X-ray reflectivity studies of confined fluids

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Introduction

Fluids confined between solid surfaces have been of great interest to researchers over the last few years [1]. This is because the structural and other properties of such fluids differ considerably from bulk fluids at the same temperature, and this has implications for our basic understanding of phenomena such as lubrication, adhesion, surface chemistry, etc. Surface force apparatus (SFA) measurements [2] and computer simulation studies [3] have found evidence for layering of the liquid molecules in liquid films confined to thicknesses of a few molecular diameters, but direct structural evidence has been lacking. (Evidence for layering near a bulk liquid/solid interface has, however, been recently obtained from x-ray reflectivity [4].)

Methods and Materials

X-ray reflectivity provides the most direct method for probing the structure of liquid films in the direction normal to the confining surfaces. However, such experiments on films confined at thicknesses of a few nanometers present significant challenges, such as (a) penetration of the beam through the confining walls and minimization of the scattering from the walls (for which extremely small and high-energy x-ray beams are essential) and (b) alignment of two solid surfaces to a controllable parallel separation of nanometers over square millimeters of area (for which the surfaces must be both highly polished and flat over such length scales, as well as dust free). In addition, the layering is rapidly destroyed by surface roughness, which typically should not exceed ~0.3 nm. We have utilized specially designed silicon substrates (see Figure 1) having a diameter of 1 inch (25.4 mm), an rms roughness of 3 Å (determined by x-ray scattering), and a convex curvature with a height variation of less than 100 Å over the whole sample area (determined by interferometry). Two grooves were etched in each surface that left a bridge of the size 2 x 4 mm^2 in the center part. The bridge is the area of confinement with a resulting height variation of less than 10 Å. For the experiment, the liquid was spread over the surface of one substrate in a class one clean room. Both substrates were put together so that the grooves formed tunnels that were the travel paths for the x-rays to the area of confinement (see Figure1). The gap distance between both silicon pieces was controlled by piezodrivers.

Results

The x-ray reflectivity experiments were performed at the Advanced Photon Source, Argonne National Laboratory. The characteristics of the setup were checked at station 2-BM-B where liquid hexadecane ($C_{16}H_{34}$) was used. Some reflectivity measurements taken at 30 keV photon energy are depicted in Figure 2. They show that the gap size shrinks linearly with increasing pressure of the piezodevices. A minimum gap size of 74 nm was achieved but no evidence was found for layering.

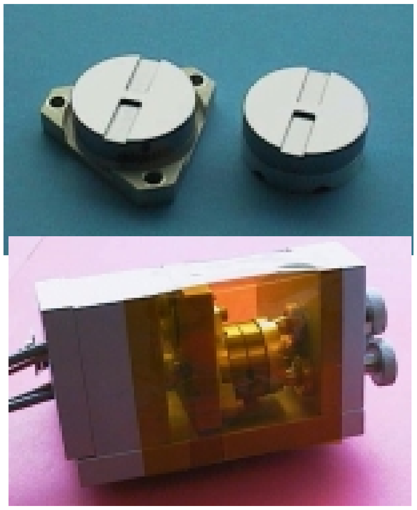

Figure 1: Components of the experimental setup for x-ray scattering on confined liquids. Top: Specially designed silicon substrates (25.4 mm diameter). The area of confinement is the bridge in the center. Bottom: The sample cell.

Further reflectivity measurements using octamethylcyclotetrasiloxane (OMCTS) were performed at station 1-ID-C, again with a photon energy of 30 keV (see Figure 3). We were able to achieve 10 times higher pressure compared to the run at 2-BM-B and thus could get much smaller gap distances. Also, the flux was much higher, allowing more details of the reflectivity to be seen.

Discussion

The reflectivity curves from OMCTS have been fitted using the following model: The silicon substrates and native oxide layers were represented with the appropriate step functions of electron density normal to the surface suitably smeared to take into account ~0.3 nm roughness and obtained by fitting to the reflectivity of the bare substrates. The OMCTS liquid between the substrates was modeled by a series of Gaussian peaks representing in-plane averaged electron densities of the molecular layers. Extremely good fits were obtained in this manner (see Figure 4). We found that both the gap and the number of molecular layers decreased in a quantized fashion with increasing pressure, from a gap size of 25.2 Å containing three close-packed layers to a gap size of 19.9 Å at the highest pressures containing two non-close-packed

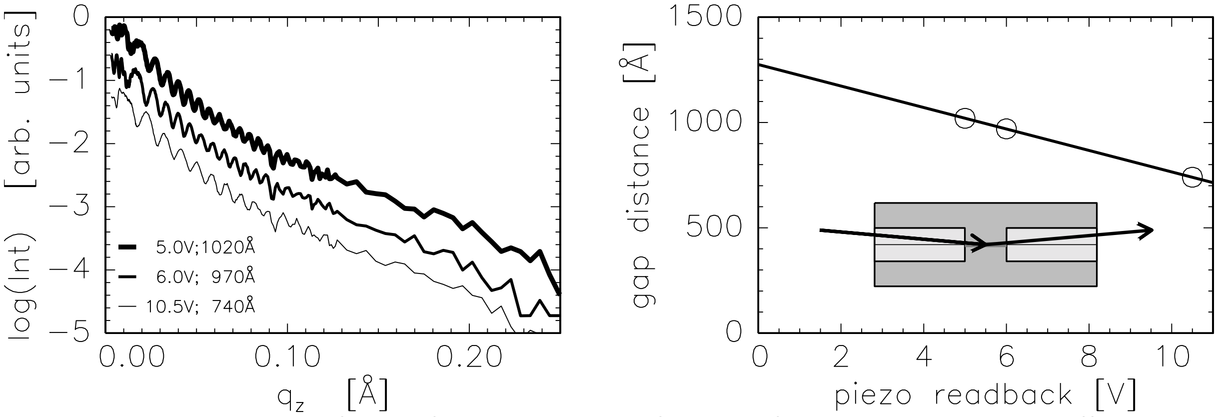

Figure 2: Gap measurements of the confined liquid setup. Left: Some reflectivity measurements at different readbacks of the piezodrivers. They show oscillations due to the gap size. Right: Characteristics of the piezodrivers and a sketch of the sample with the area of confinement in the center.

Discussion cont'd.

layers. The width of the Gaussian peaks corresponded rather well to the size of the OMCTS molecule (diameter ~8 Å).

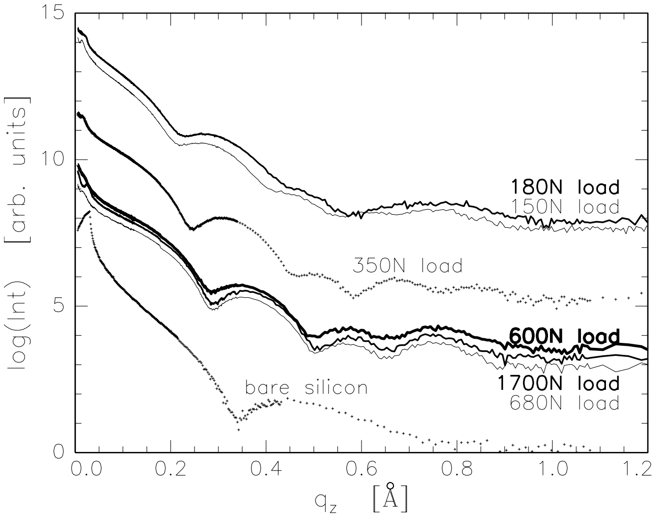

Figure 3: Reflectivities on confined OMCTS. Different pressures have been applied on the silicon substrates. Essentially, only three different reflectivities can be seen.

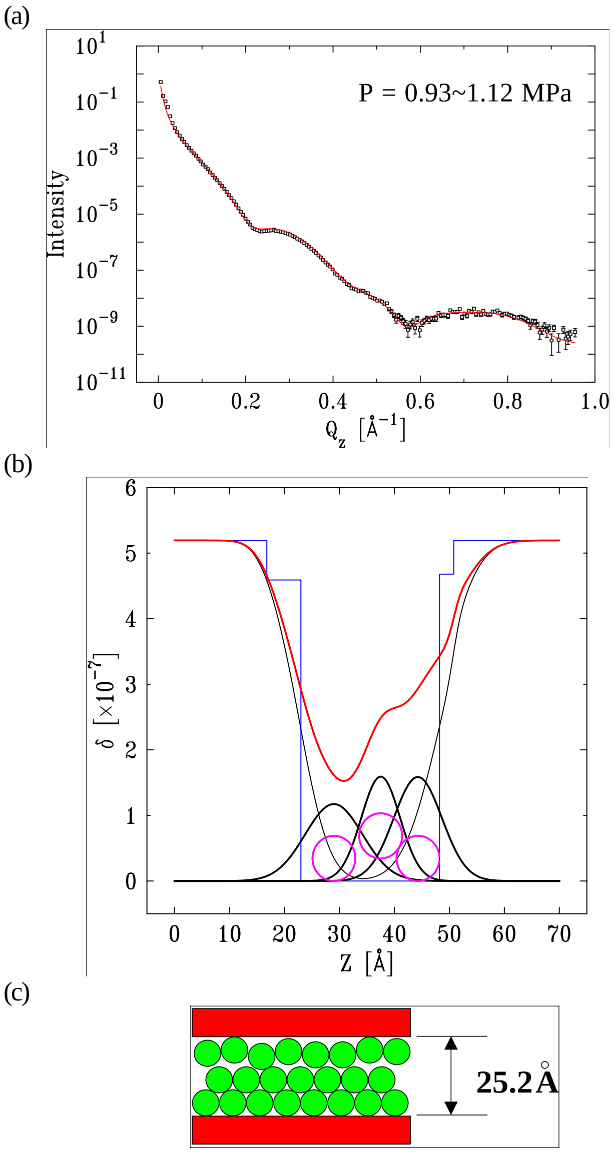

Figure 4: (a) Measured and modeled reflectivity for pressures between 0.93 and 1.12 MPa. Fitted curve uses the electron density model shown in (b). This model is schematically represented in (c).

Acknowledgments

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