Step-by-step thinning of free-standing films above the smectic-A—nematic phase transition

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Optical reflectivity of free-standing films at the smectic-A—nematic (Sm-A–N) phase transition has been studied. The Sm-A films thin in a stepwise manner in the nematic temperature interval. The film thickness can be described by a power function of maximal temperature at which this thickness is stable. The value of the exponent correlates with $\nu_\parallel$ for the smectic fluctuations in the nematic phase determined by x-ray diffraction. The step-by-step thinning is a universal phenomenon for the smectic-A—nematic phase transition.
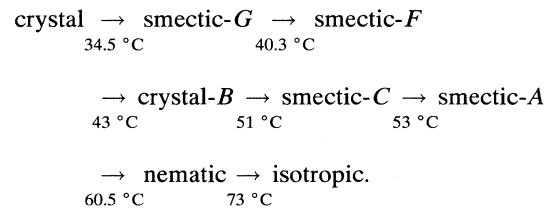
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Free-standing liquid-crystalline films are excellently suited for study of finite-size effects and surface induced phase transitions [1–11]. In previous experimental and theoretical works, films of smectic and crystalline phases with long and quasilong positional order have been studied. Recent results by Stoebe, Mach, and Huang [12] have shown that free-standing films can be stable in the isotropic liquid near the Sm-A—isotropic transition. According to [12], the Sm-A—isotropic liquid transition in partially fluorinated free-standing films occurs through the layer-thinning process, where the film thickness decreases in a stepwise manner as the temperature was increased. The bulk Sm-A—isotropic liquid phase transition is of the first order and above it the system possesses neither translational nor orientational order.

The anomalous layer-thinning behavior observed in [12] can be combined with the surface smecticity of the free boundary with temperature dependent penetration length of the surface order. From the point of view of surface ordering phenomena on the liquid-crystalline boundary the layer-thinning observed by Stoebe, Mach, and Huang can be more general, because surface freezing phenomena are typical in liquid-crystalline phases without smectic layered structure. For example, Als-Nielsen *et al.* [13] have shown that on the boundary of the bulk nematic phase smectic layers are present. Therefore, it is interesting to study the universality of the melting phenomena observed in [12] for other phases with a short range positional order. The smectic-A—nematic (Sm-A–N) transition is of special interest for such a work because in the case of the second or weak first order transitions the correlation length of smectic fluctuations in the nematic phase can be large.

The aim of this work is to study behavior of free-standing films in the nematic phase temperature interval where the bulky phase possesses only orientational order. We have observed a phenomenon of step-by-step thinning of smectic-A films in the nematic temperature interval which begins from the macroscopic lengths. The film thickness is a power function of temperature with an exponent corresponding to $\nu_\parallel$ found for the nematic phase by the x-ray measurements [14] for the Sm-A–N phase transition. This melting phenomenon was observed for all substances investigated which possess a Sm-A–N transition.

Free-standing films of 4-n-penthyloxybenzylidene-4-n-hexylaniline (5O.6) were studied in this work. Bulky samples of this material possess the following liquid-crystalline phases:

crystal $\xrightarrow[34.5\,°C]{}$ smectic-G $\xrightarrow[40.3\,°C]{}$ smectic-F

$\xrightarrow[43\,°C]{}$ crystal-B $\xrightarrow[51\,°C]{}$ smectic-C $\xrightarrow[53\,°C]{}$ smectic-A

$\xrightarrow[60.5\,°C]{}$ nematic $\xrightarrow[73\,°C]{}$ isotropic.

The phase transition N–Sm-A is weak first order with transition enthalpy 0.86 kJ/mol [15].

Films of 5O.6 with dimensions 0.1×5 mm^2 were drawn in a frame consisting of two brass rails and two movable brass blades. The experimental setup enabled simultaneous optical observations and reflectivity measurements in the visible region of wavelengths in a modified Olympus-PMG-3 inverted microscope. The number of smectic layers was determined by the optical diffraction measurements in the smectic-A phase as described in detail in [1,7]. To find the film thickness we have fitted the reflectivity curves by the expression for the light diffraction in the plane parallel plate [16]:

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

where

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

$D=Nnd$ is the optical thickness of the whole film, N is the number of layers, $n\approx1.5$ is the refractive index, and d is the average interlayer spacing. The applied method allows the exact determination of the number of layers in a broad interval of film thicknesses [7]. Figure 1 shows the reflectivity
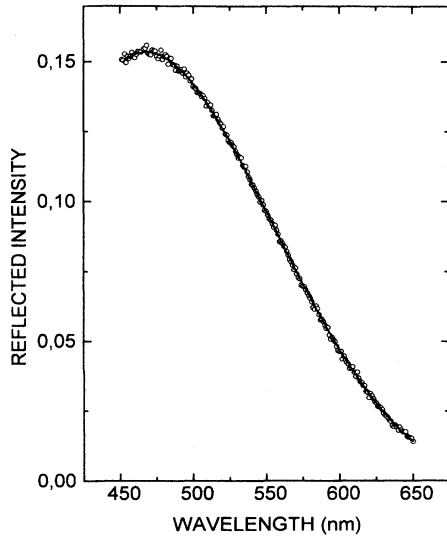
FIG. 1. Experimental reflectivity curve for $N=92$ and $T=60.77$ °C ($\bigcirc$) and the least squares fit according to the expression (1) (solid line).

curve of the 93-layer film at $T=60.77$ °C and the least squares fit curve with the expression (1) which perfectly describes the experiment.

The 2–400 layer free-standing films were prepared in the Sm-A phase, the film thickness has been determined and the films were heated with a constant rate 1–3 mK/s. The temperature of the Sm-A–N transition has been determined by changes in the film meniscus (T_c). At this temperature a part of the material in the meniscus transforms to the nematic phase and flows in the spaces between the rails and the movable blades due to the capillary forces. Above T_c the films with thickness L_1 ($L=Nd$) did not rupture in the temperature interval of the nematic phase up to the temperature $T(L_1)$ [$T(N_1)$] where the thickness spontaneously decreases to some value L_2. For a comparison, the 70-layer film was stable up to 0.5 K above the bulk transition, whereas the five-layer film remained stable more than 8 K above T_c. The temperature of the film thinning has been determined by microscopic observations with accuracy ± 10 mK. At the temperature slightly above $T(L_1)$ the heating has been stopped, the films thickness L_2 determined and the films heated up to the next jump in thickness. This procedure has been continued until the films were stable. After that the films were cooled to the Sm-A interval and the procedure repeated for some other initial thickness. Figure 2 displays the data L_i versus $T(L_i)$ which was found according to the procedure described above for three different initial thicknesses. The stable film thickness decreases by increasing the temperature $T(L)$. The experimental data can be described by the simple power law:

$$L(T)=l_0\left(\frac{T(L)-T_0}{T_0}\right)^{-\nu}, \qquad (3)$$

where T_0, l_0, ν are fitting parameters. The solid line in this figure shows the least squares fit with $l_0=1.2$ nm, $T_0=60.35, \nu=0.82$.
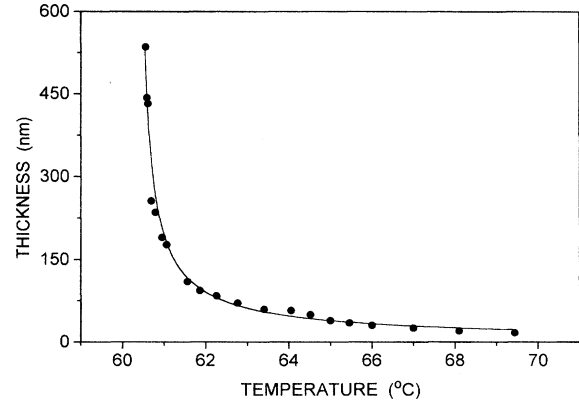

FIG. 2. The film thickness versus temperature $T(L)$. The solid line shows the least squares fit according to the expression (3).

Free-standing films can be drawn in the temperature interval of the nematic phase. The film thickness in this case is limited by some value L_{max}. The temperature dependence of L_{max} coincides with the dependence of L on $T(L)$ in Fig. 2. To avoid the ambiguities we have to underline that in the nematic temperature interval we always deal with smectic films with variable thickness.

Figure 3 shows the reflection spectra of the initially 17-layer free-standing film, which was stable up to 65 °C. This curve demonstrates that the film-thinning process takes place in the layer-by-layer regime in the case of extremely thin films. On heating we observed layer-by-layer thinning in two ways. First, we recorded the spectra near $T(17)$ and $T(15)$ on *heating* with 3 mK/s, where $T(N)$ is the maximal temperature of N-layer film stability. The jumps of the intensity on the two upper curves correspond to the decrease of the film thickness by one layer. To show this we have fitted the parts of curves for the wavelengths below and above the jumps. The difference in D corresponds to the optical thickness of one layer ($D_{min}\approx 3.8$ nm). The $N=13$ and $N=11$ curves
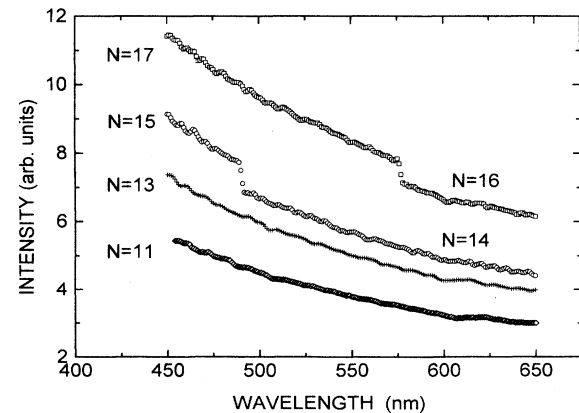

FIG. 3. Film reflectivity spectra in the region near the temperature $T(N)$ of the melting of the Nth layer for $N=17$ ($\square$) and $N=15$ ($\bigcirc$); the temperature was *increased* with the rate 3 mK/s. Spectra of the $N=13$ film (+) for some *constant* temperature T between $T(14)$ and $T(13)$, the same for $N=11$ and $T(12)$ $\leqslant T \leqslant T(11)$ ($\Diamond$).

were recorded at *fixed* temperatures far from $T(13)$, $T(12)$, and $T(11)$ and show that the film thickness remains in this case unchanged for a long period of time. From such measurements we have found that the interlayer spacing for the smectic films at 66 °C is approximately equal to 2.5 nm.

To explain our results we suppose that the smectic order occurs on the films boundary and is characterized by the penetration length ξ. Our results and results of Stoebe *et al.* [12] can be explained if we accept that the free-standing films are stable in the nematic or isotropic temperature intervals, if the film thickness equals double penetration length. Usually, steps are considered as edge dislocations moving in the interior of the films [1]. Therefore, the step-by-step thinning is an untrivial melting process of the surface ordered regions taking place in the inside of the films. The nematic phase is formed in the interior of the films and removed to the meniscus to eliminate the additional contribution to the free energy on the boundary Sm-A–nematic. It is well known that the smectic correlation length in the nematic phase is anisotropic [14]. The temperature dependences of the correlation lengths are described by power law functions similar to expression (3) with different exponents $\nu_{\parallel}$ and $\nu_{\perp}$: $\nu_{\parallel} \approx 0.74 \pm 0.1$ and $\nu_{\parallel} - \nu_{\perp} \approx 0.15 \pm 0.05$ [14]. The critical exponents found in our work ($\nu = 0.82$) and in [12] ($\nu = 0.74$) correlate with $\nu_{\parallel}$. It has to be noted that the value of the critical exponent is qualitatively different with respect to the predictions of the theory of wetting ($\nu = 1/3$). This fact correlates with our assumption that the melting process takes place in the interior of the films.

The qualitative difference of our results with respect to [12] is that we have observed the step-by-step thinning process starting from macroscopic lengths, whereas in [12] the layer thinning was reported beginning from 25 layers. This result can be explained by the different nature of phase transitions in our case and in [12] or by a difference in the

properties of boundaries. The Sm-A–N transition in 5O.6 is weakly first order. This explains the small value of difference ($\Delta T = T_c - T_0 \approx 0.15$ °C) found from fitting on Fig. 3. In the case of the second order transition this difference has to be zero. From this point of view the value of ΔT for the phase transition Sm-A–isotropic should be essentially larger, which contradicts the results of Stoebe, Mach, and Huang. The properties of the film thinning in [12] and the current work agree with the description of the critical behavior of the surface-induced order [17–19] at first order phase transitions. Indeed, the results of [12] and this paper show that in both cases ΔT and ν correlate with analogous values for the second order Sm-A–N transition and are *independent* on the type of the phase in the film interior. But to give decisive evidence for the critical behavior on the boundary air–liquid crystal in this case additional measurements are necessary.

Analogous measurements with other substances (for example, p-decyloxybenzoic acid-p-n-hexyloxyphenyl) possessing the Sm-A-nematic show the step-by-step thinning behavior similar to 5O.6. Summarizing, we would like to emphasize that the step-by-step thinning of free-standing films at the phase transitions from smectic phases into the phases without the layered structure seems to be a universal phenomenon which should be observed for a broad class of compounds and different phase transitions. The stability of the free-standing films in the temperature interval of liquid-crystalline phases without positional order is determined by the finite-size effects on the smectic fluctuations in the pre-critical region. This phenomenon deserves further attention to generalize the picture of fluctuation phenomena in free-standing films.

[1] P. Pieranski *et al.*, Physica A **194**, 364 (1993).

[2] C.C. Huang and T. Stoebe, Adv. Phys. **42**, 343 (1993).

[3] E.B Sirota, P.S. Pershan, S. Amador, and L.B. Sorensen, Phys. Rev. A **35**, 2283 (1987).

[4] E.B. Sirota, P.S. Pershan, L.B. Sorensen, and J. Collett, Phys. Rev. A **36**, 2890 (1987).

[5] S. Heinekamp, R. Pelkovits, E. Fontes, E. Yi Chen, R. Pindak, and R. Meyer, Phys. Rev. Lett. **52**, 1017 (1984).

[6] Ch. Bahr and D. Fliegner, Phys. Rev. A **46**, 7657 (1992).

[7] I. Kraus, P. Pieranski, E. Demikhov, and H. Stegemeyer, Phys. Rev. E **48**, 1916 (1993).

[8] C. Bahr, D. Fliegner, C.J. Booth, and J.W. Goodby, Europhys. Lett. **26**, 539 (1994).

[9] E. Demikhov, U. Hoffmann, and H. Stegemeyer, J. Phys. (France) II **4**, 1865 (1994).

[10] E.I. Demikhov and S.A. Pikin, JETP Lett. **61**, No. 8 (1995).

[11] E.I. Demikhov, E. Hoffmann, H. Stegemeyer, S.A. Pikin, and A. Strigazzi, Phys. Rev. E **51**, 5954 (1995).

[12] S. Stoebe, P. Mach, and C.C. Huang, Phys. Rev. Lett. **73**, 1384 (1994).

[13] J. Als-Nielsen, F. Christensen, and P.S. Pershan, Phys. Rev. Lett. **48**, 1107 (1982).

[14] *Structure of Liquid Crystal Phases*, edited by P. S. Pershan (World Scientific, Singapore, 1988).

[15] G. Pelzl (private communication).

[16] M. Born and E. Wolf, *Principles of Optics* (Pergamon, London, 1980), Chap. 7.6, p. 327.

[17] R. Lipowsky, Phys. Rev. Lett. **49**, 1575 (1982).

[18] R. Lipowsky, J. Appl. Phys. **55**, 2485 (1984).

[19] R. Lipowsky, Ferroelectrics **73**, 69 (1987).