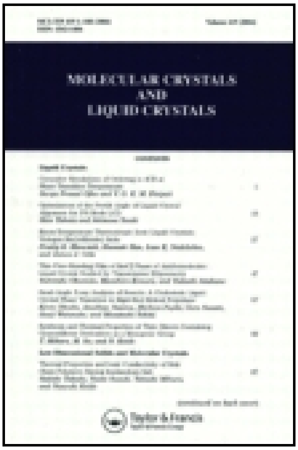

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2-Dimensional Elastic Constant in Asymmetric Films of Tilted Smectics

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2-Dimensional Elastic Constant in Asymmetric Films of Tilted Smectics

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We report on what we believe to be the first measurement of the surface elastic constant, K_1. This new elastic constant is manifested through the formation of a purely elastic instability. The instability is observed to form in thin smectic films, which are induced at the free surface of a liquid crystal droplet. Under polarising microscope, the instability is viewed as an array of interference fringes, which denote variation of both the orientation and the amplitude of the **c** director. The instability corresponds to a continuous rotation of the **c** director coupled to modulations of the molecular tilt angle θ. We propose that this mechanical instability is produced by the surface elastic term, $K_1 c^2 \mathrm{div}\mathbf{c}$. This new term to consider in the free energy density is found to be consistent both qualitatively and quantitatively with the experiments.

Keywords: smectic C_A; instability; disclination walls; elastic constant; asymmetric films; striped state

I. INTRODUCTION

Periodical textures in free standing films and Langmuir films have attracted considerable attention [1-2]. They arise in different situations and in various systems. They are instabilities and generally result from a competition between two antagonist effects. The delicate balance between them determines a threshold above which the instability may express. A very convenient system to study such instabilities is the pre-freezing smectic film, which are induced at the free surface of the isotropic droplets of liquid crystals [3]. Here, we report on a surface elastic constant K_I, which is evidenced through the occurrence of a purely elastic instability. The instability is characterised by modulations of both the orientation of the **c** director and the molecular tilt angle θ. It is hence an array of disclination walls and it produces an array of fringes when observed between crossed polarizers. By measuring the characteristics of the distortion, we deduce a magnitude order for K_I. Splay domain widths measurements performed on different thicknesses exhibit a parity effect, which proves that K_I is located at the smectic – isotropic phase interface.

II. EXPERIMENTAL

The compound used here is the 1-(methyl)-heptyl-terephtalidene-bis-amino-cinnamate, commonly abbreviated as MHTAC [4]. Because of the asymmetric carbons at the each extremity, the pure MHTAC compound is chiral. Nevertheless, our experiments are performed with a symmetric mixture of enantiomers of MHTAC in the proportions of 25% RR, 25% SS, 50% RS. The resulting compound is thus totally achiral.

This compound exhibits a SmC_A (previously called smectic O) to isotropic phase transition. During the experiments, the temperature is essentially maintained in the vicinity of the isotropic phase transition. The SmC_A phase is a lamellar phase that resembles much the SmC phase (Fig. 1a). The difference is that the molecular tilt θ occurs in alternate directions from one layer to another. The SmC_A phase is thus of the herringbone type [3].

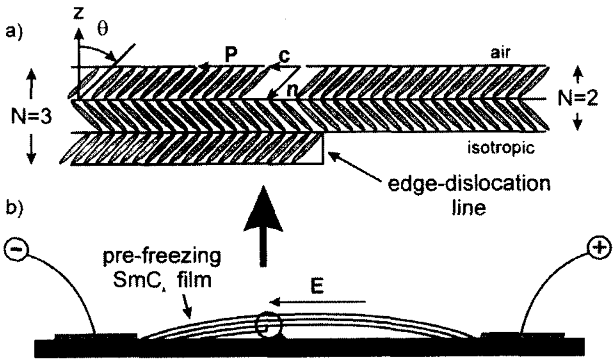

FIGURE 1 a) Herringbone structure of the SmC_A phase with the molecules tilted in alternate directions. The smectic layers are perpendicular to the z-axis; the vertical component of the electric polarization at the interface with air is not represented. b) Vertical cross section of an isotropic droplet on top of which floats a pre-freezing SmC_A film. The puddle lays on a glass substrate between two gold evaporated electrodes. The cross-section is perpendicular to a surface edge-dislocation line.

The advantage of performing experiments with MHTAC is that it exhibits an unusually large birefringence [5]. This particularity allows us to perform comfortable observations and measurements on smectic films, down to two smectic layers, using an optical polarising microscope in transmitted light.

Most of solid materials exhibit liquid pre-wetting films at the solid-air interface. On the opposite, liquid crystal materials tend to stabilise a more ordered phase at their free surface [6]. So that, a few degrees above the isotropic to smectic transition, one may generally observe the formation of the first smectic layer of the film. The film covers the whole surface of the liquid crystal droplets in the isotropic phase. This smectic film is induced by the surface fields, which tend to minimise the interfacial energy by reducing the surface contact between the liquid and the air. The induced smectic film is more ordered than its underlying bulk phase: they are pre-freezing films.

As the first smectic layer is smooth, it favours the formation of additional smectic layers, one after another one towards the isotropic phase [7]. Then, by slowly cooling down the isotropic droplet, one induces the formation of the second smectic layer that intercalates between the first smectic layer and the isotropic phase. If the temperature is decreased further, a new smectic layer appears and so on... In most liquid crystals, the pre-freezing film extends a few layers only indicating that the wetting is incomplete. In the case of MHTAC, the wetting is total and the pre-freezing film thickens in a layer-by-layer manner (Fig. 1b) until the whole isotropic droplet gets in the smectic phase [3]. This indicates that the transition is close to a critical point. Observed between crossed polarizers, the formation of a new smectic layer is viewed as a tiny line that runs through the film surface. This line is an edge-dislocation line and corresponds to the appearance of a new smectic layer. It separates two regions of different thickness as revealed by the difference of contrast between them. As a result, the most contrasted region is the thicker part of the film. This permits us to count one after the other one the smectic layers during their formation. The thickness of the film, in terms of the number of smectic layers N, is then controlled and unambiguously known.

The MHTAC constitutes therefore a very convenient experimental system because the thickness of the pre-freezing films can be sharply adjusted by means of a temperature control. In addition, the pre-freezing film is free from solid contacts since it floats on top of an isotropic liquid droplet (Fig. 1b). Thus, it is not submitted to any external parasitic perturbations and may be able to reveal subtle mechanical effects. This system thus offers a great opportunity to study experimentally thickness and surface effects on the liquid crystal properties.

The pre-freezing smectic film is in an asymmetric surrounding. It has two different interfaces, one with the air and the other one with the isotropic phase. The liquid crystal considered here wets well enough the glass substrate. The area of the isotropic liquid crystal puddle, and hence that of the pre-freezing film, which lies on its top, is typically of the order $\sim 1\,\mathrm{cm}^2$ and its height is about a few microns. The pre-freezing film may therefore be considered as flat and horizontal.

At the surface of materials there is generally a surface electric polarisation. This electric polarisation originates from the symmetry breaking and from the electronegativity difference between two media. For symmetry reasons, this surface electric polarisation is often normal to the surface of the material. Here, because the molecules are tilted, it is also tilted [3]. An electric field applied tangentially to the film plane may then couple to the in-plane component **P** of the surface electric polarisation. The whole film may therefore be oriented in this way. For the same symmetry reasons, the **c** director is a true vector here and is borne by the in-plane component of the surface electric polarisation.

The experimental set-up is quite simple. The sample is placed in a hot stage which temperature is precisely controlled with an INSTEC card, and is observed using an Orthoplan Leica microscope carefully compensated from parasitic birefringences. The microscope is equipped with a high sensitive Cohu video camera. The light intensity is digitised by a PC microcomputer through a Matrox IP-8 card. The intensity may then be accumulated in order to reduce the statistic noise. An electric field may also be applied tangentially to the film plane, allowing the orientation of the film.

Experimentally, a small amount of the liquid crystal substance is deposited on a clean glass substrate. The sample is then heated to obtain a liquid crystal droplet in the isotropic phase. Next, it is slowly cooled down until the first smectic layer has formed. Because of the surface fields influence, the first smectic layer appears a few degrees above the bulk smectic to isotropic transition. Therefore, during the experiments, the temperature is essentially maintained in the vicinity of the isotropic phase transition in order to restrict the thickness of the film to a few numbers of layers only.

III. ARRAY OF DISCLINATION WALLS

Systematically, instabilities develop on these pre-freezing films (Fig. 2). Between crossed polarizers, the instability is viewed as a set of linear and parallel stripes alternately bright and dark with a four-fringes period. The stripes are interference fringes, which are the mark of the optical axis of the rod-shaped molecules. They denote variations of the orientations of **c**. Where the fringes are dark, **c** is either parallel or perpendicular to the polarizers, where the fringes are bright, the **c** director makes a 45° angle with the polarizers. By slowly rotating the microscope hot stage, one may observe that the fringes continuously drift perpendicularly to their direction. This proves that the instability originates from a continuous rotation of **c**. The rotation sense of **c** may be deduced by noting the drifting direction of the fringes. The microscopic structure of the instability may thus be unambiguously determined. It corresponds to a continuous distortion of the director field where the **c** director rotates in splay domains separated by bend ones. The instability may be viewed as a 1D array of disclination walls. In addition, it is to be noted also that the disclination walls form spontaneously, i.e. **c** rotates by itself. So when it appears, the distorted state corresponds to a stable state.

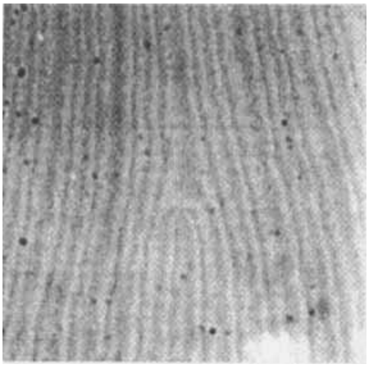

FIGURE 2. Array of disclination walls in a 2 layers thick smectic film. The splay domains are the larger dark fringes. Both splay domains have unequal widths. One disclination wall is growing, intercalating between the others.

The instability develops immediately and systematically as the first smectic layer forms [8]. The optical path difference introduced by a single smectic layer is very small, ~ 0.5nm. The contrast of the disclination walls is then very weak. Under these conditions, light intensity measurements may not be performed accurately. Nevertheless, observations are possible. The smectic film has only just formed when the disclination walls appear. Because of the weak contrast, they are only just distinguishable and seem like linear shadows. At this stage of their formation, the walls are short and not very numerous. They are closely linear but not rigorously parallel to each other. These walls grow progressively as the film extends. Simultaneously, other stripes appear and intercalate themselves between the already existing walls. Then, they slowly grow from the film borders towards its centre. The structure finally obtained is thus a radial arrangement of disclination walls. Nevertheless, the liquid crystal puddle is so large compared to the width of the walls that, obviously, they may be considered locally as linear and parallel. The formation process continues even when the first smectic layer of the film has entirely grown up. Thus, the number (and hence the density of walls) in the film increases.

IV. FREE ENERGY DENSITY

As evidenced in Sect.III, the instability originates from a spontaneous rotation of the **c** director. This feature is very surprising since any distortion of the director field should be energetically unfavourable, with an increased free energy. This is due to the quadratic Frank elastic terms. Therefore, such a stable distorted state may not be described by only considering these terms. A new term has to be taken into account. We propose that the instability originates from a surface effect and is produced by a purely elastic mechanism. As the distortions in the film have small wavevectors, this term has to be of the lowest order to contribute efficiently to the free energy and to be able to equilibrate the quadratic Frank elastic terms. In addition, this term must be linear since it has to distinguish both sign of splay domains giving them different widths. Let us recall first that the $\nabla\wedge\mathbf{c}$ terms are not considered here because the compound is achiral. For this particular striped state, chirality effects are thus excluded. The first elastic term that might be considered here is the $\nabla\cdot\mathbf{c}$ one. This term is a total derivative. Its contribution to the total free energy is therefore negligible in the case of large and free from dislocation samples, since its integral only depends on the boundary conditions.

The term of the lowest order that may account for the formation of the striped state is $K_1 c^2 \mathrm{div} c$, where K_1 is a surface elastic constant linear in the splay distortion [9]. This term has a non-trivial contribution to the total free energy with variations of the modulus of **c**. These variations are achieved through modulations of the molecular tilt angle θ, with $c^2 = \sin^2\theta$. In order to account for the tilt modulations, a Landau free energy where the c director is the order parameter of the film has to be considered. It allows one to describe the macroscopic physics of a non-chiral smectic film and, in particular, to write its free energy density:

$$f = \frac{1}{2}K_s(\bar{\nabla}\cdot\bar{c})^2 + \frac{1}{2}K_b(\bar{\nabla}\wedge\bar{c})^2 + K_1 c^2 \bar{\nabla}\cdot\bar{c} + \frac{1}{2}ac^2 + \frac{1}{4}ac^4$$

The first two terms in the free energy density expression are the classical elastic energies for the splay and bend distortion, K_s and K_b being respectively the splay and bend 2D orientational elastic constants of the film. They can be expressed in terms of the Frank elastic constants, of the molecular tilt angle θ, and the film thickness ND, where N is the number of smectic layers in the film and D the thickness of one layer. The second term is the surface elastic term linear in the splay distortions and in the modulation of θ. K_l does not depend on the film thickness, as it is a surface elastic constant. This term is linear in the splay distortion, and consistent with the symmetry of the polar film. Let us recall that the modulations of θ are easier in the vicinity of the isotropic phase transition, precisely when the instability forms. This is a consequence of the Landau terms. On the other hand, the distortion is easier to produce when the liquid crystal film is less rigid, i.e. when the film is thin, restricted to a few layers.

Both the azimuth angle φ and the molecular tilt θ are expanded as Fourier series. By developing the free energy density to the 1st order and integrating it, we obtain the expressions for the positive and negative splay domain widths and for the molecular tilt angle modulation [10]. These quantities are connected to the fundamental parameters of the smectic film (K_s, K_b, K_l, and b). They are valid only in the small wavelengths regime since the expressions are derived from a 1st order free energy density model. We find in particular a linear behavior in 1/q for S_+ and S_-, q being the wavevector of the distortion. The slope of this behavior is connected to the 2D Frank elastic constant [11]. Whereas the y-intercept is directly proportional to the K_l/b ratio, where K_l is the surface elastic constant. The tilt modulations are found to vary linearly with q. The slope of this behavior is related the K_l/b.

V. EXPERIMENTAL EVIDENCE

In practice, a rectangular window is set perpendicularly to the disclination walls direction, defined as the y-axis. A profile of the light intensity distribution may then be caught along the x-axis oriented perpendicularly to the fringes and parallel to the measurement window. The aim is to raise a map of the director field over the window in order to mark unambiguously the position of each stripe on the light intensity profile and to perform width measurements of both positive and negative splay domains. The splay domains where **c** diverges (resp. converges) are positive (resp. negative) splay domains and their widths are noted S_+ (resp. S_-). In a first step, **c** is either parallel or perpendicular to the polarizers where the fringes are dark and makes a 45° angle with them where the fringes are bright. At this stage, **c** is determined modulo π/2 only. We then apply an electric field, for a while, tangentially to the film and parallel to the disclination walls direction. Because of its coupling interaction with **c**, domains will widen out or narrow, according to the direction of **c** with respect to that of **E**. For instance, where **c** and **E** are parallel (resp. anti-parallel), the domains widen out (resp. shrink). These observations combined to the drifting direction of the fringes while the microscope stage is rotated give the rotation sense of **c**.

Light intensity profiles are then caught through an x-axis oriented parallel to the edge window and perpendicular to the disclination walls, with a direction making a 45° angle with the polarizers. In this manner, the **c** director may be determined everywhere in the film, i.e. both its amplitude $\sin\theta$ and azimuth angle φ, allowing the measurement of splay and bend domain widths. The light intensity is related to these polar coordinates through the relation $I \sim \delta^2 (1+\cos 4\varphi)$, where δ ($=\Delta n\ N\ D \sin^2\theta$) is the optical path difference of light across the film in normal incidence, D being the thickness of a smectic layer and Δn the difference between the ordinary and extraordinary refractive indices.

The distortion exhibits an asymmetry, which occurs in two ways. First, the bend domains are narrower than the splay ones because the 2D bend and splay elastic constant are different is smectics [11]. But the unexpected feature is that the splay domains have different widths according to their sign (Fig. 2). The difference between the widths of both sign of splay domain varies with the wavelength of the distortion λ. So, it is weaker for smaller λ. The difference between S_+ and S_- is nearly constant when λ is small and tends to diverge when λ becomes large.

For a two layer thick film, S_+ is systematically larger than S_- [9]. The larger splay distortion has a more favorable contribution to the total free energy than the thinner one. The other main feature is that the light intensity profiles exhibit light intensity modulations, which are related to θ through the film birefringence. In opposition to the asymmetry of the splay widths, the intensity modulations are more remarkable when λ is small, so that the measurements of the splay domain widths and the tilt angle modulations are performed on two different and distinctive ranges of λ. The splay domains width measurements for N=2 are reported in Ref. [9]. They are compared to the theoretical expansion. Asymptotic least square fits over both signs of splay width are realized. This particular fit is performed asymptotically on progressively reducing the total number of data one after another one from the large λ until stabilization of the fitting parameters. It yields $K_s/K_b \sim 5$ consistent with what is reported in Ref. [11].

The light intensity profile exhibits a modulation of the intensity maximums. Within a period, one fringe is uppered, another is lowered, the two others keeping intermediate amplitude. The intensity modulation is connected to molecular tilt angle modulation $\delta\theta_0$ through the birefringence of the film. It is significant only for the small λ and is directly connected to K_l/b. Though independent, the results obtained from the three measurements (S_+, S_-, $\delta\theta_0$) are consistent and thus confirm the model. The linear splay elastic constant is found to be of magnitude order $\sim 10^{-11} J.m^{-1}$.

VI. THICHNESS BEHAVIOR

The effect of K_l is evidenced spectacularly for a two layers thick film. However, measurements may also be performed for different thicknesses. These measurements give information about the thickness behavior of the instability and also about where K_l is located. Is it located at the Sm – air interface or the Sm – isotropic phase interface?

We present splay domain widths measurements for N=3 as a function of the wave vector inverse (Fig. 3). A parity effect is evidenced on these measurements. Indeed, when N=2, i.e. even N, S_+ is larger than S_-. When N=3, i.e. odd N, S_- becomes larger than S_+. In addition, the separation between both asymptotic least square fits, which is directly connected to the K_l to b ratio, decreases when the film thickness is increased. Thus K_l/b decreases when N is increased.

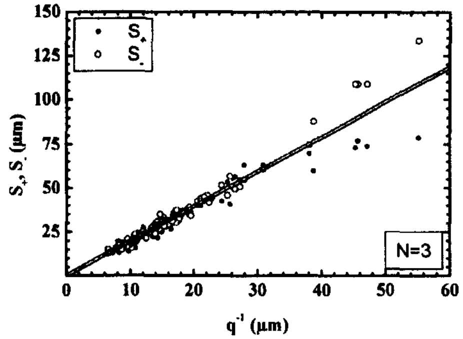

FIGURE 3. Widths of the positive and negative splay fringes, S_+ (close dots) and S_- (open dots), as a function of 1/q for a three layers thick film. Unlike a two layers thick film, S_- is larger than S_+. The separation between both widths increases with 1/q. The lines are asymptotic least square fits on the data. They yield independent measurement of K_l/b.

But, these measurements also seem to show a sign inversion for K_l/b when N is changed. This is impossible since the interface, which governs the formation of the instability and where K_l is located, must not be affected by a change of N and hence by its parity. In fact, what is measured is the whole term: $K_l c^2 \mathrm{div} c$. Since K_l may not change its sign, a parity effect may just come from a change in the sign of **c**. By defining **c** at the Sm – air interface, we implicitly made the assumption that K_l were located at that interface. But there, **c** does not change its sign when the thickness is increased. If **c** is defined at the Sm – isotropic phase interface, it changes its sign according to N is odd or even and the parity effect is then understood (Fig. 4). In the light of these consideration, it becomes easy to understand that the inequality between S_+ and S_- reverses with the parity of N. So the linear splay elastic constant is located at the Sm – isotropic phase interface.

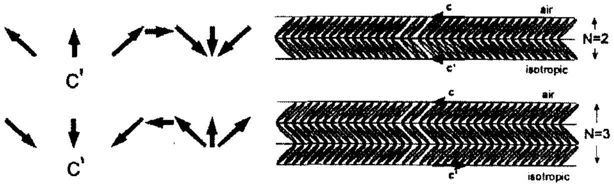

FIGURE 4. Schematic representation of the SmC_A with two and three smectic layers. Defining **c** at the Sm - isotropic phase interface accounts well for the parity effect and the splay domain widths inversion when the thickness is increased.

VII. CONCLUSION

The instability in which spontaneous variations of both the azimuth angle φ and the molecular tilt θ occur is found to be produced by a purely elastic mechanism. The corresponding microscopic structure is determined as a continuous rotation of the **c** director coupled to modulation of θ. This effect is an interfacial effect since it is not observed in bulk samples. We propose that the formation of the instability is governed by a surface elastic term $K_l c^2 \mathrm{div} c$ linear in the splay distortion. This term describes qualitatively as well as quantitatively the spontaneous distortion observed here. A value of K_l may be deduced from both splay domain widths and molecular tilt modulations. Though independent, both measurements lead to consistent results, and we found K_l to be of order $10^{-11} J.m^{-1}$. A study of the instability for different thicknesses of the film evidences a parity effect for the linear splay elastic term K_l. This proves that K_l is located at the Sm – isotropic phase interface and not at the air – Sm interface. Let us finish with noting that this elastic constant is quite general. It has been evidenced in SmC pre-freezing film of non-chiral molecules. It has also been observed in Langmuir films [12] and may probably also occur in biological systems.

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