Chapter 17

CRITICAL FLUCTUATIONS IN FREE-STANDING SMECTIC FILMS: AN X-RAY REFLECTIVITY STUDY

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We report on the x-ray reflectivity of free-standing smectic films of 8CB. At temperatures well below the second-order nematic-to-smectic transition temperature T_{NA} we find that the fluctuations of the smectic layers in the middle and at the surfaces have the same amplitude. However, on approaching T_{NA} the fluctuations of the middle layers of the film are found to diverge while those at the surfaces are still quenched. The results can be understood qualitatively by including an additional surface term in the well-known Landau-De Gennes free energy for the smectic-A phase.

Much of the interest in smectic liquid crystals is related to the fact that these systems are at their lower marginal dimensionality. As a consequence the positional ordering of the layers is not truely long-range: the thermal fluctuations diverge logarithmically with the size of the sample. If $u(\mathbf{r})$ is the layer displacement from its equilibrium position $\mathbf{r}$, the well-known expression for the mean-squared fluctuations of $u(\mathbf{r})$ is[1]:

$$\langle u^2(\mathbf{r})\rangle = k_B\, T \ln(L/a) \big/ \left(4\pi\sqrt{KB}\right) \qquad (1)$$

where K and B are the elastic constants associated with layer bending and layer compression, respectively, L is the relevant macrosopic length, a the molecular dimension in the direction of L and k_BT is the thermal energy. If the phase transition to the nematic phase is second-order, B can be expected to vanish at T_{NA}. In that case the layer fluctuations will diverge also for finite samples.

Here we report on preliminary x-ray observations of the smectic layer fluctuations on approaching T_{NA} in free standing smectic films (FSSF). These films can be obtained over a hole in a substrate and have their layers (varying in number from two to very large) parallel to the surfaces[2]. Recently FSSF have been made large enough for x-ray reflectivity

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measurements to be performed[3,4]. While conventional transmission x-ray scattering of FSSF provides information about the in-plane structure, x-ray reflectivity gives an accurate determination of the electron density profile normal to the smectic layers[5]. This allows for a direct study of the layer fluctuation profile. At temperatures well below T_{NA} we find that the fluctuations in the bulk and at the surfaces have the same amplitude. However, on approaching T_{NA} we observe a divergence of the fluctuations in the bulk of the films while the fluctuations near the surfaces are quenched and remain finite.

The compound investigated was 4-*n*-octyl-4'-cyanobiphenyl (8CB), which has a smectic Ad phase[6] with a bulk periodicity d=31.8 Å leading to $Q_0=2\pi/d=0.20$ Å^{-1}. 8CB has a second-order SAd-N phase transition[7] at $T_{NA}\approx33.5$ °C. The substance was obtained from BDH (Poole, Dorset, UK) and used without further purification. FSSF of 8CB were drawn over a hole of 10x20 mm^2 defined by four razor blades. The mosaic spread of 0.04° FWHM of the layers was due to the non-perfect planarity of the edges of the razor blades. The films were kept in a two-stage oven which was regulated to within 0.05 °C. The reflectivity data were obtained using films positioned vertically on a standard triple axis spectrometer as described in Ref.3.

Results for a 43 layer film of 8CB at several temperatures are shown in Fig. 1, together with the best fits to a model to be described below. A first qualitative interpretation of the data can be given by considering the two main contributions to the scattered intensity. In the first place there is the regular pattern of Kiessig fringes arising from the reflections against the two film/air interfaces and which extends over the whole range of Q-values. Secondly there is the smectic layering within the film leading to a finite size Bragg peak at Q_0 (equal to the bulk value) with its subsidary maxima. It is the interference between these two contributions that makes the method extremely sensitive to the electron density profile. The Bragg peak which is clearly present at 22.0 °C vanishes at temperatures close to T_{NA} indicating the disappearance of the smectic layering in the middle of the film. However, the Kiessig fringes which depend on the roughness of the film/air interfaces do not show any appreciable change with temperature, indicating almost constant layering at the surfaces. This can be directly seen from the remaining interference minimum around Q = 0.19 Å^{-1} in Fig. 1d, where the Bragg peak itself is already absent.

Starting point for a quantitative data analysis is the standard expression for the reflectivity[8]

$$R(Q) = R_F(Q)\left|\int dz \frac{\partial\rho(z)}{\partial z}\exp(iQz)\right|^2 = R_F(Q)|F(Q)|^2 \tag{2}$$

$R_F(Q)$ is the Fresnel reflectivity of a sharp flat interface and $\rho(z)$ is the projection of the electron density of the film on the z-axis normal to the film surface. We will restrict ourselves to a phenomenological form for $\rho(z)$. The simplest model for a smectic film with layer spacing d is a cosine modulation superposed on the average electron density ρ_0:

$$\rho(z) = \rho_0\,[1 - A\cos(Q_0 z)] \tag{3}$$

In order to incorporate different amplitudes at the surfaces as compared to the bulk we allow A to vary with z as a hyperbolic cosine:

$$A(z) = A_b + (A_s - A_b)\{\exp[\alpha(z-D/2)] + \exp[\alpha(-z-D/2)]\} \tag{4}$$

A(z) represents the amplitude of the density modulation, varying from the surface value A_s at $z=\pm$ 1/2 D to the bulk value A_b. F(Q) is now given by:

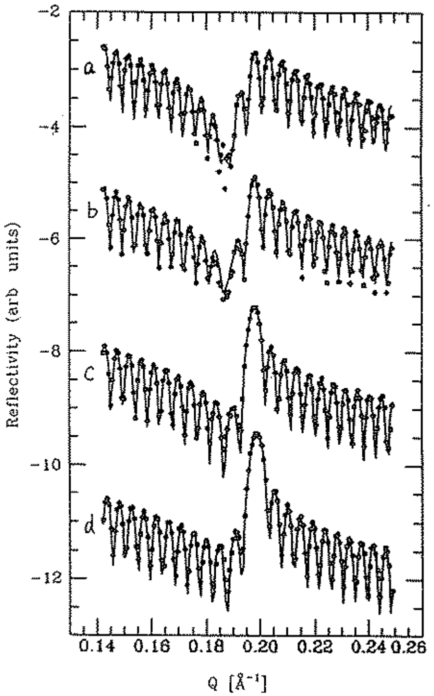

Fig. 1. Reflectivity curves of a 43 layer FSSF of 8CB at 32.8 °C, 32.0 °C, 31.0 °C and 22.0 °C, indicated as a, b, c and d, respectively. The dots are data points, the solid lines are fits using the model described in the text. The curves have been shifted for clarity.

$$\begin{aligned} F(Q) = {} & 2\sin\left(\frac{1}{2}QD\right) - (Q/Q_+)A_b\sin\left(\frac{1}{2}Q_+D\right) - (Q/Q_-)A_b\sin\left(\frac{1}{2}Q_-D\right) \\ & -(A_s - A_b)\exp\left(-\frac{1}{2}\alpha D\right)\left[\frac{Q}{\alpha^2+Q_+^2}R_+ + \frac{Q}{\alpha^2+Q_-^2}R_-\right] \end{aligned} \tag{5}$$

where

$$R_\pm = \alpha\sin\left(\frac{1}{2}Q_\pm D\right)\sinh\left(\frac{1}{2}\alpha D\right) + Q_\pm\sin\left(\frac{1}{2}Q_\pm D\right)\cosh\left(\frac{1}{2}\alpha D\right)$$

and $Q_\pm = Q \pm Q_0$.

For each temperature A_s, A_b and α were varied to obtain best fits to the experimental data. An additional structureless overlayer with a thickness of about 12 Å was needed in the model to describe the data correctly. The resulting electron-density profiles are shown in Fig.2. We conclude that the toplayers remain essentially constant over the whole temperature range. In Fig. 3 the amplitude of the middle layer and the top layers of the film is shown as a function of temperature. From this figure and the data at the next higher temperature (not shown), we conclude that the highest temperature run given in Fig.1d and 2d is within our accuracy at T_{NA}-T = 0.1 K.

A(z) as defined above still has to be related to the thermal fluctuations of the layers $\langle u^2(r)\rangle$. This can be done by noting that the layer fluctuations will smear out the projected density and thus diminish the amplitude of the modulation. This leads to

$$A(z) = S(Q_0)\exp(-Q_0^2\langle u^2(r)\rangle/2) \qquad (6)$$

where $S(Q_0)$ is the structure factor of a perfectly ordered smectic layer. We shall assume $S(Q_0)$ to be constant with temperature while $\langle u^2(r)\rangle$ is taken to be independent of x and y. The amplitude of the middle layer of the film is anticipated to be well described by Eqs.1 and 6. The behaviour of the surface layers will require an additional surface term to be added to the Landau-De Gennes free energy that is at the basis of Eq.(1). An explicit (but complicated) expression for $\langle u^2(r)\rangle$ taking such a term into account was published recently by Holyst *et al.*[9]. In Fig. 3 the predictions for the surface layer and the middle layer of the sample are shown. For B (see Ref.10), K (see Ref.11) and for the surface tension γ (see Ref.12) experimental values of bulk 8CB are taken; L/a = 43 is the number of layers. A value $S(Q_0)\approx 0.12$ was chosen to get approximately agreement with the data for low temperatures. The amplitude of the density modulation of the surface layers is predicted to be almost constant in temperature in agreement with the experiment. The general behavior of the fluctuations in the middle of the film with increasing temperature is also well described, though the functional form is less satisfactory. The predicted behavior is essentially the same as for a layer in the bulk.

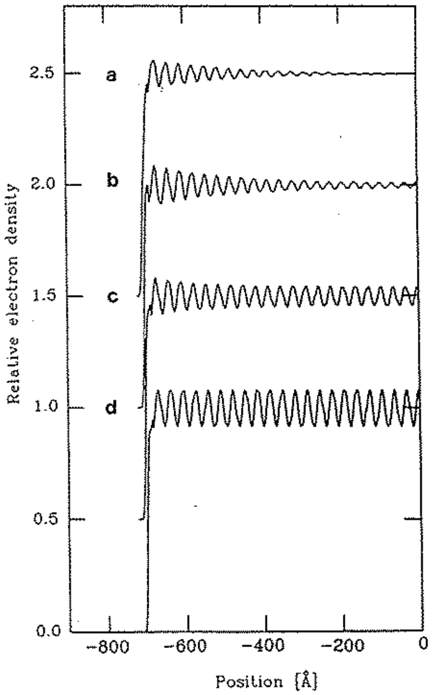

Fig. 2. Model electron densities corresponding to the curves in Fig. 1.

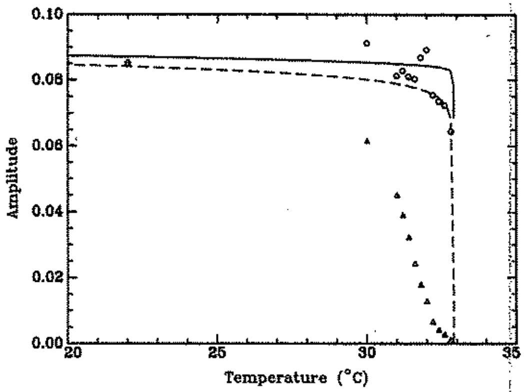

Fig. 3. Amplitude of the middle layer (triangles) and of a surface layer (dots). The lines are predictions of the Landau-de Gennes theory with an additional surface term; broken line: middle layer, solid line: surface layer.

Several uncertainties remain. The rounding off of the fluctuation profile of the middle layer in Fig. 3 could be accounted for by a temperature gradient of the order of 2°C. This seems rather unprobable, and in fact later attempts to measure the temperature gradients over the sample, indicate values on order of magnitude smaller. Alternatively it could be an artefact due to the specific form chosen for A(z). Furthermore, the nature of the observed overlayer is not clear in spite of its reproducibility in the present series of experiments.

In conclusion we have observed in a 43 layer free standing film of 8CB a divergence of the layer fluctuations in the middle of the film on approaching T_{NA} and quenching of the fluctuations of the surface layers.

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