Thermal Fluctuations of Freely Suspended Smectic-A Films from Mesoscopic to Molecular Length Scales

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The thermal fluctuations of freely suspended smectic-A films have been studied with diffuse x-ray scattering. Using a (2 + 2) scattering geometry at a synchrotron source the spectral dependence of the displacement-displacement correlation function has been determined from mesoscopic to molecular dimensions. At long in-plane length scales the fluctuations of the smectic layers were found to be conformal; i.e., all layers of the film fluctuated in unison. At decreasing length scales conformality was progressively lost, starting between the top and bottom layers of the film. [S0031-9007(97)04410-4]

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Smectic-A (SmA) liquid crystals are uniaxial systems possessing long-range orientational order. In addition, the molecules are on average arranged in equidistant layers, while the translational order is liquidlike in the other two directions. The positional order along the uniaxial direction is not truly long range but decays algebraically with position as $\mathbf{r}^{-\eta}$. This absence of true long-range order is due to the fluctuations of the smectic layers: if $u(\mathbf{r})$ is the layer displacement from its equilibrium position, $\langle u^2(\mathbf{r})\rangle$ is found to diverge logarithmically with the sample size (Landau-Peierls instability) [1]. Freely suspended SmA films have a well-controlled size and high degree of uniformity, with thicknesses varying from two to over hundreds of layers. This makes them ideal model systems for investigation of the crossover from three-dimensional to two-dimensional behavior, as well as the influence of the surfaces on the physical properties. Recently, measurements of the x-ray reflectivity of freely suspended films [2], which probe the laterally averaged density profile through the film, have been extended to the diffuse scattering [3]. Diffuse reflectivity allows the determination of the interlayer displacement-displacement correlation function $C(R, z, z') = \langle u(\mathbf{R}, z)u(0, z')\rangle$, where $\mathbf{R}$ is in the plane of the film and z along the film normal. From $C(R, z, z')$ the thermal fluctuation behavior can be deduced, which depends on the surface tension (γ) and the elastic constants for compression (K) and bending (B) of the smectic layers [4,5]. At long in-plane length scales the thermal fluctuations are predicted to be highly correlated: all the layers fluctuate conformally, i.e., they undulate in unison and $C(R, z, z')$ decays logarithmically with decreasing R. This behavior has recently been confirmed experimentally in freely suspended films [3] and other organic multilayer films [6]. On the other hand, for $R < R_c \approx 2\sqrt{L\lambda}$ [3], where $\lambda = \sqrt{K/B}$ and L is the thickness of the film, conformality is expected to vanish, starting between the top and bottom of the film. Thus, loss of conformality is expected with decreasing in-plane distance, in thick films and/or systems with a small value of B. This Letter presents the first measurements of displacement-displacement correlations of freely suspended films from mesoscopic down to molecular in-plane distances R. Furthermore, the crossover from conformal to independent thermal fluctuations in these systems could be observed.

The compound investigated is 4,4′-diheptylazoxybenzene (7AB), C_7H_{15}-Φ-N(NO)-Φ-C_7H_{15}, with a bulk phase sequence cryst 32.4 °C-SmA 52.9° C-N 69.9 °C-I. The SmA-nematic phase transition [7] is a second order one, where B is expected to vanish [1]. 7AB was obtained from Frinton (Vineland, U.S.A.) and was recrystallized several times. The freely suspended films covered an area of 28×10 mm^2 determined by four knifelike blades of a rectangular hole in a steel holder. The sample holder was mounted in a two-stage oven which was evacuated and sealed. Measurements were performed at 52.2 ± 0.1 °C, close to the bulk SmA-nematic phase transition but far enough to avoid loss of layers due to layer-by-layer thinning [8] during the experiment.

The experiment was performed at the beam line BM32 at the European Synchrotron Radiation Facility (Grenoble, France) using x rays with wave number $|\mathbf{k}| = 9.12$ Å^{-1}. Using a ′2 + 2′ surface x-ray diffractometer [9] diffuse intensity has been measured at in-plane wave vector transfers as large as 1.6 Å^{-1}, which corresponds to in-plane distances of molecular dimensions ($\approx 4-5$ Å). In our geometry, shown in Fig. 1(a), the detector and sample move out of the plane of specular reflection, while the angles of the incoming and outgoing beam are kept constant with respect to the sample surface. Similar geometries have recently been used to perform diffuse scattering measurements of multilayers [10] and amphiphilic films [11]. We have taken three types of scans for which in all cases $q_x = 0$. In reciprocal space specular scans probe the scattered intensity along q_z with $q_y = 0$. Transverse diffuse scans probe the scattered

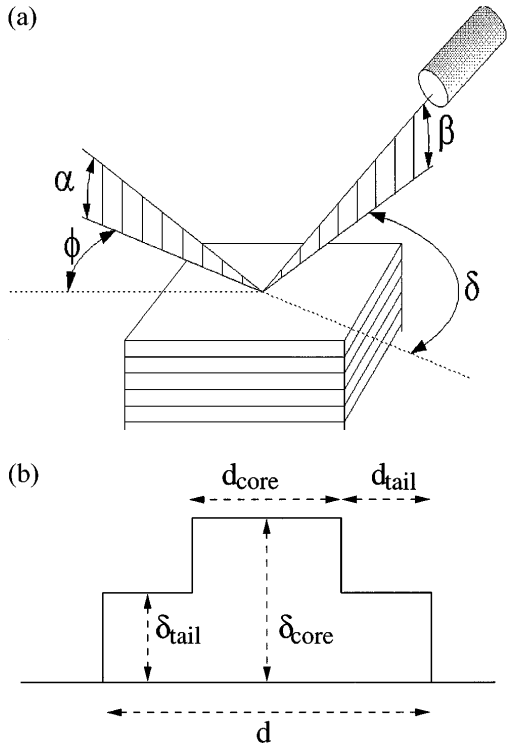

FIG. 1. (a) The scattering geometry in a $'2 + 2'$ surface diffraction setup, where in specular scans (along q_z), α and β are varied with respect to the sample surface while keeping them equal ($\delta = \phi = 0$), in transverse diffuse scans q_y is varied at fixed q_z ($\alpha = \beta$) by moving the detector out of the scattering plane over an angle δ, while rotating the sample over $\phi = \delta/2$, and diffuse scans parallel to q_z are at an offset q_y. (b) The model for a single smectic layer.

intensity along q_y at fixed q_z. Finally, in diffuse scans parallel to the specular rod q_z is varied at a constant offset q_y. In the configuration used we obtained a dynamic range of 2×10^{10}. All scans are background subtracted, where the background was measured in scans with no film present. The data were corrected for overfilling, for the changing illuminated sample area visible by the detector, and for the polarization factor [9]. Note that transverse scans with large in-plane momentum transfer q_y are possible at small q_z where the scattered intensity is high. This is in contrast with the conventional two circle diffractometer setup for diffuse scattering, where q_x is varied by rocking the sample in the beam. Correlations probed in q_x are equivalent to those in q_y as the SmA samples are liquidlike in the xy plane.

Scans along and parallel to the specular rod for a 24 layer film are presented in Fig. 2. 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 [12]. The disappearance of the interference fringes with increasing q_y indicates that the top and bottom of the film no longer fluctuate in unison. The persistence of the Bragg peak up to $q_y = 0.0414$ Å^{-1}

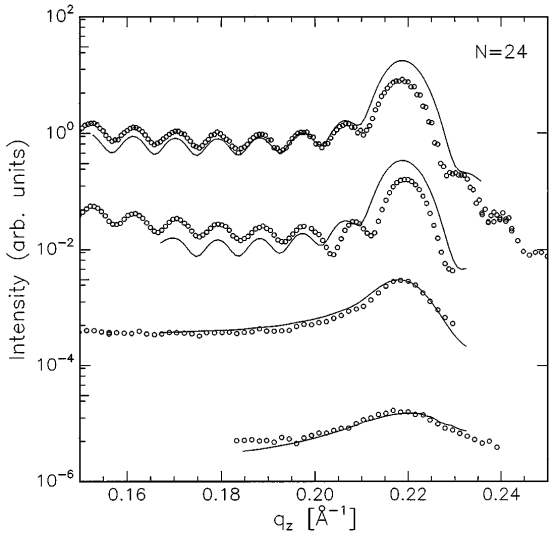

FIG. 2. Specular and diffuse scans along and parallel to q_z for a 24 layer film with, from top to bottom, $q_y = 0$, $q_y = 0.0064$ Å^{-1}, $q_y = 0.0191$ Å^{-1}, and $q_y = 0.0414$ Å^{-1}. Curves have been shifted for clarity.

($R \approx 150$ Å), however, shows that correlations between adjacent layers still exist. The broadening and weakening of the Bragg peak reveals that with increasing in-plane momentum transfers more layers fluctuate independently, and thus not all layers contribute coherently to the diffuse signal.

Additional information about the displacement-displacement correlation function can be obtained from the transverse diffuse scans. Scans were done across the first Bragg sheet where $q_z = 0.218$ Å$^{-1}(q_0)$, across a subharmonic of the Bragg peak at $q_z = 0.109$ Å$^{-1}(0.5q_0)$ and at an intermediate interference fringe at $q_z = 0.152$ Å$^{-1}(0.7q_0)$ for a 24 and a 100 layer film (Fig. 3). At small q_y the slopes of the transverse scans are more or less parallel at all q_z; therefore, all the layers are fluctuating in unison. The development of different slopes in the various scans is the signature of loss of conformality of the thermal fluctuations with increasing in-plane momentum transfer. The behavior at the Bragg sheet and at the subharmonic, where lateral correlations between adjacent and next nearest layers are contributing dominantly to the diffuse signal, respectively, is still very similar for $R < R_c$, in particular for the 100 layer film. At the same time the very different slope of the scan at $q_z = 0.7q_0$, where only correlations between more distant layers are constructively interfering, confirms that conformality between the top and bottom of the film is lost. For short in-plane distances, $R \leq 40$ Å, the diffuse intensity seems to decay logarithmically with increasing q_y. In this regime of short lateral distances the correlations between individual molecules are probed and the continuum theory cannot be applied.

As a critical comparison to the continuum theory, the data have been fitted using [3]

$$\frac{I(\mathbf{q})}{I_0} = \left\{ |R_F|^2 \exp(-q_z'^2\sigma_{\rm loc}^2)\frac{\Delta q_x \Delta q_y}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\, dy \exp[-i(q_x x + q_y y)] \exp\left(-\frac{1}{2}x^2\Delta q_x^2\right) \times \exp\left(-\frac{1}{2}y^2\Delta q_y^2\right) G(R, q_z') \right\} \otimes \exp\left(-\frac{1}{2}q_z^2/\Delta q_z^2\right), \quad (1)$$

with

$$G(R, q_z') = \sum_{m,n}^{N} \exp[iq_z'(m - n)d] \exp[-q_z'^2 g_{mn}(R)/2]. \quad (2)$$

Here the double sum runs over all N layers, and $g_{mn}(R) = \langle [u(\mathbf{R}, z_m) - u(0, z_n)]^2 \rangle = 2\sigma^2 - 2C(R, z_m, z_n)$, where $\langle u^2(\mathbf{R}, z_m) \rangle = \langle u^2(0, z_n) \rangle = \sigma^2$. An explicit expression for $g_{mn}(R)$ has been given in Ref. [3]. The average z component of the wave vector transfer in the film is $q_z' = (q_z^2 - q_c^2)^{1/2}$, where q_c is the critical wave vector transfer for total reflection. The term $|R_F|^2$ is the Fresnel reflectivity of a single layer, in which the smectic layer is approximated by the slab model of Fig. 1(b). It is smeared with a Gaussian of width $\sigma_{\rm loc}$, which approximates the local (short wavelength) contribution to the total fluctuations. The resolution convolution is performed as a one-dimensional convolution (denoted as $\otimes$) along q_z with a Gaussian of half-width Δq_z, and with real space cutoffs to the structure factor integration along x and y.

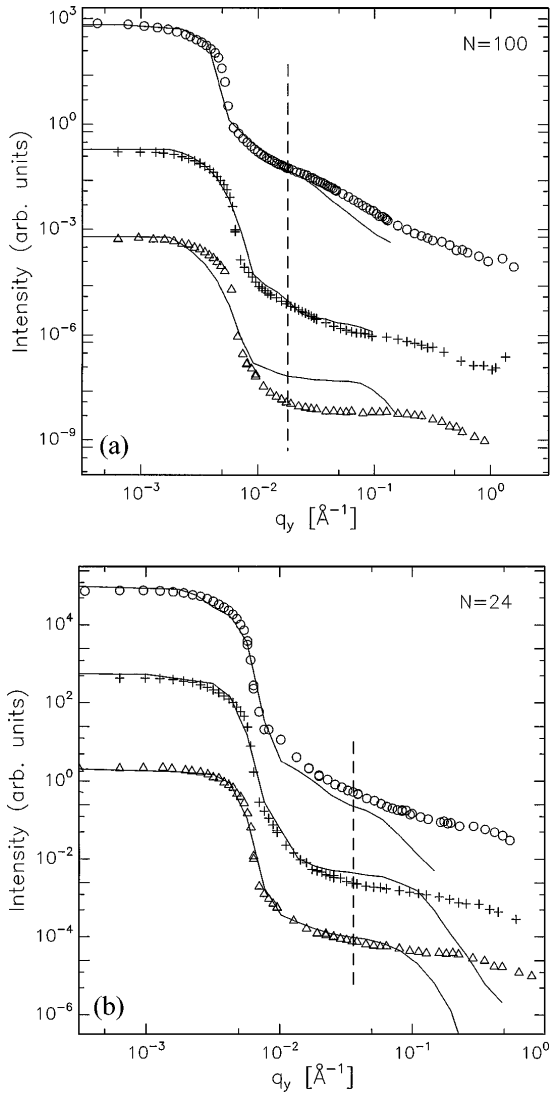

FIG. 3. Transverse diffuse scans for (a) a 100 layer film, (b) a 24 layer film, at $q_z = 0.218$ Å$^{-1}(q_0)$ (circles), $q_z = 0.109$ Å$^{-1}(0.5q_0)$ (crosses), and $q_z = 0.152$ Å$^{-1}(0.7q_0)$ (triangles). The dashed lines indicate where loss of conformality is expected. Curves have been shifted for clarity.

The positions of the Bragg peaks and the Kiessig fringes in the specular reflectivity curve fix d and N, respectively. We find $d = 28.75 \pm 0.05$ Å, independent of film thickness. Fits to the transverse scans give in principle γ, B, and K. However, in the transverse scans the range where capillary waves, and thus γ, dominate the thermal fluctuations, is hidden by the relatively large experimental resolution in the present experiment. Therefore we determined the surface tension of 7AB from the line shape of a transverse scan in a two circle reflectivity setup as in Ref. [3], yielding $\gamma = 25.0 \times 10^3$ N/m^2, in excellent agreement with the results of the direct surface tension measurements of 7AB [13]. The large q_y range caused fitting to be very time-consuming. As K is not expected to change at the nematic-SmA phase transition [1], the nematic value $K = 1.2 \times 10^{-11}$ N [14] was used. Best fits to the transverse scans using those values (see Fig. 3) result in $B = (1.0 \pm 0.5) \times 10^7$ N/m^2, in the same range as found for bulk systems close to the smectic-nematic phase transition [15]. However, although the data and fits show the same general trend, agreement is limited to small q_y values. With the above values $2\pi/R_c$ can be calculated, which are shown as the vertical dashed lines in Fig. 3. The value for the 24 layer film, $R_c \approx 170$ Å ($q_c = 0.037$ Å^{-1}), agrees with our experimental observations in the scans parallel to the specular rod: in the diffuse scan at $q_y = 0.041$ Å^{-1} the fringes have fully disappeared.

Fits using the above values for B, K, γ, and the model parameters for a single layer $\delta_{\rm core}/\delta_{\rm tail} = 1.5$, $d_{\rm core} = 0.54d$, and $\sigma_{\rm loc} = 1.0$ Å are shown as the solid lines in Fig. 2(a). The fits to the two bottom curves are rather good; however, those for the specular and first diffuse scan deviate at the Bragg peak. In fact, the specular reflectivity is not very sensitive to $C(R, z, z')$, but it does depend on the total amplitude of the fluctuations $\sigma_{\rm tot}$, where $\sigma_{\rm tot}^2 = \sigma_{\rm loc}^2 + \sigma^2$. Figure 4 displays a fit to the specular reflectivity based on the roughness profile shown in the inset. At the surfaces $\sigma_{\rm tot}$ is strongly suppressed with respect to the interior of the film. For the above

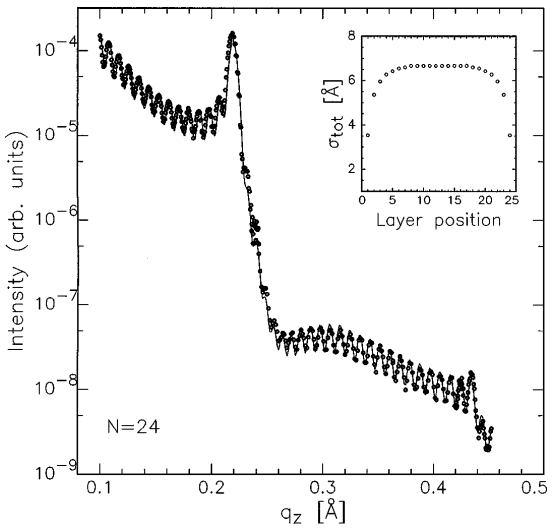

FIG. 4. Specular scan over a large q_z range. The solid line is the fit using the roughness profile shown in the inset.

values of B, K, and γ we find $\sigma = 3.4$ Å and $\sigma = 3.7$ Å at the surface and center of the 24 layer film, respectively. This implies that the total profile is mainly due to a variation of the local molecular disorder, with a fluctuation amplitude from $\sigma_{\mathrm{loc}} = 5.3$ Å at the center of the film to $\sigma_{\mathrm{loc}} = 0.9$ Å at the surface. However, the existence of a profile of σ_{loc} in the film, and thus of the smectic order parameter, should affect the correlations between the thermal fluctuations as well, because B is proportional to the square of the smectic order parameter [16]. The presence of such a profile of B could provide an explanation for the deviations between the data and the model.

In conclusion, a crossover from conformal to independent fluctuations has been observed in freely suspended SmA films. The adapted scattering geometry for diffuse scattering at a synchrotron radiation source allowed determination of the in-plane wave vector dependence of the hydrodynamic (collective) fluctuations down to length scales comparable to the distances between molecules. At decreasing lateral length scales conformality between the top and bottom of the film was progressively lost, while correlations between adjacent and next nearest layers were shown to persist down to molecular length scales. Analysis using a continuum theory indicates the need to incorporate a profile of the compressional elastic constant along the film normal throughout the film.

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