The search for Nanobubbles by using specular and off-specular Neutron Reflectometry

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Abstract

We apply specular and off-specular neutron reflection at the hydrophobic silicon/water interface to check for evidence of nanoscopic air bubbles whose presence is claimed after an ad hoc procedure of solvent exchange. Nanobubbles and/or a depletion layer at the hydrophobic/water interface have long been discussed and generated a plethora of controversial scientific results. By combining neutron reflectometry (NR), off-specular reflectometry (OSS) and grazing incidence small angle neutron scattering (GISANS), we studied the interface between hydrophobized silicon and heavy water before and after saturation with nitrogen gas. Our specular reflectometry results can be interpreted by assuming a sub-molecular sized depletion layer and the off-specular measurements show no change with nitrogen super saturated water. This picture is consistent with
the assumption that, following the solvent exchange, no additional nanobubbles are introduced at significant concentrations (if present at all). Furthermore, we discuss the results, in terms of the maximum surface coverage of nanobubbles that could be present on the hydrophobic surface compatibly with the sensitivity limit of these techniques.

Introduction

The solid-water interface has been for many years the subject of fundamental scientific research due to the relevance of interfacial phenomena to biological processes in which water plays a major role. Moreover, the push for miniaturization driven by rapidly evolving microfluidic technologies calls for a deeper understanding of the physical-chemical mechanisms that govern the processes occurring at this interface. Experiments using different model hydrophobic surfaces at the solid-water interface showed controversial results as a liquid layer of reduced density was observed sandwiched between the hydrophobic surface and the bulk water. In order to quantify the resulting depletion effects, the depletion distance \( d_2 \) was introduced:

\[
d_2 = \int \left( 1 - \frac{\rho(z)}{\rho_{\text{bulk}}} \right) dz, \tag{1}
\]

where \( \rho(z) \) denotes the density of the depleted liquid at a distance \( z \) from the interface and \( \rho_{\text{bulk}} \) represents the bulk liquid density. \( d_2 \) reduces the smeared-out density profile of the depletion to a step-like function that represents an equivalent layer of zero density. The results of neutron reflectometry (NR) studies on spin-coated deuterated polystyrene (dPS)-D\(_2\)O interfaces showed a depletion distance of \( d_2 \approx 2.6 \text{ \AA} \), however, a repeat of this experiment by another group did not show this depletion when a freshly prepared PS film was not exposed to air before the measurement. A similar scenario emerged with X-ray reflectometry (XRR) results on bulk water in contact with octadecyl-trichlorosilane (OTS) coated substrates. A depletion distance of only \( d_2 = 1.1 \text{ \AA} \) was observed although up to half of the contribution may have arisen from the hydrogen termination of the hydrophobic
coating, which is practically invisible to X-rays. Even though this topic is still controversial, the depletion between water and a hydrophobic surface, if present at all, might occur on a sub-molecular scale and may arise from preferred orientation of water molecules at the interface as suggested by molecular dynamics (MD) simulations and Raman-scattering and demonstrated for other liquids at hydrophobic surfaces.

The situation becomes increasingly complicated if water supersaturated with gas is used as the exceeding gas may condense in the form of a nanoscale layer at a hydrophobic interface. These so-called nanobubbles were initially assumed to be the cause of the hydrophobic gap and motivated further reflectometry studies to probe the influence of different gas enrichments on the water depletion yielding controversial results. A further argument of controversy is the fact that theoretical calculations predicted the lifetime of nanobubbles to be in the µs range and thus not observable on a laboratory time scale. Therefore the observation of nanobubbles has often been attributed to the invasive effect of the Atomic Force Microscopy (AFM) technique, which was mainly used to show their presence. With the introduction of a well established protocol to make nanobubbles reproducibly and at high surface coverage in this system, the so-called solvent exchange technique, it became possible to deliberately produce nanobubbles which are stable on the time scale of hours or even days by replacing ethanol by water. Eventually, nanobubbles were observed with non-invasive techniques like infrared spectroscopy and optical microscopy. However, though it is currently accepted that nanobubbles may be artificially produced locally at solid-liquid interfaces under certain circumstances their (time and space averaged) concentration and thus their influence on mesoscopic quantities in microfluidics or cell biology is still debated. We believe this is due to the fact that the techniques used so far to examine nanobubbles are either local (various microscopy techniques) or they had no particular sensitivity to the shape of the bubbles, and quantifying only the mean surface coverage (infrared spectroscopy, specular reflectometry).

The reported size of nanobubbles (50 - 10000 nm) makes them ideal candidates for investi-
gations with grazing incidence small angle neutron scattering (GISANS), specular and off-
specular neutron reflectometry. These techniques operate in the reciprocal space and provide
structural information averaged in time and over a macroscopic surface area in contrast to
the aforementioned local microscopy techniques.\textsuperscript{27} The investigation of buried interfaces, e.g.
solid-liquid interfaces, is mainly done by NR or high energy X-rays as those interfaces are
rarely accessible by soft X-rays or visible light. Neutrons have a further advantage for soft
matter interfaces since cold and thermal neutrons do not cause radiation damage of organic
specimens nor they cause alterations of the samples due to radiation induced accumulation of
charges on the surfaces.\textsuperscript{28} Neutron scattering techniques can further augment their capabili-
ties thanks to isotopic substitution, which offers a powerful tool for contrast enhancement of
the low atomic number elements typically composing soft matter.\textsuperscript{29} Off-specular scattering
(OSS), which is typically several orders of magnitude weaker than the specular reflection
is not routinely used, apart from synchrotron X-rays sources.\textsuperscript{27} However, specific examples
where neutron OSS has been used are highly ordered systems like magnetic domains or grat-
ings, especially in multilayered systems,\textsuperscript{30} or for microphase separated polymers in heavy
water.\textsuperscript{31} Other examples include capillary waves,\textsuperscript{32} lipid bilayers,\textsuperscript{33,34} polymer dewetting,\textsuperscript{35}
and organic photovoltaics,\textsuperscript{36} which all profit from the high contrast of deuterated materi-
als. Grazing incidence small angle neutron scattering has recently experienced an increasing
recognition\textsuperscript{37} partly due to the unique possibility to use TOF in combination with GISANS
to measure depth dependent patterns in a single measurement\textsuperscript{38,39} and due to advances in
analysis software.\textsuperscript{40}

Previous GISANS measurements\textsuperscript{41} on the interface between dPS and D\textsubscript{2}O were performed
on D22 at the Institut Laue-Langevin (ILL) in Grenoble, France, but the PS layer was
unstable at higher temperatures used to enhance the appearance of nanobubbles. Therefore
we used in this study silicon substrates coated with OTS that are stable at the relevant range
of temperature and performed specular and off-specular NR and GISANS on N\textsubscript{2} enriched
D\textsubscript{2}O in order to cover the relevant lateral and out of plane length-scales of depletion layers
and nanobubbles.

**Experimental Details**

The silanization of the single crystal silicon (100) block (80*50*20 mm³, Siltronix, France) was performed according to reference [42]. The advancing contact angle of *Millipore* filtered water was 102° and the receding one 70° (static contact angle was 93°). The specular and off-specular NR measurements, which took 35 min and 10 min, respectively were performed on the FIGARO horizontal sample plane reflectometer [43] at the Institut Laue-Langevin using a wavelength (λ) range from 1.7 Å to 19 Å with a relative resolution of \( \frac{\Delta \lambda}{\lambda} = 4.2\% \). The reflectivity was measured at two reflection angles (0.625° and 3.2°) with a relative angular resolution of \( \frac{\Delta \theta}{\theta} = 3.3\% \). The GISANS measurements, which were also performed on FIGARO and took 2 h each used a wavelength resolution of \( \frac{\Delta \lambda}{\lambda} = 7.4\% \) with the same wavelength range as before. The reflection angle was set to \( \theta_i = 0.393° \) with a vertical and horizontal angular divergence of \( \Delta \theta_i = 0.02° \) and \( \Delta \phi_i = 0.1° \), respectively. The detector pixel resolution corresponds to an angular spread of \( \Delta \theta_f = 0.018° \) and \( \Delta \phi_f = 0.16° \). All resolutions are given as Gaussian equivalent full width at half maximum (FWHM). The solid-liquid sample cell contained about 3 ml of liquid and was mounted with the liquid on top of the solid so that macroscopic bubbles would drift away from the interface under consideration.

The measurements were taken according to the following procedure. Firstly specular and off-specular reflectivities were recorded on the OTS-D₂O interface by using heavy water as received from *Sigma-Aldrich*, France (99.9 atom % deuteration). Then the water was exchanged by 9 ml of ethanol and after 1 min the ethanol was again exchanged within 100 s by 12 ml D₂O which was saturated with nitrogen by bubbling it with \( N_2 \) for 30 min at a temperature of 5 °C. The sample cell and the ethanol were kept at 45 °C throughout the experiment.

Fitting of the reflectivity data was accomplished using a slab model with *Motofit*. The
error in depletion distance, was determined as follows. The SLD and the thickness of the
density depleted layer were allowed to vary simultaneously until the $\chi^2$ increased by 5% as
compared to the best fit. This was done because the thickness and SLD of this layer are
highly correlated parameters in the data fitting. Then the maximum and minimum values
for the depletion distance were calculated within this parameter range. The absolute $\chi^2$
values for all NR fits varied between 4 and 5.

The GISANS patterns were reduced as follows: In order to accumulate meaningful statistics
the data was binned to wavelength bands of $\Delta \lambda/\lambda = 20\%$. For the wavelength shown here
(5 Å) this corresponds to a wavelength range of 4.5-5.5 Å. This results in a Gaussian equiva-
 lent wavelength resolution of $\Delta \lambda/\lambda = 15\%$ (FWHM). Although other wavelengths were
recorded and analyzed as well it turned out that only at 5 Å wavelength a GISANS signal
outside the specular and direct beam region above background could be observed. As can
be seen in the measured GISANS patterns the background was very low, on the order of
$10^{-6}$ with most of the pixels having 0 counts after 2h of acquisition. We therefore did not
subtract background from the GISANS images.

The analysis of the GISANS patterns was done by comparing the absolute intensities to
simulations performed with the software package BornAgain. Detector sizes and pixels,
incident and reflected angles and divergence as well as wavelength and wavelength resolution
were matched to those used in the experiment. The simulations used layer parameters from
the specular reflectivity data to form a multilayer structure to which model nanobubbles of
oblative shape with different spherical radius $r$, height $h$ and surface coverage $\sigma$ were added at
the water-OTS interface. The model used to describe the expected scattering from nanobub-
bles was the form factor of a truncated oblate spheroid with a scattering length of 0 (air)
and the measured contact angle $\theta = (180^\circ - 93^\circ) = 87^\circ$.

Structure factor contributions were not included as high nanobubble coverage would be
clearly visible by specular reflectivity and would give rise to stronger scattering than that
observed, so the simulations focussed on coverages below 25% (less than half that expected
by random sequential adsorption). Polydispersity effects were not included and would correspond to the weighted sum of the images shown in the supporting information. In-plane roughness correlations of the respective interfaces were not included in the simulation as they did not produce scattering stronger than that of the nanobubbles in the range of realistic correlation lengths (<10 nm).

Results and Discussion

The thickness and density of the OTS layers were previously determined by X-ray reflectivity on the same batch of samples. The hydrocarbon tail length was thus fixed to 21.3 Å corresponding to almost completely stretched chains with a neutron SLD of $-0.4 \cdot 10^{-6} \text{ Å}^{-2}$ and a porosity of 2%. The silicon oxide thickness was fixed to 17 Å including the silane head group of the OTS molecule. The neutron SLD of SiO$_2$ was fixed to $3.47 \cdot 10^{-6} \text{ Å}^{-2}$ and the hydration was determined to be 6%. The roughnesses of all interfaces were allowed to vary and were between 4 and 6 Å.

The specular neutron reflectivity (multiplied by $q^4$) of the untreated D$_2$O-OTS interface and of the gas enriched water after solvent exchange are plotted in Figure 1. In order to fit the data a 5 - 15 Å thick density depleted layer (50-80% depletion) sandwiched between the OTS and water had to be assumed leading to a depletion distance of $d_2 = 2.8 - 3.9 \text{ Å}$ in case of the naturally aerated water and a similar range of $d_2 = 1.6 - 3.7 \text{ Å}$ in the case of N$_2$ enriched water. These values are only slightly higher than previously mentioned X-ray reflectometry and MD simulation results and within the neutron reflectometry experiment of reference.

Also the influence of gas enrichment on the depletion distance seems to be negligible, within the error of the measurement, in accordance with earlier X-ray measurements. In any case the depletion seems to be of sub-molecular size. The assumption of a thicker density reduced layer analog to that found in reference (thickness 35 Å, roughness 5 Å, density reduced by ~ 10 % leading to $d_2 = 2.6 \text{ Å}$) impairs the quality of the fit as can be seen in Figure 1(a).
Figure 1: (a) NR multiplied by $q^4$ for the initial $D_2O$-OTS interface (black crosses) and the $N_2$ enriched water (green circles). The best fits for the two curves are plotted as solid lines in the same color. The dashed-dotted blue line corresponds to a simulation with a depletion layer as observed in [5], whereas the dashed red line denotes a simulation from a depletion layer as observed in [15]. (b) Scattering length density for the NR fits in the same color code.

The assumption of a zero-density layer as in [15] (thickness 7.4 Å, roughness 3.4 Å, leading to $d_2 = 7.4$ Å) leads to an even worse fit as can be seen in Figure 1. In order to quantify this result in terms of the maximum nanobubble surface coverage compatible with these data, we make some hypothesis on the shape and density of the nanobubble. For simplicity we will limit our analysis to oblate half-sphere shaped objects with a radius $r$ and a height $h$ filled with ambient pressure gas that can be safely assumed to result in zero scattering length density for neutrons. In this case the amount of missing material per unit area can be calculated by multiplying the volume of a oblate half-sphere $2/3\pi r^2 h$ with its surface coverage. The resulting value can be directly compared to the depletion distance $d_2$ from eq.1 which also corresponds to the missing material’s volume per interface area. By normalizing the nanobubble surface coverage to its surface area at the solid/liquid interface $\pi r^2$ we get the relative surface coverage of nanobubbles $\sigma$ in compliance with the depletion distance:

$$\sigma = \frac{3d_2}{2h}.$$  

(2)

It is evident that, as the height of the nanobubbles decreases, their contribution to the depletion distance will be smaller. We therefore limit the analysis to the minimum nanobubble
height detected in literature, which is around 5 nm to the best of our knowledge. Hence the maximum surface coverage of oblate half-sphere shaped bubbles compatible with a depletion distance of $d_2 = 3.7 \text{ Å}$ is 11%.

![Figure 2: Reflected intensity on a logarithmic scale for detector scans at an incident angle of $\theta_i = 0.625^\circ$ and a wavelength of $\lambda = 5.5 \text{ Å}$.](image)

In Fig. 2 we display the off-specular reflectivity curves for the initial interface (black crosses), the gas enriched water immediately after solvent exchange (green circles) and after 11 h (blue rectangles), respectively. The Yoneda peak intensity originates from an evanescent wave at the solid/liquid interface and is particularly sensitive to in-plane density fluctuations e.g. the presence of nanobubbles adsorbed on the surface. The Yoneda peak appears when the exit angle $\theta_f$ matches the critical reflection angle $\theta_c$ related to the SLD difference $\Delta N_b$ between that of bulk Si and the D$_2$O in the vicinity of the solid in the following way:

$$\theta_c = \lambda \sqrt{\frac{\Delta N_b}{\pi}}. \quad (3)$$

From fitting a Gaussian to the Yoneda peak in Fig. 2 a critical reflection angle of $0.35^\circ - 0.364^\circ$ for all three measurements can be derived with no systematic variation between the
measurements. By using eq.3 a minimum $\Delta N_b = 3.875 \cdot 10^{-6} \text{Å}^{-2}$ can be derived which leads to a SLD of $5.95 \cdot 10^{-6} \text{Å}^{-2}$ of the adjacent water layer after adding the known Si $N_b = 2.07 \cdot 10^{-6} \text{Å}^{-2}$. If comparing this value to the bulk water SLD of $6.26 \cdot 10^{-6} \text{Å}^{-2}$ as derived from the specular fits one can estimate a minimum water density of 95% in the vicinity of the solid. By comparing the volume of a cylinder to a half-sphere of the same radius one can calculate the maximum surface coverage of half-spheroids to be 7.5% in this case. Moreover, no additional bubbles are introduced within the sensitivity of this measurement.

In order to check for bubbles in the range of 10 nm - 400 nm, we performed GISANS measurements and compared the absolute intensities to simulations performed with the program BornAgain. A representative pattern after solvent exchange recorded at 5 Å wavelength and the corresponding simulation at 5% surface coverage of 100 nm radius spherical nanobubbles (maximum in the size spectrum of Ref.15) is shown in Fig.3. The measured GISANS pattern does not change significantly even 13 h after solvent exchange (see supplementary information). The most prominent feature in the simulated GISANS patterns resulting from nanobubbles is the diffuse scattering along the off-specular axis ($\phi = 0$) just above the specular peak (Intensity $\approx 1$) which is hidden behind a mask and the lateral lobes extending from the Yoneda scattering (at $\theta_f = 0.33^\circ$). Systematic variation of the nanobubble radius and height in the simulation (see Supplementary Information) predicts that bubbles in the range of 50-100 nm produce significant intensity in the side-lobes along the Yoneda peak for sufficiently high coverages, which is not as pronounced in the data. For an easier comparison we have plotted an out-of-plane cut along the $\phi_f$ axis at the Yoneda postion in Fig.3(c). For better statistics a range of $0.26^\circ < \theta_f < 0.36^\circ$ was integrated and the negative and positive $\phi_f$ values were binned. Even at a nanobubble concentration as low as 10% the side-lobe intensity is on the level of $2 \times 10^{-5}$ at an in-plane angle of $\phi_f \approx 0.4^\circ$ for 100 nm spherical bubbles in the simulation whereas the measured intensity is around $1 \times 10^{-5}$. For oblate nanobubbles the scattering intensity is lower, but even for a radius of 50 nm (lower limit in
Ref. [19] and a height of 10 nm the scattering intensity at 25% coverage clearly exceeds the measured values. By comparing the measured pattern to the absolute scattering intensities of the simulation at different surface coverages and nanobubble sizes we therefore estimate that the maximum surface coverage compatible with the sensitivity of the technique in this set up is around 10% for flattened spheroids and even lower for spherical bubbles.

Figure 3: GISANS pattern of the gas enriched water after solvent exchange at 5 Å (a) and the corresponding simulation for 100 nm radius spherical bubbles at 5% coverage. (b) The specular reflected beam (Intensity ≈ 1) is masked. In (c) the projected intensity at the Yoneda peak on the $\phi_f$ axis is shown for the data and for various simulations with parameters shown in the legend.

Summary

In summary, we have shown that with a combination of specular and off-specular neutron reflectometry as well as grazing incidence small angle neutron scattering it is possible to probe
a large range of momentum transfers perpendicular and parallel to the surface which correspond to the length-scales present in previous observations of nanobubbles. Nevertheless, we could not find any evidence of a change of nanobubble concentration or depletion layer through the application of the well-established technique of solvent exchange and the use of nitrogen saturated water. Clearly the maximum surface coverage of nanobubbles satisfying the presented results is on a percent level if present at all. We urge the need of quantitative surface averaging techniques for further investigations of nanobubbles.

Supporting Information Available

All simulated GISANS patterns are available in the supporting information. This information is available free of charge via the Internet at http://pubs.acs.org/.

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