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OPTICAL DETERMINATION OF SMECTIC A LAYER SPACING
IN FREELY SUSPENDED THIN FILMS

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ABSTRACT

Optical measurements of smectic A layer spacings in freely suspended thin films of three liquid crystals are reported. Although the measured spacings are close to those reported for the bulk, some anomalous behavior is noted. In addition, we report that the smectic A phase in the film can exist at unusually high temperatures.
Freely suspended liquid-crystal thin films offer a potentially powerful experimental tool for the investigation of the physics of two-dimensional systems. These films are quantized in one or more molecular layers, and can be readily created in the laboratory(1). Many of their properties have been investigated by light scattering techniques(2,3), and recently the nature of molecular order in thick films (>30 molecular layers) has been determined by x-ray scattering(4). Definitive x-ray measurements of thin films await further development of intense synchrotron-produced x-ray sources to compensate for the small scattering intensity.

We have employed a simple optical approach to deduce the layer spacing of smectic A thin films (2≤N≤15). Since these freely suspended films are much thinner than optical wavelengths, one can make use of optical interference effects to measure smectic layer spacings. Consider the case of a light beam incident on a thin uniform(5) slab of material. The reflectivity coefficients for electric fields in (R||) and perpendicular to (R⊥) the plane of incidence are given by(6)

\[ R|| = \frac{(n_{||}^2 \cos^2 i - \cos^2 r||)^2 \sin^2 a||}{4n_{||}^2 \cos^2 i \cos^2 r|| + (n_{||}^2 \cos^2 i - \cos^2 r||)^2 \sin^2 a||} \]  
\[ R⊥ = \frac{(\cos^2 i - n_{⊥}^2 \cos^2 r⊥)^2 \sin^2 a⊥}{4n_{⊥}^2 \cos^2 i \cos^2 r⊥ + (\cos^2 i - n_{⊥}^2 \cos^2 r⊥)^2 \sin^2 a⊥} \]  

where:  
- \( i \) = angle of incidence  
- \( r|| \) (\( r⊥ \)) = angle of refraction for the parallel (perpendicular) mode  
- \( n_{||} \) (\( n_{⊥} \)) = index of refraction for the parallel (perpendicular) mode  
- \( a|| \) = \( n|| k \ h \cos r|| \)  
- \( a⊥ \) = \( n⊥ k \ h \cos r⊥ \)  
- \( k \) = wavevector of light  
- \( h \) = thickness of film
The smectic A phase is birefringent and the optic axis lies perpendicular to the plane of the film (and therefore in the plane of incidence) (see Fig.1). \( n_\perp \) is therefore independent of \( \iota \) and is equal to \( n_0 \), the ordinary component of the refractive index. However, for light polarized in the plane of incidence (parallel mode), \( n_\parallel \) is given by the usual formulae

\[
\begin{align*}
n_\parallel &= \left( \frac{\sin^2 r_\parallel}{n_\varepsilon^2} + \frac{\cos^2 r_\parallel}{n_0^2} \right)^{-1/2} \\
\sin r_\parallel &= \frac{\sin \iota}{n_\parallel}
\end{align*}
\]

which easily simplify to yield a transcendental equation in the variable \( n_\parallel \). Here \( n_\varepsilon \) is the extraordinary component of the refractive index. In principle, three independent measurements of \( R_\parallel \) at three different angles \( \iota \) would yield \( n_0, n_\varepsilon, \) and the film thickness \( h \). Such a measurement, in addition to yielding the film thickness (and hence layer spacing for a film of \( N \) layers), would provide useful information about the density of the film (through the symmetric component of the dielectric tensor) as well as the orientational order (through the asymmetric component of the dielectric tensor). Nevertheless, small errors in such quantities as \( R_\parallel \) and uncertainties in \( \iota \) strongly propagate in this technique, creating large errors in the quantities of interest; the errors are sufficiently large to render this measurement meaningless.

We have consequently opted for a somewhat less ambitious measurement, though nevertheless interesting. One measurement of \( R_\parallel \) at a given angle yields a surface in \((h, n_0, n_\varepsilon)\) space (cf. eq. 1); on the other hand, a measurement of \( R_\perp \) at some angle \( \iota \) yields a line \( h \) vs. \( n_0 \). Hence, although we cannot extract absolute values of \( h \) and \( n_0 \), we can nevertheless gain some insight as to their behavior in thin films.
Three materials are investigated: octyloxy cyanobiphenyl (80CB), butyloxybenzylidene octylaniline (40.8), and cyanobenzylidine octyloxyaniline (CBOOA). Films are drawn across a 6 mm square hole in a microscope cover slide and are housed in a small oven, with a temperature stability of ±300 mk (see Fig. 1). The portholes for light passage are covered with microscope slides, tilted in the plane of incidence by 3.6° with respect to the film; this prevents light reflected by the glass window from interfering with light reflected from the film. Light from a 2 mW He-Ne laser first passes through a polarizer, a beam splitter, then into the oven, where the angle of incidence is 20° (Angles of 8° and 30° were also checked, with no systematic variation in the results). Two identical photodiodes are used and are biased in parallel with the same voltage source. One photodiode monitors the reflected intensity and the other monitors the beam-split signal, and hence is calibrated to the incident intensity. $R_\perp$ is then taken as the ratio of the reflected intensity to the incident intensity, corrected for small voltage offsets, stray light, and the transmission of the reflected light through the glass window.

Thirty to forty films are drawn at a given temperature for each material studied. The measured reflectivities are quantized, taking on well-defined values corresponding to the number $N$ of smectic layers; the scatter in data around any given value of $R_\perp$ is generally less than 1%. For thin enough films ($N \leq 15$) Eq. 2 reduces to $R_\perp \propto h^2$. Assuming that $h = a_0 N$, where $a_0$ is a constant layer spacing, one can associate a value of $N$ with each $R_\perp$ such that $R_\perp \propto a_0^2 N^2$.

We also assume that the index of refraction $n_0$ is constant and independent of film thickness; thence, from Eq. 2, we calculate a film thickness for each measured $R_\perp$ and hence $N$. In
Fig. 2a we plot $h$ vs. $N$, assuming $n_0 = 1.50^{7}$, the bulk value for 80CB at $T = 67.3^\circ C$. Performing a least squares fit to the function $h = a_0 N + b$, we obtain $a = 31.1 \pm 0.2$, $b = -1.4$, and an rms error is 2.2. The very small negative intercept is characteristic of all our results. Although it may arise from real physical effects (such as slightly thinned outer layers because of the assymmetric environment near the surface), it can also be due to a changing value of $n_0$ which is a function of $N$. This effect may be seen more easily in Figure 2b, where we have plotted $h/N$ vs. $N$. Although the scatter is about $\pm 0.2$ angstroms, it can be seen that values of $h/N$ for $N \leq 4$ are generally less than those for larger $N$. If, however, one assumes that $n_0$ were 1.49 for $N \leq 4$ (rather than 1.5), the effect would be to increase $h/N$ to values more closely resembling those of the thicker films, i.e., about 31.0 angstroms. In other words, $n_0$ may be slightly reduced in thinner films. With the present technique, however, one cannot ascertain whether a thickness-dependent refractive index is due to orientational or density considerations, if in fact there is a refractive-index effect at all.

In Figures 3a, 3b, and 3c we plot layer spacing vs $n_0^{7-10}$ for the materials 80CB, 40.8, and CBOOA respectively. We have assumed that $n_0$ is constant as a function of $N$ and therefore the layer spacing shown is the slope of the $h$ vs. $N$ line, as in Fig. 2a. If one assumes, however, that $n_0$ is $N$-dependent (cf. Fig. 2b) and that $a_0$ is simply $h/N$, then values of $a_0$ would be reduced by 0.1 to 0.2 angstroms in thicker films from those reported in Fig. 3, for a constant $n_0$. In thinner films the correction would be slightly greater. Since the error bars for $a_0$ are $\pm 0.5$ angstroms, these corrections fall within experimental error. (In addition to scatter, errors arise from a small uncertainty in angle $i$ and from local variations in the transmission coefficient through the oven's glass window.)
We have also investigated the temperature dependence of the layer spacing. For 80CB and 40.8 there appears to be no systematic temperature-dependent behavior of $h$ vs. $N_0$ in the films. In CBOOA, however, there appears to be a weak but systematic increase in $a_0$ as a function of temperature. The data shown in figure 4c are for $T = 82.3^\circ C$. Assuming a fixed $n_0$, $a_0$ decreases by approximately 0.2 angstroms at $T = 74.5^\circ C$ and increases from that shown by 0.2 angstroms at $T = 85.3^\circ C$. It is interesting to note that this is the first reported case of a smectic A film existing at temperatures which would normally be nematic in bulk; earlier measurements on the chiral material decyloxybenzylidene-$p'$-amino-2-methylbutylcinnamate (DOBAMBC) have shown the existence in films of the chiral smectic C phase at temperatures in which the bulk is in the smectic A phase.

In figure 3 asteriks show the approximate bulk behavior in the smectic A phase at $T = 64^\circ C$ for 80CB, $T = 60^\circ C$ in 408, and $T = 80^\circ C$ in CBOOA. Although the bulk data lie very close to the $a_0$ vs. $n_0$ lines, the measured values of $a_0$ are nevertheless consistently smaller than their corresponding bulk values, assuming $n_0$ is identical in film and bulk. Such an effect might arise from an asymmetric surface potential or the smeared-out nature of the film's surface. On the other hand one can also view the data from the standpoint of $a_0$ being the same in both bulk and films with $n_0$ in films being smaller than in bulk. Such an effect can arise from a decreased density in films as films tend to maintain the chemical potential of the bulk reservoir in the presence of a surface tension. It was shown in smectic C films that the density is independent of $N$; however, the density effect needed to account for our results are very small and would fall well within the error bars of the earlier experiment. A decreased $n_0$ can also be due to orientational effects.

Reflectively measurements alone cannot answer all these questions. However, our approach, in conjunction with future x-ray and light scattering experiments, should enable the elucidation of the nature of orientational ordering, possible
density effects, and of the transition from two to three dimensionality in these films.

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References


5) Molecular times are much faster than detector response times; the detector therefore integrates over thermal motions, resulting in a uniformly appearing slab, except perhaps near the surfaces.


Figure Captions

Figure 1 - Optical arrangement

Figure 2 - a) Film thickness vs. N in 8OCB at 65.5°C assuming $n_0 = 1.50$. Line is least squares fit to data points. Error bars are approximately $\pm 1\%$. b) h/N vs. N for some material.

Figure 3 - Layer spacing $a_0$ as obtained in figure 2a vs ordinary refractive index $n_0$ for three materials. Error bars are shown. Asterisks represent bulk data, where values of $a_0$ are obtained from X-ray experiments.
(a)  

h (angstroms)  

300  

200  

100  

0  

Number of layers N

(b)  

h/N (angstroms)  

31.5  

31.0  

30.5  

0  

(Fig. 2)
(Fig. 3)