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Isabelle Kraus, Christian Bahr, Pawel Pieranski. Mechanical Properties of Freely Suspended Smectic Films. *Journal de Physique II*, 1997, 7 (11), pp.1617-1634. 10.1051/jp2:1997206 . jpa-00248539

HAL Id: jpa-00248539

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Submitted on 4 Feb 2008

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Mechanical Properties of Freely Suspended Smectic Films

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(Received 22 November 1996, revised 13 June 1997, accepted 21 July 1997)

PACS.61.30.Eb – Experimental determinations of smectic, nematic, cholesteric, and other structures

PACS.68.60.Bs – Mechanical and acoustical properties

PACS.64.70.Md – Transitions in liquid crystals

Abstract. — A new experiment has been designed to investigate the effects of a mechanical perturbation applied parallel to the plane of the smectic layers of a free-standing film. Runs have been performed on films of different thicknesses in liquid, hexatic and crystal smectic phases present in the thermotropic liquid crystal compound (7o.7). We show that the thermodynamic phase of the meniscus is a crucial parameter because it determines the perturbation regime experienced by the film. In light of a theoretical framework developed in this paper, two perturbation regimes were found: a flow regime and a pure-elastic regime. Data recorded in the latter case enable us to extract the elastic constant of the smectic B and the smectic G crystal phases. We observe an unexpected discrepancy in the compressibility coefficient between the two crystal-like phases indicating that the molecular tilt angle provides the film with one additional macroscopic variable to respond to the mechanical modulation.

Résumé. — Les effets d'une perturbation mécanique appliquée parallèlement au plan des couches smectiques d'un film librement suspendu sont étudiés à partir d'un nouveau dispositif expérimental. Les expériences sont réalisées sur des films de différentes épaisseurs dans les phases smectiques dites liquides, hexatiques et cristallines. Nous montrons que la phase thermodynamique du ménisque est un paramètre crucial car il détermine le régime de perturbation que subit le film. En s'appuyant sur un modèle phénoménologique, nous distinguons deux régimes de perturbation : le régime d'écoulement et le régime élastique. Les mesures effectuées dans ce dernier cas nous permettent d'extraire la valeur de la constante élastique dans les phases cristallines smectique B et smectique G. La forte variation du coefficient de compressibilité observée entre ces deux phases indique que l'angle d'inclinaison des molécules apporte au film une variable macroscopique supplémentaire pour répondre à la perturbation mécanique imposée.

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1. Introduction

Freely Suspended Smectic Films (FSSF) have been of great interest to the scientific community for the last 20 years. They have proven to be a powerful instrument in investigating the evolution of physical properties as one passes from 3D to 2D because the thickness of such layered films can vary from thousands of layers down to 2 layers (50 Å) by increments of one layer, keeping an experimentally accessible planar area of several centimeter squares.

Many types of experiments have been performed on FSSF, including optical, mechanical and heat capacity measurements (for recent reviews see [1] and [2]). One of the characteristic facts concerning these films is that the smectic phase sequence they follow depends strongly on their thickness. This property can be expressed in three different ways: the transition temperature between two smectic phases can be shifted to higher (or lower) value as the thickness of the film is reduced; new smectic phases can appear between two “bulk-known” phases as the number of layers is decreased [3]; a first-order Smectic A (SmA) to Smectic C* (SmC*) phase transition becomes continuous below a critical thickness [4, 5].

Recently, there has been a growing interest in FSSF. Attention has been devoted to pattern formations [6–10], to heat capacity measurements in very thin films [11], to structures of antiferro- and ferroelectric phases [12], to correlations in thermal fluctuations [13], and to surface effects such as layer-by-layer phase transitions [14, 15] and critical adsorption [16].

Nevertheless, little has been done on the mechanical properties of these films. The only work that the authors are aware of are tension measurements [17–19], studies of a 2D shear-flow-induced behavior [20], along with early work on the shear constant and viscosity [21, 22]. To fill this perceived gap, we have developed a new experimental set-up that applies a mechanical constraint parallel to the plane of the film’s smectic layers. A periodic motion is generated by a piezo-electric element on one side of the film holder (the frame) so that the film will be alternately expanded and compressed in a direction parallel to the plane of the smectic layers. This allows us to investigate two new features of freely suspended films. First, we examine the elastic properties of a film under such a perturbation. We find an expected crystal behavior in the untilted smectic B phase as well as the unexpected role of the tilt angle θ of molecules in the smectic G phase during the perturbation. Second, we find support for the assumption made in reference [23] that a free standing film can not be seen as independent of the meniscus connecting the film to the frame. The meniscus acts as a reservoir of molecules for the film so that exchanges of molecules are possible when required. The “meniscus-film” entity has not been considered by previous authors. We show in this article the importance of the thermodynamic state of the meniscus in determining the mechanical properties of the film.

We begin the present paper with a description of the experimental set-up and general principles of our experiments. We then show some representative results obtained when applying a side modulation to the film for three different thicknesses. We develop a theoretical frame-work to understand the experimental results and finally we discuss the significance of these results.

2. Experimental Set-Up

In this section we describe the experimental method used to induce and to detect a mechanical perturbation applied in the plane of a freely suspended smectic film. First, we introduce the theoretical concept of the experiment, then we give a description of the set-up and finally we explain the measurement process.

2.1. CONCEPT. — To apply a mechanical perturbation to the film, we have designed a rectangular frame with one mobile side connected to a piezo-electric element. The periodic movement

imposed on the mobile side generates a contraction and dilation of the smectic film around its steady state.

We detect the effects of such a perturbation by studying the deviation of the resonant frequency of the vibrating film from its unperturbed value. In the case of a rectangular film submitted to an (n, m) vibrating mode, the resonant frequency $\Omega_{n,m}$ is given by the equation (see [17, 24]):

$$\begin{aligned}\Omega_{n,m}(t) &= \pi \sqrt{\frac{\tau}{\rho}} \left[\left(\frac{n}{x(t)} \right)^2 + \left(\frac{m}{y_0} \right)^2 \right]^{1/2} \\ x(t) &= x_0 + x_a e^{i\omega t}\end{aligned}\quad (1)$$

where τ stands for the total tension of the film, ρ is an effective 2D-density representing all materials involved in the motion, y_0 is the constant width of the frame and $x(t)$ is the length of the frame modulated at frequency ω and amplitude x_a by a piezo-electric element around the equilibrium position x_0 .

The modulation of the side affects $\Omega_{n,m}$ via $x(t)$, the tension τ and the 2D-density ρ leading to a periodic modulation $\Delta\Omega(t)$ of the resonant frequency. We measure the amplitude of $\Delta\Omega(t)$ and its phase-shift relative to the side modulation, $\Delta x(t) = x(t) - x_0$. We obtain information on the elastic behavior of smectic films parallel to the layers, as well as on the relaxation mechanism that allows molecules to flow between the meniscus and the film.

2.2. APPARATUS. — The experimental set-up consists of three main parts. The first is the frame on which the smectic film is freely suspended, together with the piezo-electric element that drives the mobile side to induce a mechanical perturbation. The second is the electrostatic excitation made up of four electrodes, which induces a transverse vibrating mode to the film. The third is the detection part that measures the perturbation's effects.

The first and central part of the experiment consists of a film holder (the frame) made of copper, installed in an oven to ensure temperature regulation better than ± 0.03 °C. One side of the frame is mobile and is connected *via* an axis to a piezo-electric element located outside the oven (Fig. 1). The constant width y_0 and the initial position x_0 of the mobile side fix the dimensions of the unperturbed film to $y_0 = 0.58$ cm and $x_0 = 0.61$ cm. The temperature measurements are obtained using two detectors located inside the oven. One is placed in the motionless metallic part of the frame and the second is suspended above the film by about 1 mm. The oven has a window on its top and bottom so that a laser or light beam can be sent to the film. It stands on top of an inverted microscope, enabling us to observe the film during a run and to measure the exact number of layers by a method described in reference [5]. The mobile side allows us also to change the number of layers one by one in the given film [5].

The second part of the experimental set-up induces and detects the (n, m) vibrating mode of the film by means of an electrostatic excitation from four electrodes coupled two by two and set a few μm from the membrane (Fig. 2a). We apply a direct voltage V_{DC} of 50 volts between the electrodes and the frame to bring charges on the film. An alternating voltage V_{AC} is then applied to the electrodes with the two pairs having opposite phases. By this method, we generate a $(2, 1)$ vibrating mode with eigenfrequency given by equation (1) and with amplitude proportional to $V_{\text{DC}} \times V_{\text{AC}}$, *i.e.*, of the order of 2 μm at resonance. A He-Ne laser beam is used to measure the resonant frequency $\Omega_{n,m}$ of the membrane. Deviations of the reflected beam are detected by a quadrant photo-diode and sent to a first lock-in detector that extracts the amplitude of the deviation and the phase-shift Φ between the reflected signal and the electrostatic signal sent to the electrodes. For better resolution, the resonant frequency is measured *via* the phase Φ at $-\pi/2$. Its value depends on the thickness of the smectic film as

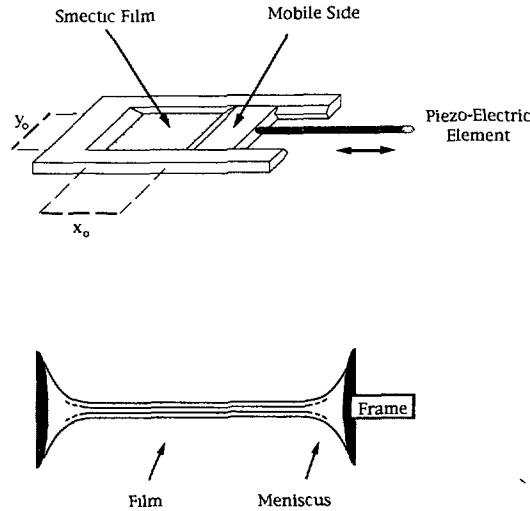


Fig. 1. — Schematic representation of the frame along with a section of a freely suspended smectic film.

well as on the temperature (see [25] for a more detailed discussion) and usually ranges from 600 Hz to 800 Hz for a film thickness of about 2000 to 5 layers, respectively. This range is small because of the contribution of the surrounding air during vibration. We call Ω_T the resonant frequency of the film at temperature T when no mechanical perturbation is applied.

We now apply to the film a mechanical perturbation by means of the mobile side of the frame connected to the piezo-electric element. The piezo is supplied by an AC voltage that generates a sinusoidal movement, $\Delta x(t) = x(t) - x_0$, at the mobile side with amplitude x_a from $1 \mu\text{m}$ to $20 \mu\text{m}$ at a frequency ω between 1 mHz to 20 Hz with no noticeable mechanical delay. As a consequence, the resonant frequency $\Omega_{n,m}$ of the film oscillates about Ω_T .

In the third part of the experimental set-up, we detect the modulation by means of the phase $\Phi(t)$, $\Delta\Omega(t) = \Omega_{n,m}(t) - \Omega_T$. During all the perturbation measurements, the voltage applied to the four electrodes is kept constant at the eigen-frequency value of the unperturbed film, *i.e.*, Ω_T . The phase Φ detected by the first lock-in is therefore periodically modulated about $-\pi/2$, so a second lock-in detector provides the amplitude A_Φ of this modulation as well as the phase-shift D_Φ between the phase $\Phi(t)$ and the side excitation $\Delta x(t)$, as shown in Figure 2b. A linear expansion of the phase Φ about the resonance allows us to relate the measured A_Φ and D_Φ to the modulation of $\Omega_{n,m}$.

We performed the experiments over a broad temperature range to investigate the different smectic phases and phase transitions. As the resonant frequency Ω_T is strongly dependent on the actual temperature of the film [25], we detect Ω_T at each temperature increment before performing the perturbation measurement.

3. Experimental Results

We examined a Schiff-base compound 4-n-heptyloxybenzylidene-4-n-heptylaniline (7o.7) [26] with bulk phase sequence presented in Figure 3. The SmB and SmG phases are crystalline smectic phases characterized by a hexagonal arrangement of the molecules, with long range positional and orientational order within the layers as well as correlations from one layer to the other. In the SmB phase the molecules' long axis is perpendicular to the plane of the layers,

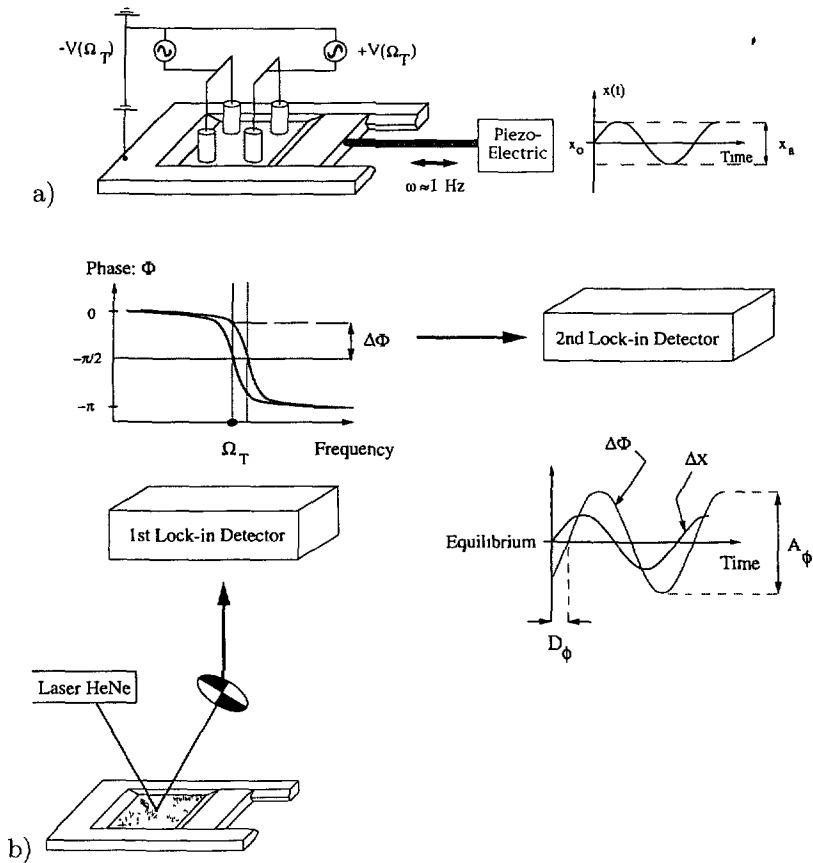


Fig. 2. — a) Excitation part of the experimental set-up: the film is brought into a ($n = 2$, $m = 1$) transverse vibrating mode with eigenfrequency Ω_T (~ 800 Hz) by means of the four electrodes. Meanwhile a sinusoidal motion $x(t)$ of amplitude x_a ($\sim 1 \mu\text{m}$) and frequency ω (~ 1 Hz) is imposed on the mobile side of the frame, generating a mechanical perturbation on the liquid crystal film. b) Detection part of the experimental set-up: a Ne-He laser beam is used to record at fixed eigenfrequency Ω_T the modulation $\Delta\Phi(t)$ of the phase-shift Φ between the beam reflected signal and the electrostatic signal sent to the four electrodes. This modulation is the consequence of the mechanical perturbation applied. A lock-in detector provides the amplitude A_Φ of this modulation and the phase-shift D_Φ between the phase Φ and the side excitation $\Delta x(t) = x(t) - x_0$.

whereas in the SmG phase the molecules are tilted to an angle θ from the normal of the free surfaces. Using X-ray measurements, Sirota *et al.* have shown that the 7o.7 phase sequence is strongly dependent on the film's thickness [27]. They found that two hexatic phases, SmI and SmF, appear between the crystalline SmB and SmG phases for sufficiently thin films. SmI and SmF are tilted hexatic phases with molecules arranged on a hexagonal pattern. They have short range in-plane positional order with no correlations from one layer to the other and long range bond-orientational order. Molecules are tilted towards their nearest-neighbors in the SmI phase and towards their second nearest-neighbors in the SmF phase. Sirota's results are summarized in Figure 4.

We performed a series of experiments on films of different thicknesses. Our results can be summarized by three curves that show the characteristic behavior of films subjected to a mechanical perturbation.

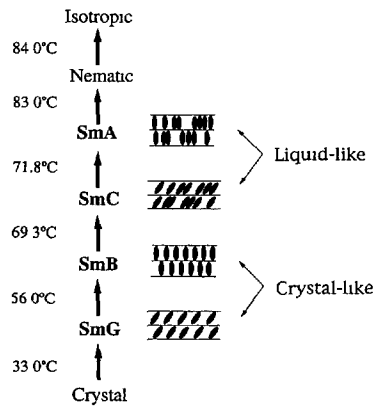
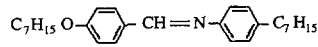


Fig. 3. — Chemical structure and bulk phase sequence of the compound (70.7) used in experiments.

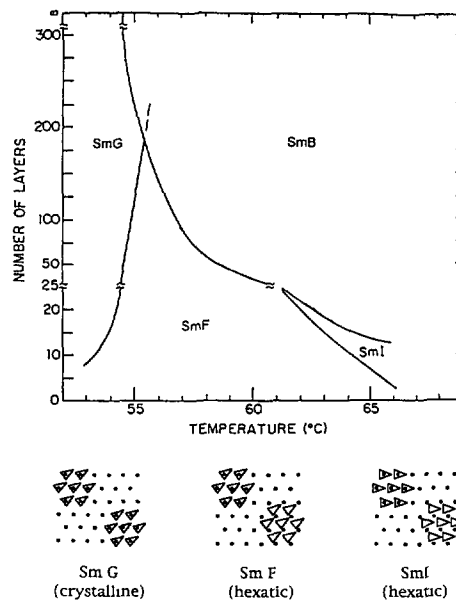


Fig. 4. — Thickness and temperature dependence of the phase sequence of (70.7) obtained by Sirota and co-workers using X-ray measurements [27]. The drawings beneath are a schematic representation of SmG, SmF and SmI phases. The dots indicate the 2D rectangular lattice describing the 6-fold in-layer packing of the rod-like molecules; the triangles represent the direction of molecular tilt within a layer.

The curve in Figure 5 is typical for a thick membrane with a large SmB crystalline phase. The run is performed on a 204 layer thick film starting at 79 °C cooling down to 44 °C and then heating back up again. The heating rate is of 0.15 °C/min with data points taken every 30 seconds. The piezo-element was driven by a sinusoidal voltage with a frequency of 4 Hz and an amplitude of 100 mV which corresponds to a displacement Δx_{max} of $\pm 1.05 \mu\text{m}$ about the

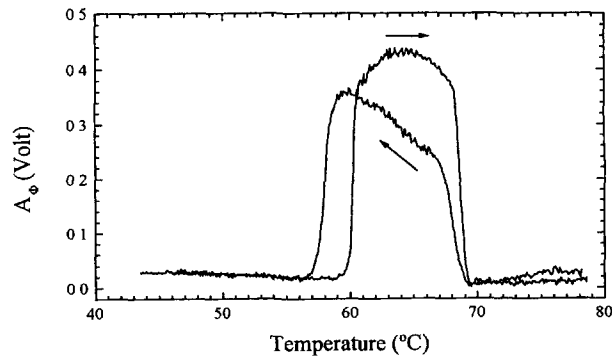
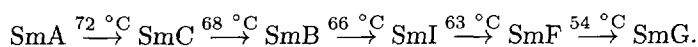


Fig. 5. — Experimental curve obtained on a 204-layer thick film with a “large” crystal SmB phase, over a thermal cycle. The perturbation applied is a modulation of frequency 4 Hz and of amplitude $\pm 1.05 \mu\text{m}$ of the frame’s length ($\sim 0.7 \mu\text{m}$).

equilibrium position x_0 . When cooling from 79 °C, the film first undergoes the SmA to SmC phase transition that is not visible on the experimental curve, but then one notices a jump in the amplitude A_Φ of the phase modulation $\Delta\Phi(t)$ when passing the SmC to SmB transition at 69.7 °C. The increase in A_Φ at the liquid SmC to crystal SmB phase transition is of a factor of 100. This can be understood as an observation intrinsic to a liquid-like to crystal-like transition and will be discussed later in this paper. At the untilted SmB to tilted SmG phase transition (60 °C on our graph), the film has an unexpected response to the external perturbation. Both phases are crystal-like and one would expect a similar order of magnitude for A_Φ . Instead the amplitude of the modulated phase has a significant drop in the SmG phase and returns to the same order of magnitude one obtains in the liquid phases. We believe that this is due to the tilt angle θ of the molecules, as we will discuss later. Identical behaviors are seen when heating the film back to 79 °C. The shift recorded between the cooling and the heating curves is due to some retardation in the first order transition, *i.e.*, is due to the finite value of the heating/cooling rate. The hysteresis in the SmB/SmG transition temperature of about 3 degrees is typical of the studied material.

We would like to emphasize the difficulty of such an experiment on thick films. The problems arise in the crystal SmB phase where the film is very sensitive to any variation of its length and tends to respond to the perturbation by creating holes, *i.e.*, domains of thinner thickness, in various layers. The holes are thermodynamically unstable in smectic films [23, 28], and they expand over the whole area of the film making it impossible to run an experiment at constant thickness. This is even more dramatic for films of very large thickness (> 500 layers), and often the film will simply break. It is therefore imperative to check constantly the homogeneity of the thickness through the inverted microscope when working in the SmB phase and to perform the experiment with small mechanical displacements $\Delta x(t)$ (typically less than $\pm 5.53 \mu\text{m}$ for $\omega = 4$ Hz).

Figure 6 shows a run performed on a 13 layer thick membrane having only a short temperature range of SmB phase. For such a thickness, the following phase sequence was expected on cooling [27]:



We start the cooling run with a mechanical excitation of $\pm 1.05 \mu\text{m}$ at a frequency of 4 Hz to ensure that the thickness of the film stays constant. When the SmB temperature range is passed, we increase the amplitude of the side’s motion to $\pm 3.16 \mu\text{m}$ to obtain a better signal/noise ratio. In the figure we have plotted the two runs on the same graph along with

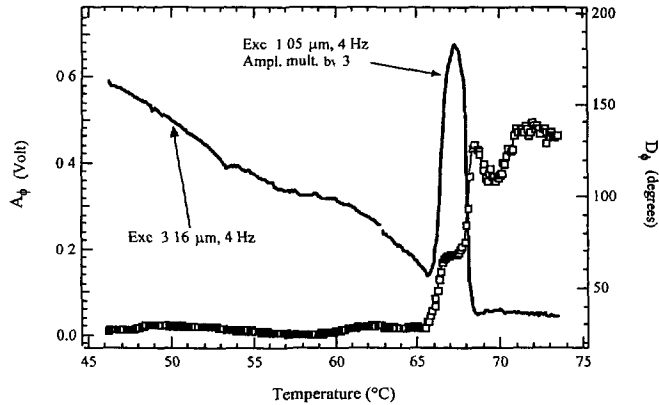


Fig. 6. — Two consecutive runs performed on a 13-layer thick film with a modulation of frequency 4 Hz. The first run is with a motion amplitude of $\pm 1.05 \mu\text{m}$ to go beyond the SmB phase; the second is with an amplitude of $\pm 3.15 \mu\text{m}$ to improve the signal/noise ratio for the SmI, SmF and SmG phases. The amplitudes recorded during the first run have been multiplied by a factor of 3 in the present Figure in order to be comparable to the ones recorded during the second run.

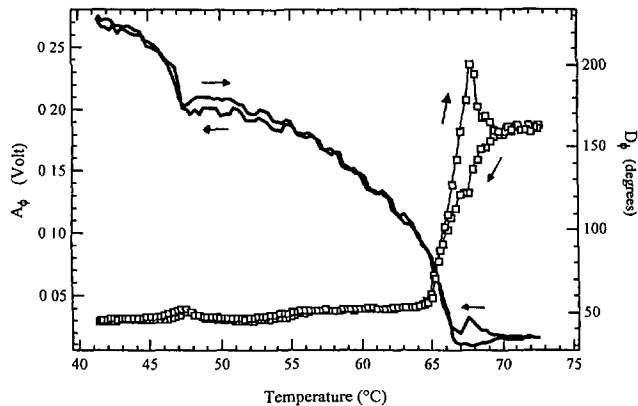


Fig. 7. — Run performed on a 9-layer thick film exhibiting no SmB phase and passing directly from the liquid SmC phase to the hexatic SmI phase. The perturbation applied is of frequency 2 Hz and of amplitude $\pm 5.53 \mu\text{m}$.

the phase-shift D_Φ of the phase $\Phi(t)$ relative to the side excitation $\Delta x(t)$. The amplitude data for A_Φ ($\pm 1.05 \mu\text{m}$) were multiplied by a factor of 3 to match the second set of data. One can observe the expected increase in A_Φ at the liquid/crystal transition temperature, 68.4°C , as well as a decrease at the SmB/SmI transition temperature. The transition SmI to SmF that should be observed at around 63°C is not detectable. But 10°C below this temperature, one can see the transition from the hexatic SmF phase to the crystalline SmG phase when checking A_Φ around 53°C . A factor of 10 between A_Φ in the liquid SmC phase and its value in the crystal SmG phase is now detectable in this run.

In Figure 7, we display a run on a 9 layer film with a side excitation of displacement $\pm 5.53 \mu\text{m}$ at frequency $\omega = 2$ Hz. The expected phase sequence should be [27]:



Our results agree only qualitatively with this sequence. We confirm the vanishing of the crystal SmB phase in thin films since the pronounced increase of the A_{Φ} values, characteristic for the SmB phase in the 204- and 13-layer films, is not observed in the 9-layer film. There are, however, some temperature discrepancies between our results and that of Sirota *et al.* [27]: the graph shows the SmC to SmI transition to be at 66.3 °C, a bit lower than expected. The SmI to SmF transition is still not seen except perhaps for a slight change around 55 °C in the slope of the continuously increasing quantity of A_{Φ} . On the other hand, the hexatic SmF to crystal SmG transition is clearly detectable in that run. A jump corresponding to a 35% increase in A_{Φ} as well as a “hiccup” in the phase-shift D_{Φ} occur at 47.3 °C on both the cooling run and the heating run with no significant hysteresis. We do not attribute the temperature discrepancy between our measurements and that of Sirota to a simple temperature shift. Indeed, the 110-degree jump in the D_{Φ} -signal due to the SmC/SmB transition in the meniscus takes place at the temperature indicated by X-ray measurements, *i.e.*, 69.5 °C. It may be that the widening of the SmI-SmF temperature range is due to the use of a chemical compound less pure than the one used by Sirota *et al.* during their measurements. The hysteresis recorded around 66 °C and 70 °C between the cooling and the heating curve is related to the fact that the data points are taken during the SmC/SmB phase transition, when both phases are coexisting in the film. Thus, the data can present a certain dispersion, particularly so since the recorded signal is weak at that time. At the same temperature interval, the D_{Φ} -curve exhibits a peak on the heating run. This feature is not well-understood.

In all cases the phase-shift D_{Φ} between the phase modulation $\Delta\Phi(t)$ and the side excitation signal $\Delta x(t)$ shows a jump of 110 degrees at the liquid-like to crystal-like (or hexatic) phase transition. The physics underlying this phenomenon can be explained by the following calculations.

4. Theoretical Development

We are interested in extracting an expression for the modulation $\Delta\Omega(t)$ of the resonant frequency $\Omega_{n,m}(t)$, introduced in equation (1), when a mechanical perturbation $\Delta x(t)$ is applied. To do so, we start with a simplified expression of $\Omega_{n,m}$, then discuss the contribution of the 2D-density ρ and of the tension τ and finally give the expanded form of $\Delta\Omega(t)$ along with the expression of the measured quantities A_{Φ} and D_{Φ} [29].

In the experiment presented above, the film holder has an approximate square shape at rest ($x_0 = 0.61$ cm, $y_0 = 0.58$ cm) and the amplitude of the side's motion is much smaller than the actual length of the film, so $\frac{x_a}{x_0} e^{i\omega t} \ll 1$. This leads to the following expression of the resonant frequency,

$$\Omega_{n,m}(t) = \pi \sqrt{\frac{\tau}{\rho}} \frac{1}{x(t)} \left[n^2 + m^2 \left(\frac{x_0}{y_0} \right)^2 \left(1 + \frac{x_a}{x_0} e^{i\omega t} \right)^2 \right]^{1/2} \approx \Pi \sqrt{\frac{\tau}{\rho}} \frac{1}{x(t)} \quad (2)$$

where the constant Π is defined as $\pi(n^2 + m^2)^{1/2}$, *i.e.*, $\Pi = \pi\sqrt{5}$.

In the expression above, we did not consider the temperature dependence of $\Omega_{n,m}$, even though we mentioned earlier that there is such a dependence in its non-perturbed value Ω_T . Ω_T , however, varies principally at the SmC/SmB transition where the freezing of the meniscus induces a “rippling effect” in the film, characterized by the additional contribution of the in-plane shear elasticity to the restoring force [25]. In the present paper, we concentrate more on the structural differences between phases occurring in 7o.7 as well as between the film and the meniscus. In order to discuss these differences, we therefore neglect the temperature dependence of $\Omega_{n,m}$ within the phases.

4.1. THE 2D-DENSITY ρ AND THE MODULATION OF THE FILM TENSION τ . — In order to expand $\Omega_{n,m}$, we first need to discuss the significance of the 2D-density ρ that appears in the denominator. ρ is the density of material involved in the vibration of the membrane, that is, the density ρ_{lc} of the liquid crystal making up the film *plus* the density ρ_{air} of the gas surrounding the film. The 2D-density ρ is then given by:

$$\rho = \rho_{lc} + \rho_{air} = \bar{\rho}_{lc}H + \bar{\rho}_{air}h \quad (3)$$

where $\bar{\rho}$ stands for a 3D material density, H is the thickness of the smectic film and h is the effective height of air involved in the vertical motion of the film. The parameter h depends on the mode (n, m) excited and was measured to be 0.27 cm for our experimental case [30]. By taking $\bar{\rho}_{air} = 10^{-3}$ g/cm³, $\bar{\rho}_{lc} = 1$ g/cm³ and the thickness of a smectic layer equal to 30 Å, ρ_{air} is of the order of 3×10^{-4} g/cm² while ρ_{lc} is of the order of 3×10^{-6} g/cm² to 3×10^{-4} g/cm² for films of 10 layers to 1000 layers, respectively. It is thus relevant to compute the contribution of ρ_{air} during data analysis.

Let us now consider the maximum variation $\Delta\rho_{lc}$ of the film density ρ_{lc} due to the modulation $\Delta A = y_0 x_a$ of the frame area. Taking our experimental conditions applied to a film of 100 layers, we calculate $\Delta\rho_{lc}$ to be 3×10^{-9} g/cm², which is negligible compared to the contribution ρ_{air} of 3×10^{-4} g/cm². The variation of the smectic film density is insignificant given the weight of the surrounding air and ρ can be considered as constant during the modulation of the film's area. Thus, only the variation of the tension and of the frame size are relevant in the $\Delta\Omega_{n,m}(t)$ expression.

There are two physical reasons for the modulation $\Delta\tau(t)$ of the tension. The first is the modulation of the film area itself: $y_0\Delta x(t) = y_0(x_a e^{i\omega t})$. The second is the variation of the number of the molecules in the film, $\Delta N(t) = N(t) - N_0$, which is a consequence of the first reason. It has been shown that a freely suspended smectic film is in thermodynamic equilibrium when both its tension and chemical potential are equal to that of the meniscus [23]. Any variation in τ generates a flux of molecules between the meniscus and the film to restore the equilibrium state. This can be expressed by the following equation:

$$\frac{\partial}{\partial t} \Delta N(t) = +c \Delta\tau(t) \quad (4)$$

where c is a constant of proportionality. The + sign emphasizes that a *positive* deviation of the tension will bring molecules *into* the film. This process takes place at the same frequency ω as the motion of the side, but there is a relaxation time for molecules to move from the meniscus to the film leading to a phase-shift in the $\Delta N(t)$ expression:

$$\Delta N(t) = N_a e^{i\omega t} e^{\omega t} = \tilde{N}_a e^{i\omega t} \quad (5)$$

Combining equations (4) and (5), we get a relationship between $\Delta\tau(t)$ and N_a . But to extract the modulation of the tension as a function of known parameters, a second relation is needed between $\Delta\tau(t)$ and the deviation $\Delta\rho(t)$ of the 2D-density of molecules in the film. This can be obtained through a linear response with slope $-\kappa^{-1}$, where κ^{-1} is the elasticity constant parallel to the smectic layers.

$$\begin{aligned} \Delta\tau(t) &= -\kappa^{-1} \Delta\rho(t) \\ &= -\kappa^{-1} \left(\frac{N(t)}{x(t)} - \frac{N_0}{x_0} \right) \frac{1}{y_0} m_{cl} = -\kappa^{-1} \rho_0 \left(\frac{N_a}{N_0} - \frac{x_a}{x_0} \right) e^{i\omega t}. \end{aligned} \quad (6)$$

We define m_{lc} to be the molecular mass of the liquid crystal compound. The minus sign in front of κ^{-1} expresses that the tension of a smectic film increases as the number of molecules

decreases at constant area. We can notice that an expansion of equation (6) around $N(t)$ and $x(t)$ combined with equation (4) gives a relation that defines the relaxation time of our system [31]:

$$\frac{\partial}{\partial t} \Delta N(t) = -\frac{1}{t_{\text{rel}}} \Delta N(t) + \frac{c\kappa^{-1}\rho_0}{x_0} \Delta x(t) \quad (7)$$

where $t_{\text{rel}} = \frac{N_0}{c\kappa^{-1}\rho_0}$, N_0 and ρ_0 being the unperturbed number of molecules and density. $(c\kappa^{-1}\rho_0)/N_0$ is defined as the inverse of a relaxation time because, if we apply a step-like modulation going from 0 to 1 at $t = 0$, the flux of molecules between the meniscus and the film will occur during the characteristic time t_{rel} .

The elimination of \tilde{N}_a between equations (4 and 6) gives the final expression for the deviation of the film tension under a periodic perturbation:

$$\Delta\tau(t) = \kappa^{-1}\rho_0 \frac{1}{1 - i\frac{1}{\omega t_{\text{rel}}}} \frac{x_a}{x_0} e^{i\omega t}. \quad (8)$$

4.2. EXPANSION OF THE RESONANT FREQUENCY $\Omega_{n,m}(t)$. — With the expression (2) of $\Omega_{n,m}$ introduced earlier, we can expand the resonant frequency of a free standing film about the tension τ and the displacement $x(t)$ to obtain the modulation $\Delta\Omega(t)$ such that:

$$\Delta\Omega(t) = \Omega_0 U \left(\frac{1}{1 - iW} - \frac{1}{U} \right) \frac{x_a}{x_0} e^{i\omega t} \quad (9)$$

where Ω_0 is the unperturbed resonant frequency, $U = \kappa^{-1}\rho_0/2\tau_0$, τ_0 is the tension of the unperturbed film and $W = (\omega t_{\text{rel}})^{-1}$. The constant U stands for the contribution of the tension modulation $\Delta\tau(t)$ to $\Delta\Omega(t)$. The contribution of the “pure-geometrical” area modulation $\Delta x(t)$ to $\Delta\Omega(t)$ can be seen in the limit of frequencies tending to zero when the film tension is constant. The minus sign in front of the ratio $1/U$ is in agreement with our experimental observations that the resonant frequency $\Omega_{n,m}$ drops as the film area increases.

During runs, we detect the fluctuations of the phase-shift Φ between the reflected beam and side motion signal. A linear expansion can be performed about the resonance such that $\Delta\Phi(t) = \mu\Delta\Omega(t)$ where μ is a measured negative value. When defining $\Delta\Phi(t)$ to be equal to $A_\Phi e^{iD_\Phi} e^{i\omega t}$, equation (9) leads to expressions for the experimentally measurable quantities A_Φ and D_Φ .

$$\begin{aligned} A_\Phi &= \left| \mu\Omega_0 U \frac{x_a}{x_0} \sqrt{\left(\frac{1}{1+W^2} - \frac{1}{U} \right)^2 + \left(\frac{W}{1+W^2} \right)^2} \right| \\ D_\Phi &= \text{arctg} \left(\frac{UW}{(U-1) - W^2} \right). \end{aligned} \quad (10)$$

4.3. LIMITING CASES. — At high frequency, $\omega \gg t_{\text{rel}}^{-1}$, the exchange of molecules between the meniscus and the film is no longer possible: the meniscus is “frozen”. Consequently, the tension modulation is very high as no molecular flow can counter the effect of the variation of the film area. Indeed, our experimental observations state that since the $\Delta x(t)$ -contribution represents not more than 1 to 2% of the actual signal $\Delta\Phi(t)$, the $\Delta\tau(t)$ -contribution dominates.

In terms of equation (9), this means that the ratio $1/U$ is negligible compared to $1/(1+W^2)$, so that:

$$\begin{aligned}\Delta\Phi(t) &= \mu\Omega_0 U \frac{x_a}{x_0} e^{i\omega t} \\ A_\Phi &= \left| \mu\Omega_0 U \frac{x_a}{x_0} \right|.\end{aligned}\quad (11)$$

This emphasizes the fact that $\Phi(t)$ is 180 degrees out of phase with the external excitation ($\mu < 0$). It is in agreement with the studied case for which no molecular exchanges are possible, *i.e.*, no physical process can generate a delay between the response of the smectic film and the perturbation. So at high frequency we investigate the pure elastic properties of the smectic film when modulating the size of the frame.

On the other hand, at low frequency, $\omega \ll t_{\text{rel}}^{-1}$, a flux of molecules occurs between the meniscus and the film. Therefore there is a phase-shift between the excitation and the response, and A_Φ and D_Φ can be rewritten:

$$\begin{aligned}A_\Phi &= \left| \mu\Omega_0 U \frac{x_a}{x_0} \sqrt{\left(\frac{1}{U}\right)^2 + (\omega t_{\text{rel}})^2} \right| \\ D_\Phi &= \text{arctg}(-U\omega t_{\text{rel}}).\end{aligned}\quad (12)$$

We can define a characteristic frequency $\omega_{\text{char}} = \frac{1}{U} \times (t_{\text{rel}})^{-1}$ under which $\Delta\Omega(t)$ is a real expression. The movement of the side is slow enough for the system to be at equilibrium at each moment, *i.e.*, for the number N of molecules in the film to be such that $a_e = A/N$ is a constant. The signal $\Delta\Phi(t)$ is then in phase with the side's excitation and the amplitude of modulation A_Φ tends towards $\left| \mu\Omega_0 \frac{x_a}{x_0} \right|$.

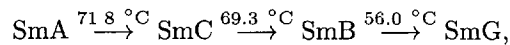
5. Discussion

The three most striking phenomena observed in our experimental data are as follows. First, the increase in the amplitude's modulation A_Φ by a factor of 100 at the liquid SmC to crystal SmB phase transition. Second, the 90-degree change of the phase-shift D_Φ between the phase modulation $\Delta\Phi(t)$ and the perturbation signal $\Delta x(t)$ at the liquid to crystal transition as well as at the liquid to hexatic phase transition. Third, the sudden drop of A_Φ at the untilted crystal SmB to tilted crystal SmG phase transition. To understand these features, we start by discussing the influence of the meniscus on our measurements. The existence of two perturbation regimes experienced by the film enables us to explain the large increase of A_Φ at the SmC/SmB transition as well as the thermic behavior of the phase-shift D_Φ . Then, we discuss the striking decrease of A_Φ at the SmB/SmG transition in light of a phenomenological model developed on a microscopic scale. Finally, we extract from our experimental curves an elastic constant associated with the compression/dilation of the layers in the crystal SmB and SmG phases.

5.1. IMPORTANCE OF THE MENISCUS IN THE OBSERVED PHENOMENA. — We mentioned in Section 4 that the meniscus plays a role during our experiment because it can exchange molecules with the film [32]. The exchange process is a coupling of diffusion in a layer and of permeation from one layer to the other. It is characterized by a relaxation time t_{rel} which is a function of the mesophase of the meniscus. The value of t_{rel} is relevant in our case because it

defines the perturbation regimes experienced by the film, when compared to the reciprocal of the mechanical excitation frequency ω^{-1} .

The meniscus has a macroscopic volume so that its phase sequence is always bulk-like:



regardless of the thickness of the film. We thus defined two regimes of perturbation depending on the ratio of t_{rel} to ω^{-1} . When the reservoir is in the liquid-like phase, SmA or SmC, t_{rel} is measured to be of the order of ω^{-1} : $t_{\text{rel}} = 0.2$ s, $\omega^{-1} = 0.25$ s. A flux of molecules takes place and we mainly observe a flow process as the size of the frame is varied. When the reservoir is in the crystal-like phase, SmB or SmG, t_{rel} is of the order of ten minutes, so that $t_{\text{rel}} \gg \omega^{-1}$. No molecular flux can take place — the meniscus is frozen — and we are able to explore the purely elastic behavior of a freely suspended smectic film, parallel to the plane of the layers. Thus the effect induced by the mechanical perturbation $\Delta x(t)$ is strongly dependent on the thermodynamic state of the meniscus.

The variation of -110 degrees recorded in the $D_\Phi(T)$ curve at $69.3\text{ }^\circ\text{C}$ (see Figs. 6 and 7) is due to the change of regimes. Indeed, when making an analogy between the perturbation regimes and the limiting cases of Section 4.3, we see that the meniscus-(SmC/SmB) transition gives rise to a jump ΔD_Φ in the phase-shift, given by:

$$\Delta D_\Phi = D_\Phi(\omega \rightarrow 0) - D_\Phi(\omega \rightarrow \infty) = -\text{arctg}(U\omega t_{\text{rel}}) \quad (13)$$

where t_{rel} is the relaxation time measured in the SmC phase. Taking experimental values obtained for U and t_{rel} [33] ($\omega = 4$ Hz), we calculate the jump to be equal to -87 degrees on cooling. The ΔD_Φ -jump occurs regardless of the phase transition that the film undergoes: it appears at the film-(SmC/SmB) transition (Fig. 6) as well as at the film-(SmC/SmI) transition (Fig. 7). This is in agreement with the fact that the thermodynamic state of the meniscus defines the perturbation regime experienced by the film. From Figure 7, we see that the phase transition in the meniscus takes place within a few degrees. This corresponds to a gradual transition of the reservoir into the SmB phase. It is a consequence of the thickness dependence of the transition temperature T_{CB} [27] correlated with the large thickness increase of the meniscus towards the frame.

At this stage, we may notice that the D_Φ -values are influenced mainly by the state of the meniscus, whereas the A_Φ -values reflect the state of the film.

The variation in the amplitude A_Φ at the SmC/SmB transition in Figure 5 also corresponds to a change in the perturbation regime. In the SmC phase the system can exchange molecules with the meniscus in order to prevent the modulation of the tension generated by the external perturbation, and the amplitude A_Φ stays small. But in the SmB phase the meniscus is frozen and the system can not counteract its length modulation with a variation of the number of molecules, so the tension is highly modulated and we get a large increase in A_Φ compared to the SmC phase case.

Another consequence of the frozen meniscus is seen optically when the film is heated up to the SmB/SmC transition. Small islands nucleating throughout the film and with a tendency to enlarge their radius can be observed at that point. For thin grey films (~ 8 layers), this is remarkable because the islands, often very thick, appear bright yellow. Hence our use of the term “constellation effect” to denote this phenomenon recalling the image of a clear night sky. At the SmB to SmC transition, molecules go from an untilted crystal phase to a tilted liquid phase, leading to an important increase in the 2D-density ρ in the film [34]. As the meniscus is still frozen, $T_{\text{BC}}(N) < T_{\text{BC}}(N \rightarrow \infty)$, the number of molecules stays constant in the film and there is an excess of molecules. The system responds to this frustrated state by exploring the

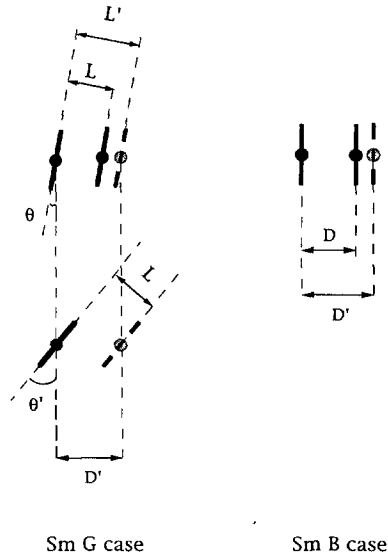


Fig. 8. — Diagram of two nearest-neighbor molecules in crystal smectic phases subjected to a horizontal expansion of their center of mass distance D — the effect of a positive increase of the frame's length in the crystal phases —. Defining the equilibrium state by the in-plane inter-molecular distance L , the increase of the center of mass distance from D up to D' brings the system into a non-equilibrium state ($L' > L$). In the case of the tilted SmG phase, molecules can keep their inter-molecular distance L constant during the perturbation by increasing their tilt angle θ as shown. In the case of the untilted SmB phase, the inter-molecular distance L varies along with D .

third dimension and creating new layers in order to reduce its 2D-density value. During runs, we avoid the constellation-effect by keeping the heating rate low enough and by minimizing the temperature gradient between the film and the frame [35].

5.2. SMB TO SMG TRANSITION. — The sudden drop in the amplitude A_Φ at the SmB/SmG transition (see Fig. 5) is the most unexpected phenomenon observed in our plots, given that the excitation $\Delta x(t)$ is constant over the entire run and that the meniscus is frozen to exchange in each phase [36]. Thus, it is the pure-elastic behavior of the film that we study in SmB and in SmG phases. We propose that the drop of a factor 100 in A_Φ arises because the coefficient of the 2D-compressibility is much higher in the SmG phase than in the SmB phase, even though both phases are crystal-like. We believe that the tilt angle θ , defined between the molecular long axes and the direction normal to the free surface, explains the recorded change in A_Φ . In the SmB phase, θ is on average zero, while in the SmG phase, θ varies with temperature from 22 to 24 degrees [27, 34].

Discussed on a microscopic level, the effect of the mechanical perturbation when the meniscus is frozen is to vary D , the nearest neighbor center of mass distance (Fig. 8). This brings the system into a non-equilibrium state and the molecular readjustment occurs either through a variation δL of the in-plane inter-molecular distance L , or through a variation $\delta\theta$ of the tilt angle θ , or through a combination of both. The energy cost δF of such an effect is:

$$\delta F = \frac{\alpha}{2}(\delta\tilde{L})^2 + \frac{\beta}{2}(\delta\theta)^2 \quad (14)$$

where α and β are phenomenological constants and $\delta\tilde{L}$ is the reduced length $\delta L/L$.

As $D = L/\cos\theta$ (see Fig. 8), we rewrite δF as:

$$\delta F = \frac{1}{2}A(\delta\tilde{D})^2 + \frac{1}{2}B(\delta\theta)^2 - C\delta\tilde{D}\delta\theta \quad (14')$$

where $A = \alpha$, $B = \alpha\tan^2\theta + \beta$, $C = \alpha\tan\theta$, and $\delta\tilde{D} = \delta D/D$. The negative coupling term contribution $-C\delta\tilde{D}\delta\theta$ indicates that the film can minimize the variation of its free energy by modulating θ together with the perturbation δD . However, this is possible only if the molecules are already tilted, as seen by the coefficient C which vanishes at $\theta = 0$. Considering that no torque is applied on a molecule during the perturbation, $\partial(\delta F)/\partial(\delta\theta) = 0$, the free energy is equal to:

$$\delta F = \frac{1}{2}E_{\text{eff}}(\delta\tilde{D})^2 \quad (15)$$

where E_{eff} is the effective elastic constant of the film, parallel to the plane of the smectic layers, such that:

$$\frac{1}{\alpha}E_{\text{eff}} = 1 - \frac{\tan^2\theta}{\frac{\beta}{\alpha} + \tan^2\theta}. \quad (16)$$

We see that the elasticity of a mesophase is strongly dependent on the initial tilt angle θ of the molecules, and that E_{eff} is lower when θ is larger. As the amplitude A_{Φ} is proportional to E_{eff} , we now understand that A_{Φ} is weaker in the tilted SmG phase where $\theta \approx 22$ degrees than in the SmB phase where $\theta \approx 0$. From the experimental data of Figure 6, we extract β/α to be equal to 1.6×10^{-3} . This leads us to the conclusion that the energy needed to increase the pre-existent tilt angle of molecules is 1000 times less than the energy needed to change the intermolecular distance L . In other words, it costs less energy to “slide” two tilted molecules parallel to each other — effect of $\delta\theta$ — than to separate two molecules — effect of δL —.

5.3. ELASTICITY COEFFICIENT IN CRYSTAL-LIKE PHASES. — Taking the data recorded when the meniscus is in a crystal-like phase, we can estimate the elasticity coefficient M parallel to the plane of the layers. In the context of the elastic constants nomenclature [37], M appears as a “mean” elastic coefficient because there is no specific crystallographic orientation of the hexagonal (SmB) or the rectangular (SmG) unit cell within a layer — *e.g.*, with respect to the film holder — on a macroscopic scale. We saw in Section 4.3 that when the meniscus is frozen to exchanges the modulation $\Delta\Omega_{n,m}(t)$ of the resonant frequency is a function of the $\Delta\tau$ -contribution only, so that:

$$\Delta\tau = 2\tau_0 \frac{\Delta\Omega_{n,m}}{\Omega_0} = 2\frac{\tau_0}{\Omega_0\mu} A_{\Phi}. \quad (17)$$

Thus, the recorded A_{Φ} -values for the SmB and SmG phases in Figure 6 are a measurement of the tension modulation $\Delta\tau$ induced by a mechanical perturbation Δx of amplitude $1.05 \mu\text{m}$. The values extracted, of 0.38 dynes/cm in the SmB phase and of 0.01 dynes/cm in the SmG phase, show that our experiment can detect very small deviations of the tension τ from its unperturbed value τ_0 .

As the tension modulation $\Delta\tau$ is proportional to the constraint σ imposed on the film by the modulation Δx of the frame’s length, the elasticity coefficient M is given by:

$$M = \frac{\sigma}{H} = \frac{x_0}{x_a} \frac{\Delta\tau}{H} \quad (18)$$

where H is the total thickness of the film. We obtain:

$$M(\text{SmB}) = 0.34 \times 10^8 \text{ dynes/cm}^2 \quad \text{and} \quad M(\text{SmG}) = 1.0 \times 10^6 \text{ dynes/cm}^2$$

for the elasticity in the SmB and SmG phases, respectively. These values are in agreement with the order of magnitude known for smectic phases ($\approx 10^8$ dynes/cm² [38–40]). The factor of 40 difference between the measurements of $M(\text{SmB})$ and of $M(\text{SmG})$, even though both phases are crystal-like, is a direct consequence of the existence of a molecular tilt angle in the SmG phase and not in the SmB phase as discussed in Section 5.2.

Finally, let us mention that when the number of molecules in the film is constant, *i.e.*, when the meniscus is frozen, we can obtain the constant κ^{-1} introduced earlier in equation (6): κ^{-1} is simply equal to the coefficient M divided by the 3D liquid crystal density $\tilde{\rho}_{\text{lc}}$ (≈ 1 g/cm³). It is interesting to notice that the value $\kappa^{-1}(\text{SmB})$ obtained for the crystal SmB phase is of the same order of magnitude as the value $\kappa^{-1}(\text{SmA})$ obtained for the liquid SmA phase [41] because in each phase the molecular tilt angle θ is on average zero.

We therefore strongly believe that the behavior difference of crystal-like phases when responding to the external excitation is associated with the value of the tilt angle of the mesogenic molecules, defined with respect to the direction normal to the smectic layers.

6. Conclusion

We have designed an experiment enabling us for the first time to investigate the behavior of a freely suspended smectic film when a mechanical constraint is applied parallel to the plane of the layers. The purpose of this experiment is to study the elastic response of the membrane when alternately compressed and expanded, as well as to see the role of the meniscus that attaches the film to the frame. Our results show three interesting features: an increase in the amplitude A_{Φ} of the recorded signal by a factor of 100 at the liquid SmC to crystal SmB transition; a 90-degree change in the phase-shift D_{Φ} at the liquid-like to crystal-like meniscus transition; a striking decrease in A_{Φ} by a factor of 100 at the SmB to SmG transition.

The first two features allow us to illustrate the importance of the meniscus, showing that its thermodynamic state determines which of the two perturbation regimes the film undergoes: the flow regime or the pure-elastic regime. The regime criterion considered is the ratio between the relaxation time t_{rel} , characterizing the molecular flow process between the meniscus and the film, and ω^{-1} , the reciprocal of the mechanical excitation frequency. When in a liquid-like phase, $t_{\text{rel}} \approx \omega^{-1}$, the meniscus can exchange molecules with the film in order to overcome the effect of the side modulation Δx ; this is the flow regime. When in a crystal-like phase, $t_{\text{rel}} \gg \omega^{-1}$, the meniscus is frozen to exchanges so that no molecular flux can counter the modulation of Δx ; this is the pure-elastic regime. These observations provide experimental evidence for the theoretical assumptions we have developed in a previous work [23], stating that the film and the meniscus should be treated together as a single thermodynamic system.

The third feature mentioned above gives an interesting outlook on the molecular process involved in responding to a mechanical perturbation. We have suggested that it arises because the compressibility coefficient is much higher in the tilted SmG phase than in the untilted SmB phase, even though both phases are crystal-like. The values extracted from our data show a factor of 40 difference between the elastic constant in the SmG phase and in the SmB phase. By developing a phenomenological model to explain this behavior on a microscopic level, we have concluded that the tilt angle of the molecules provides the film with one additional macroscopic dynamic variable that can be excited easily at low frequencies to respond to the external perturbation.

We have shown that our experiment gives interesting insights into the mechanics of freely suspended films and provides important results. Unfortunately, despite our efforts, we have not been able to detect the hexatic surface freezing referred to by Sirota *et al.* [42] in thin films of 7o.7. Also, for all film thicknesses investigated, we have not observed a significant

change of the parameters A_{Φ} or D_{Φ} at the hexatic SmI to hexatic SmF phase transition. The discrepancy between the two phases — a change in the tilt direction of the long axes of molecules, from pointing towards a nearest neighbor in the SmI phase to pointing towards the second nearest neighbor in the SmF phase — might well not be detectable by our experimental set-up. However, it may be interesting to run the same experiment under reduced pressure so that the air contribution will no longer dominate equation (3). By doing so, we might achieve a better signal to noise ratio and perhaps a greater chance of observing the SmI/SmF transition. One more interesting direction to pursue would be to employ our method on a liquid crystal compound exhibiting both the hexatic SmB phase and the hexatic SmF phase, in order to check our “tilt-angle” assumption. Also, a compound with hexatic SmB and crystal SmB phases could have interesting features to explore.

Acknowledgments

Ch. Bahr acknowledges financial support by the European Community (Human Capital and Mobility Program) and the Fond der Chemischen Industrie, and wishes to thank all members of Pawel Pieranski's group for their very kind hospitality. I. Kraus wishes to thank A.G. Percus for his careful reading of the manuscript.

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