EUROPHYSICS LETTERS 15 June 1990

Europhys. Lett., 12 (4), pp. 341-345 (1990)

X-Ray Reflectivity of Free-Standing Smectic Films.

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(received 8 January 1990; accepted in final form 23 April 1990)

PACS. 61.10 – X-ray determination of structures.
PACS. 61.30E – Experimental determinations of smectic, nematic, cholesteric, and lyotropic structures.
PACS. 68.55 – Thin film growth, structure, and epitaxy.

Abstract. – The X-ray reflectivity has been measured of free-standing smectic liquid crystalline films, which provides information on the electron density perpendicular to the layers. An extraordinary sensitivity is reached due to the interference between the signal from the fringes arising from multiple reflections against the two parallel interfaces and the signal from the Bragg peak and its satellites. Experiments on two smectogenic compounds, 12CB and 8CB, provide examples of a commensurate and an incommensurate structure in which the film thickness is an integer/noninteger times the bulk periodicity of the smectic layer structure, respectively.

During recent years X-ray reflectivity has proven to be a powerful tool in surface physics [1]. In particular using liquid crystals as model systems of low-dimensional order [2], a variety of interesting effects have been observed related to the nematic-to-smectic phase transition [3]. At this transition, in addition to the orientational order of the elongated molecules typical for the nematic phase, a one-dimensional density wave develops parallel to the preferred direction of the molecules. This leads to what is loosely called the smectic layer structure. In the smectic phase it is possible to draw free-standing films over a hole in a substrate, in which the layers (varying in number from two to very large) are parallel to the surfaces of the film [4]. These free-standing films have been used in X-ray diffraction studies [5], though only in transmission, thus restricting the information to the in-plane structure. Apart from a single particular case of a multilamellar lipid system [6], no X-ray reflection studies of free-standing smectic films have been published. In this letter the potential of this method—which gives information about the layering itself—will be explored and demonstrated on two examples. It will be shown that X-ray reflection of free-standing smectic films provides a sensitive measurement of the electron density perpendicular to the layers, including information on the surface. Because of the interference between the signal from the fringes due to reflections against the two parallel interfaces and the signal from the Bragg peak and its satellites, a very large sensitivity is reached.

Free-standing smectic films were drawn over a $(10 \times 25)\,\text{mm}^2$ hole defined by four razor

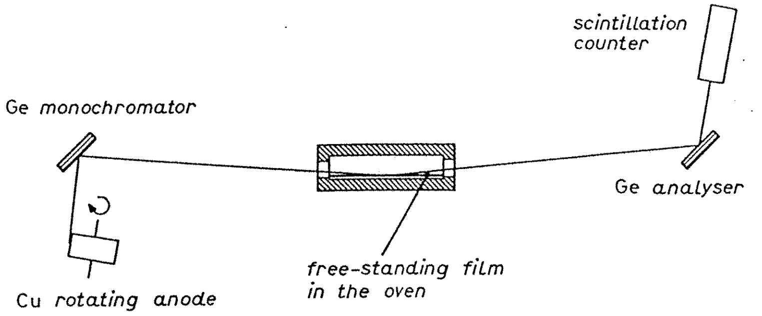
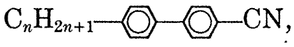


Fig. 1. – Top view of the experimental configuration.

blades. In this configuration the central part of the film was flat enough for X-ray reflectivity measurements to be performed (see fig. 1) over an angular range of $(0.8 \div 5.0)°$ (2θ). Below 0.8° the incoming and reflected beam were obstructed by the sample-holder, and above approximately 5° the reflected intensity was too low. The «mosaicity» was typically 0.04° FWHM. The samples were mounted vertically on a triple-axis X-ray spectrometer equipped with two flat Ge(111) monochromators resulting in a 2θ resolution of 0.006° FWHM. No averaging over the mosaicity was required. $\mathrm{CuK}_{\alpha 1}$ radiation with $\lambda = 1.542$ Å was obtained from an Enraf-Nonius GX-21 rotating anode operator operated at 6 kW. The compounds studied were the octyl and dodecyl members of the p, p′-alkylcyanobiphenyls



nCB.

These compounds have a smectic Ad phase with bulk periodicities of 31.8 Å (8CB) and 39.1 Å (12CB), respectively. The S_{Ad} phase has a liquid in-plane structure. It is called a partially double-layer phase because of the antiparallel correlation of the polar molecules with overlapping aromatic cores, leading to a layer periodicity larger than the length of a fully stretched molecule.

The refractive index of condensed matter in the X-ray regime differs slightly from unity: $n = 1 - \delta$, where $\delta = \lambda^2 r_0 \rho_{\mathrm{el}} / 2\pi$, r_0 being the classical radius of the electron and ρ_{el} the electron density. In spite of the small value of δ ($3.1 \cdot 10^{-6}$ for organic material, $7.6 \cdot 10^{-6}$ for silicon), this allows for the direct observation at X-ray wavelengths of typical optical effects like reflection and interference. To illustrate this point, consider the simplest model of a free-standing film: a thin dielectric slab of constant electron density. For reflection the momentum transfer $q = 4\pi \sin\theta/\lambda$, where θ is the angle between the incoming beam and the reflecting surface, is perpendicular to the film. An X-ray beam incident onto such a film is totally reflected for $q < q_{\mathrm{c}} = \sqrt{(8\pi r_0 \rho_{\mathrm{el}})}$. Above q_{c} the refracted beam is partially reflected at the second interface and the two reflected beams interfere with each other giving rise to a series of fringes of equal inclination (Kiessig fringes). The intensity of this pattern decays like q^{-4}, which corresponds to the reflecting power of a single interface (Fresnel's law). The results for the reflectivity R can be summarized as [1]

$$R = R_{\mathrm{F}} |F(q)|^2 \quad \text{with} \quad F(q) = 2 \sin(qD/2), \tag{1}$$

and where D is the thickness of the film and R_{F} the reflectivity of an infinitely thick film. Results for this model are shown in fig. 2*a*). The spacing of the fringes is reciprocal to D, which thus can be measured with an accuracy that is of the order of the wavelength used.

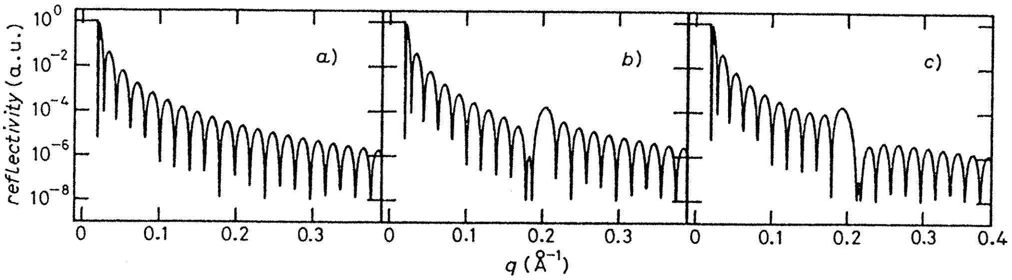


Fig. 2. – Reflectivity curves from some model calculations for 10 layers of 8CB with $d = 31.8$ Å. *a*) Kiessig fringes for a structureless film of 318 Å. *b*) Commensurate smectic film with a 15% harmonic density modulation and maximum-density terminations. *c*) As *b*) with minimum-density terminations.

In order to model the real structure of a smectic film we add a harmonic modulation $A \cos(2\pi z/d)$ perpendicular to the surfaces to the constant electron density. Here A is the relative amplitude of the modulation, d the period, and $z = 0$ defines the midplane of the film. The scattering from this periodic structure gives rise to a Bragg peak centred at $q_0 = 2\pi/d$. Due to the finite number of layers the peak is broadened and accompanied at both sides by a set of subsidiary maxima. The final reflectivity pattern is the result of the interference between the Kiessig fringes and the Bragg peak with its satellites. It proves to be extremely sensitive to the positioning of the density modulation with respect to the limiting surfaces of the film. Fourier transformation of the model-electron density leads to the following expression for $F(q)$:

$$F(q) = 2\sin(qD/2) + A[q/(q+q_0)]\sin[(q+q_0)D'/2] + A[q/(q_0-q)]\sin[(q_0-q)D'/2], \quad (2)$$

where $D' = Nd$, N being the number of smectic layers. In the simplest case the modulation period is commensurate with the thickness of the slab and $D' = D$. Figures 2*b*) and *c*) show the reflectivity according to this model taking for the harmonic modulation the maximum and the minimum electrondensity at the interfaces, respectively. The first case could be expected to be the common situation for a classical smectic A structure; the latter case could apply to a film with a bilayer S_{A2} structure in the bulk and monolayers on top. Of interest is also the case that the film thickness is not an integer times the bulk layer spacing; then the top layers are altered with respect to the bulk structure. This can be incorporated in the formalism by adding a third term corresponding to the top layer structure to $F(q)$ in eq. (2). For instance, a model with $D = (N + \Delta)\,d$ with $0 < \Delta < 1$ would correspond to a monolayer S_{A1}

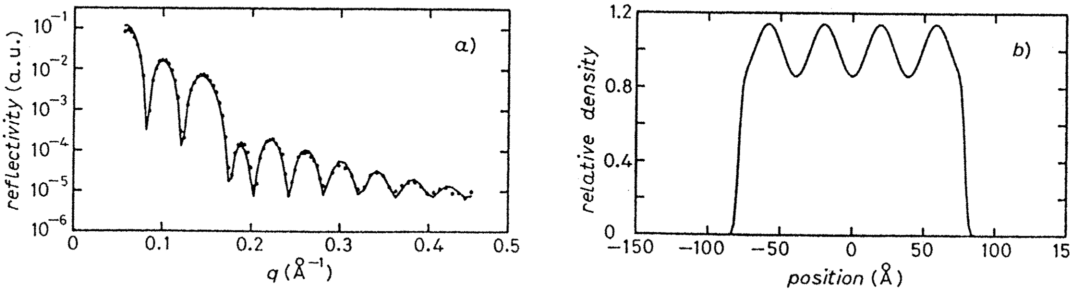


Fig. 3. – Results for a commensurate 4-layer film of 12CB at 55.0 °C. *a*) Experimental reflectivity and fit to the model with $q_c = 0.02$ Å^{-1}, $A = 0.15$ and $\sigma = 3.0$ Å. *b*) Associated electron density profile.

structure in the bulk with S_{Ad}-type double layers on the surface [7], or alternatively to a bulk S_{Ad} structure with S_{A2} layers on top. Another incommensurate model with $D = (N - \Delta) d$ may correspond to tilted top layers. Essential is that incommensurability leads to asymmetric changes in the spacings of the fringes around the Bragg peak.

Reflectivity data for a thin film of 12CB are shown in fig. 3*a*). At high q-values the signal-to-noise ratio is limited by the dark current of the detector (3 counts/min). From the spacing of the fringes far from the Bragg-peak the thickness of this film is determined to be (156 ± 1) Å, which indicates a commensurate structure with 4 smectic layers. The model for the corresponding electron density is straightforward and is shown in fig. 3*b*). Fluctuations of the smectic layering are included by applying a Debye-Waller factor to eqs. (1), (2) with a RMS value $\sigma = 3.0$ Å. Reflectivity data for a thin film of 8CB are shown in fig. 4*a*). The thickness of this film is determined to be (149 ± 1) Å, which is clearly incommensurate with the bulk layer spacing. A possible solution is a four-layer model with expanded top layers (which then correspond to twice the length of a fully stretched 8CB molecule) or alternatively nonexpanded layers with additional material on top. The latter solution is pictured in fig. 4*b*). A five-layer model can be ruled out because of the difference in the phase-relation for interference between the Bragg peak and the Kiessig fringes in case of an odd and an even number of layers. A six-layer model with heavily tilted top layers—though somewhat unlikely—strictly cannot be excluded. This type of surface behaviour has been observed in several films of very different thicknesses. The constant top layer on an increasing number of «bulk» layers seriously limits the possibilities of interpretation in terms impurities. To complicate things further, also cases of commensurate 8CB films have been found. The origin of this behaviour is currently under investigation; the purpose of this paper is to illustrate the sensitivity of the method to the surface structure.

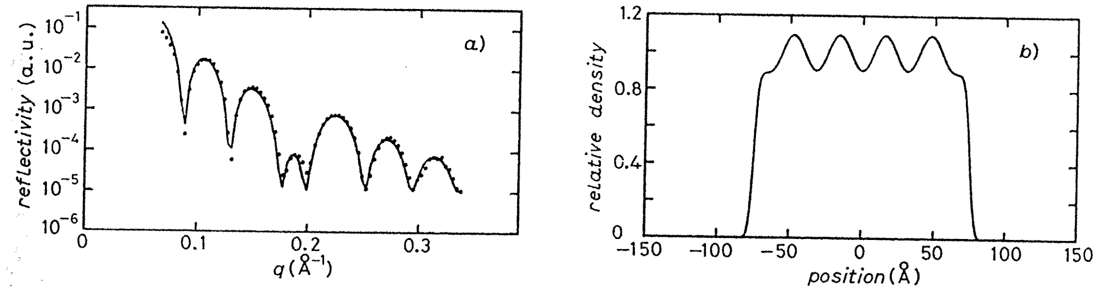


Fig. 4. – Results for an incommensurate 4-layer film of 8CB at 23.0 °C. *a*) Experimental reflectivity and fit to the model with $\Delta = 0.36$, $q_c = 0.02$ Å^{-1}, $A = 0.11$ and $\sigma = 3.6$ Å. *b*) Associated electron density profile.

In conclusion we have shown that X-ray reflectivity of free-standing smectic films provides a powerful new tool to investigate surface structures. The application of the method to various types of smectic structure should provide important information that could not be obtained so far. Two points are of particular interest. In the first place, with decreasing number of layers N the surface field may quench fluctuations causing a cross-over from three-dimensional to two-dimensional behaviour [8] (1). Secondly, compared to surfaces of an infinitely thick sample no bulk scattering is present that could limit the

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(1) After the completion of this work a preprint by L. B. Sorensen and coworkers came to our attention investigating this point using the same technique.

possibilities to study the surface. In the absence of a substrate also no other background scattering is found, which effectively limits the signal-to-noise ratio in many other layered systems. Hence by increasing the intensity (for example, by using synchrotron radiation) rather large q-values should be attainable. This would allow for an almost direct measurement of molecular form factors.

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This work is part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for the Fundamental Research of Matter, FOM) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research, NWO).

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