

Ordering of Liquids Near Solid Interfaces

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Introduction

Thin liquid films are central to a wide range of biological, geological, and technological processes. Wetting and dewetting behavior, lubrication, nucleation, growth, and boundary-layer friction are all closely related to the atomic-scale structure and molecular interactions at the interface. In addition to force measurements, [1] several experiments have shown the layering of liquid near free surfaces [2] or – more recently – solid interfaces. [3,4] Because of experimental difficulties, however, the nature of liquid ordering near interfaces is still poorly understood.

Methods and Materials

Preliminary experiments have concentrated Ga near a Si_3N_4 x-ray window. A schematic of the experiments is shown in Fig. 1, where the x-rays are shown penetrating the 2000\AA window from below. Using this cell, which is mounted in an 8-circle Huber diffractometer on the MRCAT 10-ID line, x-ray reflectivity and evanescent-wave XAFS measurements [5] are performed. Although the initial experiments were performed at room temperature, future studies will be studying ordering as a function of temperature.

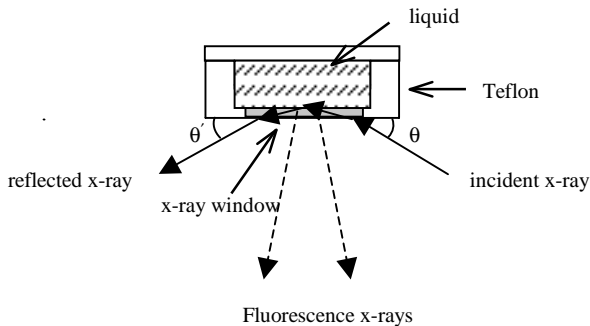


Fig. 1. Experimental configuration for x-ray reflectivity evanescent-wave XAFS measurements of liquid Ga. The temperature-controlled cell has a thin ($\sim 2000\text{\AA}$) x-ray window made of Si_3N_4 which is approximately 2mm wide \times 4mm long. To simplify sample handling, the beam is deflected downward and the fluorescence detector is mounted below the sample cell.

Results

Fig. 2 shows our reflectivity data measured at 10.6 keV (above the Ga K absorption edge). At low Q_z – below the critical angle of reflection – the x-rays are totally reflected from the surface of Si_3N_4 . Above the critical angle, x-rays easily penetrate the 2000\AA Si_3N_4 window to reach the Ga liquid. The oscillatory structure above this angle is a result of the interference between the reflected beam from the surface of Si_3N_4 and the beam from the interface between Ga and Si_3N_4 . Here we note that Si_3N_4 is a lower density material than Ga, so in the region between the critical angles of the two materials, x rays penetrate the solid completely and only the evanescent wave reaches the interface region of the liquid into $10\text{-}40\text{\AA}$, which is suitable for interface

studies. The data at lower angles is of high quality but at angles higher than 0.3 deg , long integration time is necessary to obtain high quality data. To determine the atomic layering of the liquid, higher-angle measurements of up to $Q_z = 2.5\text{-}3\text{ \AA}^{-1}$ ($10\text{-}15\text{ deg}$ at 10.6 keV) are necessary in order to probe a possible layering structure of period $3\text{-}4\text{ \AA}$. For these preliminary measurements, count rate limitations have thus far kept us from detecting a possible peak in this angular range. Beamline and sample improvements, and the dedication of more beam time to this work will enable much better quality high-angle data in the future.

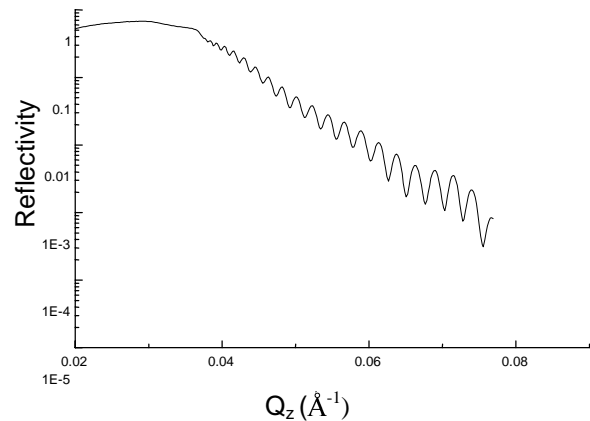


Fig. 2. X-ray reflectivity from liquid Ga with a 2000\AA Si_3N_4 window overlying the liquid. The x-ray energy is fixed at 10.6 keV , slightly above the Ga K edge. The high frequency oscillations are due to interference of the beams reflected from the outer window surface and the window-liquid interface. Slower oscillations, not immediately apparent from this figure, are presumably due to further structure (e.g. layering) in the liquid itself.

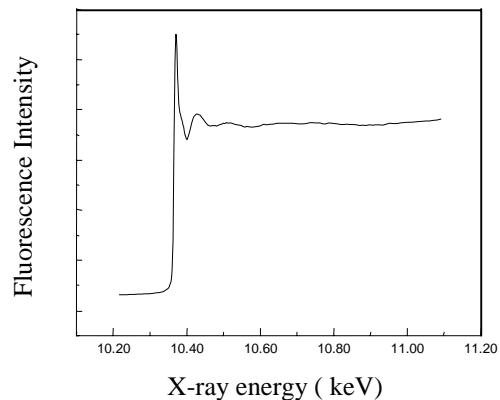


Fig. 3. Grazing-incidence fluorescence XAFS measurements of liquid Ga, at an angle corresponding to a penetration depth of a few tens of Angstroms into the liquid. For this scan, the x-rays were polarized in the plane of the interface, so that in-plane ordering of the Ga atoms would be observed. Future measurements will also involve the sample cell rotated about the beam axis, probing out-of-plane ordering as well.

Discussion

The combination of x-ray reflectivity and evanescent-wave XAFS has the possibility of probing structure in systems that have been difficult to previously study. Reflectivity is sensitive to density oscillations due to layering, and the polarization-dependent XAFS reveals short range order parallel and perpendicular to the interface.

The results shown here represent the first step in a more ambitious program to study ordering phenomena in liquids near interfaces. Other liquids to be investigated include GeBr_4 and other liquids exhibiting different surface tension. Other windows are also being investigated, including diamond. These results will be compared with theoretical predictions and molecular dynamics and Monte Carlo simulations.

Acknowledgments

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