SOFT MATERIALS & LIQUIDS

X-RAY SCATTERING REVEALS THE STRUCTURE OF LIQUIDS NEAR SOLID-LIQUID INTERFACES

A number of present and developing technologies, including applications of coatings, numerous chemical processes, thin film growth, and lubrication techniques, depend on the properties of liquids near solid-liquid interfaces. Until researchers used x-ray scattering at the Materials Research Collaborative Access Team (MR-CAT) beamline 10-ID at the APS and beamline X-18A at the National Synchrotron Light Source to examine these interfaces, the interfacial liquid structure remained poorly understood, because other experimental techniques do not permit the direct investigation of the internal structure.

In these experiments at the MR-CAT beamline, normal liquids (nonmetallic, nonpolar, nonreactive, Newtonian liquids composed of spherical, nonentangling molecules) were studied. Normal liquids were chosen in order to eliminate any added complexities. The experiments were done at room temperature, far above the freezing points of the liquids.

The (111) silicon substrates with amorphous native oxide were cleaned thoroughly and stored under deionized water until the samples were prepared. The silicon x-ray reflectivities were measured before the deposition of liquid films to measure the roughness and check that there were no adsorbed impurities. Thin (45-90 Å) and thick (5000 Å) liquid films were prepared and studied. To make thin films, tetrakis(2-ethylhexoxy)silane, or TEHOS, was dissolved in hexane. The substrates were dipped and then withdrawn at constant speeds to ensure uniform film thicknesses. To make thick liquid films, pure liquids were simply poured onto the substrates and then allowed to drain until visible interference patterns appeared. Three liquids were studied in this way: TEHOS, octamethylcyclotetrasiloxane (OMCTS), and tetrakis(trimethylsiloxy)silane (TTMSS).

Shown in Fig. 1 are specular and off-specular reflection data for thick TTMSS films, represented by solid and open circles. The inset shows the true specular reflectivity obtained by subtracting the off-specular data from the specular data. These scans were extended to unusually high q-values (1.6 Å^{-1}). Note that there are two peaks from bulk TTMSS (off-specular data), but the second peak does not appear in the background-subtracted reflectivity. This indicates that the structure of the bulk liquid is not merely enhanced in the z-direction but is also changed.

TEHOS liquid films were prepared on smooth, rough, and contaminated silicon substrates. On smooth surfaces, evidence of layering is observed, but one cannot directly determine whether these layers are near the solid-liquid interface or liquid-air interface. This problem was overcome by studying liquid films deposited onto substrates with various surface conditions: rough and contaminated surfaces. Any changes in the reflectivity data from smooth surfaces should be from the solid-liquid interface, because the air-liquid interface is far from the solid-liquid interface and the condition of the substrate surface should not affect it. For rough substrates, no layering was indicated in the data, demonstrating that the internal layers in the liquid must be forming near the solid-liquid interface. In liquid films on contaminated substrates, slow growth of the diffraction peaks is observed as impurities diffuse into the bulk liquid, further confirming that the layering is at the substrate-liquid interface.

In all three liquids, x-ray reflectivity measurements revealed layering at the solid-liquid interfaces. The liquids that were used are all normal, “spherical”-molecule liquids, so it is expected that such layering occurs in all liquids. Further, these experiments establish that layering occurs at a single solid-liquid interface, not just in ultrathin, doubly confined liquid films, as once thought.

The studies described here have sought to determine the structure of the liquid side of the solid-bulk liquid interface. The high brilliance of APS undulator radiation is an asset because these studies look at small density oscillations in weakly ordered materials (liquids), by using x-rays incident at small angles.

See: C.-J. Yu, A.G. Richter, J. Kmetko, S.W. Dugan, A. Datta, and P. Dutta, “Structure of interfacial liquids: X-ray scattering studies,” Phys. Rev. E **63**, 021205-1 to 021205-8 (February 2001).

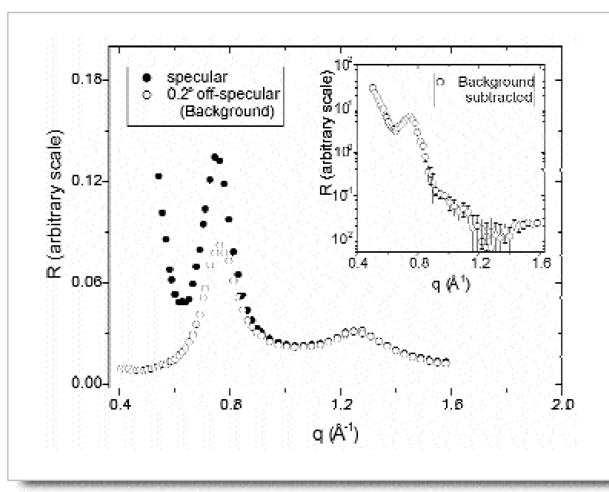

Fig. 1. X-ray scattering from a ~0.5-μm liquid film of TTMSS on a clean, smooth (~3-Å FWHM) silicon substrate. The solid circles are for wave vector q in the specular direction, and the open squares are for q at 0.1° away from the specular direction. Inset: Specular reflectivity data after substracting the background, semi-log scale.

Reprinted from APS Science 2002, ANL-03/15