# Destruction of a first-order smectic- $A \rightarrow$ smectic- $C^*$ phase transition by dimensional crossover in free-standing films

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Shifting and destruction of phase transitions due to the finite thickness of free-standing smectic films are examined. The behavior of smectic films is studied as a function of the temperature and the thickness in a material showing a first-order smectic-A (Sm-A) $\rightarrow$ smectic- $C^*$  (Sm- $C^*$ ) bulk phase transition. Measurements of the optical reflectivity and direct observations in an inverted polarizing microscope reveal that the first-order phase transition between Sm-A- and Sm- $C^*$ -like structures takes place in films that are thick enough  $(N > N_c = 90)$ . In thin films  $(N < N_c)$  this transition disappears. For  $N \approx N_c$ , a critical behavior is detected. A theoretical scheme for interpretation of phase transitions in smectic films is proposed and on its basis a conjecture on tension-induced phase transitions is formulated.

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#### I. INTRODUCTION

The most striking effects due to the finite size of thermodynamic systems are shifting or destruction of singularities associated with phase transitions [1]. The purpose of the present paper is to deal with such effects in free-standing smectic films.

In order to distinguish smectic films more precisely from other finite-size systems, one can use a simple classification scheme based on the following two criteria.

- (1) Dimensionality: Thermodynamic systems can be of finite size in one (I), two (II), or all three (III) dimensions of space.
- (2) Type of confinement: One must distinguish between systems that possess a finite size by virtue of an external confinement (a) due to some walls or (b) due to a self-confinement.

In terms of this classification, clusters containing a finite and fixed number of atoms belong to the category IIIb, while the droplets in the so-called polymer-dispersed liquid-crystal composite materials [2] belong to the category IIIa. Free-standing strands of discotic liquid crystals [3] and fluids confined in cylindrical pores [4] are representative of classes IIa and IIb, respectively.

The smectic films discussed in the present paper are examples of systems confined in one of the three dimensions and because of this unidimensional character of the confinement their thermodynamic properties should resemble those of other slablike systems. In the past, most attention has probably been devoted to the so-called problem of capillary condensation concerning the liquid-gas transition in narrow pores [4]. In the field of liquid crystals the isotropic-nematic phase transition has also attracted much attention [5]. Let us note, however, an essential difference between smectic films and these two

examples. Smectic films are self-confined while in the above examples the confinement was due to the action of parallel walls.

The property of self-confinement of smectic films results from their layered structure; smectic films are stacks of N well-defined molecular layers, each layer being identified by its index i = 1, ..., N in the stack. Due to this property, smectic films offer an opportunity to control easily and with accuracy the pertinent size parameter. Indeed, the number N of molecular layers composing films can be reduced so much that their structures and properties are visibly different from those of the bulk sample. For example, x-ray studies in films of 4-(n-heptyloxy)-benzylidene-4-(n-heptyl)aniline(7O.7) have shown that different structures occur in the temperature range of the bulk smectic-B (Sm-B) phase when the thickness N is small enough [6]. More recently, ellipsometric measurements of Bahr and Fliegner [7] on thin films of 4-(3-methyl-2-chloropentanoyloxy)-4'-heptyloxybiphenyl (C7) have revealed that the average tilt discontinuity, characteristic of the smectic-A (Sm-A) $\rightarrow$ smectic-C(Sm-C) first-order phase transition, disappears for Nsmaller than 15 layers.

In the present paper we also study the  $Sm-A \rightarrow Sm-C$  transition in liquid-crystal (LC) films, but our experimental and theoretical methods differ in several aspects from those in Ref. [7]. First of all, our interest in phase transitions in smectic films has its origin in the previous work on transitions involving changes in the number N of layers [8]. Therefore our experimental procedure for producing, detecting, and quantifying phase transitions is an adaptation of the former one. It is described briefly in Sec. II where we show how well it gives us total control on the thickness of smectic films and how it is used to detect the phase transitions. The experimental results we

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have obtained with this method concern the Sm- $A \rightarrow \text{Sm-}C^*$  phase transition in a different material: ALLO-902C13M5T (see Sec. II C). Finally, the theoretical phenomenological scheme we use here for interpreting the Sm- $A \rightarrow \text{Sm-}C^*$  phase transition is a necessary generalization of the procedure used in Ref. [8].

### II. EXPERIMENT

In order to study phase transitions in free-standing films, we have developed an optical method that consists of measuring the spectrum  $I(\lambda)$  of the light reflected by the films. Our procedure presents three considerable advantages. First, the exact number of layers at any location in the film can be obtained from such spectra with no restriction on the total thickness of the film as in the case of methods using reflection of a laser beam or the ellipsometry. Second, due to the use of an inverted microscope in our optical setup, one can observe directly the film during the run of the experiment and especially during a phase transition. Finally, using a mobile frame, layers of the films can be removed or added by a defined and well-controlled number down to two layers.

#### A. Setup

The general scheme of the experimental setup is presented in Fig. 1. In our experiment, we create a free-standing film on a rectangular frame. One side of the frame is mobile and a micrometer screw allows us to have precise control of its motion. This apparatus permits a variable surface area of the free-standing film. The frame is held by an open metallic support over an inverted polarizing microscope. A monochromatic beam is generated from a halogen source followed by a grating monochromator. The monochromator is driven by a stepping motor and controlled by a microprocessor system which

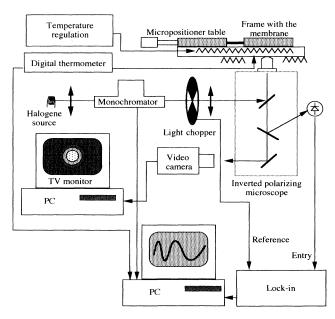


FIG. 1. Diagram of the experimental setup.

delivers a continuous voltage proportional to the actual wavelength of the beam. This voltage is sent to a computer via a numerical voltmeter.

In between the monochromator and the microscope, a lens forms the image of the monochromator's slit on the sample. The dimensions of this image depend on the magnification of the microscope objective and can be as small as  $100 \times 10 \ \mu\text{m}^2$  for the objective  $\times 20$ . This is essential for measurements in the temperature range where the smectic-A-like and smectic-C-like phases coexist in the film. Such a small slot image can be located precisely in adjacent domains so that characteristic spectra of the two coexisting phases can be taken separately. Thus any possible optical discontinuity can be resolved. The positioning of the slit image on domains is done in the configuration where the image of the film is sent via the microscope to a video camera for direct observation of the film. The same image can then be sent on a silicon photodiode connected to a lock-in (via a current preamplifier) for intensity measurements.

A light chopper is set just after the monochromator. It modulates the beam at a frequency of 300 Hz. By using the lock-in detector, one can extract the useful spectrum without taking care of perturbative light sources like daylight, for example.

The temperature of the film can be changed and controlled with a set of resistances placed under the metallic support of the liquid crystal's frame. A digital thermometer connected to the computer measures the temperature by the means of a  $100-\Omega$  platinum probe. All data acquisition and parameter fitting are then controlled by the computer.

## B. Control and measurements of the thickness N

A free-standing film obtained on the rectangular frame is characterized by its number of layers, but also by the meniscus which assures contact between the frame and the smectic film.

When a film is formed it is generally not homogeneous and we can see a series of steps which define domains of various thicknesses. In Ref. [8] we have discussed conditions for equilibrium of such a system of steps. In general these steps are not in equilibrium because their curvature is not adapted to the difference in the tension  $\tau$  in adjacent domains. This lack of balance generates a motion of steps which makes certain domains grow, decrease, or even vanish. The step's motion is possible because of the existence of the meniscus which acts like a "reservoir" of molecules, i.e., like a donor or an acceptor of molecules. After a time of relaxation, the domain's walls collapse or move outward to the meniscus, into an equilibrium stage such that all parts of the film are homogeneous in thickness.

By taking advantage of such a process, we can remove one layer when a short but strong increase in tension is applied on the membrane by pulling on the mobile side of the frame. A "hole" is thereby generated in the film and it presents few concentric steps next to its boundary. We can then control the number of layers in this hole by opening the frame more or less, so that the desired variation of layers between the film and the hole is obtained. If the radius of this hole is larger than the critical one  $R_C$  [8], it will extend to the frame reaching an equilibrium stage after a time of relaxation. We also can generate an additional layer by closing the frame until the radius of the first step in the meniscus becomes smaller than  $R_C$ . After the collapse of this step the frame is slowly opened. In brief, we see that the number of layers in a free-standing film can be well controlled with a frame of variable surface area.

The experimental method presented in this paper can also give the exact number of layers in any domain of the free-standing film. The image of the monochromator's slit is focused on a selected place of the film. We measure the intensity spectrum  $I(\lambda)$  of the reflected beam as a function of the wavelength of the incident monochromatic beam. The layers are removed (or added) one by one until we reach the minimum number of layers characteristic of a smectic free-standing film; i.e., two layers. For each intermediate thickness, the above measurement is repeated on the same spot of the film. The experimental curves  $I(\lambda)$  shown in Fig. 2 are then fitted using the equation (see Ref. [9])

$$I(\lambda) = \frac{f \sin^2 \left[ \frac{2\pi D}{\lambda} \right]}{1 + f \sin^2 \left[ \frac{2\pi D}{\lambda} \right]} , \qquad (1)$$

$$f = \frac{(n^2 - 1)^2}{4n^2} , (2)$$

with D = Nnd, where N is the total number of layers in the selected spot, n is the refractive index, and d is the average thickness of one layer.

The obtained values of D are plotted versus the corresponding number of layers  $N_{\rm arb}$  (the first number is taken arbitrarily but the next ones have to follow chromatically). The values plotted in Fig. 3 come from several series of measurements, each series being obtained on a different film. The plot is a straight line whose slope represents the value of nd at a given temperature  $T_m$ . In

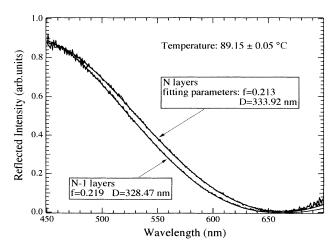


FIG. 2. An example of curves fitting on reflective spectra of a film of thickness N and N-1 layers. Here N=61.

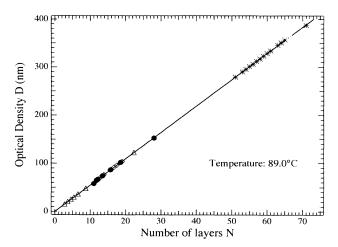


FIG. 3. Plot of the optical density D as a function of the number of layers for four different series of measurements. The slope of the straight line gives the value of the optical density per layer nd for the ALLO-902C13M5T material.  $nd = 5.47 \pm 0.01$  nm.

the case of Fig. 3,  $T_m$  was taken to be 89 °C and the obtained value of the average optical thickness per layer is

$$nd = 5.47 \text{ nm} \pm 0.01 \text{ nm}$$
.

The uncertainty of the above measurement is estimated from the scatter of values *nd*, determined individually for each different series.

The exact number of layers for any experiment is then obtained by shifting  $N_{\rm arb}$  such that the straight line passes through the origin. Any thickness N can then be calculated with accuracy from a simple measurement of the spectrum  $I(\lambda)$  at the temperature  $T_m$  through the above plot.

## C. Substance

We have investigated phase transitions in free-standing films of a new material ALLO-902C13M5T. The chemical formula of ALLO-902C13M5T is shown in Fig. 4(a). Its liquid-crystalline phase sequence as established by cooling is indicated in Fig. 4(b). The free-standing films made from this material are stable over several weeks.

## III. RESULTS

## A. Measurements of the optical thickness as a function of the temperature

For each film, we start our measurements by determining its number of layers N. This is done using the intensity spectrum recorded at 89 °C (range of the bulk smectic-A phase). From such a spectrum we determine the optical thickness D and the coefficient f using the fit to Eq. (1), as explained in Sec. II B. Knowing D and nd, we calculate N.

The temperature of the membrane is then lowered by decrements  $\Delta T$  that are made smaller in the vicinity of the phase transition. For each temperature, we record

$$C_{9}H_{19}O - \bigcirc C = CCO_{2} - \bigcirc CO_{2}CH_{2}C*H(CI)C*H(CH_{3})CH_{2}CH_{3}$$

$$(Q)$$

$$I. \xrightarrow{126.0^{\circ}C} BPI, II, III \xrightarrow{123.8^{\circ}C} CHOL. \xrightarrow{102.4^{\circ}C} SmA* \xrightarrow{99.2^{\circ}C} SmA \xrightarrow{82.1^{\circ}C} SmC* \xrightarrow{72.0^{\circ}C} CRYST.$$

$$(b)$$

FIG. 4. (a) Chemical formula of ALLO-902C13M5T; (b) sequence of liquid-crystal bulk phases of ALLO-902C13M5T. I denotes isotropic; BP, blue phase; CHOL, cholesteric; CRYST, crystalline.

the spectrum  $I(\lambda)$  and determine the coefficients D and f. For a film of a given thickness, we notice a temperature dependence of the coefficient of reflectivity f and of the optical thickness D when passing through the phase transition Sm- $A \rightarrow$  Sm- $C^*$ . Typical variations are plotted in Fig. 5 for a film of 126 layers. Similar variations D(T)appear also for all the thicknesses we have investigated. When using the theoretical expression (2) and the data from Fig. 5, we see that the variation of f over a range of temperatures from 95 to 75 °C is related to the change of the refractive index n from 1.53 to 1.59, representing a relative increase of +4%. Meanwhile, the variation of D = Nnd in the same range of temperature consists of a decrease from 390 to 340 nm, giving a relative change of -13%. Thus we conclude that the decrease of the optical thickness D takes place in spite of the increase in n, and so it must be an intrinsic phenomenon due to a change in the film's structure.

In Fig. 6, we present the temperature dependence (when cooling) of the optical thickness for different thicknesses of the ALLO-902C13M5T film. We use here the "reduced" optical thickness nd = D/N in order to compare results for films of different thicknesses. The curves present a common behavior when the temperature varies. The optical density is almost constant in the Sm-A temperature range; i.e., from 100 °C to approximately 84 °C. When passing through the bulk Sm- $A \rightarrow$ Sm-C\*

FIG. 5. Temperature dependence of the coefficient f(+) and of the optical thickness  $D(\bullet)$  in a 71-layer-thick membrane.

transition temperature  $T_{AC}^*$ , we see an important decrease in nd over a range of 10 °C until the system reaches the optical thickness of the Sm- $C^*$  phase. The decrease represents approximately 15% of the optical thickness value in the Sm-A phase.

In Figs. 7(a) and 7(b) one can observe different behavior depending on the film thickness in the vicinity of the temperature  $T_{AC}*$ . Figure 7(a) represents the plot D(T) for a film of thickness N=212 layers. A jump in the optical thickness D at  $T=82.5\,^{\circ}\mathrm{C}$  can clearly be seen. We have also found this discontinuous behavior in films with a number of layers N=126 and N=480. The discontinuity is a signature of a first-order phase transition taking place in relatively thick films. This phase transition in smectic films can be seen as inherited from the behavior of the bulk ALLO-902C13M5T material which is known to display a first-order Sm- $A\to$ Sm- $C^*$  transition [10]. Indeed, in the limit  $N\to\infty$ , smectic films should exhibit bulk behavior.

The height of the jump in the optical thickness  $\Delta D$  decreases with decreasing number of layers. We see in Fig. 7(b) that for an 80-layer-thick film there is no discontinuity at all in the plot of D vs T. The same observation is made for the 71-layer-thick film.

We conclude that there exists a critical thickness  $N_c$  such that for  $N < N_c$ , the discontinuity inherited from the bulk Sm- $A \rightarrow$ Sm- $C^*$  transition is lost.

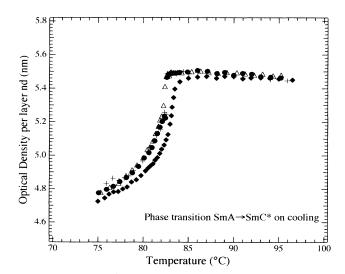
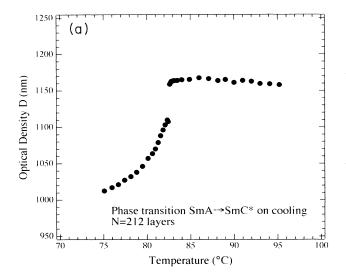


FIG. 6. Temperature dependence of the optical density per layer nd for the films consisting of 80 layers ( $\spadesuit$ ), 126 layers ( $\triangle$ ), 212 layers ( $\spadesuit$ ), and 480 layers (+).



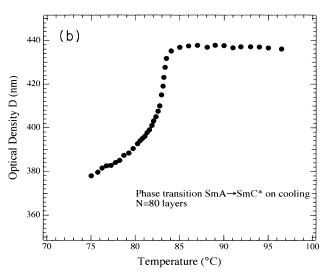


FIG. 7. Temperature dependence of the optical thickness D. (a) The 126-layer-thick film exhibits a discontinuity in D at the transition Sm- $A \rightarrow$  Sm- $C^*$  temperature  $T_{AC}^*$ . It is a proof that a first-order phase transition takes place. (b) The 80-layer-thick film. The variation of D is continuous through  $T_{AC}^*$ .

## B. Direct observation of the first-order phase transition

The existence of the first-order phase transition in ALLO films was confirmed by direct observations with an inverted polarizing microscope.

Observations in monochromatic illumination were done in thick films (more than 126 layers) at the temperature  $T_{AC}*(N)$  corresponding to the jump  $\Delta D$  in the optical thickness. They reveal the existence of well-defined circular domains in the plane of the film, with the optical thickness  $D_{C}*$  smaller than the one,  $D_{A}$ , of the surrounding matrix (Fig. 8). These domains exist in a narrow temperature range ( $\approx$ 1°C) around  $T_{AC}*(N)$  and their size depends on the temperature. These observations indicate clearly that there is a first-order structural transition in such thick films and that due to the presence of some im-

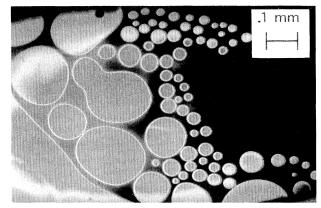


FIG. 8. Phase coexistence of  $Sm-C^*$ -like domains in a Sm-A-like matrix. Domains have a tendency to be circular. The "pear"-shape domain is created by coalescence of two adjacent domains. Once relaxed, it will take a circular shape (view in monochromatic illumination).

purities, the Sm-A-like and Sm-C\*-like domains coexist in a narrow temperature range.

We shall refer to this situation as the "horizontal" phase coexistence between the Sm-A-like and Sm-C\*-like phases in the film. This film is then considered to be a two-dimensional thermodynamic system in the xy plane parallel to the surfaces (see Sec. IV). We introduce this definition in contradistinction to another phenomenon named the "vertical" phase coexistence, which involves a stratification in the film along the z axis. It arises at higher temperatures in the whole range of the Sm-A-like phase (in the sense defined as "horizontal"). Indeed, two faint and independent schlieren textures (Fig. 9) are visible in the polarizing microscope at high temperatures. This means that for a thickness  $N > N_c$ , smectic films have a tripletlike structure made of a Sm-A core "sandwiched" between two uncoupled Sm-C\* films of thickness  $H_{C*} \ll H/2$  (Fig. 10). The thickness  $H_{C*}$  increases on cooling so that the schlieren textures become more contrasted and coupled as the phase-transition temperature  $T_{AC}^{\phantom{AC}*}$  is approached. This increase of the thickness  $H_{C*}$  with decreasing temperature becomes very rap-

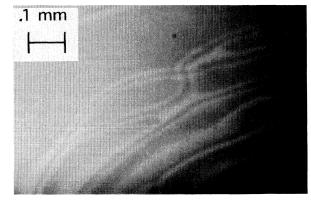
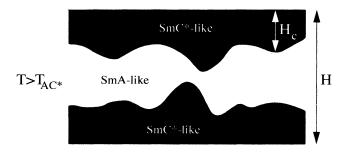


FIG. 9. Crossing of two independent schlieren textures in an ALLO-9O2C13M5T film of thickness  $N > N_c$  far from the Sm- $A \rightarrow \text{Sm-}C^*$  transition temperature.



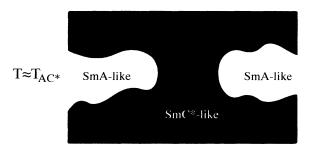


FIG. 10. Representation of a "vertical" phase coexistence. In the upper panel we have a Sm-A core "sandwiched" between two uncoupled Sm- $C^*$  strata. In the lower panel the two Sm- $C^*$  strata touch each other and form a well-defined Sm- $C^*$  domain through the entire thickness of the film.

id in the vicinity of  $T_{AC}^*$  and results in the decrease of the optical thickness D. It is clearly visible in the vicinity of the jump in the plot of Fig. 7(a).

The stratification of the Sm-A-like phase is crucial for nucleation of domains of the Sm- $C^*$ -like phase. Indeed, we observed that the thickness  $H_{C^*}$  is not uniform in the films so that the Sm- $C^*$ -like domains nucleate in well-defined areas where we believe that the Sm- $C^*$  boundary layers touch each other. These variations in the thickness must be related to the schlieren textures because the nucleation takes place preferentially along  $\pi$  walls.

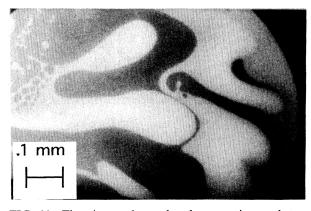


FIG. 11. The picture shows the phase coexistence between domains of Sm-A- and Sm-C\*-like structures. The thickness of the film is close to the critical thickness  $N_c$ . One can compare the "wavy" shape of the domains with the circular one of the thick film presented in Fig. 8.

# C. Behavior of the interphase in the vicinity of the critical point

When the critical point is reached  $(N \approx N_c)$ , the Sm- $C^*$ -like domains cease to present their circular shape. Indeed, their shape becomes irregular and dependent on the schlieren textures as shown in Fig. 11. Also, the optical contrast between the Sm- $C^*$ - and Sm-A-like domains becomes very poor.

Besides the heterogeneous nucleation we observed a spinodal decompositionlike transformation when the system is rapidly quenched below the transition line in the vicinity of the critical point. The study of the spinodal decomposition is postponed to another paper.

## IV. DISCUSSION AND CONCLUSIONS

#### A. Thermodynamics of smectic films

It results from the above observations that the structure of molecular layers composing smectic films is drastically perturbed by the vicinity of surfaces. Indeed, it is a function of the layer's position *i* in the stack when considering a film of fixed thickness *N*. For this reason the notion of a homogeneous thermodynamic phase such as defined in three-dimensional materials loses its significance and must be reformulated.

Inspired by the theoretical scheme developed previously [8], we find it useful and pertinent to introduce the following reformulation.

- (1) We treat as a thermodynamic phase any given molecular structure that is homogeneous in the xy plane of a film.
- (2) From the microscopic point of view, each phase is characterized by a set of some parameters  $\{p_i\}$  describing the structure inside each layer i in the stack  $(i=1,\ldots,N)$ . These parameters concern the positional and orientational order of molecules in layers.
- (3) From the phenomenological point of view, we treat smectic films as two-dimensional systems by averaging over the i dependence of thermodynamic potentials such as the free energy per molecule  $f_N$  (or the chemical potential) and by using two-dimensional quantities such as the area per molecule a. This area is defined as the ratio of the projected area A of a given domain of thickness N to the number  $\mathcal N$  of molecules in this domain [11].
- (4) The behavior of the film is then characterized by some equation of state such as

$$f_N = f_N(T, a) , (3)$$

where the average free energy per molecule  $f_N$  is a function of the temperature T and of the average area per molecule a.

The distinction introduced in Sec. III B between the "horizontal" and "vertical" types of phase coexistence now becomes clear. According to the above scheme, the former is a true phase transition in the film treated as a thermodynamic system in two dimensions. On the other hand, the "vertical" phase coexistence loses its meaning in the above scheme because of the averaging over i.

The "horizontal" transition takes place between the

Sm-A- and Sm-C\*-like structures. These structures, considered as phases, are characterized by the sets  $\{\theta_i\}$  of average tilt angles  $\theta_i$  in each layer i composing the films. For temperatures higher than the bulk Sm- $A \rightarrow$  Sm-C transition temperature  $T_{AC}$ , we will have  $\theta_1 = \theta_N = \theta_{\text{surf}}$  [12] and  $\theta_i \approx 0$  for the others. It is clear that on average the axial symmetry of the bulk Sm-A phase is broken in such a structure so that a second-order transition is not possible in the films. For T lower than  $T_{AC}$  the structure inherited from the bulk Sm-C phase is characterized by some distribution  $\{\theta_i\}_C \approx \theta_{\text{bulk}}$ .

### B. Conditions for the phase coexistence in smectic films

In a previous paper [8] we have examined questions on the equilibrium between adjacent domains of different thicknesses coexisting in smectic films, and on the equilibrium between a film of constant thickness and the meniscus which assures contact between the film and its frame. In this last case we have emphasized the fact that the meniscus acts as a reservoir of molecules. Because of its large volume, it fixes the chemical potential  $\mu_m$  in the system so that  $\mu$  must be the same at any position (x,y,z) of the film. Thus the chemical potential  $\mu_N$  of each domain must be equal to the chemical potential of the meniscus  $\mu_m$ .

By definition, the chemical potential is given by the Legendre transformation of  $f_N$  with respect to a:

$$\mu_N = f_N - \tau a , \qquad (4)$$

where

$$\tau = \frac{\partial f_N}{\partial a} \tag{5}$$

represents the tension of the film. The requirement of equality of chemical potentials

$$\mu_N = \mu_m \tag{6}$$

at equilibrium fixes the tension  $\tau_N$  of the film and the area per molecule  $a_N$  [13].

We shall use here the same procedure and examine a more general case where, for a given N, the function  $f_N(a,T)$  has more than one minimum. In the case of the Sm- $A \to \text{Sm-}C^*$  transition, if one supposes that there are no thermodynamically competing structures other than  $\{\theta_i\}_A$  and  $\{\theta_i\}_C$ , then the function  $f_N(a,T)$  is expected to have two minima for T close to  $T_{AC}$ .

For a given chemical potential of the meniscus  $\mu_m$  the equilibrium between the two structures is found by the construction of a common tangent (see Fig. 12). As the depths of the two minima vary with T, this condition is satisfied only for some particular temperature  $T_{AC}$  and for a given value of the tangent's slope, viz., the tension  $\tau_{AC}$ .  $T_{AC}$  and  $\tau_{AC}$  define the conditions needed so that the phase transition from structure A to structure C takes place. By analogy with considerations presented in the previous reference [8], the function  $f_N(a,T)$  is different for each N so that the temperature  $T_{AC}$  and the tension  $\tau_{AC}$  are functions of N:

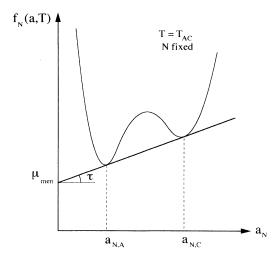


FIG. 12. Common tangent construction corresponding to a first-order phase transition in a film of thickness N.

$$T_{AC} = T(1/N)$$
,  $\tau_{AC} = \tau(1/N)$ . (7)

These two functions define parametrically a line  $\zeta$  in the three-dimensional space  $(\tau, T, 1/N)$ .  $\zeta$  is represented in Fig. 13.

For another choice of the chemical potential  $\mu_m$ , one gets another line in this space. By changing  $\mu_m$  continuously, one gets a surface  $\Sigma_{AC}$  in the space  $(\tau, T, 1/N)$  (Fig. 13). This surface represents the first-order phase transition between structures A and C in the three-dimensional phase diagram.

Experiments show that for  $N < N_c$  the first-order Sm-A-Sm- $C^*$  transition is destroyed. In terms of our theoretical scheme it means that for  $N < N_c$  the function  $f_N$  exhibits only one minimum instead of two. In this case, the surface  $\Sigma_{AC}$  must be limited by a line of critical points:  $L_{\rm crit}$ .

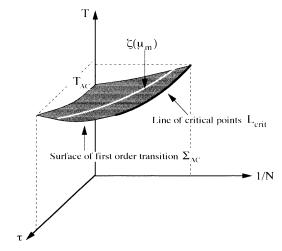


FIG. 13. Possible phase diagram showing the surface  $\Sigma_{AC}$  of a first-order phase transition terminated by the line  $L_{\rm crit}$  of critical points.

## C. Conjecture on tension-induced phase transitions in smectic films

When the surface  $\Sigma_{AC}$  is oblique with respect to all three coordinate axes, then the transition from structure A to structure C can be induced by a change in any of the three variables  $(\tau, T, 1/N)$  of the phase diagram as shown in Fig. 13. In the present paper we have explored the phase diagram in two of its dimensions. However, the possibility of varying the tension should not be excluded because it has already been shown experimentally that  $\tau$  can be changed dynamically by moving one side of the frame [8]. For example,  $\tau$  increases when one pulls on

the frame. The increase of the tension  $\tau$  favors the phase with the lower area per molecule. In the present case it means that when starting from the Sm-A-like phase, the Sm- $C^*$ -like phase could be induced by pulling on the frame. We intend to verify this conjecture in the near future

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- [1] K. Binder, Ferroelectrics 73, 43 (1987).
- [2] J. W. Doane, N. A. Vaz, B. G. Wu, and S. Zumer, Appl. Phys. Lett. 48, 269 (1986).
- [3] M. Gharbia, A Garbi, M. Canion, and G. Durand, J. Phys. 51, 1335 (1991).
- [4] A review of the capillary condenstion can be found in R. Evans, J. Phys. Condens. Matter. 2, 8989 (1990).
- [5] A review on the surface effects in liquid crystals can be found in B. Jérôme, Rep. Prog. Phys. 54, 391 (1991).
- [6] An excellent review and a collection of articles on free-standing smectic films can be found in P. S. Pershan, Structure of Liquid Crystal Phases (World Scientific, Singapore, 1988). Among these articles let us quote a representative one: E. H. Sirota, P. S. Pershan, L. B.

- Sorensen, and J. Collet, Phys. Rev. A 36, 2890 (1987).
- [7] Ch. Bahr and D. Fliegner, Phys. Rev. A 46, 7657 (1992).
- [8] P. Pieranski et al., Physica A 194, 364 (1993).
- [9] M. Born and E. Wolf, *Principles of Optics* (Pergamon, New York, 1980).
- [10] J. Goodby (unpublished).
- [11] F. David and S. Leibler, J. Phys. (France) II 1, 959 (1991).
- [12] At temperatures higher than  $T_{AC}$  the external layers can already be tilted. Similar observations have been made previously in other materials; for example, S. Heinekamp et al., Phys. Rev. Lett. **52**, 1017 (1984).
- [13] A similar problem concerning "black films" was considered in F. Brochard, P. G. de Gennes, and P. Pfeuty, J. Phys. (Paris) 37, 1090 (1976).

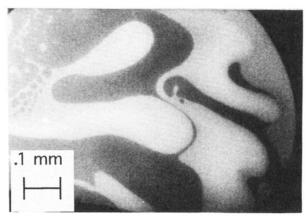


FIG. 11. The picture shows the phase coexistence between domains of Sm-A- and Sm-C\*-like structures. The thickness of the film is close to the critical thickness  $N_c$ . One can compare the "wavy" shape of the domains with the circular one of the thick film presented in Fig. 8.

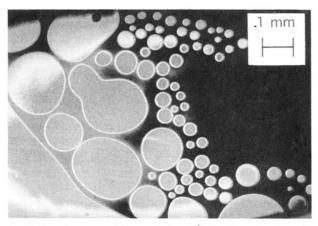


FIG. 8. Phase coexistence of  $Sm-C^*$ -like domains in a Sm-A-like matrix. Domains have a tendency to be circular. The "pear"-shape domain is created by coalescence of two adjacent domains. Once relaxed, it will take a circular shape (view in monochromatic illumination).

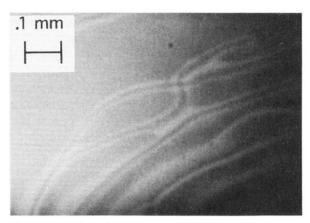


FIG. 9. Crossing of two independent schlieren textures in an ALLO-9O2C13M5T film of thickness  $N>N_c$  far from the Sm- $A\to {\rm Sm-}C^*$  transition temperature.