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## Liquid and liquid crystal surfaces

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Specular reflection of x-rays is shown to be a powerful tool for measuring the structure along the direction of the surface normal for gas-liquid or gas-solid interfaces. For x-rays incident at an angle  $\theta$  from the surface there is essentially 100% reflectivity for  $\theta < \theta_c$ , where the critical angle  $\theta_c \approx 0.2^\circ$ – $0.3^\circ$ . One can show that, for x-rays incident at angles  $\theta \gg \theta_c$ , the ratio between the actual reflectivity  $R(\theta)$  and the theoretical reflectivity  $R_F(\theta)$ , from an ideal flat surface with a sharp boundary, is given by (1):

$$\frac{R(\theta)}{R_F(\theta)} = \left| \frac{1}{\rho} \int dz e^{iQz} \left\langle \frac{\partial \rho}{\partial z} \right\rangle \right|^2, \quad [1]$$

where  $Q \equiv (4\pi/\lambda)\sin \theta$ ,  $\lambda$  is the x-ray wavelength, and  $\langle \partial \rho / \partial z \rangle$  is the derivative of the total electron density  $\rho$ , taken along the normal  $z$  and averaged over the  $x$ - $y$  plane of the surface.

For example, the effect of a mean-square surface roughness  $\sigma^2 \equiv \langle u^2 \rangle$  is to change  $\rho^{-1}(\partial \rho / \partial z)$  from  $\delta(z)$ , as expected for a flat surface with a sharp boundary, to the Gaussian form  $(1/2\pi\sigma^2)^{-1/2} \exp(-z^2/2\sigma^2)$ . The result obtained on taking the Fourier transform described in Eq. 1 is that the ratio  $R(\theta)/R_F(\theta)$  is reduced by a Debye-Waller factor,  $\exp(-Q^2\sigma^2)$ . We have measured the x-ray reflectivity from  $H_2O$ ,  $CCl_4$ , and  $CH_3OH$  and found this Gaussian law (2, 3).

One of the more interesting features of the reflectivity measurements is that for these simple liquids the measured roughness depends on the resolution of the spectrometer (2, 3). Consider thermally excited capillary waves at a wave vector in the plane of the surface  $q$ . If the energies of the capillary waves are dominated by surface tension (i.e.,  $\gamma$ ) the value for  $\langle u^2 \rangle$  is approximately given by

$$\langle u^2 \rangle = \frac{k_B T}{4\pi^2 \gamma} \int_{L_1}^{L_2} \frac{d^2 q}{q^2} = \frac{k_B T}{2\pi \gamma} \ln \left( \frac{L_2}{L_1} \right), \quad [2]$$

where the upper limit  $L_2 \approx (\text{molecular size})^{-1} \equiv (\pi/a)$  and the lower limit is essentially equal to the reciprocal of the spectrometer resolution  $\Delta q^{-1} \approx 1/L_1$ ,  $k_B$  is the Boltzmann constant, and  $T$  is absolute temperature. It follows that the roughness is proportional to the logarithm of the resolution: e.g.,  $\langle u^2 \rangle \propto \ln(\Delta q a / \pi)$ .

The real-space interpretation of this result can be understood in terms of the phase shift between x-rays reflected from two points on the surface a distance  $r$  apart:  $\langle \exp(iQz: [u(r) - u(0)]) \rangle \approx \exp\{-[Qz^2 \langle (u(r) - u(0))^2 \rangle] / 2\}$ . The predicted ratio  $R(\theta)/R_F(\theta)$  is given by integrating this exponential over the "x-ray coherence area" defined by the spectrometer resolution. The integrand is essentially the same as that of Eq. 2

when  $qr \gg 1$ ; however, since it goes to zero for  $qr \ll 1$ , the result is approximately the same as that of Eq. 2 if the lower limit is replaced by  $L_1 = \pi/r$ . In fact, a spectrometer that has a resolution  $\Delta q$  measures a reflectivity that is averaged over a length scale of the order of  $r \approx \pi/\Delta q$  and the apparent surface roughness increases as the resolution  $\Delta q$  becomes finer.

According to theory the average  $\langle (u(r) - u(0))^2 \rangle$  that defines the surface roughness for simple liquids is dominated by surface tension effects so long as the distance  $|r|$  is less than something of the order of the depth of the liquid. The measured value of the roughness of  $H_2O$ , averaged over a spectrometer-limited correlation area  $\approx 200 \text{ \AA} \times 5000 \text{ \AA}$  is  $\sigma = 3.2 \pm 0.5 \text{ \AA}$ . The value calculated from Eq. 2 by using the published value for the surface tension and this spectrometer resolution was  $2.8 \text{ \AA}$ . The agreement is improved when the finite size of the water molecule is taken into account—e.g.,  $\approx 1.9 \text{ \AA}$ .

For temperatures at which the bulk liquid crystal is in either the nematic or isotropic phases the angular reflectivity from gas-liquid crystal interfaces exhibits structure at  $Q = (4\pi/\lambda)\sin \theta \approx Q_0 = 2\pi/d$ , where  $d$  is the smectic layer spacing (4). In the nematic phase, but near to a second-order nematic to smectic-A (NA) transition, there is a temperature-dependent peak in the specular reflectivity due to the surface-induced local smectic order. The half width at half maximum (HWHM) of that peak is identical to the reciprocal of the longitudinal correlation length  $\xi_{||}(T)$  of the critical fluctuations of the bulk nematic (1, 4, 5). Since  $\xi_{||}(T)$  diverges as  $T \rightarrow T_{NA}$ , the HWHM approaches a value that is limited by only the spectrometer resolution. We interpret this to mean that the thickness of the surface-induced smectic region is diverging as  $T \rightarrow T_{NA}$ . Within a few mK of  $T_{NA}$  the measurements place a lower limit on the thickness of the surface smectic region that exceeds 2 or 3  $\mu\text{m}$ .

Surface-induced smectic order is also observed at the gas-isotropic phase interface near to a first-order isotropic to smectic-A (IA) transition. In the case of the molecule dodecylcyanobiphenyl (12CB), as the temperature approaches  $T_{IA}$ , the number of smectic layers increases in a stepwise manner from 0 up to 5 layers. There is a triple point in the concentration ( $n$  12CB)-temperature phase diagram, and for mixtures corresponding to  $n$  less than approximately 9.55 a nematic phase intervenes between the isotropic and smectic-A phases (6). For  $9.0 < n < 9.55$  the NA transition is first order, but there is a tricritical point at  $n = 9$ , and for  $n < 9.0$  the NA transition is second order (7, 8). Although the numbers of surface layers are comparable for decyl-, undecyl-, and dodecylcyanobiphenyl, the stepwise growth becomes washed out in changing from dodecyl- to decylcyanobiphenyl (9). Although it is not surprising that the thickness of the surface-induced smectic-A layer should diverge as the temperature approaches a second-order NA transition, it is surprising to find that the width of the region of surface-induced smectic order also appears to diverge near to a first-

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order NA transition for which  $\xi_{||}(T)$  remains finite (10).

Other liquid surfaces that have been studied include the microemulsion formed from sodium di-2-ethylsulfosuccinate/water mixtures (unpublished results), and the lyotropic liquid crystal formed from micelles of cesium perfluorooctanoate (11).

Specular reflection can also be used to study the surfaces of solids, and we have carried out experiments in collaboration with George Whitesides on the structure of silane-coated silicon wafers. Destructive interference between the x-rays reflected from the air-hydrocarbon interface and from the hydrocarbon-substrate interface provides information on the uniformity of the silane coating, on the roughness of the two interfaces, and on other features of the structure along the surface normal (12).

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