

## Ordering of liquid squalane near a solid surface

Haiding Mo, Guennadi Evmenenko, Pulak Dutta \*

*Department of Physics and Astronomy, Northwestern University, Rm F225, 2145 Sheridan Road, Evanston, IL 60208-3112, United States*

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### Abstract

X-ray reflectivity is used to study the interfacial structure of liquid squalane on SiO<sub>2</sub>/Si(1 0 0) substrates. The data show that there are density oscillations ('layers') near the interface, with the squalane molecular long axes parallel to the substrate. The results are compared to those from molecular dynamics simulations and recent force measurements.

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Liquids near solid surfaces play essential roles in lubrication, coating, adhesion, wetting, chemical and biological processes, etc. Many experiments have suggested that the structure and properties of liquids near interfaces are different from that of the same liquid in the bulk. For example, surface force measurements of liquids between two smooth solid surfaces find that there are oscillations in the force acting between the solid surfaces as a function of the distance between the two surfaces [1–3]. X-ray scattering studies of liquid metals at free interfaces [4,5], and of spherical-molecule liquids near solid–liquid interfaces [6,7], show that these liquids form layered structures near single surfaces/interfaces.

The interfacial structure of liquid branched alkanes at solid interfaces has been a subject of numerous molecular dynamics (MD) simulations [8–11]. These simulations predict that branched alkanes, when confined between two solid surfaces, form layered structures in which the density oscillates as a function of the distance from the solid interface, though the density oscillations are not as pronounced as those in linear alkane systems [8,9]. However, the experimental situation is less clear. Early surface force apparatus (SFA) measurements were interpreted to indicate that the side chains in squalane disrupt molecular layering, resulting in a monotonic force–distance curves [12,13]. More

recent SFA measurements of liquid squalane confined between two mica surfaces, and atomic force microscope (AFM) measurements of liquid squalane between Si AFM tips and highly oriented pyrolytic graphite (HOPG) substrates, show that the force oscillates as the distance is varied, implying that the confined squalane is layered [14,15], but similar AFM measurements between Si AFM tips and mica surfaces do not clearly show oscillatory forces.

Moreover, as Landman et al. [8,9,16] pointed out, the force curves of branched alkanes such as squalane depend on the mode of response to the confinement, and it is conceivable that the force profiles could also depend on geometry of the confined surface. Thus, the force profiles obtained from force measurements in such systems could be substantially different from the actual density profiles of the system. Force measurements have other limitations. They cannot be used to study the liquid near an isolated liquid–solid interface, but single interfaces are important in their own right. Also, because of the dramatic increase in surface force as the two enclosing surfaces approach closer than ~1 nm, it is difficult for force measurement methods to characterize the first two squalane monolayers adjacent to the hard surface [1–3,14,15].

X-ray reflectivity has become a powerful tool for studying the structures of various interfaces, especially since synchrotron radiation became available. Indeed, this method has been used extensively to investigate the structure of free liquid interfaces [4,5,17–19], thin solid films

\* Corresponding author. Fax: +1 847 491 9982.

E-mail addresses: [h-mo@northwestern.edu](mailto:h-mo@northwestern.edu) (H. Mo),  
[pductta@northwestern.edu](mailto:pductta@northwestern.edu) (P. Dutta).

on solid interfaces [20–24], and Langmuir monolayers on water surfaces [25,26]. However, there are very few studies using X-ray scattering techniques to examine the interfacial structure of liquids, since it is relatively difficult to access the solid–liquid interface because of high attenuation by the bulk material. It has been previously shown [7] that this problem can be minimized by reducing the thickness of the liquid film to less than 1  $\mu\text{m}$ . In this Letter, we show X-ray reflectivity evidence that liquid squalane on  $\text{SiO}_2/\text{Si}(1\ 0\ 0)$  substrates forms layered structures at solid–liquid interfaces.

Polished (1 0 0) silicon substrates were purchased from Semiconductor Processing, Inc., and cleaned and stored using methods described previously [7]. Squalane was purchased from Sigma–Aldrich with a purity of 99% and used as supplied. Squalane is a branched alkane with 24 carbon atoms in the carbon backbone and 6 methyl side groups located symmetrically about the center of the molecule as illustrated in Fig. 1. It is a colorless liquid at room temperature and its melting temperature is 235 K. Thin squalane films on silicon substrates were prepared using the method described in [7]. In brief, a few drops of liquid squalane were spread on a silicon substrate; the substrate was then held vertically, allowing the liquid to drain until visible interference patterns appeared on the substrate surfaces. This takes about 30 min. Excess liquid at the lower edge was then absorbed with paper tissues. The regions studied with X-rays were at least 5 mm away from the draining edge. The film thicknesses are estimated to be about 5000  $\text{\AA}$ , but the exact thickness is immaterial. The relevant point is that the liquid film is sufficiently thick that there are no Kiessig fringes due to the total thickness, since the X-rays reflected from the solid/liquid and the liquid/air interfaces are not coherent. At the same time, the liquid films are thin enough that absorption of X-rays going to the solid–liquid interface is small.

Specular X-ray reflectivity studies were performed at Sector 10 (MRCAT) of the Advanced Photon Source at Argonne National Laboratory. The beam size was  $\sim 0.4$  mm vertically and  $\sim 1$  mm horizontally. The samples were under flowing helium during the measurements to reduce background scattering and radiation damage. In addition to specular scans, slightly off-specular ‘background’ scans were performed and subtracted from the specular data, thus removing bulk (isotropic) features in the data.

Fig. 2 shows specular reflectivity data and two ‘background’ scans taken  $\pm 0.1^\circ$  off the specular direction. All scans show peaks at  $\sim 1.28 \text{\AA}^{-1}$ , which gives a  $d$ -spacing of  $\sim 4.9 \text{\AA}$ . However, the peak in the specular direction is stronger than the off-specular peak. The off-specular peaks are

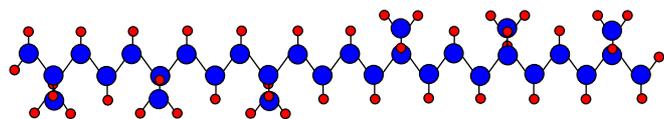


Fig. 1. Structure of squalane as projected onto its carbon backbone plane.

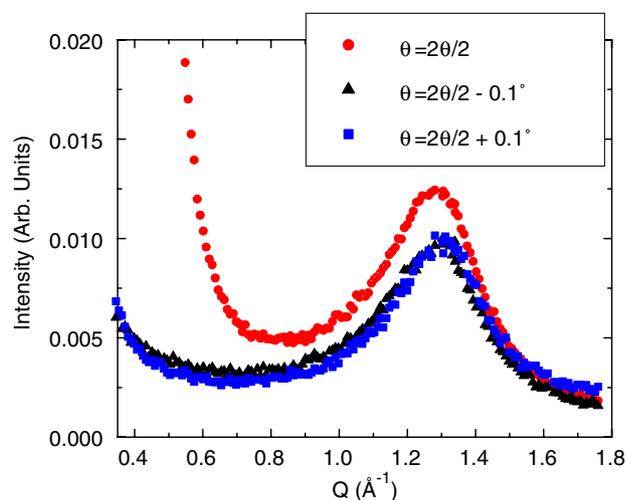


Fig. 2. X-ray specular scattering scan and slightly off-specular ‘background’ scans for a thin film of liquid squalane on a polished oxidized silicon substrate.

due to the isotropic short-range order in the bulk liquid. When squalane is deposited on an unpolished substrate, the specular peak has the same intensity as the off-specular peak, i.e. there is no peak in the background-subtracted data. Comparing the data on polished vs. unpolished substrates tells us that the layers are formed at the solid–liquid interface. The position of the background-subtracted peak gives us a  $d$ -spacing of  $4.95 \pm 0.05 \text{\AA}$ . The peak FWHM is  $\sim 0.25 \text{\AA}^{-1}$ , corresponding to a coherence length of  $\sim 25 \text{\AA}$ . The  $d$ -spacing of the peak is comparable to the width of the molecule, which indicates that the molecules near the solid–liquid interface are ‘lying down’ with their molecular long axes *preferentially* parallel to the substrate. This is consistent with results from MD simulations of liquid alkanes near solid substrates [8–11,27].

While the peaks near  $1.25 \text{\AA}^{-1}$  establish that there is a density-layered interfacial structure, fitting the specular reflectivity data with model electron densities is required to extract more details. We first fitted the data assuming that the electron density is an exponentially decaying sine function [28]

$$\Delta\rho(z) = A \exp\left(-\frac{z}{L_d}\right) \sin\left(2\pi\frac{z}{L} + \varphi_0\right),$$

where  $\Delta\rho$  is the small deviation from the uniform bulk electron density of liquid squalane. This simple model fits the data reasonably well (Fig. 3). The best fit gives an electron density oscillation amplitude of  $A = (0.150 \pm 0.005) \rho_{\text{Si}}$  and a decay length of  $L_d = (5.6 \pm 0.1) \text{\AA}$ . This electron density is plotted in Fig. 4, and shows there are two to three layers of squalane near the interface. The amplitude of the density oscillations is about twice that previously found for TEHOS, a spherical molecule [29]. This may be a consequence of the anisotropic shape of the squalane molecules [30]. It appears that the decay lengths are proportional to the widths of the molecules, which results in about the same number of layers near the interface for both liquids, although the width of a TEHOS molecule is about twice

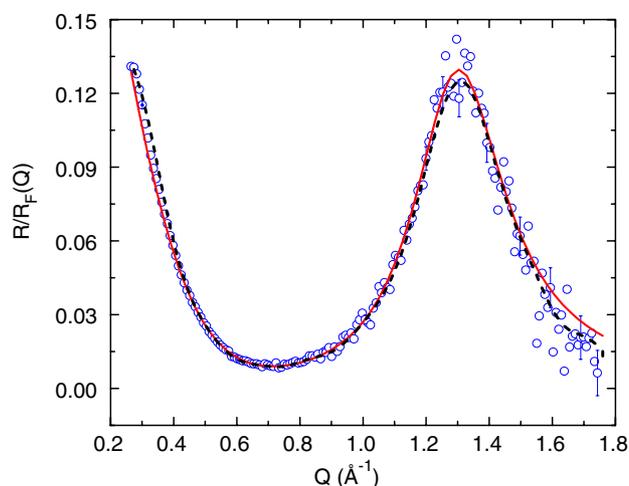


Fig. 3. Specular reflectivity data from the silicon-squalane interface after normalized to the Fresnel reflectivity. The solid and the dashed line are exponentially decaying sine fit and model-independent fit, respectively.

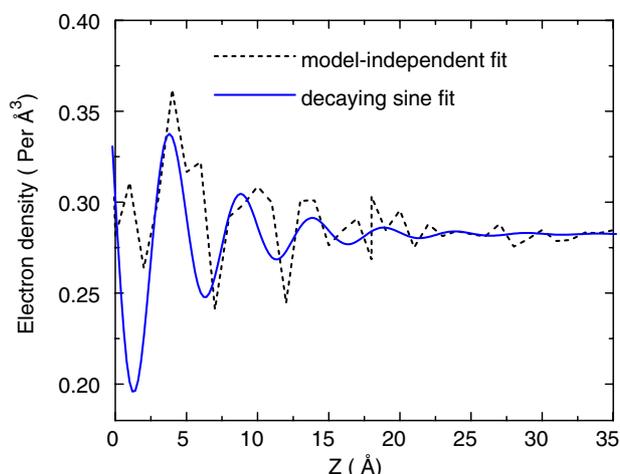


Fig. 4. The decaying sine function electron density (solid line), and the model-independent electron density (dashed line) that best fit the reflectivity data. In both cases, the electron density of the substrate is not shown.

of that of squalane and the structures of the two molecules are different.

Although this exponentially decaying sine function density profile fits the data well, both MD simulations and force measurements [8,9,14,15] indicate that the actual interfacial structure could be more complex. For example, Lim and O'Shea [14] found that spacing between the second and third layers was  $5.1 \pm 0.2$  Å, about 0.7 Å less than the average spacing of layers further away from the substrate. Therefore, the data were also fitted using a model independent approach, as described in [6]. The liquid squalane within 40 Å of the solid surface was divided into forty 1 Å slices, with a constant electron density in each slice. The liquid further away from the substrate was modeled as a uniform slab. The data were fitted by varying the electron densities of slices independently.

Overall, the two approaches fit the data very similarly, except that at high  $Q$ s the model-independent fit fits the data better than the decaying sine fit. The results of the model independent fit are shown in Fig. 3 as a dashed curve. This fit is inevitably less smooth, but still clearly indicates two well defined layers. A third layer may be present, but this is obscured by the noise in the data.

The maximum electron density of the first layer is about 10% higher than that of the second layer, and 25% higher than that of the bulk liquid, indicating that the first layer packs more tightly than the second layer. The layer spacing from X-ray scattering is in good agreement with the spacing between the second and third layers ( $5.1 \pm 0.2$  Å) and smaller than that between layers further away from the substrate ( $5.7 \pm 0.6$  Å) observed in the force measurements [14].

As noted earlier, the squalane molecules at the interface organize with their long axes preferentially parallel to the substrate. This is consistent with MD simulations [8,9,27]; however, these simulations predict much larger density oscillations than we observed. These simulations use ordered and perfectly smooth metal substrates, which may explain the difference (our polished substrates have  $\sim 3$  Å roughness). Previous experiments have shown that the amplitude of density oscillations strongly depends on the surface roughness of the substrate [6], and similar results were obtained in recent MD simulations of confined liquids between solid substrates [31,32].

In summary, our X-ray scattering results indicate that squalane forms 2–3 density layers near an oxidized silicon interface, with molecular long axes preferentially parallel to the substrate. The layer spacing is in agreement with that of layers close to the surfaces, but smaller than that of layers further away from the substrate as seen in recent AFM measurements, which suggest that additional loose bound layers in confined liquid squalane might be induced by the confinement.

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