Glancing-Angle Neutron Diffraction from Smectic C Liquid-Crystal Surfaces

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Abstract
Glancing-angle neutron diffraction has been used to study the variation in smectic layer tilt in high- and low-pretilt smectic C cells with distance from the surface. Evidence for varying tilt regions within high-pretilt smectic C cells exists; however, complete analysis is not possible without the appropriate depth-resolved information. Cells containing a liquid crystal and either rubbed polyimide or 5° obliquely evaporated silicon monoxide alignment layers were studied. A partially deuterated liquid crystal was used so that total external reflection could be achieved. Using the D17 diffractometer at the ILL, measurements were made in and around the regime of total external reflection. The tilt angle of the smectic layers was determined from the azimuthal angle of their Bragg reflection on the area detector. Below the critical edge, the penetration depth of the transmitted evanescent wave could be limited to ~300 Å, thus ensuring surface specificity. Varying penetration depths were achieved by alteration of the angle of incidence. Analysis of the Bragg reflection has shown the surface of the SiO cell to have a layer tilt of about 3° higher than that of the bulk. Negligible difference between surface and bulk chevron arm tilts was encountered for the polyimide cell. In both cases, the degree of surface specificity and the accuracy of the layer tilts obtained is discussed.

1. Introduction
In the past decade, the technology required for the development of surface-stabilized ferroelectric liquid-crystal displays (SSFLCs) (Jones, Towler & Hughes, 1993) has made great progress. In these devices, liquid crystal in the smectic C* phase is sandwiched between two glass plates approximately 2 µm apart. The under-sides of the glass are treated with conducting indium tin oxide and then with an alignment layer that constrains the molecules to lie approximately parallel to the cell surface. The structure within the cell was first revealed by Rieker et al. (1987) using X-ray scattering techniques. They observed a chevron structure (Fig. 1) instead of the usual bookshelf geometry that is characteristic of the smectic A phase.

Since it is the uniaxiality of the liquid crystal that is exploited for good optical performance, any directional deviations of the optic axis within the cell would degrade the contrast between the light and dark states. Unfortunately, the chevron structure falls into this category. Using half-leaky guided modes, Yang & Sambles (1993) carried out a detailed study of the optic tensor profiles within such devices. They observed a boundary layer of director reorganization near the cell surface, particularly when SiO alignment layers were used that induce a high surface pretilt (tilt of liquid crystal with respect to the surface). Taylor, Richardson, Ebbutt, Jones & Haslam (1995) also observed anomalous tilted regions within these devices from X-ray rocking-curve studies. However, in the absence of any depth-resolved information, the higher tilted regions could not be located. In this experiment, depth-dependent glancing-angle neutron diffraction has been used to elucidate the nature of the liquid-crystal-alignment layer interface because establishing these boundary conditions would advance the progress of current attempts to theoretically model the system.

Traditionally, the technique of surface diffraction has been most widespread using X-rays, where the good scattering cross sections and bright synchrotron sources have assisted the acquisition of the otherwise low-intensity diffraction data. With a highly collimated beam of X-rays in the regime of total external reflection, the limited penetration depth of the evanescent waves has facilitated the structure determination of many surface crystallographic planes (Dosch, 1987; Robinson, 1986). However, in a liquid-crystal device, the incident medium must be a solid (rather than air or a vacuum) so the only...
way to achieve total external reflection was to use neutrons and a deuterated liquid crystal.

In comparison to X-ray diffraction, the advance of glancing-angle neutron diffraction has been slow. Hindered by even weaker scattering cross sections and significantly lower-intensity incident beams, attempts to obtain surface specificity have been limited. Nevertheless, some surface-sensitive neutron scattering experiments have been successfully performed on crystal surfaces (Al Ulsta, Dosch & Peisl, 1990; Dosch, 1993), including the pioneering experiment by Zeilinger & Beatty (1983) on the silicon (211) surface. In this paper, we explore the potential for this technique to study interfaces other than the air–crystal surfaces, namely the solid–liquid-crystal interface. The depth dependence of the layer tilt has been established for devices containing the liquid crystal MH222 (Gray, Hird, Lacey & Toyne, 1989) and either rubbed polyimide (Negi et al., 1993) or obliquely evaporated silicon monoxide (Kaho, Masumi, Tahata, Mizunuma & Miyake, 1991) alignment layers. The accuracy of the layer-tilt determination and the degree of surface specificity achieved are discussed for each case.

2. Theory

2.1. Scattering from a smooth surface

The fundamental quantity controlling the interference effects associated with waves emerging from media is the refractive index, \( n \). For neutrons, this is given to a good approximation by

\[
n = 1 - \left( \frac{\lambda^2 \rho}{\pi} \right) - i \left( \mu \lambda / 4 \pi \right) = 1 - \delta - i \beta.
\]

In this formula, \( \lambda \) is the wavelength of the incident radiation, \( \beta \) is related to the linear-absorption coefficient, \( \mu \), by \( \beta = \lambda \mu / 4 \pi \), and \( \rho \) is the scattering-length-density of the medium given by \( \rho = \sum_i N_i b_i \), where \( N \) and \( b \) are the number density and scattering length of element \( i \), respectively. The refractive-index variation at surfaces is exploited in surface-diffraction experiments to achieve surface sensitivity.

Consider the boundary shown in Fig. 2 between two semi-infinite media of refractive indices \( n_1 \) and \( n_2 \), where \( n_1 > n_2 \). From Snell’s law, \( (n_1 / n_2) \cos \theta_1 = \cos \theta_2 \), it can be shown that, at a critical value of \( Q \), \( Q_c = (16\pi \Delta \rho)^{1/2} \), where \( \Delta \rho = \rho_2 - \rho_1 \) is the difference in scattering-length density between the incident and transmitted media, the condition for total external reflection is achieved. In this regime, transmission into the sample is greatly reduced. If we resolve the expression for the transmitted wave \( \psi_t = \psi_0 \exp[i(k \cdot r - \omega t)] \) into \( z \) and \( y \) components, we find that, for \( Q < Q_c \),

\[
\psi_t = \psi_0 \exp[i(\pi/2\gamma) \exp[i(k \cos \theta_1 - \omega t)]. \quad (2)
\]

For transparent media and with neglect of higher-order terms,

\[
\gamma = (2 \omega / \lambda) [2(\delta) - \sin^2 \theta]^{1/2}, \quad (3)
\]

where \( \Delta \delta = \delta_2 - \delta_1 \). Thus, in the second medium, the evanescent field decays exponentially in the \( z \) direction and travels parallel to the sample surface. Since only scattering centres in close proximity to the surface are illuminated, any resulting diffraction data will be surface specific. The appropriate penetration depth is given by the depth in which the scattered intensity falls to \( 1/e \) of its original value. This ‘scattering depth’ \( \Lambda \) (Dosch, Batterman & Wack, 1986) is obtained from the imaginary part of the \( z \) component of \( Q \) within the sample, \( Q'_z \) (Dietrich & Wagner, 1984), where

\[
Q'_z = (2\pi / \lambda) [\sin^2 \theta_1 - 2(\Delta \delta) - 2i\beta]^{1/2} + [\sin^2 \theta_1 - 2(\Delta \delta) - 2i\beta]^{1/2} \]

\[
\Lambda = |\text{Im}Q'_z|^{-1} = \lambda / 2\pi(l_f + l_f), \quad (5)
\]

and

\[
l_f = (1/2^{1/2}) [(2\Delta \delta - \sin^2 \theta_1) + [(\sin^2 \theta_1 - 2(\Delta \delta)^2 + (2\beta)^2]^{1/2}. \quad (6)
\]

The effects of absorption and self shielding due to incoherent scattering have been incorporated into the calculation via the use of \( \beta \) in this expression. Fig. 3 illustrates the dependence of \( \Lambda \) on angle of incidence in an ideal situation of zero beam divergence. Typically, \( \Lambda \) could be limited to 300 Å in this experiment. For \( Q > Q_c \),

![Fig. 2. Refraction of neutrons at a boundary where \( n_2 > n_1 \).](image-url)

![Fig. 3. Variation in scattering depth, \( \Lambda \), with angle of incidence, \( \mu = 0.14 \text{ mm}^{-1} \).](image-url)
\( \Lambda \) is primarily governed by the value of \( \beta \) and hence the linear-absorption coefficient, \( \mu \). In this regime, the incident radiation penetrates into the lower-refractive-index medium. The relative intensities of the reflected and transmitted waves are given by the modulus squared of the Fresnel reflection and transmission coefficients (Born & Wolf, 1970), \( r_{12} \) and \( t_{12} \), where

\[
\begin{align*}
r_{12} &= \frac{(n_1 \sin \theta_1 - n_2 \sin \theta_2)}{(n_1 \sin \theta_1 + n_2 \sin \theta_2)} \\
t_{12} &= \frac{2n_1 \sin \theta_1}{(n_1 \sin \theta_1 + n_2 \sin \theta_2)}.
\end{align*}
\]

(7)

For \( \theta_1 \geq \theta_c \), the refraction of the incident beam towards the surface on entry of the lower-refractive-index medium enables some degree of surface specificity to be retained. However, as \( \theta_1 \) is increased further, \( \Lambda \) very quickly reaches the order of microns and the surface specificity is lost. For this reason, smooth surfaces and small beam divergences are imperative in any depth-sensitive surface-diffraction experiment since the diffracted intensity from stray transmitted radiation will dominate over any evanescent diffracted intensity.

2.2. Scattering from semi-infinite smectic C layers

Unlike in techniques such as low-energy electron diffraction, the interaction between neutrons and matter is relatively weak. This, with the mosaic nature of the liquid crystal, enables us to use the kinematic description of the scattered intensity (Vineyard, 1982), i.e.

\[
I(Q) = V_{\text{ill}}|T - i^2 S(Q)|T_f|^{2},
\]

(8)

where \( V_{\text{ill}} \) is the illuminated volume of the sample and \( S(Q) \) is the appropriate scattering law determined by the structure of the liquid crystal.

The liquid-crystal scattering-length-density profile, \( \rho(r) \), can be represented by an infinite set of tilted lattice planes, truncated by a smooth surface as shown in Fig. 4. Since \( S(Q) \) is the modulus squared of the Fourier transform (FT) of \( \rho(r) \), we can use the convolution law

\[
\text{FT}[g(r) * h(r)] = \text{FT}[g(r)] \odot \text{FT}[h(r)].
\]

(9)

Given that

\[
\text{FT}[H(-z)] = \Delta \rho[\pi \delta(z) - (i/Q_z^2)]
\]

(10)

and

\[
\text{FT}[\rho_s \sin(k \cdot r)] = 2i \rho_s \delta(Q_x - \kappa \cos \alpha, Q_y, Q_z - \kappa \sin \alpha),
\]

(11)

where \( \alpha \) is the tilt of the planes with respect to the surface, the result is then a set of diffraction rods whose intensity decreases as \( Q_z^4 \) away from the position of the Bragg peak. The layer tilt and spacing can then be extracted from the diffraction data as indicated in Fig. 5. Thus, position analysis of the diffraction spots obtained from glancing-angle neutron-diffraction data yields the depth dependence of the layer tilt and spacing. In addition, a study of the intensity decay along the diffraction rods should indicate the nature of the truncation of the liquid-crystal layers at the alignment-layer interface.

3. Experimental

3.1. Sample preparation

The liquid crystal MH222 (Gray et al., 1989) is a single-component mesogen whose structure is illustrated in Fig. 6. In this experiment, it was prepared in partially deuterated form to increase its scattering-length density above that of the incident medium, thus meeting the criterion for total external reflection. The hydrogenous core was retained and only the alkyl tails were deuterated so that the amplitude of the sinusoidal wave of scattering-length density across the smectic C layers was enhanced,

![Fig. 4. \( \rho(r) = \rho_s \sin(k \cdot r)(-z) \). Schematic representation of the scattering-length-density profile of the sample. \( H(-z) \) is the Heaviside function, \( \rho_s \) is the difference in scattering-length density of the core and tails of the liquid-crystal molecules making up the lattice planes and \( k \) is the wave vector associated with the planes whose modulus is equal to \( 2\pi/d \).](image)

![Fig. 5. Schematic representation of the diffraction data obtained from a truncated set of tilted lattice planes.](image)

![Fig. 6. Schematic representation of MH222, \( m = 6, n = 8 \).](image)
thus increasing the Bragg intensity. The following phase sequence is exhibited by the mesogen:

\[ K \rightarrow S_C \rightarrow S_A \rightarrow N \rightarrow I. \]

Silicon was chosen as the incident medium as it is virtually transparent to neutrons and has a lower scattering density than the liquid crystal, and the (111) planes can be highly polished to obtain an optically flat surface. Glass was used for the cell base to enable the uniformity of the liquid-crystal film inside to be assessed. Three such cells were prepared; one containing a rubbed polyimide alignment layer and the other two 'SiO 5\( ^\circ \)'. The latter was prepared by oblique evaporation of SiO onto Si(111) at an angle of 85\( ^\circ \) to the substrate normal. This resulted in an approximately 500 Å thick layer of SiO pillars tilted at an acute angle with respect to the surface normal. A 10% solution of polyamide–polyimide mixture PI-32 (Ciba-Geigy, Germany) in \( n \)-methyl pyrrolidone was spun-coated onto the Si(111) at 3000 rev min\(^{-1}\) for 30 s. The substrate was baked and then rubbed using a Buehler Rayval rayon cloth attached to a rotating roller. This process is believed to elongate the polymer chains in the direction of rubbing. The liquid crystals align parallel to the rubbing direction owing to resulting anisotropic van der Waals interactions between the liquid crystal molecules and the polymer chains.

Using two Melinex (polyethylene terephthalate, Goodfellow Metals) strips ~6 μm thick as spacers, two of the cells were assembled with the rubbing/pillar tilt directions parallel to each other to induce the chevron structure and the remaining cell was constructed with the pillar tilts in the antiparallel configuration. 0.5 g of the liquid crystal in the isotropic phase was then introduced into the cell by capillary action under vacuum. The cell was then cooled slowly to room temperature to avoid the formation of air bubbles.

Owing to the elevated temperature at which the smectic C phase forms, it was necessary to heat the sample in situ during the diffraction experiment. Before any diffraction measurements, the sample had to be reheated to the isotropic phase, then cooled slowly to the smectic C phase to re-establish the correct surface alignment, which is lost on crystallization. Table 1 summarizes the specifications of the three cells and the temperatures at which the diffraction measurements were performed.

### Table 1. Summary of the cell specifications

<table>
<thead>
<tr>
<th>Cell number</th>
<th>Alignment layer</th>
<th>Configuration</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyimide</td>
<td>Parallel</td>
<td>339</td>
</tr>
<tr>
<td>2</td>
<td>SiO 5( ^\circ )</td>
<td>Antiparallel</td>
<td>344</td>
</tr>
<tr>
<td>3</td>
<td>SiO 5( ^\circ )</td>
<td>Parallel</td>
<td>335</td>
</tr>
</tbody>
</table>

3.2. Diffraction measurements

Neutron surface-diffraction measurements were made using the D17 diffractometer at the Institute Laue–Langevin, Grenoble. Using the 10% velocity selector, neutrons of wavelength 8.5 Å were extracted from the main beam. Despite the coarse wavelength resolution, it was still possible to obtain accurate layer tilts since the resulting broadening occurred in the radial direction in reciprocal space and the appropriate layer-tilt information was obtained from the azimuthal position of the peak. However, the wavelength resolution will have a detrimental effect on the scattering depth similar to that of the beam divergence. Hence, both angular divergence and wavelength resolution are discussed in some detail later in this paper, where the degree of surface specificity achieved is addressed.

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Fig. 7. Schematic representation of the sample environment.

Fig. 8. Plan of the D17 diffractometer.

Fig. 9. Sample geometry during diffraction measurements.
The scattering geometry of Figs. 8 and 9 was realised. The sample was mounted on a two-circle goniometer in a vertical configuration. By tilting through the Bragg angle on the \( \phi \) circle, the condition for diffraction from the layers was achieved and the maximum possible intensity of the diffraction peaks on the area detector was obtained. Careful adjustment of the sample slit size enabled the beam divergence to be kept minimal (\( \sim 0.4^\circ \)) without reducing the diffracted intensity at low angles of incidence to the extent that it was unmeasurable. The sample was then rotated about the \( \Omega \) axis to vary the angle of incidence. For each sample, measurements in and around the regime of total reflection were made. The layer tilts were then extracted from the azimuthal angle of the diffraction spot on the area detector.

4. Results and discussion of results

Initial reflectivity measurements were made using a wavelength \( \lambda = 15^\circ \) so the critical edge was not obscured by the beam stop. Given the scattering-length density of silicon, \( \rho_{\text{Si}} = 2.1 \times 10^{-6} \text{Å}^{-2} \), a liquid-crystal scattering-length density of \( 4.80 \times 10^{-6} \text{Å}^{-2} \) was obtained from the position of the critical edge. The number density of the liquid crystal was subsequently calculated and the absorption coefficient, \( \mu \), found to be \( 0.10 (1) \text{ mm}^{-1} \). Since the diffraction measurements were to be made at \( \lambda = 8.5 \text{ Å} \), the corresponding critical angle was calculated before the experiment and was found to be \( 0.454 (8)^\circ \).

Figs. 10(a)–(c) illustrate typical diffraction data obtained from glancing-angle diffraction measurements for each sample. Note that the two different-temperature SiO 5° data sets came from separate samples.

No obvious truncation rods were observed. We believe this was due to the poor signal-to-background ratio when the sample was orientated below the critical angle. It could also be due to the layers becoming poorly defined near the surface, giving a sharp decay of rod intensity.
Bragg condition that emerged from the silicon side of the sample.

Comparison of the results with those from bulk X-ray diffraction measurements of MH222 (P. L. Phillips & L. Taylor, unpublished work) showed that the layer tilt was significantly higher than the corresponding molecular tilt (with respect to the smectic C layer normal) at that temperature (see Table 2). This is not normally observed in the chevron structure; however, X-ray rocking-curve measurements carried out by Taylor et al. (1995) have encountered this phenomenon to a lesser degree for some parallel aligned cells containing other liquid crystals. At present, the origin of this effect is unclear.

Care was required when analysing the diffraction data due to the beam refraction at the liquid-crystal–Si interface. Subsequently, the observed and real diffracted angles were no longer equal. Steps were taken to correct for this before extracting the layer-tilt information. Also, the wavelength and angular resolutions of the incident beam were carefully assessed and by incorporating these parameters into a routine, the mean transmission angle.

Table 2. Summary of results

<table>
<thead>
<tr>
<th>Cell number</th>
<th>Structure</th>
<th>No. of Bragg spots</th>
<th>Bulk layer tilt (°)</th>
<th>Molecular tilt (°)</th>
<th>Pillar tilt (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chevron</td>
<td>4</td>
<td>21.5</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>UTL</td>
<td>2</td>
<td>27.5</td>
<td>7</td>
<td>45±5</td>
</tr>
<tr>
<td>3</td>
<td>Chevron, θ &lt; θc</td>
<td>22.2</td>
<td>13</td>
<td>45±5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>θ &gt; θc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 11. The zigzag effect.

Fig. 12. Schematic representation of the liquid crystal layer tilt and SiO pillar tilt.

Fig. 13. Layer tilt and scattering depth versus angle of incidence for (a) Si/polyimide/MH222, T = 339 K (cell 1), (b) Si/SiO 5°/MH222, T = 344 K (cell 2) and (c) Si/SiO 5°/MH222, T = 335 K (cell 3).

Fig. 14. Bragg spot intensity (●) and illuminated volume (●) versus angle of incidence for (a) Si/polyimide/MH222, T = 339 K (cell 1), (b) Si/SiO 5°/MH222, T = 344 K (cell 2) and (c) Si/SiO 5°/MH222, T = 335 K (cell 3).
for a given incident angle was established. Thus the true layer tilt and corresponding scattering depth could be extracted. The error bars shown incorporate these effects and the ambiguities of the analysis process itself. A detailed account of the data-interpretation procedure can be found in the Appendix.

Layer-spacing results are not presented here as difficulties were encountered in placing the centre of the sample exactly over the $\Omega$ axis of rotation. Subsequently, the foot of the beam traversed the sample with increasing angle of incidence, thus varying the sample–detector distance particularly for the first and most important low-angle measurements. Therefore the layer spacings calculated from the actual sample–detector distance and the layer tilts were not accurate.

Figs. 14(a)–(c) illustrate the (001) Bragg spot intensity. Also displayed is the calculated peak intensity evaluated from the effective illuminated volume and transmission factor at each angle of incidence. Again, wavelength resolution and beam divergence were accounted for as well as the absorption effects encountered by the beam on traversing the sample (see Appendix).

4.1. Discussion of the degree of surface specificity achieved

Plots of Bragg spot intensity versus angle of incidence provide a useful means of assessing how surface specific the measurements were. An increase in intensity occurs at the critical angle where the beam begins to transmit into the liquid crystal. The sharpness of this rise is determined by the angular divergence and the wavelength spread of the beam. The downward slope after the steep rise is essentially determined by the thickness of the liquid-crystal layer. A very thick layer would give the intensity only weakly dependent on the angle of incidence whereas a very thin layer would result in a rapid decay with increasing angle of incidence as the transmitted beam swings away from the plane of the liquid-crystal film, thus illuminating very little of it. Another effect that would show up in these plots is that some form of surface roughness (perhaps due to small air bubbles or the SiO pillars) would permit a high transmission below the critical angle. In order to check that our data are consistent with diffraction of a beam penetrating a smooth interface we have fitted the Bragg spot intensity to that predicted by (8) (with the terms $V_{\parallel 1}$ and $T_i$ calculated as outlined in the Appendix) using the beam divergence (estimated from the slit sizes on the instrument), the cell thickness and a variable scale factor.

For the polyimide sample, a good fit was obtained between the measured and calculated spot intensities indicating that our wavelength and angular resolution estimations were adequate. However, only the first few data points were situated in the region before transmission occurred, characterized by the sharp rise in the diffracted intensity. Thus the surface-specific region of the data set was somewhat limited but nevertheless confirmed the absence of any layer-tilt variation at the surface. Attempts to obtain data for lower incident angles only produced diffraction data of too weak intensity for analysis indicating that perhaps the layers became somewhat diffuse on approaching the surface.

Little or no surface-specific data were obtained from cell 2 (SiO antiparallel) simply due to the absence of any data points where all the beam was incident below the critical angle. Owing to the beam divergence and the close proximity of the lowest-angle data point to $\theta_c$, the evanescent diffracted intensity was overcome by the transmitted intensity; thus, the surface-specific information was obscured. The invariance in the layer tilt observed was then due to the measurements being manifest on the bulk.

The cell 3 (SiO parallel) data exhibited a good contrast between transmitted and evanescent diffracted intensities in addition to a broad region of data points below the critical edge; thus, a good range of surface-specific data was obtained. The fit of the Bragg spot intensity to the illuminated volume was adequate; however, a slight mismatch between the points was evident at the critical edge that could not be remedied by altering the resolution functions. The reluctance of the (001) spot intensity to rise at the critical edge may have been due to the reduction of the incident intensity by the small-angle scattering from the SiO pillars.

Let us now question the depth sensitivity of the data. Loss of surface specificity is most likely to have arisen from two separate sources: (i) surface roughness; (ii) poor wavelength resolution and angular divergence. The latter was accounted for in the data analysis routine as described in the Appendix; however, accounting for some degree of surface roughness is not so easy. Since depth sensitivity was crucial to the success of the experiment we shall now assume a rough surface, decide a means of analysis, execute it and then decide whether or not it was appropriate for our data.

Consider the extreme case of a smooth silicon surface and a very rough SiO–liquid crystal interface as shown in Fig. 15. Schematic representation of the beam transmission at a rough surface.
It could be argued that with a rough interface as illustrated it would be unnecessary to apply the reflection correction outlined in the Appendix because the rays are incident at a high angle to the liquid-crystal surface. This raises the possibility that the variation in tilt angle observed is an effect of applying the correction when it is not required. We have therefore repeated the analysis of cell 3 (SiO parallel) without making this correction and the result is shown in Fig. 16.

Clearly the correction makes very little difference, hence the variation in layer tilt angle with scattering depth seems to be valid.

4.2. Discussion of the influence of the alignment layer on the surface structure

Little variation in the layer tilt for the polyimide cell was encountered. In contrast, the SiO parallel cell exhibited a higher tilt region in the upper 0.1 μm of the cell. The two different behaviours may be explained by the chevron structure and the ‘pinning’ of the liquid-crystal molecules at the surface.

Two possible chevron structures can form depending on whether the layer tilt has the same (C1) or opposite (C2) sign to the surface pretilt, β (Fig. 17) (Clark & Lagerwall, 1986; Elston, 1995). Which type of chevron forms depends on the magnitude of the pretilt, cone angle and layer tilt. Since the polyimide PI-32 induces a low pretilt, during the $S_d$ to $S_c$ phase transition, the layers can tilt either way, resulting in the formation of both chevrons and zigzag defects (Handschy & Clark, 1984). In contrast, SiO 5° alignment layers induce a high pretilt that generally biases the formation of the C1 chevron. In this structure, the molecular long axis moves round the cone angle to accommodate the high surface pretilt. Hence, one explanation for the higher tilt region is that the molecular rotation round the cone is limited because the director deviates from the alignment direction (in the plane of this page). Hence further increases in surface pretilt can only be incorporated into the C1 chevron if the cones tilt away from the surface as illustrated in Fig. 18, resulting in a higher layer tilt at the surface. This is only a speculation; however, it is in agreement with more direct profile measurements made by Elston & Sambles (1991).

Using half-leaky guided mode techniques, they observed an ~0.04 mm thick surface layer in which the director reorientated back to the surface-alignment direction. The thickness of this surface layer corresponds well with that of our high-tilt region, thus supporting the surface-alignment–pretilt conflict used to explain the origin of this elevated tilt region at the cell surface.

For cell 3 it should also be noted that, although the majority of the diffracted intensity arose from the C1 chevron (where the molecular layers lie in the opposite direction to the pillar tilt), weak diffraction peaks from the C2 chevron were also present. This highly unfavourable C2 probably formed among damaged outer regions of the alignment layer. Owing to the large sample size required to obtain any significant diffracted intensity (in comparison to X-ray measurements where the sample size is considerably smaller), these rogue areas fell into the vicinity of the incident beam, thus contributing towards the final diffracted intensity. Also, evidence exists to suggest that the alignment is lost on crystallization (P. E. Dunn, unpublished work). If so, this could also explain the small amount of C2 chevron formed in cell 3.

5. Conclusions

The experiment has confirmed the equality of the surface and bulk layer tilts of parallel aligned smectic C cells containing the rubbed polyimide PI-32 and the liquid crystal MH222. In contrast, equivalent cells containing SiO 5° alignment layers have a surface region of 0.1 mm...
thick in which the layer tilt increases between 3 and 6°. In both these cells, the chevron structure formed. In comparison, the antiparallel SiO sample exhibited a uniform tilted layer structure with the molecular long axes aligned in the direction of the pillar tilt; however, no depth dependence of the layer tilt was obtained.

We believe that we have demonstrated the potential of the technique of glancing-angle neutron diffraction to elucidate the structure of interfaces other than the air-solid surface. Despite poor intensities, with careful assessment of resolutions, refraction effects and surface roughness, depth-specific information can be obtained and interpreted.

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References