Smectic-Layer Growth at Solid Interfaces

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X-ray reflectivity is used to study the temperature-dependent smectic layering of the cyanobiphenyl compounds (nCB) in the isotropic phase at alkylsilane-coated silicon surfaces. Layer-by-layer growth is observed for 11CB and 12CB. Comparison of the layering-transition temperatures with measurements at the vapor interface is used to determine the relative anchoring strengths at the two interfaces.

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Subtle changes in the interactions at interfaces may have dramatic effects on wetting properties;[1] the sign of these atomic interactions determines whether the surface melts or freezes before the corresponding bulk phase transformation.[2,3] With few exceptions, the structure of these surface-induced phases is poorly understood. Ion-channeling and x-ray-scattering measurements of the (110) surface of lead[3,4] suggest that the surface layers disorder before the bulk melts. In contrast, liquid-crystal surface layers order above the bulk freezing.[5,6] The present x-ray-reflectivity measurements, conducted at a liquid/solid interface, provide the first microscopic picture of how a bulk isotropic liquid-crystal phase orders at a solid interface. These experiments clearly demonstrate the utility of x rays as a probe of the bulk liquid/solid interface.

Liquid crystals exhibit diverse wetting phenomena since both orientational and positional order can be induced by an interface at temperatures where the bulk phase is disordered. At cleaved graphite surfaces, scanning-tunneling-microscopy studies have revealed that liquid-crystal molecules form an ordered array with the long axis in the plane of the surface.[7] In contrast, at the vapor interface the surface molecules align with the long axis normal to the interface. In this geometry, the orientational order parameter $\hat{\mathbf{n}}$ and the smectic order parameter ψ may exhibit complete or incomplete wetting behavior.[8-10] Previous measurements in the isotropic phase of dodecylcyanobiphenyl (12CB), which probed the behavior of ψ at a vapor interface, revealed a unique series of five discrete layering transitions.[6] The present investigation has been motivated by these previous studies at the vapor interface and by the possibility that solid surfaces might exhibit new and interesting wetting behavior. Additional interest in the problem has been stimulated by detailed density-functional calculations[11] and lattice-gas models.[12] In order to explore the universality of how the smectic phaes "wets" surfaces we have carried out x-ray-reflectivity measurements of liquid crystals at an alkyl-coated solid interface. The behavior of the smectic order parameter at each layer is obtained from detailed analysis of the x-ray specular-reflectivity profiles.

The experiments reported in this paper were performed at beam lines X22B and X22C at the National Synchrotron Light Source. These setups provided an intense monochromatic beam, with approximately 10^{10} photons/s in a spot 0.5 mm high and 1.0 mm wide. Experiments were carried out at $\lambda = 1.39$ Å (X22C) and $\lambda = 1.49$ Å (X22B). In the specular geometry, $q_z = 4\pi/\lambda \sin(\theta)$ is the momentum transfer normal to the surface. The incident x rays traversed a temperature-controlled beryllium can (7 mm diam) filled with liquid crystal and were reflected from a solid surface immersed in the liquid (Fig. 1, lower inset). Measurements were performed on nCB samples, $n = 10, 11, 12$, with transition temperatures T_{IA} of 44.0, 52.7, and 56.9 °C, respectively, on silicon (100) wafers which have been chemically coated with alkylsilane, Si-$(CH_2)_{m-1}$-CH^3 (Cm), monolayers with $m = 10, 12, 18$.[13]

The surface sensitivity of the liquid/solid reflectivity technique is apparent from the rocking curve shown in

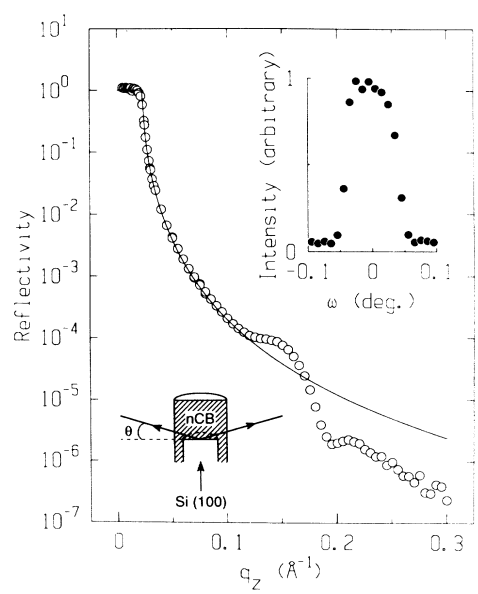

FIG. 1. X-ray reflectivity for 12CB at a C12 interface in the isotropic phase, shown as circles, at $T - T_{IA} = 0.05$ °C. The solid line is the Fresnel law of optics. Upper inset: A typical rocking curve at $q_z = 0.15$ Å^{-1}. Lower inset: The scattering geometry.

the upper inset of Fig. 1 for 12CB on C12-coated silicon at $q_z = 0.15$ Å. The peak at $\omega = \theta - 2\theta/2 = 0$ corresponds to the specular scattering, where the width $\Delta\theta = 0.08°$ is primarily determined by the detector acceptance angle. In order to obtain the specular reflectivity the background at all q_z is measured at $\omega = \pm 0.1°$. Since the beam is uniform and broader than the sample, the background-subtracted data are divided by q_z to correct for the area of the incident beam. Absolute reflectivity is achieved by scaling the data at small angles to obtain unity reflectivity. In Fig. 1 the absolute reflectivity versus q_z in the bulk isotropic phase is plotted at 0.05 °C above the isotropic-to-smectic-A transition as circles. A weak peak is observed at $q_z \sim 0.15$ Å^{-1}. At the isotropic-to-smectic transition this broad peak condenses into a sharp peak at $q_z \sim 0.160$ Å$^{-1} = 2\pi/L$, where L is the bulk smectic-layer spacing.

In Fig. 2, the intensity of the specularly reflected signal at $q_z \sim 0.15$ Å^{-1}, obtained upon cooling, is shown for 12CB, 11CB, and 10CB on the C18-coated surface, for 12CB on the C12-coated surface, and for published data on the 12CB/air interface.[6] Detailed line-shape analysis, presented below, supports the notion that the steplike features in Fig. 2 are a consequence of layer-by-layer growth of a smectic phase at the interface. Identical behavior was obtained on heating and cooling cycles. For the solid as well as the air interface, the wetting is incomplete. It is remarkable that the formation of a single bilayer can be resolved since the 0.5-mm-wide incident beam illuminates the equivalent of 10^6 layers.

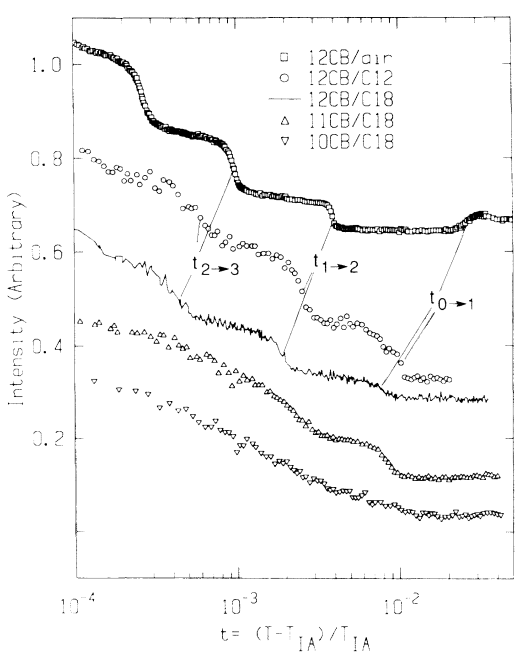

FIG. 2. X-ray-reflected intensity at $q_z \sim 0.15$ Å^{-1} for 10CB, 11CB, and 12CB at the C12, C18, and air interfaces vs reduced temperature. For graphical clarity the data have been scaled by arbitrary factors.

Several important differences emerge between the air and solid interfaces for 12CB as shown in Fig. 2. Five layering transitions were observed at the air interface, whereas only three are observable at the solid interface. In addition, the layering transitions are considerably broader at the solid interface; i.e., they appear more continuous. Finally, there is a clear shift in the transition temperatures. For 12CB on the C18-coated surfaces the layering transitions occur at $t_{0\to1} = 7.6\times10^{-3}$, $t_{1\to2} = 1.8\times10^{-3}$, and $t_{2\to3} = 4.5\times10^{-4}$ corresponding to the formation of a single bilayer, two bilayers, and three bilayers. For 12CB on the C12-coated surface the layering transitions occur at $t_{0\to1} = 1.0\times10^{-2}$, $t_{1\to2} = 2.3\times10^{-3}$, and $t_{2\to3} = 6.0\times10^{-4}$. At the 12CB/vapor interface, the corresponding transition temperatures are higher with $t_{0\to1} = 2.5\times10^{-2}$, $t_{1\to2} = 3.8\times10^{-3}$, and $t_{2\to3} = 9.6\times10^{-4}$.

The reduction in the layering-transition temperatures can be interpreted in terms of a Landau free-energy density

$$F(z) = at\,|\psi(z)|^2 + B\,|\psi(z)|^4 + C\,|\psi(z)|^6 - \alpha F_s(z)\,|\psi(z)|^2, \quad (1)$$

where the last term induces smectic ordering at the surface when $F(z)$ is negative. The surface field $\alpha F_s(z)$ is short range and is reasonably described by an exponential form, since the steps are nearly equally spaced on a logarithmic scale,[2,14] and not a $\frac{1}{3}$ power-law divergence as predicted for van der Waals forces. Ideally, the free energy should also include a periodic term to account for the quantized nature of the layering.[11,12] If $F_s(z)$ is a universal function, then the reduced layering-transition temperatures for different interfaces scale as α/a, where a depends on the liquid crystal. Conversely, the relative values of α/a can be deduced from the measured layering-transition temperatures. The ratios of the anchoring terms for the alkyl and vapor interfaces for 12CB on the C18 surface $\alpha_{CH_2}/\alpha_{air}$ are 0.30 ± 0.07, 0.47 ± 0.1, and 0.47 ± 0.1, obtained from the values of $t_{0\to1}$, $t_{1\to2}$, and $t_{2\to3}$, respectively. These ratios are slightly larger for the C12 surface. There is a clear shift to smaller anchoring at the alkyl interface. Two layering transitions are clearly resolved for 11CB at a C18 surface. The reduced temperatures of these transitions are indistinguishable from those of 12CB at the same interface (see Fig. 2). Since α is the same, this result requires that a [Eq. (1)] must be nearly identical for 11CB and 12CB.

For shorter-chain liquid-crystal compounds within the isotropic phase, the nematic-isotropic-smectic triple point is approached[9] and the quantized nature of the ordering disappears, as is apparent from Fig. 2. Indeed, for 10CB which is fairly close to the triple point (9.45CB in mixtures of 9CB and 10CB), there are no discrete layering transitions.[9,10] The loss of discrete transitions results

from the increased nematic susceptibility which acts to roughen the interface.

Actual density profiles have been determined from an analysis of the reflectivity spectra. In analogy with the air interface, the reflectivity for an arbitrary density profile can be calculated as a perturbation of the reflectivity for a perfectly sharp interface. The latter is given by the Fresnel law of optics,[13] $R_F=[q_c/2q_z]^4 \times |T(q_z/q_c)|^4$, where T is the surface enhancement factor. For the present geometry, the critical q vector q_c equals $[16\pi e^2(\rho_S-\rho_L)/mc^2]^{1/2}$, where ρ_S and ρ_L are the electron densities of the bulk solid (silicon) and liquid phases, respectively. In Fig. 1 the calculated R_F is shown as a solid line. Up to ~ 0.10 Å^{-1} there is good agreement between R_F and the data.

For interfaces which are not perfectly sharp, the actual reflectivity normalized to that of the sharp interface (R_F) may be approximated by

$$\frac{R(q_z)}{R_F(q_z)} \cong \left| \frac{q_z}{\langle \rho_S-\rho_L\rangle} \int_{-\infty}^{\infty} \langle \rho(z)\rangle e^{iq_z z}\, dz \right|^2 = q_z^2 |\phi_1+\phi_2(t)|^2 \qquad (2)$$

in the Born-approximation limit, i.e., $q_z \gg q_c$. The first term ϕ_1 is temperature independent and represents the contribution from the Si/Si-oxide/alkyl/liquid interfaces. The second term is from the surface smectic layers and varies with temperature. Asymmetry in the reflectivity line shape is primarily controlled by the amplitude and phase of the smectic density wave with respect to the amplitude from the alkyl/silicon surface. Analysis of the profile provides a reliable measure of the alkylsilane thickness D. The first term is given by

$$\phi_1 = \frac{-i\exp(q_z^2\sigma_S^2/2)}{q_z} |(1-\Delta)+\Delta\exp(iq_z D)| , \qquad (3)$$

where $\Delta=(\rho_C-\rho_L)/(\rho_S-\rho_L)$ and ρ_C is the electron density of the alkyl coating. The Si/Si-oxide/alkyl interface is described by a single Gaussian [Eq. (3)]. Including a separate Si/Si-oxide as well as a Si-oxide/alkyl interface did not significantly improve the fits over the range of the present measurements.

The symmetric, molecular bilayer smectic form factor $C(q_z)$ for 12CB has been calculated in terms of the atomic positions as described by Gramsbergen, de Jeu, and Als-Nielsen.[15] This calculation has been guided by the measured spacing for the bulk nCB series, $L=2\times(0.906n+8.5)$ Å for $8<n<12$. For fully extended molecules $dL/dn=2(1.22$ Å$)$. Consequently, a $42° = \cos^{-1}(0.906/1.22)$ tilt of the aliphatic tails, with respect to the layer normal, has been used in the form-factor calculation.

The density-wave amplitude for the liquid-crystal layers ϕ_2 is given in terms of a sum over bilayers,

$$\phi_2 = \frac{\rho_L}{\rho_S-\rho_L} C(q_z)\exp\left[iq_z\left(D-\frac{L}{2}\right)-\frac{q_z^2\sigma^2}{2}\right] \times \sum_{k=1}^{4} A_k \exp(iq_z kL) , \qquad (4)$$

where A_k is the occupation of the kth layer. For perfectly formed smectic layers $A_k=1$, whereas in the isotropic phase $A_k=0$. An alternative approach, allowing σ to vary for each layer with A_k fixed at unity, gives rise to large oscillations in the reflectivity at small q_z which are not observed.

The analysis of the reflectivity profiles of the 12CB freezing at the C12 surfaces proceeds as follows. Parameters Δ, D, and σ_S were chosen by performing a least-squares analysis at $t=0.00015$ in which these three parameters and the amplitudes A_1-A_4 were allowed to vary. Data over the range 0.07 Å$^{-1}<q_z<0.27$ Å^{-1} were included in the fits. The best fit gives $\Delta=-0.10\pm0.05$ and $\sigma_S=5.5\pm0.5$ Å, where $L=39.15$ Å was fixed at the bulk value. Because of the strong coupling between A_k and σ, σ has been fixed at 5.5 Å. The fitted thickness of the alkylsilane layer at the liquid interface $D=15.6\pm1$ Å is close to the value obtained at an air interface.[13]

Reflectivity data, shown as circles in Fig. 3, have been fitted by the model given by Eqs. (3) and (4). In order to describe the data the occupancy parameters A_1-A_4 are allowed to vary in the analysis at every temperature. Reflectivity profiles, generated by the fits, are shown in Fig. 3 as solid lines and the order parameters A_1-A_4 obtained are shown in Fig. 4. The essential features of the data including the broad peak at $q_z=0.15$ Å^{-1} and the

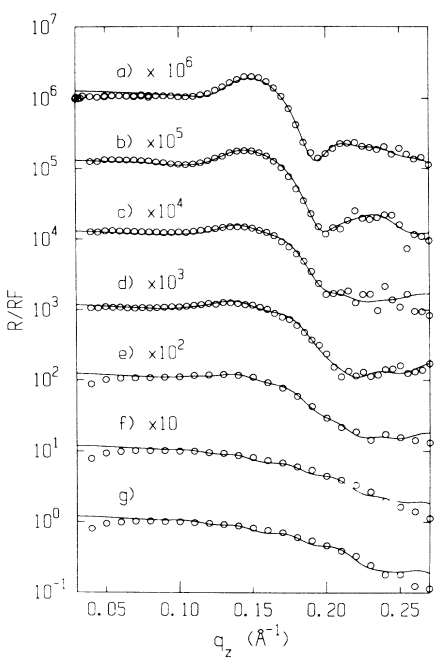

FIG. 3. Measured x-ray-reflectivity profiles, divided by R_F, in the isotropic phase of 12CB at a C12 interface at t equal to 0.00015 (curve a), 0.0012 (b), 0.0024 (c), 0.0039 (d), 0.0067 (e), 0.015 (f), and 0.023 (g), shown as open circles. The data have been offset for clarity. The solid lines are fits to the data where the fitted parameters are shown in Fig. 4.

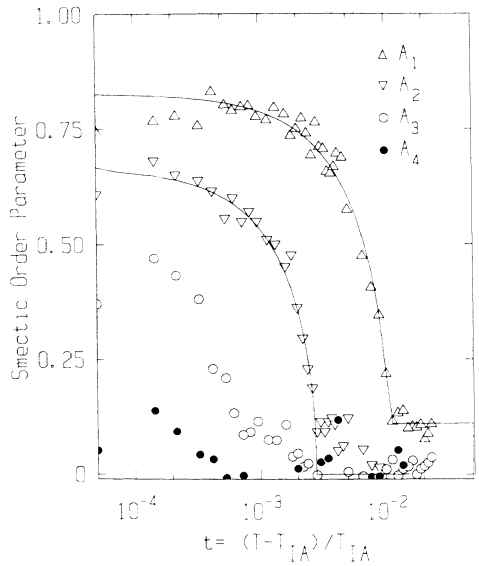

FIG. 4. Layer-dependent order parameters for 12CB at a C12 interface, A_k, obtained by least-squares analysis described in the text. The solid lines are fits by a $\frac{1}{2}$ power law.

subsequent dip are well described by the model with a typical R factor of 0.01. Similar fits were also obtained for 12CB and 11CB on a C18 surface with $D=22\pm1$ Å and for 12CB on a C10 surface with $D=12\pm1$ Å. In all cases the value of D obtained by independently measuring the x-ray reflectivity of the alkylsilane surface in air agrees within 1 Å with the value obtained from the liquid-crystal analysis. This result establishes that the liquid-crystal molecules are in close contact with the alkyl coating, although penetration of the liquid-crystal molecules into the alkyl coating by several angstroms cannot be ruled out.

Layer-by-layer growth was anticipated for 12CB on the C12 interface from the behavior of the reflected intensity at fixed q_z (Fig. 2), but the details of the structure could not be ascertained. With $\sigma=5.5$ Å, the limiting values $A_{1\text{-}3}=0.75$, 0.70, and 0.5, are all less than unity, the value expected for a fully formed layer. Because of the strong coupling between A_k and σ in the analysis, there is a large uncertainty in the scale factor of A_k. This does not affect the temperature dependence of $A_{1\text{-}4}$. The behavior of $A_{1\text{-}3}$ is not consistent with a first-order jump predicted by density-functional calculations.[11] However, a continuous growth of the order parameters for the first few layers has been predicted by lattice-gas models,[12] although the expected linear growth is not observed. Instead, the layering order parameters $A_{1\text{-}2}$ are consistent with $(t-t_{(k-1)\to k})^{0.5}+K_{(k-1)\to k}$ as shown by the solid lines in Fig. 4 with $t_{0\to1}=1.03\times10^{-2}\pm3\%$ and $t_{1\to2}=2.7\times10^{-3}\pm6\%$ and with $K_{0\to1}=0.10$ and $K_{1\to2}=0.07$. The constants $K_{0\to1}$ and $K_{1\to2}$ are significantly smaller if a more realistic model of the Si/Si-oxide/alkyl interface is utilized. However, the overall temperature dependence of A_k is the same. An order-parameter exponent of $\beta=\frac{1}{2}$ is expected for second-order transitions ($B>0$) and not for first-order transitions such as the isotropic-to-smectic-A phase transition. If β is allowed to vary in the fitting procedure, $\beta=0.6\pm0.15$. The continuous nature of the transitions at the solid interface may be a manifestation of surface roughness which is not, as yet, addressed by any of the current theories for liquid-crystal wetting.

In conclusion, the technique of x-ray reflectivity as a structural probe of liquid/solid interfaces has been demonstrated. Layer-by-layer surface freezing transitions[3] are observed for 12CB at a hydrocarbon interface. Comparison with freezing data at a vapor interface reveals a decrease in the transition temperatures, suggesting a smaller anchoring field. The exact behavior of the layering order parameters appears to obey a $\frac{1}{2}$ power law which is not consistent with first-order transitions. Measurements on non-methyl-terminated surfaces would provide detailed insight on how the short-range interactions modify the microscopic and macroscopic wetting behavior.

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