

**The fluorocarbon-water interface: how water meets  
a very hydrophobic surface**

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## **Abstract**

When water sits on a surface that repels it, is there an intervening nanoscale low-density region such that the bulk water never touches the surface? Resolution-limited X-ray and neutron scattering experiments have presented evidence both for and against this possibility. We have used synchrotron X-rays to study the interface between water and fluoroalkylsilane self-assembled films, which are significantly more hydrophobic than the previously studied surfaces. The width of the depleted region is found to increase with aqueous contact angle, making unambiguous measurements possible. When the advancing contact angle is  $120^\circ$ , the effective depletion layer thickness is  $\sim 5\text{\AA}$ . While X-rays cannot determine directly whether or not there are interface fluctuations, the data place an upper limit of  $3.5\text{\AA}$  on the RMS interface width attributable to such fluctuations.

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## **Introduction**

The hypothesis that thin density-depleted regions exist between water and hydrophobic surfaces has been actively discussed for several decades (1-6). It is a compelling idea for many reasons, for example it provides a simple explanation for the large slip lengths seen in studies of shear flow at superhydrophobic surfaces (7). A microscopic description of the water-hydrophobic interface is essential to understanding how proteins fold in aqueous environments, how membranes interact with water, and the physics of interfaces within colloids. Both theoretical studies and computer simulations (3-6) predict depleted interface regions. Neutron and X-ray reflectometry, very widely used today, are direct nanoscale probes of the density profile normal to an interface. It is therefore surprising that experimental consensus has proved so elusive.

Several specular neutron reflectivity studies (8-10) have reported remarkably wide ( $\sim 10\text{-}30\text{\AA}$ ) depletion regions, but this is now attributed (11,12) to the lower resolution of neutron reflectivity and the consequent broadening of finer features. Another neutron experiment reported no depletion at all (13). The three most recent and detailed X-ray (11,12) and neutron (14) studies are worth reviewing here. Synchrotron X-rays were used by Poynor et al (11) to examine the octadecyltriethoxysilane (OTE) - water interface, and by Mezger et al. (12) to examine the octadecyltrichlorosilane (OTS) - water interface. Both substrates are methyl-terminated at the upper surface. Synchrotron beams have higher intensities, and thus the specular reflectivity technique achieves better resolution normal to the plane with X-rays than with neutrons (the width of the resolution function is  $\pi/q_{z,\text{max}}$  where  $q_{z,\text{max}}$  is the highest momentum transfer reached by the specular

reflectivity scan). These X-ray experiments found depletion layer widths of a few Å, in the same range as the X-ray resolution and the surface roughness. Mezger et al. therefore calculated the product of the width ( $D$ ) and the electron density *deficit* relative to the bulk electron density ( $\rho_{\text{H}_2\text{O}} - \rho_{\text{dep}}$ , where  $\rho_{\text{dep}}$  is the density of the depleted region) which they found to be a more robust parameter. We have converted this product to the parameter used in Ref. 14, namely the equivalent width of a zero-density gap,  $D_{\text{eq}} \equiv D(\rho_{\text{H}_2\text{O}} - \rho_{\text{dep}})/\rho_{\text{H}_2\text{O}}$ . The Mezger et al data yield  $D_{\text{eq}} \approx 1.0 \text{Å}$ , while the Poyner et al. data yield  $D_{\text{eq}} \approx 1.8-3.3 \text{Å}$ . It may appear that there is qualitative agreement, but Ocko et al. (15) have pointed out that the terminal hydrogen atoms of the SAM molecules have a negligible electron density and are invisible to X-rays (indistinguishable from air/vacuum) at a dry surface. When sandwiched against water, however, there is a density contrast and the hydrogen atom layer shows up as an electron-depleted layer. This effect is intrinsic to all methyl-terminated surfaces, and has nothing to do with hydrophobicity.

Indeed Poyner et al later reported (16) that the ethanol-OTE interface also shows a depletion, corresponding to  $D_{\text{eq}} \approx 1.0 \text{Å}$ , even though the contact angle of ethanol on OTE is small. This number is essentially the same as the estimate of Ocko et al. extracted from lamellar alkane and lipid data in the literature (the depletion in these systems must be divided by 2 because there is one terminal hydrogen atom from each side of a bilayer). This “hydrogen gap” explains essentially all of the depletion reported in ref. (12), while the gap reported in ref. (11) is  $\sim 0.8-2.3 \text{Å}$  after subtracting the hydrogen gap.

Using neutrons, Maccarini et al. (14) studied the interface of water with various partially-deuterated alkanethiol monolayers. Here as well, depletion was observed with both water and nonpolar liquids. They therefore subtracted the non-hydrophobic depletion from that seen with water. The corrected depletion has error bars that include 0, for example, at pH=5.5,  $D_{eq}=1.4 \pm 1.6\text{\AA}$ .

Thus, in answer to “Is there a hydrophobic gap?”, one might say that the data of Ref. (11) say yes, the data of Ref. (12) say no, and the data of Ref. (14) say maybe. How can these very important measurements be made definitive? One possibility is to improve the experimental resolution, but gaining a mere factor of 2 in resolution would require several orders of magnitude increase in incident X-ray intensity. Such intensities are not currently available, and if available would undoubtedly destroy the samples. The other approach is to seek a substrate on which there is a stronger and thus more easily measured hydrophobic depletion.

## Results

We have studied the interface between water and fluoroalkylsilane self-assembled monolayers (SAMs) adsorbed on silicon substrates. Specifically, we have made SAMs using  $\text{CF}_3(\text{CF}_2)_{11}(\text{CH}_2)_2\text{SiCl}_3$  and  $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ , referred to in the rest of this paper as FS14 and FS8. These monolayer materials are more hydrophobic than methyl-terminated monolayers: the measured advancing contact angles were  $120^\circ$  for FS14 and  $111^\circ$  for FS8. This trend as a function of chain length is the same as that previously reported (17). Moreover, the atoms at the surface are fluorine atoms ( $Z = 9$ ) rather than hydrogen atoms. Using the relevant atomic numbers and atomic radii, and the average

electron density of the SAMs as measured in our experiments, we estimate that the top layer of F atoms has roughly half the electron density of water. Thus the density contrast is roughly the same whether the material on top of it is air or water. The F layer, unlike an H layer, contributes to the observed electron density profile of the dry SAM surface, and no special corrections are needed to account for “invisible” atoms.

The sample cell consisted of a thin film of water sandwiched between the SAM-coated silicon substrate and a 7.5 $\mu\text{m}$  thick window made of Kapton (Fig. 1). Similar sample cells have been used in other liquid-solid interface studies (e.g.(11,18)). We initially found this configuration to be difficult to achieve, because the tendency of water to bead is stronger for these more hydrophobic surfaces. However, if the window material is sufficiently hydrophilic, that renders it energetically favorable for a thin film of water to remain between the two interfaces. Kapton as purchased is only weakly hydrophilic, but the windows were made more hydrophilic (and simultaneously cleaned) by treatment in an oxygen plasma for 3 minutes (19). After this treatment, stable water films  $\sim 1\mu\text{m}$  thick were readily formed.

In Fig. 2, the top panel shows X-ray reflectivity data for the FS14 surface and the FS14-water interface. It can immediately be seen that the phase shift between the dry and wet reflectivity oscillations, which is attributable to the gap, is much larger here than in the OTS/OTE-water system (11,12). This is the qualitative basis for the fitted numbers reported below.

The dry FS14 data were fitted using the commonly used Parrat formalism. Uniform-density slabs, with error-function-rounded interfaces, were used for the silicon substrate, the silicon oxide layer, and the SAM (two slabs). The slab parameters were varied

to obtain the best fit, shown as lines through the data in Fig. 2 (top panel). The dry SAM density profile thus obtained is shown in the inset. Reflectivity studies of similar SAMs were first performed by Geer et al. (20), and our results match well with theirs. Since the density profiles of dry SAMs are not of specific interest here, further details will be published elsewhere.

The FS14-liquid interface reflectivity data were fitted by taking the dry profile and adding variable slabs for the interface region and for the semi-infinite water region, with rounded interfaces. The electron density of water is constrained to its known value. The best fit profile is shown in the lower panel of Fig. 2, with the dotted lines indicating the slabs (without interface rounding) and the solid line indicating the final profile (with rounded interfaces as determined by the fits). The width of the unrounded depletion region is  $D = 8.6 \pm 0.12 \text{ \AA}$  and the electron density in this region is  $\rho_{\text{dep}} = 0.13 \pm 0.02$  electrons/ $\text{\AA}^3$ . Since water has  $0.334$  electrons/ $\text{\AA}^3$ , we get  $D_{\text{eq}} = 5.1 \pm 0.5 \text{ \AA}$ .

Some additional information of interest is contained in the contours of  $\chi^2$  in the  $D$ - $\rho_{\text{dep}}$  plane near its minimum value (inset, lower panel of Fig. 2). These contours were constructed by determining  $\chi^2$  for an 11x11 matrix of  $D$  and  $\rho_{\text{dep}}$  values, and then interpolating. The line through the plot indicates the path along which  $D_{\text{eq}} \equiv D(\rho_{\text{H}_2\text{O}} - \rho_{\text{dep}})/\rho_{\text{H}_2\text{O}}$  is the same as its value at the center of the contours. If this constant- $D_{\text{eq}}$  curve were to follow the major axis, it would mean that  $\partial(\chi^2)/\partial D_{\text{eq}}$  is the largest possible, in other words  $D_{\text{eq}}$  (or equivalently, the integrated density depletion quoted in refs. (12,15,16) would be the most robust combination of fitting parameters. However, that is not the case here. We suggest that this is because our depletion region is wider than the resolution function (width  $\pi/q_{\text{max}} \approx 3.5 \text{ \AA}$ ). In the limit where the depleted region is *much*

larger than the resolution, we speculate that the two parameters will be completely uncorrelated and the axes of the ellipse will be parallel to the axes of the graph.

Fig. 3 shows reflectivity data and the fitted profile for FS8. In this case the gap is both narrower and less deep; we find  $D = 6.5 \pm 0.12 \text{ \AA}$  and  $\rho_{\text{dep}} = 0.24 \pm 0.01 \text{ e/\AA}^3$ . Thus  $D_{\text{eq}} \approx 1.85 \pm 0.25 \text{ \AA}$ , not very far from the OTE/OTS-water. Recall that the contact angle in this case is  $\sim 111^\circ$ , lower than that of the FS14 SAM.

## Discussion

It is not surprising that the same forces that cause the contact angle to increase should cause the width of the gap to increase. Recent computer simulations (21,22) confirm the expected (and now experimentally observed) trend, although they predict smaller gaps than are actually observed in our systems. (This may be because of the assumptions in the models: for example, they do not allow increased  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  concentrations at the interface (23).) In retrospect, searches for hydrophobic depletion have been conducted on a wide variety of hydrophobic surfaces, from paraffin to polystyrene to alkanethiol SAMs on gold to alkylsilane SAMs on silicon, but these apparently different surfaces have one thing in common: they are all relatively low on the contact angle scale. But hydrophobicity is not a step function at  $90^\circ$ . Thus the results of previous studies are in fact consistent rather than contradictory, once it is recognized that the effect is marginal for the surfaces studied given the experimental resolution and substrate roughness. This point is illustrated in Fig. 4, which summarizes our results and the other recent results discussed in this paper. (This graph shows  $D_{\text{eq}}$  because, as

discussed previously, the gap width and gap density are not individually as reliable for the prior results quoted.)

The effect reported here is larger than might have been expected, but since the size of the effect is clear even in the raw data (Fig. 2, upper panel), it is not an artifact of data analysis procedures. The fact that SAMs of different chain lengths, handled the same way, gave different results, makes it less likely that the gaps are due to extraneous factors. However, X-ray scattering is not chemically sensitive and cannot directly determine the composition of the depleted layer. Could the observed effect be due to interface segregation of dissolved impurities, such as organic molecules or gases? The electron densities observed in the depletion regions are too low to be attributed to bulk organic materials, which generally have 85-95% of the density of water (any gaps in an impurity layer would fill with water and this would raise the average density). On the other hand the densities are too high to be attributed to bulk gases. Our studies were conducted both with ultrapure water (from a Milli-Q system, resistivity 18.2 M $\Omega$ -cm) and bottled deionized filtered water (resistivity 0.5 M $\Omega$ -cm), with identical results.

Of course water purification systems do not remove dissolved gases. A previous experiment (10) reported that dissolved gases changed the gap width, but the reported differences were too small to have been reliably observed given the experimental resolution. Higher-resolution experiments have found no significant change in the observed depletion on OTE/OTS when degassed (11) or gas-saturated (12) water was used. We note that water does contain abundant quantities of a gas that cannot be removed by degassing: if the gap must be attributed to a gas, water vapor easily fills the role.

It has recently been found using vibrational spectroscopy (23) that the water/OTS interface is negatively charged, and carries adsorbed  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  ions. Thus the interfacial region has a composition different from pure water, and this could result in an interfacial ‘phase’ with an intermediate density such as that observed. None of our results can be attributed to nanobubbles, for the same reasons already discussed in detail by Poynor et al. (11) and Mezger et al. (12). Like them, we cannot rule out the presence of small numbers of ‘mesobubbles’ ( $\sim 500\text{\AA}$  or larger), since these would not be visible to X-ray reflectivity,

It has been proposed (24,25) that the water-hydrophobic interface, delicately suspended between attractive and repulsive interactions, will be subject to large fluctuations driven by soft modes. Interface fluctuation mechanisms could include cavity formation (23). Our technique gives time-averaged information and does not observe the dynamics directly, but it is sensitive to the resulting smearing of the interfacial density profile. Looking at the interface between bulk water and the depleted region for FS14, i.e. the left side of the density dip in Fig. 2 (lower panel), the RMS interface width is  $3.4\pm 0.1\text{\AA}$ . But the SAM-air interface is also rough (RMS width  $3.9\pm 0.1\text{\AA}$ ); of course this roughness is static, but the water-depletion interface may be partly conformal to the substrate, especially at longer wavelengths. Thus the water interface width attributable to dynamics should be less than the total observed interface width. How much of the water interface width is due to its being conformal with the rough substrate is not known, and so the best measure of fluctuation amplitude obtained from these data is that the RMS interface width due to fluctuations is anywhere between  $0\text{\AA}$  and  $3.5\text{\AA}$ . For comparison, the interface width at the free surface of water as would be observed with our q-resolution

(26,27) is  $\sim 3.4\text{\AA}$ . This width is also due in part to thermal fluctuations (capillary waves). In other words the amplitude of density fluctuations normal to the interface, if present, is no larger than that seen at the free surface.

## **Materials and Methods**

FS8 was purchased from Aldrich and FS14 from Synquest Inc; both were used as supplied. SAMs were deposited using the methods of Paso et al. (17) Prior to deposition, polished Si wafers were treated with piranha solution ( $\sim 7:3 \text{ H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ) for 30 min to remove organic contamination from the surface. 1mM solutions of the SAM reagents were prepared in a mixture of anhydrous isooctane and carbon tetrachloride solvents,  $\sim 7:3$  by volume, and the substrates were immersed in the solution for 1h. After deposition, the samples were thoroughly rinsed, first with chloroform and then with methanol. The surfaces were then thermally treated at  $150^\circ\text{C}$  for 30min.

X-ray reflectivity studies were performed at Sector 33-BM-C of the Advanced Photon Source, Argonne National Laboratory. The X-ray energy was 19KeV, and the beam size was  $\sim 0.4\text{mm}$  vertically and  $\sim 1\text{mm}$  horizontally. The momentum resolution was  $\sim 0.007\text{\AA}^{-1}$ . In addition to specular reflectivity scans, slightly off-specular “background” scans were performed and subtracted from the specular data, thus removing the scattering from all diffuse sources including that from the rough Kapton surface and the Kapton-water interface. Our samples were exposed to X-rays for less than  $\sim 4$  hours, and over this time period, successive reflectivity scans were identical. However, radiation damage effects become apparent after much longer exposure times. (Radiation damage will reduce the observed gap, not increase it.) The use of a bending magnet beamline (less

intense than state-of-the-art undulator beamlines) may be one reason why more rapid radiation damage was not encountered.

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## Figure Legends

Fig. 1: Schematic diagrams of the sample cell, shown in cross-section. The thin water film is stabilized on the hydrophobic substrate (at center) by the thin Kapton window, which has been made hydrophilic by plasma treatment. X-rays penetrate the Kapton and are reflected from the water-substrate interface. The thickness of the water films is  $\sim 1\mu\text{m}$ .

Fig. 2: *Upper panel*: Reflectivity data, scaled by the reflectivity of an ideally sharp interface  $R_F$ , for the FS14 SAM surface (stars, red line) and SAM-water interface (circles, blue line). The y-axis numbers are not absolute; there is an unknown multiplicative constant. Inset shows the fitted electron density profile of the dry SAM. *Lower panel*: density profile of the water-SAM interface. Inset shows contours of  $\chi^2$  in the plane of the fitting parameters  $D$  and  $\rho_{\text{dep}}$ , near their optimum values. Each contour represents a 1% increase in  $\chi^2$ . The line shows the path along which  $D_{\text{eq}}$  is constant.

Fig. 3: Density profile for the interface between water and an FS8 SAM. Inset: reflectivity data from dry SAM surface (stars) and SAM-water interface (circles).

Fig. 4: Dependence of the equivalent depletion width on advancing contact angle. From left to right, the first error bar represents the data in ref. 14 for  $\text{pH} = 5.5$ ; the circle represents the data of ref. 12 after subtracting the “hydrogen gap” (contact angle estimated, not reported in source paper); and the next error bar represents the data of Ref. 11, also after subtracting the hydrogen gap. The last two points are data from the present paper. The dashed line is a guide to the eye.







