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Thickening of a smectic membrane in an evanescent X-ray beam

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Abstract. We report an unusual thickening of smectic membranes under the influence of X-ray irradiation below the critical angle. In the case of a four-layer film the thickness was found to grow at the footprint of the beam, reaching within minutes tens of layers. The effect is attributed to the localized energy dissipation of the evanescent wave. The "island" thus created is not connected to the meniscus and after the beam is switched off the film returns to its original state. A possible explanation is given in terms of a local disrupture of the tension of the smectic membrane.

PACS. 61.30.-v Liquid crystals – 61.30.Hn Surface phenomena: alignment, anchoring, anchoring transitions, surface-induced layering, surface-induced ordering, wetting, prewetting transitions, and wetting transitions – 52.25.Os Emission, absorption, and scattering of electromagnetic radiation

In grazing incidence diffraction an X-ray beam is incident on a surface at a small glancing angle $\alpha < \alpha_c$, where α_c is the critical angle for total external reflection. Under these conditions only an evanescent wave propagates along the film-air interface with an intensity exponentially decaying with depth. This penetration depth of the X-rays depends on α and can be as low as 5–10 nm ($1/e$ value), allowing to probe surface-induced ordering [1,2]. We have applied this technique to smectic-A (Sm-A) membranes consisting of a liquid crystal suspended over an opening in a solid frame [3]. Such smectic membranes can be described as stacks of liquid layers. They have a high degree of uniformity and a controlled thickness ranging from two to over thousands of layers [4,5]. Quite unexpectedly, we observed that these membranes can become unstable under irradiation at glancing angles below α_c. The film thickness grows at the footprint of the beam and can reach in a few tens of minutes hundreds of layers ($\gtrsim 0.5$ μm). In this paper we discuss the conditions under which this remarkable effect occurs and give a possible explanation in terms of local heating at one side of the smectic membrane and disruption of its tension.

Measurements were done on the compound N-(4-*n*-butoxybenzilidene)-4-*n*-octylaniline, abbreviated as 4O.8, obtained from Aldrich and purified via several recrystallization steps. In bulk it shows the following phase sequence (temperatures in °C): Cr-B 48.5 Sm-A 63.5 N 78 I, where Cr-B, N and I stand for the crystal-B, nematic and isotropic phase, respectively. Smectic membranes varying from 3 to 80 layers were drawn in the Sm-A phase on large-size holders. These were made in stainless steel or brass and have either a rectangular (10×60 mm^2) or a circular (50 mm diameter) hole with sharp edges. The films were equilibrated and investigated around 50 °C in an evacuated two-stage oven [6]. The experiments were carried out at the undulator beamline BW2 of Hasylab (DESY, Hamburg, Germany) at an energy of 7 keV (wavelength $\lambda = 0.177$ nm). The wave-vector transfer is given by $\mathbf{q} = \mathbf{k}_{\rm out} - \mathbf{k}_{\rm in}$, in which $\mathbf{k}_{\rm out}$ and $\mathbf{k}_{\rm in}$ are the outgoing an incoming wave vector, respectively, and $q = |\mathbf{q}| = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle. The experimental resolution was set by slits to $\Delta q_z = 0.03$ nm^{-1} (full width at half maximum) in the scattering plane and to $\Delta q_y = 0.03$ nm^{-1} in the out-of-scattering plane. In this situation the incident intensity is given by $I_0 \simeq 4 \times 10^{11}$ photons/s. Specular scans along the surface normal q_z allowed us to determine the number of layers in each film from the interference oscillations (Kiessig fringes).

We observed that 4O.8 membranes thicken under the influence of X-ray irradiation below the critical angle $\alpha_c \simeq 0.18°$. For example, the thickness of a four-layer film was found to grow at (and only at) the footprint of the beam, reaching within minutes many tens of layers. This can be seen even by eye due to the appearance of interference colors along the footprint area. The thick island thus formed is not connected to the meniscus and the surrounding area keeps the original thickness as schematically drawn in Figure 1. The necessary material for the thicker part must be provided by the meniscus and can only flow via the smectic layers of the original film. We

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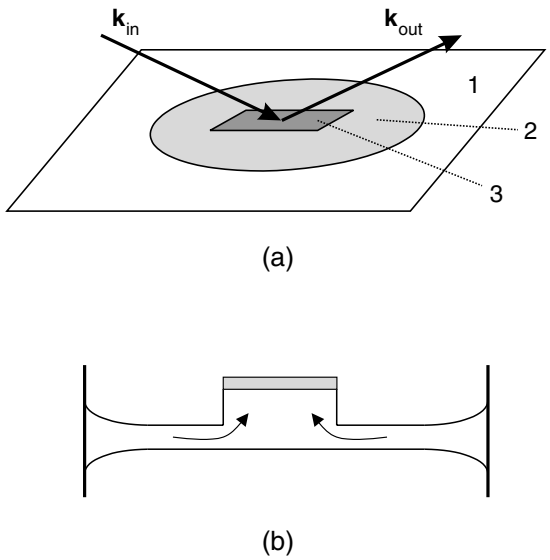

Fig. 1. Thickening of a smectic membrane under irradiation. (a) Schematic overview: 1, film holder; 2, smectic membrane; 3, thick part at the footprint of the beam. (b) Sketch of the growth of the thicker region. The grey area represents a nematic or isotropic phase, the arrows indicate flow of material from the meniscus.

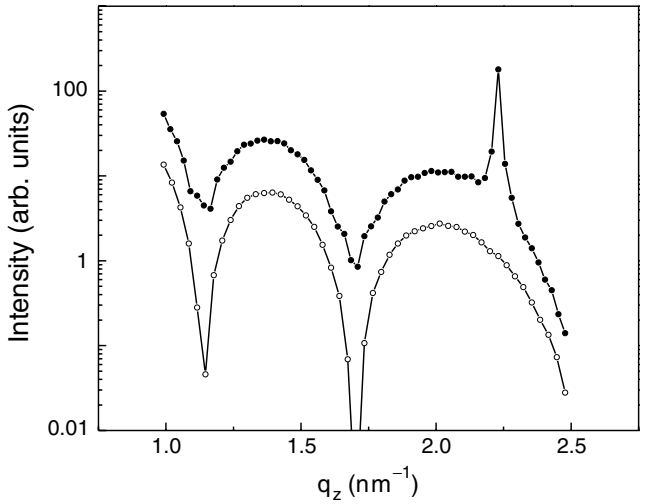

Fig. 2. X-ray reflectivity of a four-layer smectic 4O.8 membrane before (open circles) and directly after thickening (dots). The curves have been shifted for clarity.

emphasize that for incoming angles $\alpha > \alpha_c$ the thickening does not occur and the film remains stable. This is a crucial observation suggesting strongly that the dissipation of energy by the evanescent wave in a thin surface layer might be responsible for the thickening. The effect is quite general and has also been observed in membranes of other compounds. The process is not irreversible like the radiation damage observed in many polymer and liquid films under high-flux synchrotron irradiation. After the illumination is switched off the footprint "island" slowly breaks up. A typical reflectivity curve measured in this situation is displayed in Figure 2. The curve has the typical feature of broad Kiessig fringes corresponding to a thin film, with on top a Bragg peak at $q_0 \simeq 2.2$ nm^{-1} from the thicker part of the footprint ($q_0 = 2\pi/d$, where d is the layer spacing). The Bragg peak has a narrow width reflecting the large thickness of the area from which it originates. Finally, with time the various thick parts disappear in the meniscus and the film returns to its initial state. The only difference in the thickening of thin membranes (three or four layers) and thicker ones (tens of layers) is that the latter need more time to thicken.

Since the early work of Pieranski *et al.* [7] the (meta)stability of smectic membranes has been discussed by several authors [8–10]. As is well known, across a flat liquid interface in equilibrium no pressure difference can exist. This is not true anymore for a smectic surface because the layers are elastic and can support a normal stress that will equilibrate any small pressure difference $\Delta p = p_{\rm air} - p_{\rm sm}$. In addition to the surface tension γ this pressure difference contributes to the tension Γ along the smectic membrane:

$$\Gamma = 2\gamma + \Delta p\, L\,, \qquad (1)$$

where $L = Nd$ is the thickness of the film. The contribution of the stress to Δp depends on the shape of the meniscus between the membrane and its support. For relatively thick films the meniscus has a circular profile of radius of curvature R, which matches tangentially the free surface of the membrane. The value of R fixes the pressure difference inside both the meniscus and the film via $\Delta p = \gamma/R$, which is of the order of 10–100 N/m^2. The thickness of smectic membranes can be modified by variation of Γ by nucleation of edge-dislocation loops [8, 9]. Application of a local heat pulse, which brings the membrane locally close to a phase transition to the nematic or isotropic phase, can generate such an elementary loop. Subsequently, the size of the loop increases or decreases depending on the initial radius. This behavior is related to the phenomenon of thinning transitions. This refers to the effect that smectic membranes can be heated above the bulk smectic disordering temperature without immediately rupturing, and instead undergo successive layer-by-layer thinning transitions as the temperature is increased [11–13]. Thinning transitions have been found rather systematically at the Sm-A–isotropic transition of fluorinated mesogens, as well as at the Sm-A–nematic phase transition of certain mesogens [14,15].

Let us consider in some detail the X-ray absorption of a four-layer smectic membrane (thickness say $D = 10$ nm) around the critical angle. In the transmission regime $\alpha > \alpha_c$, an X-ray beam passes through the film along a trajectory with a length $D/\sin\alpha \simeq 3$ μm (taking $\alpha = 0.2°$). The absorption of hydrocarbons over this length is about 0.15% of $I_0 \simeq 4 \times 10^{11}$ photons/s, which amounts to 6×10^8 photons/s. At 7 keV this is equivalent to about 7×10^{-7} W. For an incident beam of width W (say 50 μm) and height H (say 2 mm) perpendicular to the scattering plane, the absorption takes place in a volume $V = (D/\sin\alpha)WH \simeq 3 \times 10^{-4}$ mm^3. For a density $\rho = 10^3$ kg/m^3 and a specific heat of 2×10^3 J/(kg °C), this leads to an increase of the initial temperature in the

illuminated volume of the order of 1 °C/s. The absorption volume is imbedded in the membrane and the heat is expected to spread out easily through the film by conduction. Across the thickness of the film the heat transfer will be fast. As the membranes are kept in vacuum, the lateral route will be the main pathway to get rid of the heat. In standard reflectivity scans around the Bragg angle of about 1.8°, the average absorption will be an order of magnitude less and in practice no influence of the absorption is observed.

The situation $\alpha \lesssim \alpha_c$ differs in two aspects from the previous case. First, at $\alpha \simeq \alpha_c$ the transmitted intensity is about a factor four higher due to constructive interference of the reflected and transmitted waves [16]. Second and even more importantly, below the critical angle the intensity of the evanescent wave decays exponentially. At $\alpha \simeq 0.8\alpha_c$ the evanescent wave typically penetrates over $L_e \simeq 6$ nm ($1/e$ decay length), which corresponds to the top two layers only. Taking again $W \simeq 50$ μm the incident beam propagates along the footprint $W/\sin\alpha \simeq 20$ mm. Consequently, the evanescent wave is approximately dissipated in a volume $V_e = (W/\sin\alpha)L_eH \simeq 2 \times 10^{-4}$ mm^3. Taking the difference in the absorbed intensity and volume into account, the total heat yield will be about six times more than in the case of the fully transmitted wave. This leads to an increase of the initial temperature in the smectic top layers of the order of 6 °C/s. Again the final temperature will be determined by the balance between heat accumulation in time and heat conduction away from the absorption volume. However, the absorption volume is now concentrated at one side of the membrane and as long as heat is supplied necessary a temperature gradient will exist across the film. This gradient must be small because heat conduction across the (thin) membrane is fast. Locally, a transition to a nematic or isotropic phase could be reached. We note that in a different context stable nematic and isotropic "droplets" have been reported in smectic membranes [17,18].

The observations leave us with a dilemma. As the thickening occurs only for $\alpha \lesssim \alpha_c$ the asymmetry associated with the evanescent wave should play a role. On the other hand, heat conduction is fast and any temperature gradient across the film can only be small. Let us nevertheless speculate on a possible mechanism. If due to the temperature increase the smectic layering at the top membrane surface disappears, it cannot support a pressure difference anymore. Because of the local absence of a restoring stress at the footprint of the beam, the pressure difference will push smectic material out of the membrane. In this new situation the volume in which the heat is dissipated moves up with the elevated material. As a result a chain reaction is triggered off in which more and more material is pushed out of the footprint area, which is supplied by the meniscus via transportation through the smectic layers of the original film. As any temperature gradient across the film must be small, at the footprint area initially the whole membrane could reach the nematic or isotropic phase. In that situation thickening occurs at both sides. However, as the membrane gets thicker the localization of the evanescent wave in the elevated area becomes more important while in this region also lateral heat transport becomes more difficult. As a result the symmetry of the film thickening will be broken and the bottom interface becomes gradually much less involved in the process. The absence of thickening above the critical angle necessarily imposes such an asymmetry.

The equilibrium thickness of the film with N_{eq} additional layers in the elevated area can be crudely estimated as follows. According to equation (1) the change of the membrane tension due to melting of say two top layers is given by $\Delta\Gamma = 2d\Delta p$. The corresponding decrease of the surface energy in a footprint area S is $2d\Delta pS$. In the elevated region the line tension associated with N_{eq} additional layers should compensate for this decrease (Fig. 1b). If P is the perimeter of the footprint, the corresponding gain in the surface energy is given by $N_{eq}dP\gamma$. Thus, the number of additional layers can be estimated as $N_{eq} = 2\Delta pS/(P\gamma)$. For typical values $\gamma \simeq 0.02$ N/m, $\Delta p \simeq 100$ N/m^2, $S \simeq 40$ mm^2 and $P \simeq 40$ mm, we arrive at $N_{eq} \simeq 10$, which is the right order of magnitude.

Though the idea of a local absence of stress leading to mass transport is appealing and accounts well for the observed effect, several questions remain open. The role of heat conduction, normal to the membrane as well as along the large dimensions of the system towards the meniscus, has not been incorporated. Evidently, also several questions are associated with the various time scales involved and the role of the dynamics of the whole process. A prime experiment would be to measure optically *in situ* the time dependence of the thickening. Such an experiment —which is not planned anymore— could also throw light on the precise mechanism of the thickness growing, which likely involves the energy of generating dislocation loops. In this context, we note that the dynamic behavior of dislocation loops in smectic membranes is strongly coupled via dissipation in the meniscus [19].

In conclusion, we have observed a remarkable thickening of smectic membranes over the footprint of a synchrotron X-ray beam incident below the critical angle of total reflection. This effect is attributed to local heating due to absorption of the evanescent wave at one side of the membrane. This is a unique situation of asymmetric heating that cannot be accomplished otherwise, and can cause a phase transition to a nematic or isotropic phase in the top layers of the film and possibly, initially, in the whole film. As a result, locally, the pressure difference over the smectic membrane is not supported anymore by an elastic stress of smectic layers, triggering off a chain reaction of material flow.

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