Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Free-Standing Smectic Films Above SmA-N, SmA-Iso Transitions

Yewgeni I. Demikhov [a b] & Vladimir K. Dolganov [c]

[a] Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia

[b] Research Technology Instruments, Technologiepark 12-13, 33100, Paderborn, Germany

[c] Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia

Version of record first published: 04 Oct 2006

To cite this article: Yewgeni I. Demikhov & Vladimir K. Dolganov (1997): Free-Standing Smectic Films Above SmA-N, SmA-Iso Transitions, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 193-207

To link to this article: http://dx.doi.org/10.1080/10587259708039425

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 193–207
Reprints available directly from the publisher
Photocopying permitted by license only

FREE-STANDING SMECTIC FILMS ABOVE SmA - N, SmA - Iso TRANSITIONS

YEWGENI I. DEMIKHOV

Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia and Research Technology Instruments, Technologiepark 12-13, 33100 Paderborn, Germany and

VLADIMIR K. DOLGANOV

Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia

Abstract. Spontaneous stepwise thinning of free standing films was observed above the phase transitions SmA - iso, SmA - N in several compounds. The free standing films thickness decreases on heating above these transitions in successive steps. A decrease of thickness occurs at some temperature $T_{max}(N)$ above which the N-layer film cannot be stable. The film thickness can be described by a power law function of T_{max}. Mechanism of the phenomenon is discussed.

1 Introduction

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 quasi-long positional order has been studied. Recent investigations have shown that free standing films can be stable in the isotropic liquid above the SmA - isotropic [12] and in the nematic phase above SmA - Nem [13] transition. According to [12], the SmA - 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.

From the point of view of surface ordering on the liquid-crystalline boundary the layer-thinning transition can be more general, because surface freezing phenomena

are typical in other phases without smectic layered structure. For example, Als-Nielsen et al. [14] have shown that on the boundary of the bulk nematic phase smectic layers are present. Similar behaviour was observed for the free surface of the isotropic phase [15]. Therefore, it is interesting to study the universality of the layer thinning transition for other phases with a short range positional order. In this paper we present our results on the layer thinning transition for the compounds with SmA-Iso, SmA-Nem and SmA-Nem-Iso phase sequences. The SmA - N transition is of special interest for such a work because in the case of the second or weak first order transitions the surface correlation length of smectic fluctuations in the nematic phase can be large. We studied the phenomenon in thick ($\approx$ 100 layers) and extremely thin ($<$ 20 layer) films. In the nematic temperature interval the regular step-by step thinning can begin from the macroscopic lengths. The film thickness is a power function of temperature with an exponent $\nu \approx 0.8 \pm 0.1$.

2 Experimental

Following compounds have been studied in this work

- 4-n-hexyloxyphenyl-4'-n-decyloxybenzoate (6O.10) (all transition temperatures are given in degrees centigrade): Sm C(77) SmA(83) Nem (89) Isotropic. The SmA - Nem transition is second order [16].
- 4-n- penthyloxybenzylidene -4-n- hexylaniline (5O.6) cryst (34.5) Sm G (40.3) Sm F (43) Cr B (51) Sm C (53) Sm A (60.5) Nem (73) Isotropic. The phase transition N-SmA is weak first order with transition enthalpy 0.86kJ/mol [17]
- 14P1M7 [18, 19] Isotropic (92.3) SmTGBA (88.2) SmC* (57.7) SmC_{ferri} (47.7) SmC_{anti} (40) Cry

Free-standing films with dimensions 0.1×5 mm^2 were drown in a frame consisting of two brass rails and two movable brass blades. The small films width was important to observe layer-thinning transition in the nematic phase. The experimental set-up enabled simultaneous optical observations and reflectivity measurements in 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

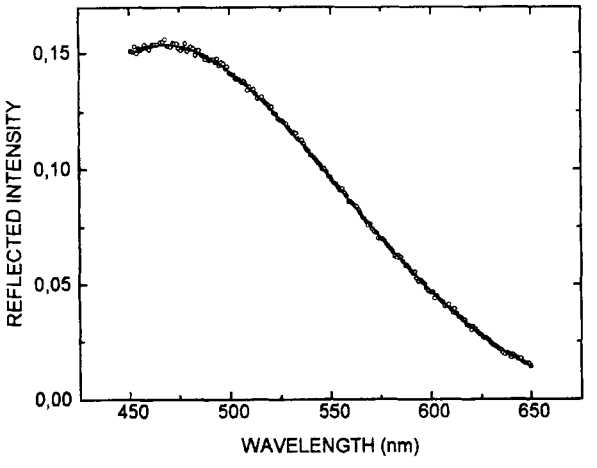

Figure 1: Experimental reflectivity curve for N=92 and T=60.77°C (o) and the best mean square fit according to the eqn. 3 (solid line)(5O.6).

fitted the reflectivity curves by the expression for the light diffraction in a plane parallel plate [20]:

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

where

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

D=N n d is the optical thickness of the whole film, N is the number of layers, n is the refractive index and d is the average interlayer spacing. The applied method allows the exact determination of number of layers in a broad interval of film thicknesses [7]. Figure 1 shows the reflectivity curve of the 93-layer film at T=60.77°C and the least squares fit curve with the eqn.1 which perfectly describes the experimental curve. To study the layer-thinning transition 2-400 layer free standing films were prepared in the SmA phase, the film thickness has been determined and the films were heated with a constant rate 1-3mK/s. SmA - N and SmA - Iso transition temperatures have been determined by changes in the film meniscus (T_c). Above T_c the films with thickness L_1 (L=Nd) did not rupture in the temperature interval of the nematic or isotropic phase up to the temperature $T(L_1)$ ($T(N_1)$) where the thickness spontaneously decreases to some value L_2. The temperature of the film thinning has been determined by microscopic observations with accuracy ±10mK.

At the temperature slightly above $T(L_1)$ the heating has been stoped, 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 SmA interval, a new film was drown and the procedure repeated for some other initial thickness.

3 Results

3.1 Films thinning above SmA - Nematic transition

Figure 2 displays the data L_i versus $T(L_i)=T_{i,max}$ which was found according to the procedure described above for three different initial thicknesses. Interesting feature of figure 2 observed for the first time is that the film thinning starts from microscopic thicknesses of about 200 layers. The stable film thickness decreases by increasing the temperature T(L). The experimental data can be described by the simple power law:

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

where T_0, l_0, ν are fitting parameters. The solid line in this figure shows the best mean square fit with $l_0 = 1.2nm, T_0 = 60.35, \nu = 0.82$. The other important films property

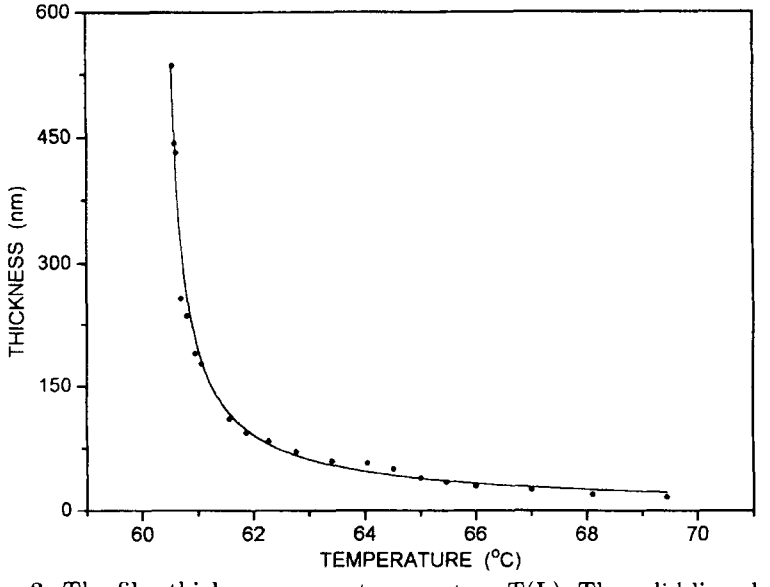

Figure 2: The film thickness versus temperature T(L). The solid line shows the best mean square fit according to eqn.3 (5O.6).

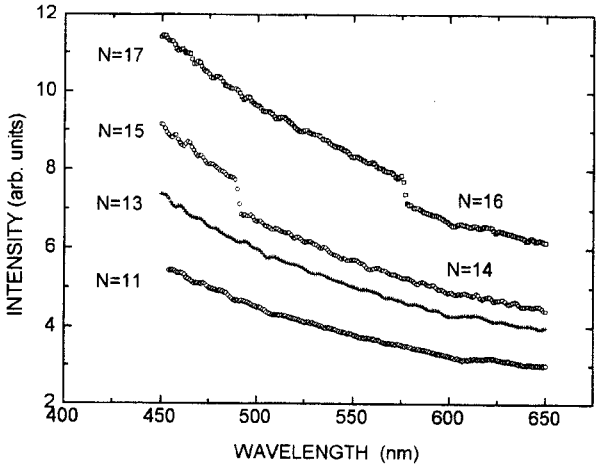

Figure 3: Films reflectivity spectra in the region near the temperature T(N) of the melting of the Nth layer for N=17 (□) and N=15 (○); the temperature was *increased* with the rate 3mK/sec. Spectra of the N=13 film (+) for some *constant* temperature T between T(14) and T(13), the same for N=11 and $T(12) \leq T \leq T(11)$ (◇) (5O.6).

is that they can be drown in the temperature interval of the bulk nematic phase as

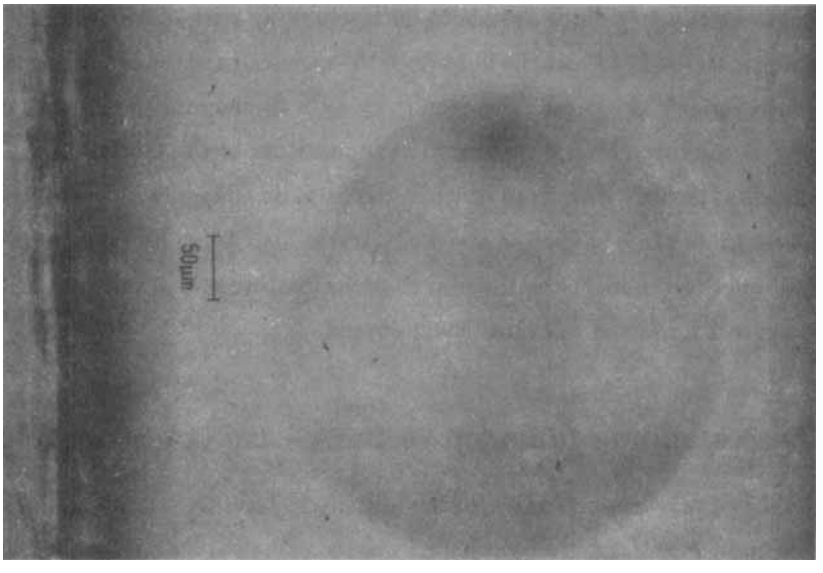

Figure 4: Large nematic droplet on the N=20 film of 5O.6 at a temperature slightly above the SmA - N transition (See Color Plate II).

well. 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) on figure 2. To avoid the ambiguities we have to underline that in the nematic temperature interval we 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 3mK/sec, where T(N) is the maximal temperature of N-layer film stability. The jumps of the intensity on the two upper curves correspond 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 the optical thickness of one layer (D_{min} ≈3.8nm). The N=13 and N=11 curves 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 approximatelly equal to 2.5nm. Figure 4 show a very interesting microscopic observation of the thinning of a very thick film (>400 layers). In this case the films thins spontaneously to a thickness about 20 layers (gray parts of the image). After the thinning material flows into the films from the meniscus and forms a large nematic droplet with variable thickness. The droplet changes its shape with time but can be stable several minites a then disappears in the meniscus or the film breaks. This is the reason why the films with large width in the nematic phase are as a rule unstable. This process takes place only close above the transition. After disappearance of the nematic droplet in the meniscus the film thinning continues in accordance with the curve of figure 2 for initial thickness N=20 layers.

3.2 Free standing films above SmA - Iso transition

Figure 5 shows the reflection spectra of the initially 10-layer free standing film, which was stable up to 95.6°C. Each curve on fig.5 was recordered at a constant temperature between the temperatures of successive thinning transitions and corresponds to a constant number of layers. On heating we observed the layer-by-layer decrease of the film thickness. To find the film thickness we have fitted the diffraction curves by

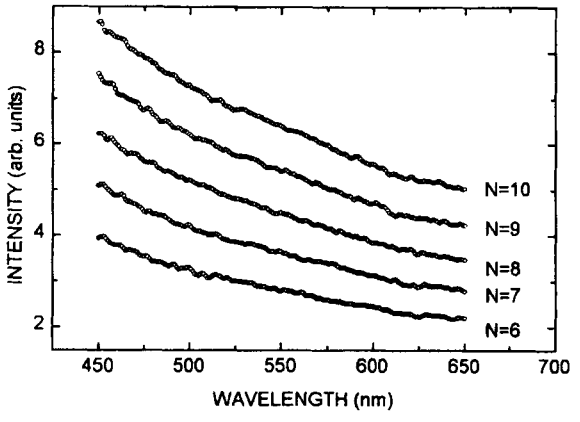

Figure 5: Films reflectivity spectra for N=6-10 films recorded in accordance with procedure described in text (14P1M7).

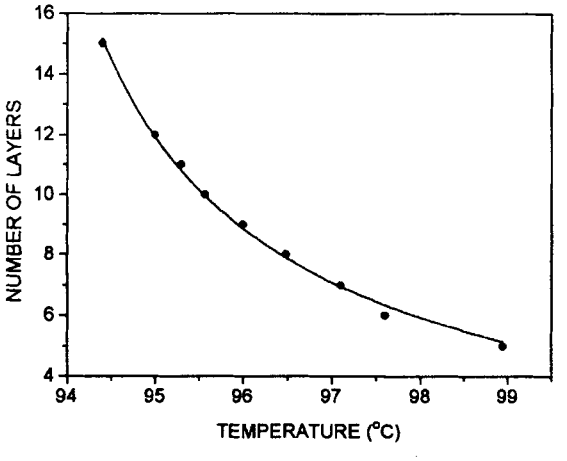

Figure 6: The film thickness versus temperature $T_{max}(N)$. The solid line shows the best mean square fit according to eqn.3 (14P1M7).

the eqn.1. From such measurements we have found that the interlayer spacing for the smectic films at approximatelly 96°C is about 4.4nm. Figure 6 displays the film thickness versus $T_{max}(N)$. The solid line in this figure shows the best mean square fit

with $l_0 = 0.6nm, T_0 = 92.4°C, \nu = 0.9$. Interesting is that free-standing films can be produced in the temperature interval of the *isotropic phase* approximatelly 7 degrees above it. The maximal film thickness which can be obtained in the isotropic liquid at a given temperature is limited. The maximal thickness decreases in a stepwise manner on the increasing temperature in accordance with fig.6.

Figure 7 shows a very interesting observation of the film thinning mechanism. Close above each T(N) small round shaped droplets spontaneously occur in some places on film area. Such droplets show a continuous variation of interference colors and we estimated their thickness to be about $1\mu m$. After the droplets are born, its diameter grows till some maximal value is reached. The droplets are approximatelly equal in size and do not recombine. After some small heating, a step is born, which removes all the droplets on its motion over the whole film area and reduces the thickness by one layer.

3.3 Free standing films above bulk SmA - Nem - Iso transition

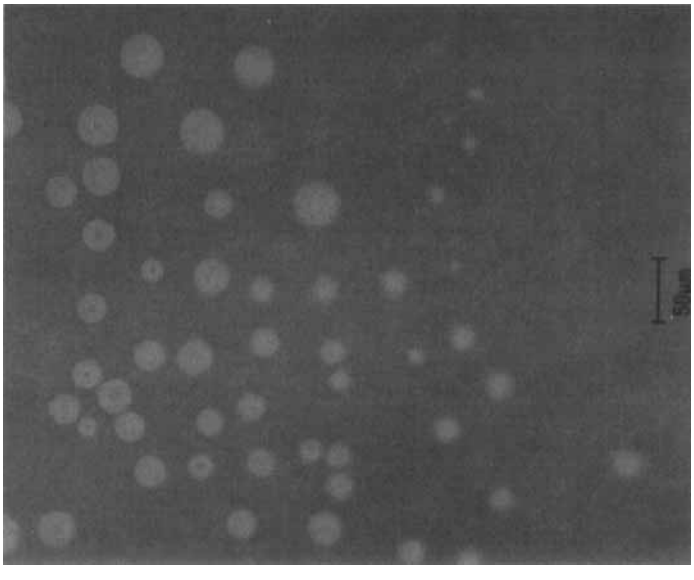

Figure 7: Droplets formation in the isotropic phase inside of a film with N=9, at T=95.74°C (14P1M7).

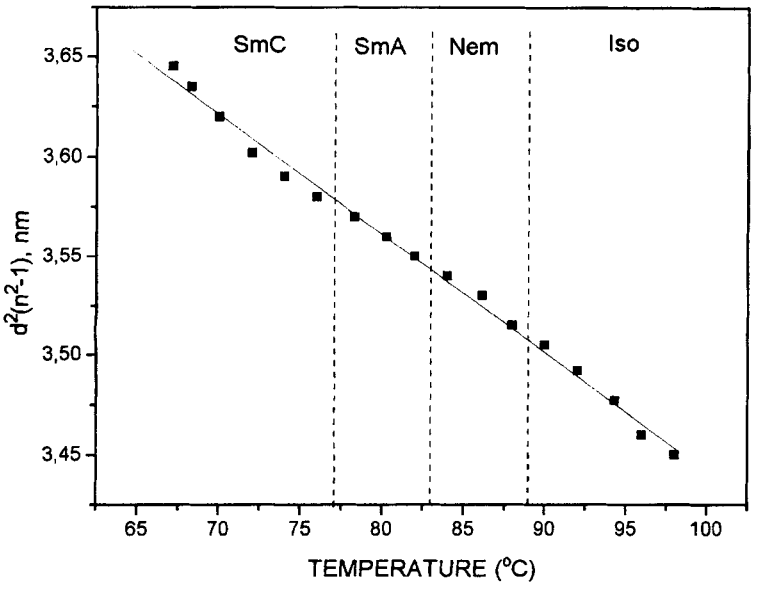

Figure 8: Temperature dependence of the optical thickness per one layer $d(n^2-1)$ for 2-layer film (•) (6O.10).

The SmA - Nem transition in 6O.10 is the second order [16]. The temperature interval of the smectic phase for ultrathin free-standing films is considerably expanded to higher temperatures. The temperature dependence of the optical thickness per one layer $d(n^2-1)$ for 2-layer film is shown in Figure 8. The 2-layer smectic film is stable in the bulk nematic and isotropic temperature intervals up to 104°C. In previous studies, it has been found that boundary layers were tilted near the SmA-SmC transition in the temperature interval of SmA phase [5]. On figure 8, the optical thickness is approximatelly linear function of temperature and no peculiarities are observed at the SmA - C, SmA -N, N-iso transitions. In the case of the bulk SmC phase, the tilt angle increases on heating in thin films below T_{A-C} [5]. The position of the maximum of the X-rays reflectivity curve in the SmC phase can be well described by a function: $d_c(T) = d_A cos\theta_0((T_c - T)/T_c)^\gamma$, where T_c is the Sm-A-Sm-C phase transition temperature and γ is a critical exponent [22], γ=0.3±0.04 [21]. In the isotropic and nematic phase well above the SmA-Nematic transition temperature the position of the broad X-ray diffraction peak corresponds to mean intermolecular distances (2.4nm) and is temperature independent. Consequently, we should expect an increase of the smectic layer spacing, d, with increasing temperature. In contrast

to this expectation, we observed a remarkable decrease of $d(n^2-1)$ with the increase of temperature for ultrathin film in the whole temperature range. This behavior can be attributed to the decrease of the refractive index in ultrathin films on heating and is qualitatively different to the bulk samples of this material [21]. Figure 9 shows the temperature dependence of the reflected intensity from the initially 8-layer film (heating rate is 10mK/s). Universally, we observe that films undergo thinning. The steps correspond to decrease of the film thickness by one or several layers. If the jumps of the intensity correspond to a single layer, the height between successive steps is nearly 3.6nm. Within each step, the reflected intensity is nearly temperature independent. The fluctuations in the reflected intensity combined with spontaneous occurrence of droplets like on figure 7 can be only observed near the transitions between successive states.

4 Discussion

In accordance with the results of [14, 15] it is natural to assume that the smectic A layers occur on the films boundary. It was suggested [12, 13] that the smectic order

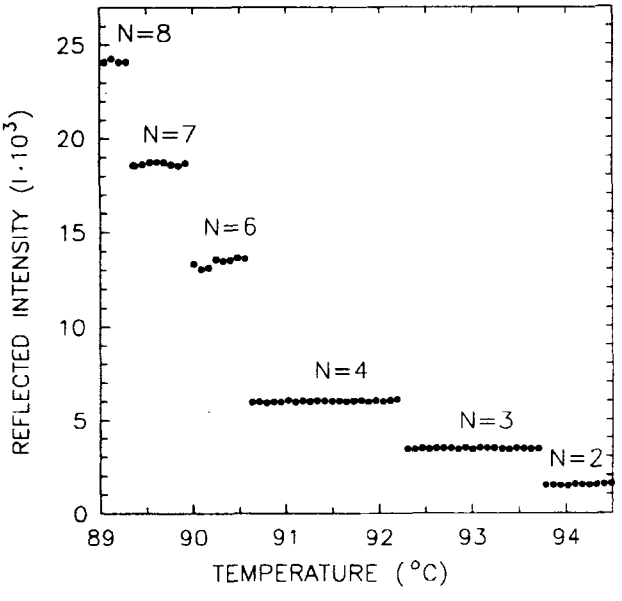

Figure 9: Optical reflectivity above the bulk Sm-A-Nematic transition from the initially 8-layer film, λ=550nm, heating rate 10mK/s (6O.10)

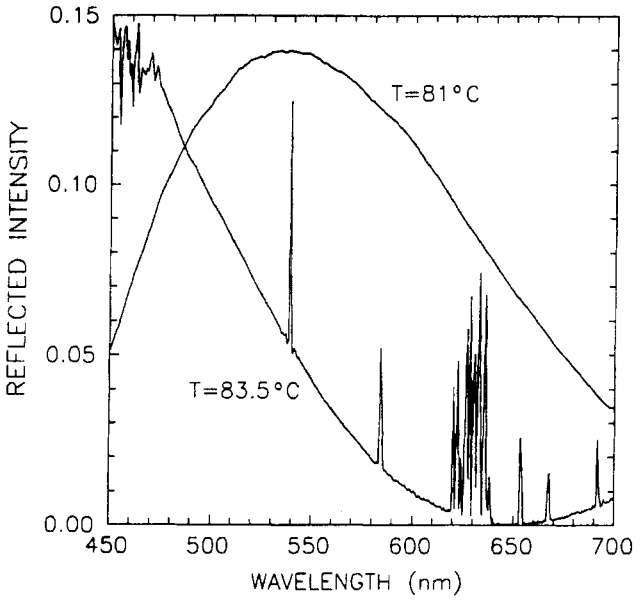

Figure 10: Reflection spectra for the 90 layer (81°C) and 72 layer (83.5°C) films.

was generated by the film-vapor interfaces and was characterized by the penetration length ξ. Free- standing films can be stable in the bulk nematic and isotropic temperature intervals if the film thickness is equal or less than $L_c = 2\xi$. The temperature dependence of the film thickness L_c is related to the temperature dependence of ξ. In the case of thin films the properties of the layer-thinning transitions are in general agreement with previous description [12, 13]. The thinning process takes place via the step motion over the whole film area. Usually, steps are considered as edge dislocations moving in the films interior [1]. Therefore, the step-by-step thinning can be considered as an untrivial melting process of the surface ordered regions taking place in the films interior. The nematic or isotropic phase is formed in the films interior and removed to the meniscus to eliminate the additional contribution to the free energy on the boundary SmA - nematic. This picture correlates with microscopic observations of figure 7. The question which remains open here is very large droplet size. The interference colors show that the droplet diameter is about several hundreeds of nanometers. In [23] a theoretical model was proposed, where this idea was elaborated with more details. The author has developed a mean field model for the layer thinning process and found a qualitative correlation with experiment. The quantitative discrepance of the theory [23] and experiment can indicate that the

mean field theory cannot be applied to describe processes in ultrathin films.

A different behavior can be observed for thick free-standing films. Figure 10 shows the reflectivity curve of 90-layers film of 6O.10 (SmA phase, 81^{0}C). The layer spacing for the bulk sample was d=3.023 nm at 81^{0}C. The film was thermostated in the SmA phase for a long time and then fast heated. At the temperature above the bulk SmA-Nematic transition temperature the heating was stopped and the reflectivity spectrum was measured (Figure 10). Increasing the temperature to 83.5^{0}C results in spontaneous decrease in film thickness to L_2=218 nm (about 72 molecular layers). In 72 layer film a lot of large jumps in the reflected intensity have been registered. This behaviour is qualitatively different with respect to thin films. Direct observations in an inverted optical microscope indicated the presence of nematic-like droplets in thick films moving in the film plane. The jumps of the reflected intensity on figure 10 correspond to the crossing of the light beam by such a droplets. It should be noted that the parts of curve for the wavelengths below and above the jumps correspond to the same thickness. At the temperature 83.5^{0}C, the thickness of an initially 90-layer film is propably more than the critical thickness L_c. This film becomes thinner as its interior layers undergo the SmA-Nematic transition and the nematic phase forms droplets (see figure 7). The difference of figure 10 to the figure 7 is that in the later case we observed the small droplets close above the thinning transition and the jumps on the figure 10 correspond to the droplets below the transition. It is interesting that these droplets do not thin or thick the free-standing film when moving in the plane of the film. After the droplets disappear in the meniscus at the edges of the film plate, the smectic surface becomes uniform. Another type of instability was observed in 6O.10 films thicker then 120 layers. Significant changes of the reflected intensity were observed in such films on heating well above the bulk SmA-Nematic transition temperature. Below the bulk SmA-Nematic transition temperature the reflected intensity, and, consequently, the film thickness, was constant. When we increase the temperature well above the SmA-Nematic transition, chaotic change of the reflected intensity can be observed. The rate of this change depends on the temperature. In Figure 11, the broken line indicates the reflected intensity versus time for the smectic film consisting from about 135 layers (L=409nm, λ=550nm, 81^{0}C). This effect is most pronounced above the bulk Nematic-Isotropic transition temperature (solid line, Figure 11). The curve was recorded at fixed temperature

from a part of the sample with dimensions $50 \times 50\mu$m. The time dependence of the reflected intensity suggests a continuous change of the film thickness. Direct observation in an inverted microscope reveals that the whole film is drastically perturbed. The material becomes very mobile and moves from the meniscus into the plane of the film. This phenomena is analogous to the observation of figure 4. The velocity of this flow can change over a wide range. Chaotic motion leads to the change of the color of different parts of the film (from blue to red) and change of the reflected intensity. In this case, there are no individual droplets and unstable behaviour is observed over the entire film. The change of the color and reflected intensity correspond to the change of the thickness in several times. Such a chaotic behaviour can be observed for a long time (>10min). Note that in the case of the layer-by-layer thinning transitions in thin films the layers drain out of the film for a very short time (<0.1s). Once an excess of the material has moved to the bulk reservoir through the meniscus, the film becomes uniform. The thickness of this film, as a rule, corresponds to the critical thickness L_c. After that the free-standing films thin through the layer-by-layer transitions as the temperature is increased.

The layer thinning above SmA - Nem and SmA - iso phase transitions have

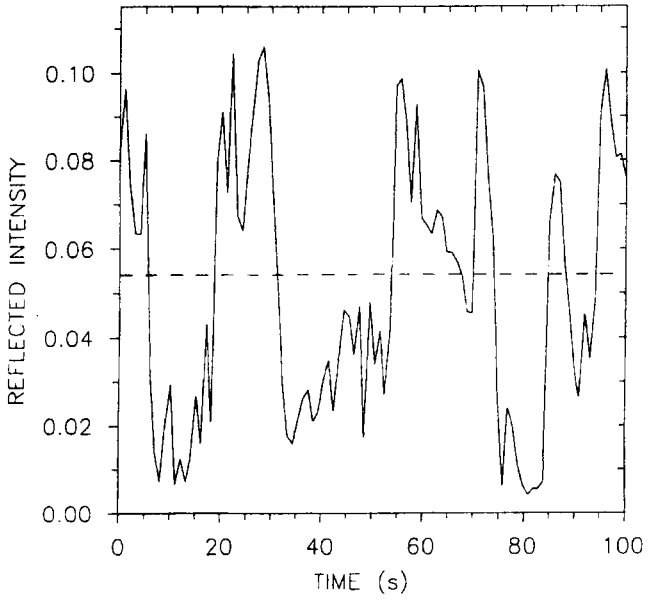

Figure 11: Reflected intensities versus time for the free-standing film at 81°C (broken line, $N \approx 135$) and at 90°C (solid line) (6O.10).

many similarities inspite of different nature of these transitions. The film thickness is a power law function of temperature with exponent $\nu \approx 0.8 \pm 0.1$. The value $(T^* - T_c) \approx 0$ which is typical for the second order phase transitions. The SmA-N transition in 5O.6 is weakly first order. This could explain the small value of difference $(\Delta T = T_c - T_0 \approx 0.15^\circ C)$ found from fitting on figure 3. From this point of view the value of ΔT for the phase transition SmA - isotropic should be essentially larger which contradicts to the results of [12] and this work. These features demonstrate that the layer thinning transition is probably determined by properties of the surface liquid crystal-air and is independent on the nature of the phase transitions in bulk.

Several problems are not clear in the framework of this qualitative description. The critical behaviour of the surface penetration length is determined by the type of the surface and the type of intermolecular interaction [24] - [26]. Because the smectic layers are parallel to the free surface we can assume that the surface is smooth. In this case the *Van-der Waals long range interaction would give the exponent 1/3, the Kasimir long range forces give 1/2.* The exponent 0.8 does not correspond to these potentials. This value could mean that we deal with a new type of long range intermolecular interaction in the system.

In the case of SmA - Nem - Iso phase sequence power law description was not applicable for the temperature dependence of the film thickness. This could be explained by possibility of some phase transition on the boundary. But this is practically excluded by the result of figure 8 where the temperature dependence of the optical thickness per one layer in a 2-layer film is shown. This dependence indicated no phase transitions. All these contradictions show that additional experimental and theoretical efforts are necessary to understand the nature of the layer-thinning transition.

Acknowledgements. The authors are grateful to Prof. J. Goodby and Dr. A. Slaney (University of Hull, UK) for the 14P1M7; to C.C. Huang for the discussions. The Deutsche Forschungsgemeinschaft (Germany), INTAS program of the EU (Project 94 -4078) and Russian Foundation for Fundamental Research (Project 95 -02 -05343-a) are acknowledged for the financial support.

References

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

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

[3] E.B. Sirota, P.S. Pershan, S. Amador and L.B. Sorensen, Phys. Rev. **A35**, 2283 (1987).

[4] E.B. Sirota, P.S. Pershan, L.B. Sorensen and J. Collett, Phys. Rev **A36**, 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] E.I. Demikhov, Mol. Cryst. and Liq. Cryst. **265**, 403 (1995)

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

[10] E.I. Demikhov and S.A. Pikin, JETP Lett. **61**, 686, (1995).

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

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

[13] E.I. Demikhov, V.K. Dolganov and K.P. Meletov, Phys. Rev. E **52**, 1285 (1995)

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

[15] B.M. Osko, A. Braslau, P.S. Pershan, J. Als-Nielsen and M. Deutsch, Phys. Rev. Lett. **57** (1986) 94.

[16] M.A. Anisimov, V.P. Voronov, A.O. Kulkov and F. Kholmurodov, J. Physique 46 (1985) 2137.

[17] G. Pelzl, private communication.

[18] J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak and J.S. Patel, J. Am. Chem. Soc. **111**, 8119 (1989).

[19] A. Slaney, private communication.

[20] M.Born and E.Wolf, Principles of Optics, Pergamon Press (1980), chapter 7.6, 327.

[21] V.K. Dolganov, E.I. Demikhov, R. Fouret and C. Gors, in press.

[22] P.G. De Gennes, C. R. Acad. Sci. Ser. B 274 (1972) 785.

[23] L.V.Mirantsev, Phys. Lett. A 205 (1995) 412.

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

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

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