Interface profiles of polar and nonpolar liquids at hydrophobic surfaces

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Abstract

A density-depleted region (“gap”) is known to exist between water and hydrophobic surfaces. Using X-ray reflectivity, we have observed similar gaps between hydrophobic self-assembled monolayers (SAMs) and four other polar liquids. For these liquids as well as for water, the observed electron density depletion can be largely attributed to the lower-electron-density layer of hydrogen atoms at the SAM surface. On the other hand, the observed X-ray reflectivity from the interfaces between SAMs and three nonpolar liquids studied can be explained either without gaps or with smaller gaps. Thus polar liquids (including but not limited to water) stand away from even the terminal hydrogen atoms at hydrophobic surfaces, while nonpolar liquids interpenetrate and thus partially or completely fill in the gap. There is no identifiable correlation between the size of the gap and the liquid-SAM contact angle or the relative polarity of the liquid.

How does a liquid make contact with a solid surface? The profile of a solid-liquid interface is relevant to many real-world processes and applications such as lubrication, chemical reactions, drug delivery, coating adhesion and labs-on-a-chip. In particular, the interface between water and hydrophobic surfaces has been the subject of much theoretical and experimental attention [1-10].

Water is of course a crucially important liquid, but it is not the only liquid of interest in real-world applications. Tribology, for example, often involves organic lubricants. The interactions between molecules and surfaces are complex and include electrostatic forces, van der Waals forces, hydrogen bonding, etc. Is every liquid different, or are there some general features

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regarding how liquids make contact with surfaces? We addressed the question by studying the interface profiles between octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) hydrophobic surfaces and several molecular liquids (four polar liquids in addition to water, and three nonpolar liquids).

Although there are spectroscopic methods sensitive enough to detect molecular orientation and bonding at interfaces [11], there is no probe of interfacial density profiles other than synchrotron x-ray reflectivity (XRR) that approaches the necessary sub-nanoscale resolution. (Neutron reflectivity is in principle similar, but neutron beams have much lower usable intensities and therefore poorer spatial resolution [8].) Therefore, in the present study we have used synchrotron X-ray reflectivity to look at various liquid-SAM interfaces.

In all cases we have fitted the observed X-ray reflectivities from the liquid-SAM interfaces using slab models with (and also without) gap layers (Fig. 1). We have then plotted some confidence regions (explained below) in the plane of gap width ($D_g$) and gap electron density ($\rho_g$) parameters. Because the confidence regions are irregularly-shaped rather than perfect ellipses, they cannot be fully described by quoting the best-fit values and uncertainties of the individual parameters. On the other hand, visual inspection of these confidence regions clearly reveals the underlying phenomena.

Past X-ray reflectivity studies have found that the gap, when present, is resolution limited in most cases; for a discussion see Ref. 9, 10. A consequence is that one cannot measure the specific shape of the gap, but must approximate it as a square well (Fig. 1) with error-function-rounded edges. Even then, the method does not determine either the width ($D_g$) or the electron

Figure 1. LEFT: The box model interfacial density profile used to fit the XRR data at liquid-SAM interfaces. The interfaces are shown in the figure as sharp steps for clarity, but in the actual data analysis are rounded using error functions. Note that the SiO$_2$ layer at far left, and the liquid layer at far right, are modeled as semi-infinite slabs because they are much thicker than the photon coherence length. RIGHT: Schematic diagram showing the geometry of the XRR experiment using a transmission cell.
density (\(\rho_g\)) of the gap with great accuracy. It has been pointed out that the method more accurately measures a combination of these variables [4]: the integrated depletion \(D_g(\rho_L - \rho_g)\), or equivalently the ‘effective gap thickness’ defined by \(D_{eq} = D_g(\rho_L - \rho_g)/\rho_L\), where \(\rho_L\) is the electron density of the bulk liquid. This combination of gap width and gap electron density can be interpreted as the width of a hypothetical ‘empty’ (\(\rho_g=0\)) gap that has the same integrated depletion.

Multiple X-ray observations of the gap between water and OTS SAMs [4-7] imply effective gap thicknesses \(D_{eq}\) of close to 1 Å. For example, Mezger et al. report data corresponding to \(D_{eq} = 1.1\) Å in three papers [4,6,7]. The data in Poynor et al yield similar but slightly higher numbers (2-3Å). In addition to water, molten octadecanol has been reported to show an interfacial gap with a similar \(D_{eq}\) [13]. However, Ocko et al [14] have pointed out that 1Å is roughly the density depletion due to the layer of CH\(_3\) groups at the surface of the SAM molecules, which have a lower electron density than CH\(_2\) groups. We can equivalently attribute this depletion to the terminal H atom (circled in Fig. 1) of each SAM molecule. (Water also shows a gap at fluorocarbon SAMs [7,9,10], even though these do not have a low-density terminal layer. However, those substrates are more hydrophobic than hydrocarbon SAMs.)

Our OTS SAMs were prepared following Wang et al [14] with a few modifications. We used polished thermal (thick) silicon oxide. This eliminates the extra Si-SiO\(_2\) interface that exists in silicon wafers with thin (~10Å) native amorphous oxide. The structure of that interface [15] is of no interest in the present study or in most studies, but adds unnecessary variable parameters to the data fits that increase the uncertainty in the parameters of actual interest. Our thick oxide substrates also facilitate comparison of reflectivity data from one sample to another, unlike Si wafers with native oxide where the Si-SiO\(_2\) interface position and profile may vary from sample to sample. The samples are mounted to the transmission cell, made of Teflon with Kapton windows, using a Teflon screw. The transmission geometry is shown in Fig. 1; more details of such cells can be found elsewhere [4-10]. About 2mL solvent is injected into the transmission cell with a glass syringe. All studies were performed at room temperature.

The X-ray reflectivity measurements were performed at Beam Line 12BM-B of the Advanced Photon Source. The x-ray energy was 19.5 KeV. The beam was focused to 0.2 mm x 0.2mm. The data were collected with a Pilatus 100K area detector. The off-specular background was determined from the area detector data by taking the counts in directions shifted \(+0.2^\circ\) and \(-0.2^\circ\) from the specular direction and averaging them. These directions are sufficiently far from the specular direction that they represent the uniform background. This background was subtracted from the specular counts.

The quality of the OTS film is key for liquid – solid interface studies. This is especially true for XRR measurements since the X-rays cover a large footprint on the sample, and lateral variations will blur the phenomena of interest. Poynor et al [5] have found that bad-quality samples show quite different reflectivity patterns from normal samples. Our samples were examined with water contact angle measurements (VCA Optima XE), and had \(>115^\circ \pm 3^\circ\) advancing contact angles, in agreement with the literature [14,16]. The reflectivity measurements were also performed on
OTS films in contact with air, showing clear oscillations up to 0.84 Å⁻¹ (Fig. 2, center column, top). Fitting of dry OTS data gave parameters (see Supplemental Material [17]) that are in agreement with other published results [18].

When a liquid replaces the ambient air, the electron density contrast at the interface is reduced, and the XRR curves are different from the dry OTS curve (Fig. 2). All the minima shift to higher q values compared to dry OTS. The polar liquids show stronger peaks and valleys in the reflectivity compared to the nonpolar liquids. To fit reflectivity data, the electron density of the OTS SAM/solvent system is modelled as a succession of slabs (Fig. 1). The model reflectivity was calculated by Parratt’s recursive method. The fitting merit function used is the logarithmic form [10,19]:

\[ \gamma^2 = \beta \sum_{i=1}^{N} \left[ \log R_{exp}(q_i) - \log R_{cal}(q_i) \right]^2 \]

Here N is the number of data points, and \( R_{exp}(q_i) \) and \( R_{cal}(q_i) \) are the experimental and calculated (model) reflectivities at wave vector \( q_i \). This logarithmic merit function [19] has a better fitting weight over the whole range and is not dominated by the much more intense low-q region of the reflectivity [17].

Following Steinrück et al [18], the OTS layer was represented by three slabs: the first slab represents the silane anchor at the substrate; the second slab accounts for the higher density Si-O-Si group, and the third slab represents the hydrocarbon chains. Unlike Ref. 18, our silicon substrate has a thick oxide layer and therefore requires only one semi-infinite slab. For the XRR data from OTS-solvent interfaces, a gap layer was introduced into our fits, as well as a semi-infinite layer of liquid of known electron density. (All these slabs are shown in Fig. 1.) Fits were also performed without a gap but with the semi-infinite liquid.

Since the SiO₂ layer and liquid layer are semi-infinite and have known electron densities, our model contains the following variable parameters: four slab widths (\( D_{\text{head1}}, D_{\text{head2}} \) and \( D_{\text{chain}} \) for the SAM, and \( D_{g} \) for the gap), four slab electron densities (\( \rho_{\text{head1}}, \rho_{\text{head2}}, \rho_{\text{chain}} \) and \( \rho_{g} \)), and five interface widths (\( \sigma_{\text{Si-head1}}, \sigma_{\text{head1-head2}}, \sigma_{\text{head2-chain}}, \sigma_{\text{chain-gap}}, \sigma_{\text{gap-liquid}} \)). In each group, the last variable is obviously not used for fits that do not include a gap. We used our own fitting program to vary these parameters and to generate the data for the confidence region plots (discussed further below). The allowed ranges of these parameters were restricted to prevent the software from arriving at unreasonable values. All interface widths were required to be \( >1\AA \), and SAM layer densities were allowed to vary no more than 5% from the values obtained in a dry-SAM XRR fit.

A slab model with a gap layer (as shown schematically in Fig. 1) will fit the XRR data from all liquids (Fig. 2, left). Without the gap layer (Fig. 2, middle), the fitting for the nonpolar liquids pentane and hexane still works well. The no-gap fit for heptane is not very good. For all the polar liquids as well as water, the no-gap fit fails badly--- the best-fit reflectivities (solid lines) do not conform to the data. Thus a gap is necessary to fit the polar liquid reflectivity data. Parameters for the fits in Fig. 2 are tabulated in the Supplemental Material [17].
Figure 2. Reflectivity data normalized by the Fresnel reflectivity for the dry OTS film (labeled ‘air’) and OTS films with liquids (labeled with liquid name). The lines through the data show fits to slab models of the interfacial profiles (Fig. 1) LEFT: Best fits including a density-depleted gap layer. MIDDLE: Same data, with best fits not including a gap layer. RIGHT: Electron density profiles for the gap fits shown in the left panel, i.e. for the fits that include gaps. (The model parameters for these fits can be found in the Supplemental Material [17]).

It has been frequent practice in the reflectivity literature to report only a single set of best-fit parameters as determined by fitting software. In fact, one cannot attribute any particular significance to the single fit corresponding to the global or local minimum of the merit function [20]. If the data points are randomly shifted up or down by less than their statistical error, the best fit parameters will change as well. Thus, crucial information is contained in the confidence regions of parameter space: a 68% confidence region, for example, means that there is only a 68% likelihood that the true parameters (i.e. the parameters that will fit infinitely accurate data) fall within that region. Fig. 3 shows the 68%, 95%, 97% and 99% confidence regions [20] in the $D_g$-$P_g$ plane. Incidentally, the “best fit” by itself would occupy a 0% confidence region. Further discussion of the merit function and confidence intervals are in the Supplemental Material [17].
Figure 3. Contour maps showing the 68%, 95%, 97% and 99% confidence regions for the parameters $D_g$ and $\rho_g$ used in fits to reflectivity data with models that include a gap. The dashed curved line in each plot corresponds to $D_{eq} = 1.0\text{Å}$. This is approximately the electron density depletion due to the terminal $H$ atoms in the SAM; it is not an exact value, and the line is merely a guide to the eye. The red dashed horizontal line corresponds to the bulk liquid electron density: along this line $\rho_g = \rho_L$ and therefore there is no gap. There is also no gap at points along the $y$-axis because $D_g = 0$ there.

Each of the eight contour maps in Fig. 3 is constructed from 14400 (120x120) fits at equally spaced points across the $D_g-\rho_g$ regions shown. At each point, $D_g$ and $\rho_g$ were fixed and the other parameters were allowed to vary until the best fit at the point is found. The resulting minimized
merit functions were then used to determine the confidence regions. (Note that this is quite different from keeping all the other parameters fixed and simply calculating the non-minimized merit function at each point in the plane, as some canned fitting programs will do.)

The confidence regions do not generally have the idealized elliptical form from which a mean value and an error estimate for each parameter can be individually determined. Rather, the regions have irregular shapes: the mean value of $\rho_g$ and its uncertainty depend on the value of $D_g$, and vice versa. Further, there is no absolute criterion to tell us what confidence level should be used; thus some qualitative assessment is always required. In the present case, the conclusions described below are robust, i.e. independent of the specific confidence region chosen.

Each panel in Fig. 3 contains two lines as guides to the eye. The horizontal dashed line is the bulk electron density of the liquid used. When a dark region (low merit function, i.e. excellent fit) reaches this line, it means that the gap has the same density as the bulk liquid, i.e. there is no gap. The same thing is true along the y-axis, where $D_g=0$. The dashed curved line connects all $D_g$ and $\rho_g$ values corresponding to $D_{eq}=1\,\text{Å}$, approximately what is expected for a gap due to the layer of terminal H atoms [12] but not an exact number.

Water and the four other small-molecule polar liquids (acetone, methanol, ethanol and 1-propanol) show quite similar merit function contours. The confidence regions never include either the horizontal $\rho_g=\rho_L$ lines or the y-axes. These regions have a tendency to mimic the shape of the $D_{eq}=1\,\text{Å}$ line, confirming that $D_{eq}$ is more significant than $D_g$ or $\rho_g$ individually. For water, acetone, methanol and ethanol, the confidence regions are below the 1Å line, with $D_{eq}$ averaging roughly 1.5Å. For 1-propanol, the confidence region is roughly symmetric about the 1Å line, i.e. $D_{eq} \approx 1.0\,\text{Å}$. Given the widths of the confidence regions, we attach no particular significance to the specific numbers above. These data are consistent with published data for water [4-7] and octadecanol [13]. We see no obvious trends within this group of liquids as functions of relative polarity---this varies from 1.0 (water) to 0.36 (acetone), but the gap is not significantly different. (A table of relative polarity values is in the Supplemental Material [17]).

Pentane and hexane (short chain nonpolar liquids) are quite different. The confidence regions are much broader, and spread out to include the horizontal $\rho_g=\rho_L$ line and the y-axis, where $D_{eq}=0$. They also include the $D_{eq}=1\,\text{Å}$ line, but parsimony requires the simpler model, i.e. one with no gap. Gaps are not required to fit the pentane and hexane data, as also illustrated in Fig. 2. Adding more variable parameters to any model generally results in improved fits, but that is not true here.

Heptane, which is the longest molecule of all the liquids studied, occupies an intermediate position. A gap is required to fit the data (the zero-gap lines are outside our confidence intervals, although just barely). The confidence regions are predominantly above the 1Å line, i.e. $D_{eq} < 1\,\text{Å}$.

The magnitude of the gap is not correlated with the OTS-liquid contact angle. For example, our OTS surfaces show a contact angle of $115 \pm 3^\circ$ with water. Published data [21] show that acetone
has a contact angle of 9.5° on OTS, close to that of heptane (<10°). Yet water and acetone show similar gap contours, whereas heptane is completely different.

We conclude that polar liquids stand away from the terminal H atoms, even when the molecules are small; in other words, polar liquids ‘mind the gap’. Nonpolar liquids, on the other hand, tend to fall into the gap and reduce its effective size, with smaller-molecule nonpolar liquids completely filling in the gap.

Much of the previous relevant literature on the topic of the interfacial gap [4-10] has been about water. Studying multiple liquids under otherwise identical conditions clarifies the situation considerably. We can now see that for polar liquids, the gap does not depend strongly on the liquid used, but is largely a property of the substrate. Indeed, while there is an extensive body of work [1-3] focusing on water as a presumably unique liquid, we find nothing special about water as far as the gap at a hydrophobic alkane surface is concerned.

Our results might appear to imply that the gap is merely a detail deriving from the near-ideal molecular arrangement of the OTS SAM. In fact, however, this arrangement provides us with a particularly sensitive measure of how different liquids interact with common hydrophobic interfaces. Less-ordered hydrocarbon surfaces will also have hydrogen atoms at the surface, but not as many. We suggest that the local environment of each H atom at the surface will still be the same as what we see in OTS monolayers, but the surface-averaged gap size will be smaller. This is consistent with the 0-0.5Å gap reported for interfaces between liquid alkanes and water [22].

It is known that water is oriented at hydrophobic interfaces [11,23,24]; it is likely that other polar liquids are oriented also. This may result in a hydrogen-bonded interfacial network that helps keep the liquids away from the solid surface. Nonpolar liquids, on the other hand, are attracted to the hydrophobic molecules. The result is that polar and nonpolar liquids form quite different interfaces, a finding that is likely to have implications for tribological response, adhesion and many other solid-liquid interface processes.

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References

17. See Supplemental Material at [URL will be inserted by publisher] for tables/graphs/discussion of fitting parameters and merit functions