Experimental report

09/02/2016

Proposal:	**9-11-1749**	**Council:**	4/2015
Title:	Water density profile at a hydrophobic - water interface investigatedby neutron reflectivity		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples: Poly(Ethyl-Methacrylate)

Instrument	Requested days	Allocated days	From	To
D17	3	0		
FIGARO	0	3	20/11/2015	23/11/2015

Abstract:

It is planned to investigate the aqueous interface of smooth hydrophobic polymer-coated substrates by neutron reflectivity. The water density profile determination will allow the hydrophobic water gap to be characterized both in terms of spatial extent and of nature (a dewetted region, a depleted region with water reduced density, or a precursor gas region?). In particular the effects of dissolved gasses (inert or non polar such as Ar, N_2, CO_2, or polar such as CO) in the water will allow insights to be gained.

Experimental Report-Experiment n° 9-13-581

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1 Context

One of the pertaining issues in the discussion of the interaction of water with surfaces is the property of water in direct contact with solids [1]. In particular the nature of the contact region between water and a hydrophobic surface has long been recognized to hold the key to the understanding of the hydrophobic effect. Hydrophobic interactions play an important role in diverse phenomena in biology and technology including protein folding, amphiphilic self-assembly, mineral flotation. A number of theoretical works have suggested that the water density is reduced at a hydrophobic substrate / water interphase [2, 3]. Indirect conclusions derived from surface measurements on the structure of water confined between two hydrophobic surfaces have shown that significant dewetting of the contact region takes place (cavitation) [4]. However, the microscopic details of how water meets a hydrophobic substrate are still not settled. Molecular dynamics simulations indicate a water depletion region extending at most 0.3 nm from the hydrophobic surface [5] while previous neutron [6, 7, 8] and X-ray [9, 10] reflectivity have suggested a 1- to 4-nm depleted region where the water density at the interface is reduced. The experimental situation is further complicated as AFM has revealed that submicroscopic bubbles may lye at the hydrophobic substrate / water interface (for a recent review see [11]). These concerns have precluded not only the extent of the depletion region to be measured with confidence (in several reported reflectivity experiments the samples have generally multicomponent layers leading to uncertainty in the layer thickness), but also have questioned whether the latter is a dewetted or a precursor gas layer. Resolution of this question requires further experimental investigations, which is the object of this study.

2 Experimental

Taking advantage of well previously characterized hydrophobic substrates [12] poly(ethyl methacrylate) (PEMA) spin coated films present several advantages to be used for neutron reflectivity. Indeed, quadruple criteria are satisfied: smoothness, homogeneity, electroneutrality, and integrity as surface-stable entities in aqueous solutions. No film delamination is observed with time [12] thanks to a preliminary coating with cerium oxide nanoparticles (5 nm diameter) irreversibly adsorbed onto the silicon wafer [13]. In addition, as the water contact angle is about 76°, below 90°, the criterion of ref. [11] is fulfilled: submicroscopic bubbles cannot form at the surface spontaneously. All these characteristics combine to facilitate the reflectivity curves analysis (see below). Spin coated protonated PEMA layers about 70 nm thick (M_w=300000 g/mol) deposited onto silicon oxide blocks were prepared in ILL using Soft Matter Lab facilities. To avoid any surface contamination (as pointed in [8]) the PEMA film were prepared immediately before neutron experiments using the spin-coater at the PSCM of ILL. High resolution was sought (2.7% in $\Delta q/q$). The instrument FIGARO worked well allowing us to study 5 different samples under different solvent contrasts (H_2O, D_2O, and mixtures around polymer water match (PMW) and SLD 4 (4PMW)). In total we obtained 43 reflectivity curves. We present below a first preliminary analysis of these measurements.

3 Results

First we characterized the silicon oxide blocks coated with a cerium oxide layer. The latter is constituted of a dense and relatively homogeneous flat film comprised of ceria nanoparticles assembled in a single layer (thickness

5 nm) and irreversibly adsorbed onto the wafer over long periods as many days [13]. Coating the substrates with nanometric particles gives a surface smooth at the nanometre scale only as indicated by Fig.1. The reflectivity curves performed with four aqueous solution contrasts all lead to infer a SLD of 3.8 for the cerium oxide layer with a solvent penetration of 55%.

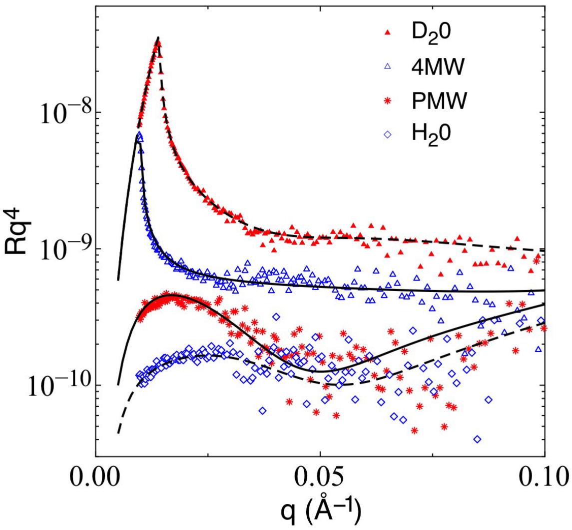

Figure 1: Reflectivity curves of ceria coated-silicon oxide blocks with 4 different aqueous solution contrasts (H_2O, PMW, 4PMW and D_2O).

Then, the deposited protonated PEMA film was characterized in air (see Fig.2). Using the same parameters of thickness, roughness and SLD for the ceria layer (as determined from Fig.1), the spin coated PEMA film is 65 nm thick. It appears smooth (1 nm roughness for its outer interface with air). The polymer chains lodge between the ceria particles (35 % penetration into the adsorbed monolayer) allowing the PEMA film to be stable with absence of any delamination over long periods as many days [12, 13]. Note that ellipsometry also carried out onto these films have confirmed their homogeneity and smoothness. In addition the water advancing and receding contact angles of 76 ± 1° and 63 ± 1° respectively confirmed the good homogeneity of the hydrophobic substrate over macroscopic areas [12].

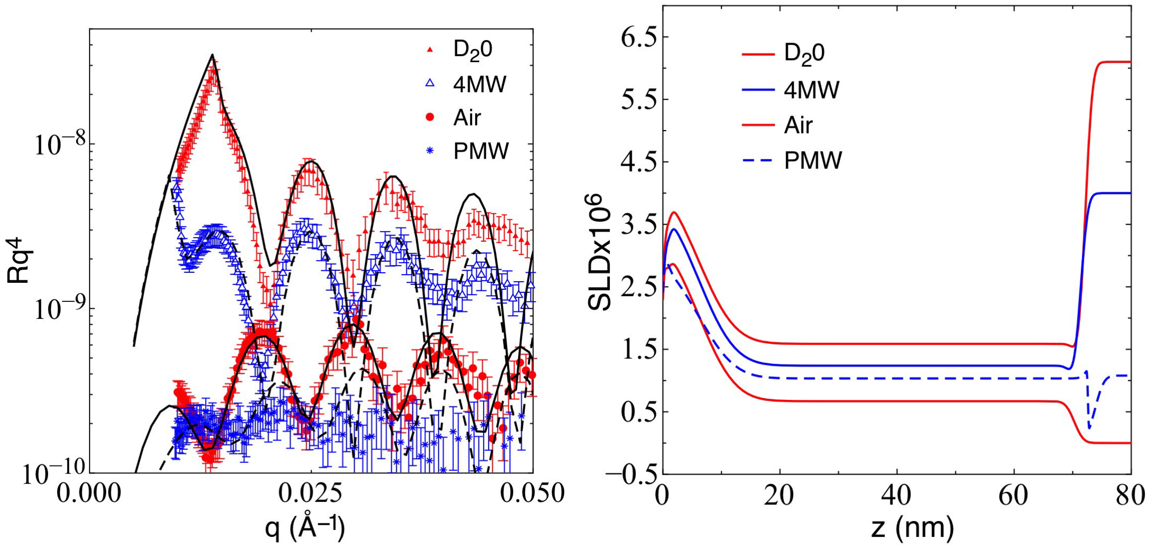

Figure 2: Reflectivity curve of spin coated PEMA film in 4 different aqueous solution contrasts (air, D2O, 4PMW and PMW) and corresponding SLD profiles.

The aqueous interface of these smooth hydrophobic polymer-coated substrates was investigated under different aqueous solvent contrasts. Fig.2 shows the reflectivity curves for 3 different contrasts (PMW, 4PMW and D_2O). None of these curves can be reproduced by a model for the scattering densities at minimum layer number (that would be with a semi infinite bulk solvent). Conversely a good agreement can be found when an air gap layer is introduced between the PEMA layer and the semi-infinite solvent layer. Remarkably this air gap layer is thin (thickness between 0.5 and 1 nm) with the a roughness value comparable to that of the polymer film ($\sim$ 1 nm).

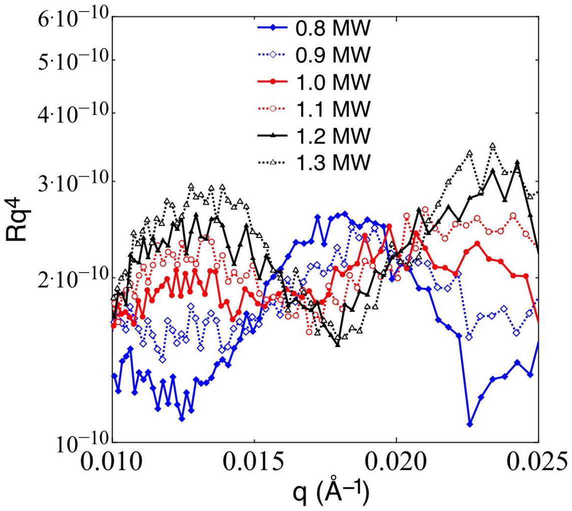

Figure 3: Reflectivity curve of spin coated PEMA film in 6 different aqueous solution contrasts around the PEMA SLD.

In order to confirm this result, we did a solvent contrast variation around the expected polymer SLD (1.08). Our results are presented in Figure 3. Remarkably, despite the almost polymer match contrast, the reflectivity curves always present oscillations corresponding to the polymer film thickness. Further quantitative analysis is in progress, but it is already a good indication of the presence of the air gap (in the absence of the latter, we should observe the disappearance of these oscillations).

4 Conclusion

High resolution reflectivity performed on the model hydrophobic substrate used in these experiments suggests the presence of a thin air gap at the interface of the hydrophobic layer and the water. The thickness of this contact region is small ($\leqslant 1$ nm) in good agreement with previous X-ray [9, 10] reflectivity on another system and molecular dynamics simulations [5]. This gap interpreted here as an air gap could also be viewed as a water depletion region with a water density reduced at the hydrophobic substrate / water interphase [2, 3]. The remaining question to address is whether the latter is a dewetted or a precursor gas layer leading to ultimate nanobubbles formation under applied mechanical load as induced by an AFM tip [12]. To get insights into the nature of both the spatial extent and the nature of this region, the influence of dissolved gases (inert, non polar or polar) in the water must be further investigated.

References

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