Fluctuations of Freely-suspended Smectic Films as Observed by Diffuse X-ray Reflectivity

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The possibilities to measure the diffuse X-ray reflectivity of interfaces and thin films are only being fully developed thanks to synchrotron sources. At BM32 during the experiment, we could determine the spectral dependence of the thermal fluctuations in freely-suspended smectic liquid crystalline films down to molecular dimensions. While at long wavelengths the top and bottom of such a film fluctuate in unison, at shorter wavelengths a cross-over to independent fluctuations could be observed.

Fluctuations in less than 3-D

Long-range translational order is a defining quality of 3-D crystals; it leads to the existence of Bragg reflections. It is well known that such a translational periodicity is destroyed by thermal fluctuations in 2-D and 1-D systems. However, we do not need a low-dimensional world to observe such effects; similar arguments apply in 3-D to smectic liquid crystals. These consist of stacks of fluid monolayers, where rod-like molecules order into a density wave along one direction, but remain fluid in the other two (Figure 1). In such a system the '1-D' translational order of the fluid layers is not truly long-range but decays algebraically with relative position as $\mathbf{r}^{-\eta}$. This is due to the fluctuations of the smectic layers: if u(**r**) is the layer displacement from its equilibrium position, $\langle u^2(\mathbf{r})\rangle$ diverges logarithmically with the sample size [1] (see intermezzo).

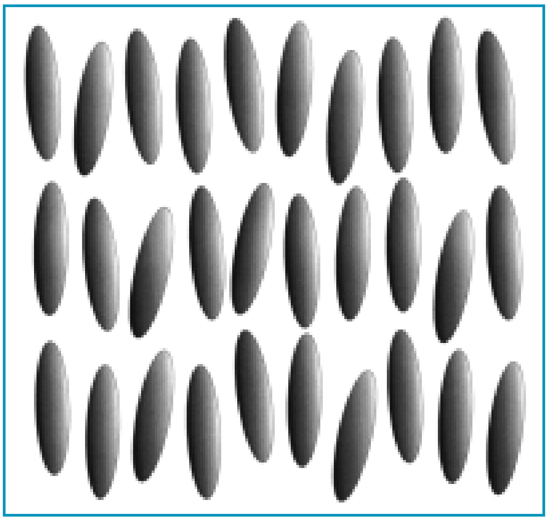


Fig. 1: Stacks of fluid layers forming a smectic phase.

Freely-suspended smectic films

A unique property of smectic liquid crystals is their ability to form films that are freely suspended over an aperture in a frame. In such a film the smectic layers align with a high degree of uniformity parallel to the two flat air-film interfaces. To accomplish X-ray reflectivity measurements – which give a large footprint at small incident angles – we succeeded in making films as large as 1 x 3 cm^2 [2]. Even for such areas, the film thickness L can be easily varied from several hundreds of molecular layers (some μm and thus essentially bulk systems) down to two layers (typically 5-6 nm). Because of these properties, freely-suspended smectic films constitute ideal model systems.

Conformal and independent fluctuations

Similarly to rough surfaces [3], the thermal fluctuations of the smectic layers in a film give rise to diffuse scattering off the specular ridge. The spectral dependence of the intensity is determined by the layer displacement function $<u^2(0,z)>$ and the interlayer displacement-displacement correlation function $C(\mathbf{R},z,z') = <u^2(\mathbf{R},z)u^2(0,z')>$, where **R** is in the plane of the film and z along the normal [4], via the surface tension γ and the elastic constants B and K (see intermezzo). At long in-plane length scales $R > R_c$ all the layers are found to fluctuate conformally, i.e. they move in unison [2]. For $R < R_c$ such a conformality is expected to vanish (see bottom of Figure 2), starting between top and bottom of the film [4]. In general, $R_c \approx \sqrt{L/B}$, hence loss of conformality can be expected at large in-plane wave vectors (small R) for thick films and/or systems with a small value of B.

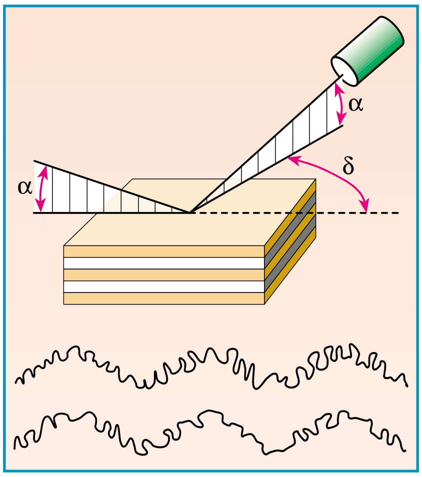


Fig. 2: Top: freely-suspended smectic film and X-ray scattering configuration. Bottom: conformal and independent fluctuations of top and bottom at different wavelengths.

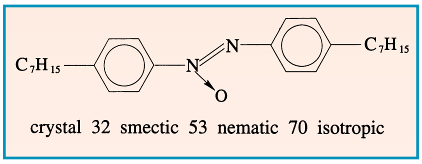


Fig. 3: The compound 7AB and its phase transitions (°C).

EXPERIMENTAL

Using a (2 + 2) surface scattering configuration, the diffuse reflectivity has been probed along q_y, normal to the (q_z, q_x) scattering plane (see Figure 2). Hence the detector was moved out of this plane, keeping the incoming and outgoing angle in the plane constant. The liquid crystalline compound used was *p,p'*-diheptylazoxybenzene (7AB) (see Figure 3). We worked about 0.5 °C below the second-order smectic-nematic phase transition where B can be expected to become small, and with two film thicknesses (24 and 100 layers). The observed intensity is essentially the Fourier transform of $C(\mathbf{R},z,z')$ [2, 3].

RESULTS OF THE SPECULAR AND DIFFUSE REFLECTIVITY

Specular (along q_z at $q_y = 0$) and diffuse longitudinal scans (along q_z at constant q_y) for a 24-layer film are presented in Figure 4a. At small q_y the film is conformal and the diffuse scattering is the coherent superposition of scattering from each layer, showing maxima and minima at the same positions as the specular reflectivity [5]. The disappearance of the interference fringes at large q_y indicates that the top and bottom of the film no longer fluctuate in unison. At the same point the broadening and weakening of the Bragg peak reveals that less than the total number of layers contributes coherently to the diffuse signal. The similar slopes of the transverse diffuse scans at the Bragg peak and its subharmonic (Figure 4b) indicate that lateral correlations between adjacent and next nearest layers persist down to molecular length scales. At the same time the very different slope of the scan at $q_z = 0.7q_o$ confirms the absence of conformality between the top and bottom of the film. A more quantitative description is given elsewhere [6].

INTERMEZZO: SMECTIC LAYER FLUCTUATIONS

In smectic liquid crystals two types of layer deformation play a role.

• Bending of the liquid layers (stiffness constant K), during which the layer spacing is maintained (**Figure A**).

• Compression and dilatation of the layers (constant B, **Figure B**).

The energetics of these two effects can be expressed in the Landau-De Gennes free-energy density:

$$f = \tfrac{1}{2}B\left(\frac{\partial u}{\partial z}\right)^2 + \tfrac{1}{2}K\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2$$

Expanding u(r) in a Fourier series leads to an expression for the free energy density in terms of the modes of the wave vector q. Next the equipartition theorem can be used to assign an energy 1/2 kBT to each mode. Integrating over all modes leads to the expression for the mean-squared layer fluctuations:

$$<u^2(r)> = \frac{k_B T}{8\pi\sqrt{BK}} \ln\left(\frac{L}{d}\right)$$

Here L is the sample size and d the smectic layer spacing. Hence introducing the number of layers N=L/d, the divergence takes the form ln(N).

Fig. A

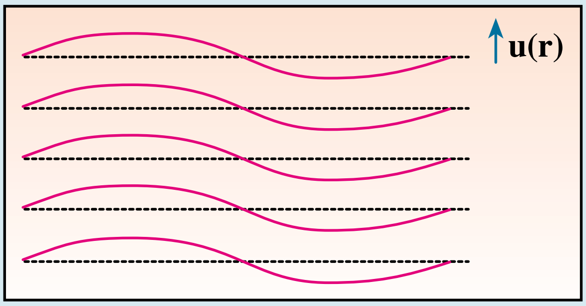
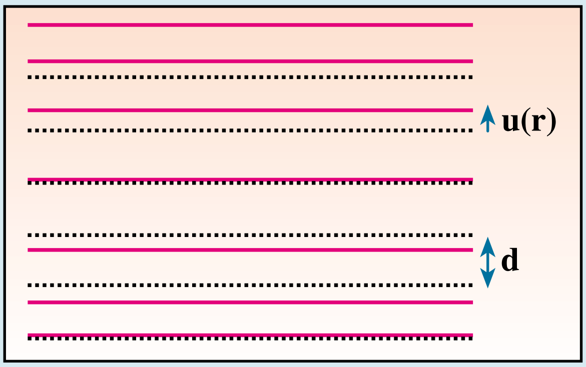


Fig. B



CONCLUSIONS

A cross-over from conformal to independent fluctuations has been observed in freely-suspended smectic films. The (2 + 2) scattering geometry to measure the diffuse scattering in combination with the large dynamic range (> 2 x 10^{10}) at BM32 allowed us to probe wave vectors down to inverse lateral distances between molecules.

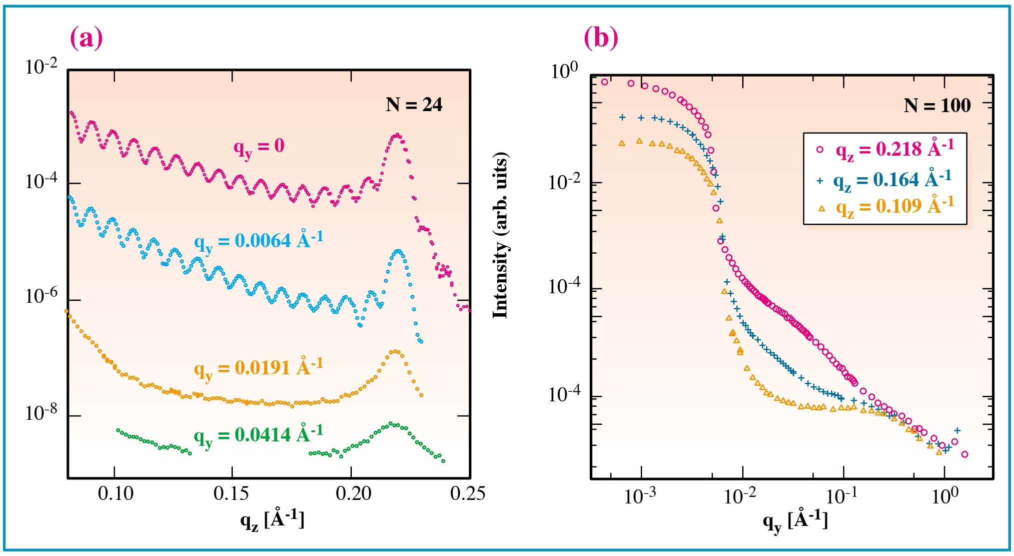


Fig. 4: (a) Longitudinal diffuse scans of a 24 layer film. (b) Transverse diffuse scans (100 layer film) at the Bragg peak ($q_z = q_o$) (red curve), at a subharmonic ($q_z = 0.5q_o$) (blue curve), and at an intermediate position $q_z = (0.7q_o)$ (orange curve).

References

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