

## Behavior of a surface phase transition in freely suspended liquid-crystal films

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(Received 4 August 1995)

The smectic-A–smectic-C transition at the free surface of freely suspended liquid-crystal films with thicknesses between three and several hundred smectic layers has been studied by ellipsometry. The results indicate that the temperature dependence of the tilt angle near the surface transition is influenced by the film thickness even in the range up to  $\approx 100$  layers and that not only the first smectic layer at the surface is involved in the transition. In films of medium thickness (between 30 and 100 layers) a splitting of the transition into two steps is observed which probably does not correspond to the layer-by-layer behavior observed frequently for other liquid-crystal phase transitions.

PACS number(s): 64.70.Md, 61.30.Eb, 68.10.-m

Thermotropic liquid crystals are prime examples of systems possessing enhanced surface order. Corresponding experimental studies are frequently carried out using freely suspended films which can be prepared from smectic (i.e., layered) liquid-crystal phases. Freely suspended films [1,2] consist of an integral number (between some thousands and only two) of molecular smectic layers, the layer planes being parallel to the two free surfaces. The surface-induced order becomes apparent near the phase transitions between different smectic phases: approaching a phase transition from the high-temperature side, the surface layers of freely suspended films transform into the low-temperature phase several kelvins above the bulk transition temperature. On further approaching the bulk transition, the thickness of the ordered surface domain grows either via a series of individual layer-by-layer transitions [3–6] or continuously without reflecting the layered structure of the smectic phases [7,8] (a recent review is [9]). In both cases, however, the results reported so far indicate that the surface transition, i.e., the transition where the first deviation from the structure of the high-temperature phase occurs when the temperature is decreased, is restricted to the first molecular layer at the surface. The exact origin of the enhanced surface order at free liquid-crystal surfaces is not clarified; it is usually ascribed to the quenching of fluctuations because of the surface tension. Studies of the dependence of the surface transition temperatures on the film thickness probe the influence of the closeness of the second surface to the first and may thus yield information about the penetration depth of the surface ordering. As expected, two-layer films always show the highest transition temperatures; with increasing film thickness the surface transition temperatures decrease until the thickness amounts to a value typically between four and ten layers; a further increase of the film thickness does not change the surface transition temperatures leading to the conclusion of fairly short penetration depths of the surface order.

In this paper we report an unusual behavior of a liquid-crystal surface transition: our results show that several layers (not only the first molecular layer at the surface) can be involved in the transition and that the detailed behavior, e.g., the temperature dependence of the order parameter, can be influenced by the film thickness even in the range up to 100 layers. Furthermore, a unique splitting of the transition into two steps is observed.

We regard the phase transition between the two simplest smectic phases, smectic-A (Sm-A) and smectic-C (Sm-C), which do not possess any in-plane order, i.e., these phases may be considered as stacks of molecular layers, each layer corresponding to a two-dimensional liquid. In Sm-A, the rodlike molecules are on average parallel with their long axis to the layer normal, whereas in Sm-C, which is the low-temperature phase to Sm-A, the mean direction of the long molecular axis is tilted with respect to the layer normal. When, in a freely suspended film, the Sm-A–Sm-C transition is approached from the high-temperature side, the first nonzero tilt appears 20–30 K above the bulk transition temperature [7,8,10]. In contrast to transitions involving hexatic and/or crystalline smectic phases, where the layer-by-layer behavior is observed, the thickness of the ordered (i.e., tilted) surface domain grows in the case of the Sm-A–Sm-C transition continuously with decreasing temperature [7,8]. Nevertheless, detailed measurements of the temperature dependence of the tilt angle in freely suspended films of the well-known compound DOBAMBC [11] have led Amador and Pershan [8] to the conclusion that the Sm-A–Sm-C surface transition is also restricted to the first smectic layer at the surface.

In the present study, we investigate the compound 2-methylbutyl 4-octanoyloxybiphenyl-4'-carboxylate (labeled in the following as MBOBC, the molecular structure is shown above Fig. 1), which shows as a bulk sample the transition temperatures  $\text{Sm-C} \leftarrow 41^\circ\text{C} \rightarrow \text{Sm-A} \leftarrow 60^\circ\text{C} \rightarrow \text{isotropic}$ . Freely suspended films are drawn in the Sm-A phase using a rectangular variable-surface frame described in [2]. The area of the films is approximately  $4 \times 10 \text{ mm}^2$ . Our experimental method is ellipsometry and details about our

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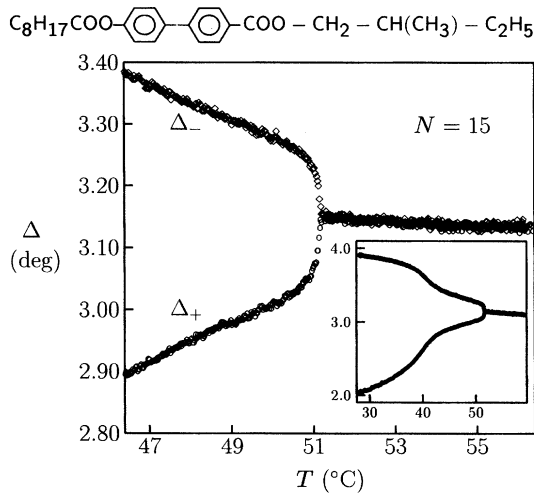


FIG. 1. Temperature dependence of  $\Delta_+$  and  $\Delta_-$  around the surface Sm-A–Sm-C transition in a 15-layer film of the compound MBOOBC (the molecular structure is shown on top). The inset shows the whole temperature range studied and one can distinguish between regions where the tilt is zero in all layers ( $T > 51^\circ\text{C}$ ), where mainly the surface layers are tilted ( $45^\circ\text{C} < T < 51^\circ\text{C}$ ), and where all layers are tilted ( $T < 40^\circ\text{C}$ ).

setup can be found in [12]. We determine the parameters  $\Delta$  and  $\Psi$  describing the polarization of a laser beam ( $\lambda = 633$  nm) which transmits the film under an angle of incidence of  $45^\circ$ ; here,  $\Delta = \delta_p - \delta_s$  is the phase difference between the  $s$ - and  $p$ -polarized components of the transmitted light and  $\Psi$  is related to the ratio of the amplitudes  $|T_s|$  and  $|T_p|$  of the  $s$  and  $p$  components as  $\tan\Psi = |T_p|/|T_s|$ ; the polarization of the incident light is described by  $\Delta = 0$  and  $\Psi = 45^\circ$ . The values of  $\Delta$  and  $\Psi$  measured in the Sm-A phase enable the determination of the film thickness as described in [12]. The value of  $\Delta$  is also sensitive to a tilt of the optical axis (and thus to a tilt of the molecules) of the film. Our experimental setup allows the application of a d.c. electric field (perpendicular to the plane of incidence) which we use to predetermine the tilt direction in the ferroelectric Sm-C phase (via the coupling between the directions of tilt and spontaneous electric polarization [13]). According to the field polarity, the molecules tilt either away from or towards the incident laser beam giving rise to two values  $\Delta_+$  and  $\Delta_-$ , the difference  $|\Delta_+ - \Delta_-|$  being a measure of the tilt angle of the optical axis of the film; when all layers of a film are in the Sm-A state, we measure  $\Delta_+ = \Delta_-$ . We have to note, however, that ellipsometric measurements do not yield direct information about the tilt profile across the film; rather, we measure a mean tilt angle  $\langle\theta\rangle$  corresponding (for an  $N$ -layer film) to  $\langle\theta\rangle = (1/N)\sum_{i=1}^N \theta_i$  ( $\theta_i$  being the tilt angle in the  $i$ th layer; details of the determination of  $\langle\theta\rangle$  from the values of  $\Delta$  can be found in [12]).

Figure 1 shows the temperature dependence of  $\Delta_+$  and  $\Delta_-$  for a 15-layer film. At temperatures above  $51^\circ\text{C}$  all layers of the film are obviously in the Sm-A state because we measure  $\Delta_+ = \Delta_-$ . At  $51^\circ\text{C}$  a sharp transition takes place where  $\Delta_+$  becomes different from  $\Delta_-$  and a finite tilt appears. With decreasing temperature, the difference

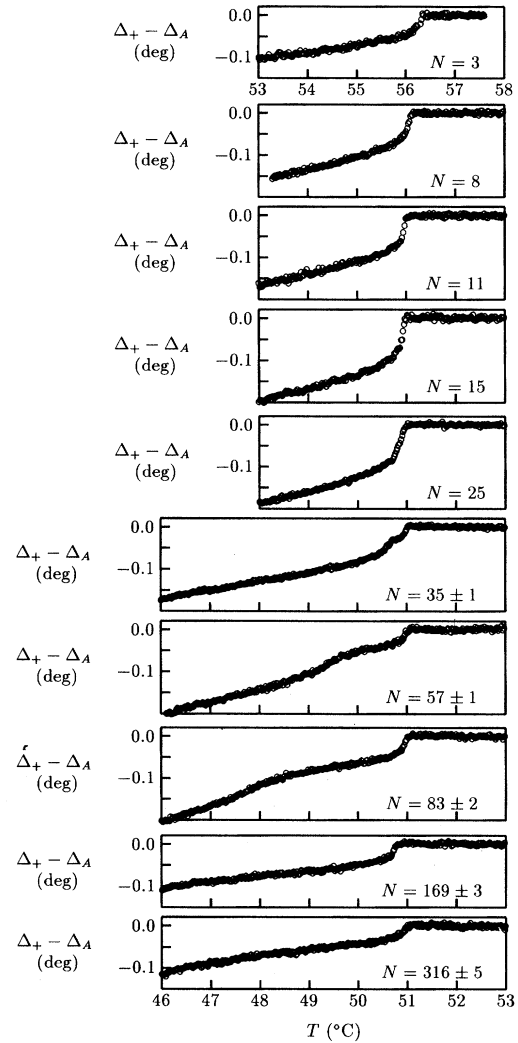


FIG. 2. Temperature dependence of the difference  $\Delta_+ - \Delta_A$  ( $\Delta_A$  being the  $\Delta$  value in the Sm-A phase) in films with the thicknesses between three and  $\approx 300$  layers (given by  $N$ ) of MBOOBC. The amount of  $|\Delta_+ - \Delta_A|$  is a measure of the total amount of tilt, i.e., the value  $\langle\theta\rangle N$ , in the different films. (Note that the temperature scale of the three-layer film is shifted by 5 K with respect to the other films).

$|\Delta_+ - \Delta_-|$  (and thus the mean tilt angle  $\langle\theta\rangle$ ) grows smoothly showing an S-shaped feature around the bulk transition temperature ( $41^\circ\text{C}$ ) where  $\langle\theta\rangle$  obviously grows somewhat “faster” with decreasing temperature because of the increasing contribution of the interior layers to  $\langle\theta\rangle$ . In the following, we concentrate on the surface transition where  $\langle\theta\rangle$  starts to deviate from zero.

An overview of our results for film thicknesses between three and  $\approx 300$  layers is given in Fig. 2 showing the temperature dependence of the difference  $\Delta_+ - \Delta_A$  ( $\Delta_A$  being the  $\Delta$  value when all layers of the film are in the Sm-A state); the amount  $|\Delta_+ - \Delta_A|$  is in good approximation proportional to the mean tilt angle  $\langle\theta\rangle$  of a given film [12]. When comparing films of different thickness, one has to take into account that the amount of  $|\Delta_+ - \Delta_A|$  is a direct measure

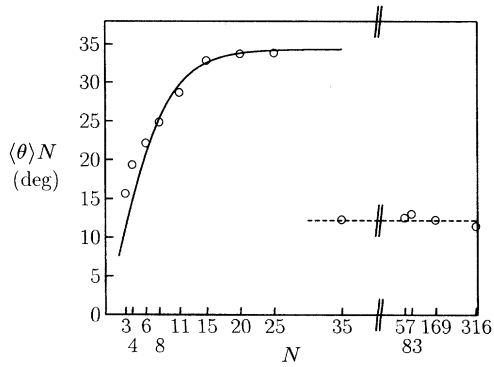


FIG. 3. Values of  $\langle \theta \rangle N$  (corresponding to the total amount of tilt in a  $N$ -layer film) as a function of thin film thickness  $N$  at a temperature 0.3 K below the surface transition. The solid line is calculated according to Eq. (2); the dashed line is only a guide to the eye. (Note that the scale of the  $N$  axis changes at  $N = 40$ .)

of the total amount of tilt present in the different films. By “total amount of tilt” we mean the value of  $\langle \theta \rangle$  multiplied by  $N$  ( $N$  being the number of layers) or, equivalently, the sum  $\sum_{i=1}^N \theta_i$ . Two films showing the same value of  $|\Delta_+ - \Delta_-|$  possess also the same value of  $\langle \theta \rangle N$ . As can be seen in Fig. 2 the surface transition is influenced by the film thickness up to  $\approx 100$  layers (although its temperature depends on the film thickness only for  $N < 8$ ): From three to  $\approx 30$  layers, the transition is characterized by a steep increase of the tilt angle within  $\approx 0.3$  K; the amount of this increase becomes larger with increasing film thickness. In the 35-layer film, the steep increase of  $\langle \theta \rangle$  has been split into two steps, the first of which (at the higher temperature) corresponds at first glance to a monolayer transition at the surface because its amount is approximately the same as we would expect for a two-layer film. The second step at lower temperatures gets more and more smeared out and is shifted to lower temperatures with increasing film thickness but is still perceptible in a 83-layer film. Above  $\approx 100$  layers only the apparent monolayer surface transition, which remains independent of the film thickness, is discernible.

The total amount of tilt, which appears at the surface transition, is given in Fig. 3 as a function of film thickness. We have plotted for each  $N$ -layer film the value of  $\langle \theta \rangle N$  at a temperature 0.3 K below the surface transition temperature  $T_{\text{surf}}$ , i.e., the  $\langle \theta \rangle N$  values just after the steep increase characterizing the transition. For thin films, the  $\langle \theta \rangle N$  values first increase with increasing  $N$  and then tend to saturate for thicknesses  $N > \approx 20$ . For thicknesses larger than  $\approx 30$  layers, we observe significantly smaller  $\langle \theta \rangle N$  values at  $T_{\text{surf}} - 0.3$  K because of the splitting of the transition into two steps; these smaller  $\langle \theta \rangle N$  values are within our experimental resolution independent of  $N$  for all films between 30 and  $\approx 600$  layers.

How can our results be understood in the light of existing theories? The bulk Sm-A–Sm-C transition of MBOBC is of the second-order type; thus, if we had a semi-infinite sample with enhanced surface order, our systems should enable the observation of critical adsorption [14,15], i.e., the thickness growth of the ordered surface domain with decreasing temperature should be governed by the divergence

of the corresponding correlation length  $\xi$  of the bulk material. Far above the bulk transition temperature, the order parameter profile  $m(z)$  ( $z$  being the direction of the film normal) near the surface should follow a simple exponential decay  $m(z) \propto e^{-z/\xi}$  [15]. In films of finite thickness  $L$ , the mean field theory predicts a profile  $m(z)$  describable by a cosh function [5,16]

$$m(z) = m_{\text{surf}} \frac{\cosh[(2z-L)/2\xi]}{\cosh(L/2\xi)} \quad (1)$$

with  $m_{\text{surf}}$  being the value of the order parameter at the surfaces ( $z=0, L$ ). Measuring the lengths in units of smectic layers, one gets for an  $N$ -layer film a total amount of tilt  $\theta_{\text{tot}}$  according to

$$\theta_{\text{tot}} = \sum_{i=1}^N \theta_i = \sum_{i=1}^N \theta_{\text{surf}} \frac{\cosh\{[2(i-\frac{1}{2})-N]/2\xi\}}{\cosh[(N-1)/2\xi]}. \quad (2)$$

The initial increase and the saturation of our experimental values of  $\theta_{\text{tot}} = \langle \theta \rangle N$  are fairly well described by Eq. (2) if we set  $\xi = 4$  layers and  $\theta_{\text{surf}} = 3.8^\circ$  (we have neglected here the dependence of  $\theta_{\text{surf}}$  on  $N$  which is, within the mean field theory, significant only in very thin films where  $N \approx \xi$  [5,16]). The dependence of our  $\langle \theta \rangle N$  values on  $N$  and the resulting value of the correlation length,  $\xi = 4$  layers, clearly indicate that just after the surface transition considerably more layers than just the first surface layer are tilted. Our results are in contrast to the results obtained for the compound DOBAMBC where the  $\langle \theta \rangle N$  values were found to be independent of  $N$  even for very thin films (3 to 11 layers) [8]. A reason for this may consist of a smaller value of  $\xi$  in DOBAMBC where the surface transition temperature is shifted by 20 K and more above the bulk transition whereas in MBOBC this temperature shift amounts to only 10 K; since  $\xi$  decreases with increasing temperature difference to the bulk transition, the  $\xi$  value just below the surface transition will be in DOBAMBC certainly smaller than in MBOBC.

At the moment, we have no conclusive explanation for the splitting of the surface transition and the resulting smaller  $\langle \theta \rangle N$  values at  $T_{\text{surf}} - 0.3$  K observed for  $N > 30$ . If we still assume that the tilt profile and the resulting  $\langle \theta \rangle N$  values are described by equations (1) and (2), we have to assume a considerably reduced value of either  $\xi$  or  $\theta_{\text{surf}}$  for film thicknesses above  $\approx 30$  layers. There is no reason at all why the correlation length  $\xi$ , which is a bulk property, should exhibit such a behavior. Rather we believe that we observe a kind of crossover behavior between two thickness regions with different strengths of surface-induced order: thin films ( $N < 30$ ) show in the whole temperature range the “stronger” surface order (i.e., larger value of  $\theta_{\text{surf}}$ ), whereas in thick films ( $N > 100$ ) only the “weaker” surface order (i.e., smaller value of  $\theta_{\text{surf}}$ ) is observed. It seems that in films of medium thickness ( $30 < N < 100$ ), which show the weaker order at higher temperatures, the stronger order can be still recovered when the temperature becomes smaller (or, equivalently, when the correlation length becomes larger) than a certain value. This hypothesis, however, leaves as an open question why  $\theta_{\text{surf}}$  apparently changes stepwise and not

smoothly with increasing film thickness; also, we cannot explain why at all the value of  $\theta_{\text{surf}}$  should change in this thickness region.

Another interpretation of our results would consist of the assumption that the two steps observed in films of medium thickness correspond to a transition occurring at higher temperatures in the surface layers only and a transitionlike phenomenon occurring at lower temperatures in the layers adjacent to the surface layers, i.e., in medium thick films a kind of rudimentary layer-by-layer behavior is observed, which is, by some reason due to the closeness of the two surfaces, suppressed in thin films. Then, however, one cannot explain why in thick films again only one transition is observed (rather, one would expect that the more steps appear the thicker the films are).

In conclusion, we have presented a study of the smectic-*A*–smectic-*C* transition at the free surface of freely suspended liquid-crystal films with thicknesses between three and several hundred smectic layers. Whereas the transition

temperature depends on the film thickness in very thin films ( $N < 8$ ) only, the temperature dependence of the tilt angle near the transition is influenced up to a thickness of  $\approx 100$  layers. In films thinner than  $\approx 30$  layers, our values of the mean tilt angle just below the transition are consistent with a tilt profile describable by a cosh function with a correlation length of four layers, indicating that not only the surface layers are involved in the transition. When the thickness is increased above 30 layers, a splitting of the surface transition into two steps is observed which vanishes again in films thicker than  $\approx 100$  layers. The reasons for this behavior are not yet understood and further studies are needed.

This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 335). One of us (C.J.B.) acknowledges financial support by the European Community (Human Capital and Mobility Program). Thanks are due to G. Heppke for stimulating discussions.

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- [1] C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978).
- [2] P. Pieranski, L. Beliard, J.-Ph. Tournellec, X. Leoncini, C. Furtlehner, H. Dumoulin, E. Riou, B. Jouvin, J.-P. Fénerol, Ph. Palaric, J. Heuving, B. Cartier, and I. Kraus, *Physica A* **194**, 364 (1993).
- [3] B. D. Swanson, H. Stragier, D. J. Tweet, and L. B. Sorensen, *Phys. Rev. Lett.* **62**, 909 (1989).
- [4] T. Stoebe, R. Geer, C. C. Huang, and J. W. Goodby, *Phys. Rev. Lett.* **69**, 2090 (1992).
- [5] R. Geer, T. Stoebe, and C. C. Huang, *Phys. Rev. E* **48**, 408 (1993).
- [6] A. J. Jin, T. Stoebe, and C. C. Huang, *Phys. Rev. E* **49**, 4791 (1994).
- [7] S. Heinekamp, R. A. Pelcovits, E. Fontes, E. Y. Chen, R. Pindak, and R. B. Meyer, *Phys. Rev. Lett.* **52**, 1017 (1984).
- [8] S. M. Amador and P. S. Pershan, *Phys. Rev. A* **41**, 4326 (1990).
- [9] Ch. Bahr, *Int. J. Mod. Phys. B* **8**, 3051 (1994).
- [10] Ch. Bahr and D. Fliegner, *Phys. Rev. Lett.* **70**, 1842 (1993).
- [11] DOBAMBC is the 2-methylbutylester of 4-decyloxybenzylidene-4'-aminocinnamic acid.
- [12] Ch. Bahr and D. Fliegner, *Phys. Rev. A* **46**, 7657 (1992).
- [13] When a tilted smectic phase like Sm-*C* is composed of chiral molecules, it possesses a spontaneous electric polarization  $\vec{P}_s$  in each smectic layer; R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. (Paris) Lett.* **36**, L69 (1975). Because the direction of  $\vec{P}_s$  is coupled to the direction of the molecular tilt, one can use an external electric field in order to fix the tilt direction.
- [14] M. E. Fisher and P.-G. de Gennes, *C. R. Acad. Sci. Ser. B* **287**, 207 (1978).
- [15] A. J. Liu and M. E. Fisher, *Phys. Rev. A* **40**, 7202 (1989).
- [16] K. Binder, *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1986), Vol. 8.