Two-Stage surface freezing of a single top layer in a smectic-*A* membrane

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The crystallization of a single liquid top layer of smectic membranes of the compound 4O.8 has been studied with grazing-incidence x-ray diffraction. As this process takes place in two steps, involving an intermediate hexatic smectic-*B* layer before the final crystalline-*B* surface structure is reached, it provides a model for melting in two dimensions. The positional order has been investigated quantitatively by measuring the scattering profiles and the associated correlation lengths. The surface liquid-hexatic phase transition is found to be continuous, while the hexatic-crystal transition is weakly first order with an abrupt change of the in-plane positional correlations. The surface phase transitions do not modify the liquid in-plane structure of the interior layers.

Melting in two dimensions remains one of the unresolved and challenging problems in condensed matter physics. Berezinskii [1] and Kosterlitz and Thouless [2] proposed a theory for transitions in *XY* models, based on topological defects. Two-dimensional (2D) crystallization belongs to the same universality class, and the relevant topological point defects are dislocations and disclinations. The theory of defect-mediated melting of 2D crystals was generalized by Halperin and Nelson [3] and Young [4]. They found that the dissociation of dislocation pairs produces an anisotropic (hexatic) liquid. The 2D hexatic phase is characterized by a quasi-long-range bond-orientational order, while the positional order is short range and the shear modulus is zero. Only after subsequent disclination unbinding is an isotropic phase realized. Phases with hexatic order have been found in several systems, such as electrons at the surface of helium, charged polymer colloids, and smectic liquid crystals [5–8]. However, the mere existence of an hexatic phase does not provide a proof of a specific melting mechanism, and the origin of hexatic order and its relation to defect-mediated melting transitions is still controversial. Smectic liquid crystals are particularly suitable to investigate these problems, as they can be suspended over an opening in a solid frame. Such smectic membranes have a controlled thickness ranging from two to over thousands of layers [8], which allows to study a crossover of the phase transitions from 3D behavior in thick films to 2D behavior in thin ones.

Smectic-*A* (Sm-*A*) membranes can be described as stacks of liquid layers. Upon cooling an hexatic Sm-*B* phase may occur, which shows a long-range bond-orientational order, while the positional order is limited to a finite correlation length. Additionally, at lower temperatures a 3D crystalline-*B* phase (Cr-*B*) may be found with an hexagonal in-plane lattice and a weak coupling between the crystalline layers. We want to concentrate on these orthogonal phases using

N-(4-n-butoxybenzilidene)-4-n-octylaniline (abbreviated as 4O.8), which compound possesses in the bulk a first-order transition from the Sm-*A* to the Cr-*B* phase at 48.5 °C. However, early mechanical studies on 4O.8 membranes [9], followed by heat-capacity and optical reflectivity measurements [10], indicated a whole cascade of phase transitions. Subsequently, transmission electron diffraction [11] provided an evidence that the Sm-*A* phase proceeds into the Cr-*B* phase in a layer-by-layer fashion involving an intermediate hexatic Sm-*B* phase that does not exists in the bulk. Further x-ray reflectivity studies [12] revealed clear changes in the layer-displacement fluctuation profile across the film in dependence of the various crystallization steps. Conformal fluctuations throughout the membrane provide an explanation of the epitaxy of the Cr-*B* lattices of the outermost surface layers [11] that occurs in spite of the intermediate liquid layers. With decreasing temperature the surface layers undergo transitions (in °C) Sm-*A* 61.1 Sm-*B* 54.5 Cr-*B*, well before the second set of layers start their own freezing transitions at 51.1 °C. Hence, the top layer at each side of the membrane may serve as a perfect model system to study crystallization of a liquid in 2D. Earlier electron diffraction gave rather ambiguous results [13]: At the liquid-hexatic transition a jump in the positional order was reported without any attendant change in the hexatic order. The latter ordering was found to develop only at 3 °C below the phase transition. In this paper we report results of high-resolution grazing-incidence x-ray diffraction (GIXD) on such a membrane that provide full quantitative information on the positional ordering in the single top layers during the two-stage melting process. Contrary to the results from electron diffraction, the surface liquid-hexatic phase transition is found to be continuous. In addition, the hexatic-crystal transition is weakly first order with an abrupt change of the in-plane positional correlations.

The compound 4O.8 was obtained from Aldrich and was purified additionally via several recrystallization steps. Smectic membranes varying from 3 to 80 layers were drawn in the Sm-*A* phase and then cooled into phases with hexatic or crystalline surface order. Special large-size holders were
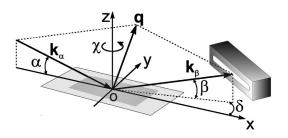
FIG. 1. Scattering geometry with linear detector. The incident plane is defined by $\mathbf{k}_\alpha$ and the surface normal Oz, the scattering plane by $\mathbf{k}_\alpha$ and $\mathbf{k}_\beta$.

made in stainless steel or brass, with either rectangular (10×60 mm^2) or circular (50 mm diameter) holes with sharp edges.

In GIXD the x-ray beam is incident on the surface at a small glancing angle α. For $\alpha < \alpha_c$, the critical angle of total reflection, only an evanescent wave penetrates into the film. The wave-vector transfer is given by $\mathbf{q} = \mathbf{k}_\beta - \mathbf{k}_\alpha$, where $\mathbf{k}_\beta$ and $\mathbf{k}_\alpha$ are the outgoing and incoming wave vectors, respectively (see Fig. 1). The scattered radiation is measured at various in-plane and normal components of $\mathbf{q} = (\mathbf{q}_\perp, q_z)$, thus detecting any in-plane periodicity in dependence of the penetration depth of the x rays [14]. In the situation $\alpha > \alpha_c$, GIXD can still be performed, but depth resolution is lost, because the x-ray beam is transmitted. The films were mounted vertically at beamline ID10B of the ESRF (Grenoble, France), and illuminated with 8 keV radiation selected by a diamond(111) monochromator. The beam was focused in the horizontal plane to about 24 μm. A linear position-sensitive detector was mounted vertically at a distance of 0.5 m from the sample, thus catching in a single shot the line shape associated with the in-plane positional ordering. The films were routinely characterized by x-ray reflectivity, which showed a Bragg peak from the smectic layering at $q_{z0} = 2\pi/d \simeq 2.2$ nm^{-1}. The mosaic distribution of the smectic layer normal was typically about 0.01° as measured from rocking curves. For GIXD the angle of incidence and the exit angle were symmetrically set at 0.6°, corresponding to a fixed momentum transfer of q_z

$\simeq 0.85$ nm^{-1} and a footprint of about 2×0.25 mm^2 ($H \times V$). As this value is well above α_c, the in-plane structure of all layers was measured. We were forced to this choice because early trial experiments at beamline BW2 of HASYLAB (Hamburg, Germany) at $0.8\alpha_c$ lead to thickening instabilities of the smectic membrane [15]. To monitor any mosaicity variations in the top layers, the film was rotated about its layer normal (χ scans), as indicated in Fig. 1. The resolution function was close to a Gaussian with $\Delta q_\perp = 0.039$ nm^{-1} (FWHM), giving rise to a spatial resolution $2\pi/\Delta q_\perp \simeq 160$ nm. This corresponds to the profile of the direct beam and also to the width of a Bragg reflection from a fully Cr-B membrane. All data were background corrected by subtracting the corresponding measurement of an empty sample holder.

Figure 2 shows for a seven-layer film the diffraction peak at $q_{\perp 0} \simeq 14.3$ nm^{-1}, corresponding to a local in-plane hexagonal packing with $a = 4\pi q_{\perp 0}/\sqrt{3} \simeq 0.51$ nm. Our trial experiments at HASYLAB, probing approximately the two outer top layers only, indicate an in-plane diffraction peak at the same position. This proves explicitly that the crystallization starts indeed at the surfaces of the membrane. Figure 2(b) indicates the general feature of the scans: A relatively narrow diffraction peak originating from the outermost hexatic Sm-B layers on top of a broad liquid peak from the "substrate" of five interior Sm-A layers. The integrated intensity I_{surf} of the former part is independent of the membrane thickness, while I_{int} of the latter part scales linearly with the number of liquid interior layers. For each film thickness, this puts a constraint on the ratio I_{surf}/I_{int}. Intensity modulations in χ scans did not exceed 10%, indicating a mosaic average over the footprint of the beam. Fits were made using the sum of a Lorentzian to represent the interior liquid layers

$$S(q_\perp) \sim [(q_\perp - q_{\perp 0})^2 + \kappa^2]^{-1}, \qquad (1)$$

and a square-root Lorentzian to describe the surface hexatic contribution

$$S(q_\perp) \sim [(q_\perp - q_{\perp 0})^2 + \kappa^2]^{-1/2}. \qquad (2)$$
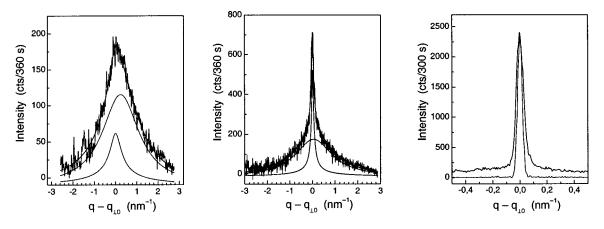

FIG. 2. X-ray scattering profiles from the in-plane hexagonal ordering of a seven-layer 4O.8 membrane. (a) 62.0 °C, Sm-A phase and (b) 60.0 °C, hexatic Sm-B surface layer. Solid lines are fits to the sum of a Lorentzian and a square-root Lorentzian. (c) 52.5 °C, Cr-B top layer, with lower curve as the instrumental resolution.
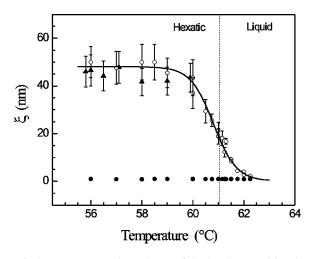
FIG. 3. Temperature dependence of the in-plane positional correlation lengths in 4O.8 membranes. Single hexatic surface layers for a seven-layer membrane (open circles) and for a 43-layer membrane (triangles); (filled circles) interior liquid layers for the seven-layer membrane.

Here $\kappa = \xi^{-1}$ is an inverse correlation length. The structure factor of Eq. (1) is typical for conventional 3D and 2D liquids and several other disordered systems. The form of Eq. (2) arises from coupling between the liquid density and the fluctuations of the bond-orientational order parameter, and was successfully used before to describe the radial line shapes [16–18]. In fact, the measured intensity is a convolution of $S(q_\perp)$ and the resolution function $R(q_\perp)$ of the diffractometer. As a 2D Fourier transformation of Eq. (2) gives $S(r_\perp) = r_\perp^{-1} \exp(-\kappa r_\perp)$, the folding theorem can be used to calculate the experimental scattering profile as

$$I(q_\perp) \sim 2\pi \int S(r_\perp) R(r_\perp) J_o(q_\perp r_\perp) r_\perp dr_\perp . \qquad (3)$$

Here $R(r_\perp) = \exp[-r_\perp^2 (\Delta q_\perp)^2/2]$ is the Fourier transform of $R(q_\perp)$ and $J_o(q_\perp r_\perp)$ is the Bessel function of zero order. The combination of Eqs. (2) and (3) for the scattering from the surface Sm-B ordering and Eq. (1) for the liquid layers, together with the integrated intensities constraints, provides a good fit to the data over the entire temperature range of the top-layer Sm-B phase. This yields the temperature dependence of ξ shown in Fig. 3. The Lorentzian width of the interior Sm-A layers corresponds to in-plane positional correlations of about 1 nm and is independent of temperature. Evidently, the interactions between the freezing outermost layers and the liquid interior "substrate" layers are very small.

With decreasing temperature the positional correlation length ξ of the top layers increases between 62.5 °C and 60 °C continuously from about 2.5 nm to more than 40 nm, and then saturates at lower temperatures. Clearly a pretransitional growth of ξ is present above the hexatic-isotropic transition at T_i. Such a behavior implies large hexatic fluctuations that couple to the density fluctuations, causing the x-ray scattering to become singular at T_i [19]. Such a critical behavior in the x-ray structure factor has also been observed

in thick membranes of the compounds 65OBC [20] and 46OBC [16], that exhibit a Sm-A-Sm-B transition through the whole film. We did not observe any thermal hysteresis in the hexatic linewidth, which indicates that the hexatic-isotropic transition in a 4O.8 surface layer is second order. These results are in strong contradiction to the 4O.8 data from electron diffraction [13]. Our results support similar conclusions from multilayer membranes of tilted hexatics [6], and are in agreement with ac-heat-capacity measurements in an eight-layer 4O.8 film [10]. These indicate that the Sm-A-Sm-B transition in the outermost layer is continuous with a divergent, nearly symmetric specific heat anomaly. We conclude that the grazing-incidence x-ray diffraction results for the isotropic-hexatic transition in a 4O.8 top layer are in qualitative agreement with defect-mediated theory. On the other hand, the observed singular behavior in the specific heat contradicts this theory, which predicts only a broad bump at the high-temperature side of the transition.

Hexatic ordering in thin hexatic membranes has been studied extensively by electron diffraction [21,22]. For several degrees below the liquid-hexatic transition, the surface layers of thin 4O.8 membranes showed no sixfold modulation of the scattering intensity in the $q_\perp$ plane [13]. Electron diffraction of one- and two-layer films suffers from the same problem [22]. As possible explanation an intermediate phase between isotropic and hexatic Sm-B was suggested. Our results for the positional ordering in Fig. 3 do not indicate anything special in this region. We assume that the absence of a modulation in the electron diffraction is due to the occurrence of multiple hexatic domains of random orientations within the small area of about 50×50 μm^2 probed, whose size becomes larger than the probing area with decreasing temperature. The larger area averaged over in GIXD would be insensitive to such an artifact.

Finally, upon cooling the seven-layer 4O.8 membrane further, at 55.5 °C, the diffuse hexatic peak condenses into the sharp, resolution-limited peak of the top-layer Cr-B phase [see Fig. 2(c)]. In addition, for large values of $q_\perp$ intense diffuse scattering, characteristic of a 2D crystal, can be seen. Only the lowest-order (110) peak of the hexagonal lattice is observed; the 2D lattice fluctuations and the molecular form factor cause the peak intensities to decay rapidly with increasing $q_\perp$. Simultaneously, the rather uniform in-plane mosaic of the Sm-B phase becomes discrete. In χ scans narrow peaks with a mosaicity of about 1° (FWHM) are measured, indicating a well-defined ordering of the lattice sites. However, their orientation varies with time: the peak positions in χ change in rather random way on the scale of minutes ("moving mosaic"). These problems prevent us from obtaining reliable line shape data to check the expected behavior $\sim (q_\perp - q_{\perp 0})^{2-\eta}$ for the diffuse scattering of the 2D Cr-B phase of a surface layer. No thermal hysteresis is observed at the hexatic-crystal transition. At this transition also no anomaly is found in the specific heat [10]. The evolution of the hexatic linewidth above the Sm-B-Cr-B transition indicates no pretransitional growth within the resolved temperature accuracy $\lesssim 0.05$ °C. These results suggest that the hexatic-crystal transition in a 4O.8 top layer is abrupt, and belongs to the class of weakly first-order transitions.

In conclusion, we have presented grazing-incidence x-ray diffraction results for the two-step surface freezing of a single top layer in smectic membranes of the compound 4O.8. In contrast to earlier electron diffraction results no anomalous phase is observed below the surface liquid-hexatic phase transition. We find that this transition is continuous, while the hexatic-crystal transition is weakly first order with an abrupt change of the in-plane positional correlations. These single-layer data provide a firm basis for existing results for multilayer membranes of tilted hexatics, as well as for complementary data on the hexatic ordering still needed.

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[15] Rather surprisingly we observed that 4O.8 membranes thickened under the influence of x-ray irradiation below the critical angle. 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. As the effect does not occur for $\alpha > \alpha_c$, it is probably associated with the localized energy dissipation of the evanescent wave. The ''island'' thus created is not connected to the meniscus. After the beam is switched off, it breaks up and disappears in due time and the film returns to its original state. Hence no irreversible effects of radiation damage are involved.

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