Alumina-Water Interface Structure: Ab-initio Molecular Dynamics and X-ray Reflectivity

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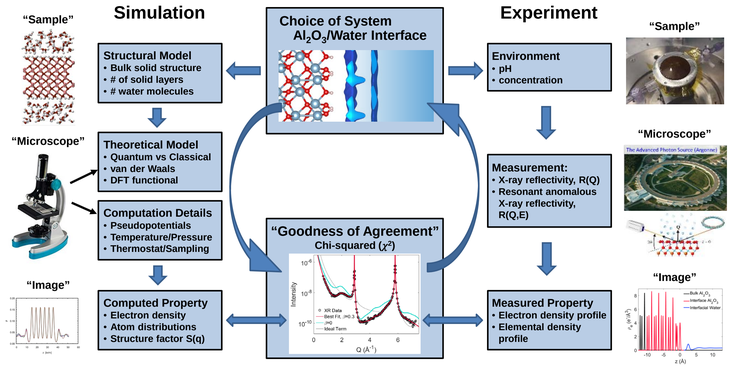
Introduction

- The Al_2O_3(001)-water interface structure serves as an ideal test case for validating ab initio molecular dynamics (AIMD) simulations as it is a relatively simple system containing key features that present challenges for computational tools: (1) symmetry breaking at the interface and (2) complex hydrogen bond (HB) networks. This system has been explored by a number of experimental means and is relatively well understood[1].
- Using direct, quantitative comparisons between experimental X-ray reflectivity (XR) data and XR signals calculated from AIMD predicted structures[2], we assess how different simulation properties affect the level of agreement with the data[3], specifically with respect to the predicted adsorbed water structure.
- A significant discrepancy in the adsorbed water height between theory and experiment may suggest a difference in the experimental and simulated HB networks at the interface. XR data of the pH-dependent structure of the alumina/water interface and non-specular XR measurements of the 3D adsorbed water organization have been acquired and will be compared to simulated structures to determine if there is a difference in alumina surface charge or in the lateral organization of water between the AIMD predictions and experimental system.

Methods

Validation Protocol



Simulations: 1. PBE ab initio molecular dynamics (AIMD) implemented in Qbox
2. Classical MD and optB88 (AIMD) for various tests of simulation conditions

Experiments: Specular and non-specular X-ray Reflectivity (XR) (Fig. 1) at APS Sector 33-ID-D

$$R(\vec{Q}) \sim \left| \int \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}}\, dr \right|^2 \qquad \chi^2 = \frac{1}{N - N_p} \sum_Q \left(\frac{R(Q) - R_{calc}(Q)}{\sigma(Q)} \right)^2$$

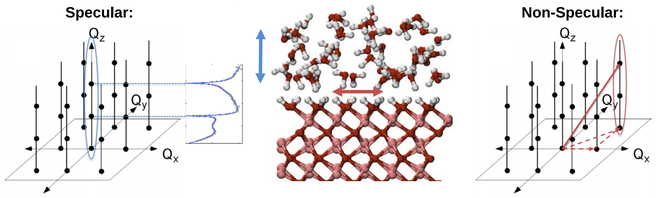


Figure 1. X-ray reflectivity schematic: Specular XR probes the interfacial structure along the surface normal and non-specular XR probes the in-plane structure.

Specular XR Comparison[3]

Ab-initio Molecular Dynamics vs. XR Data

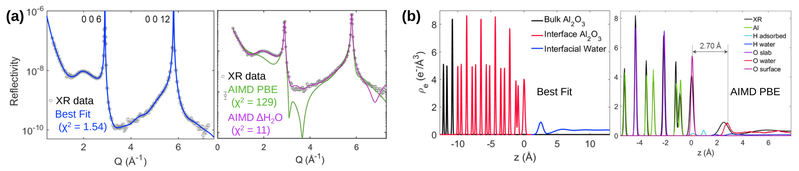


Figure 2. PBE AIMD vs. experimental best fit. **(a)** Comparison of the experimental data, XR best fit, and the reflectivity calculated from the initial and optimized PBE structures. Shifting the predicted water height results in a improvement of χ^2. **(b)** Comparison of the best fit model and the predicted PBE with the PBE water height overestimate shown.

Origin of χ^2 Disagreement

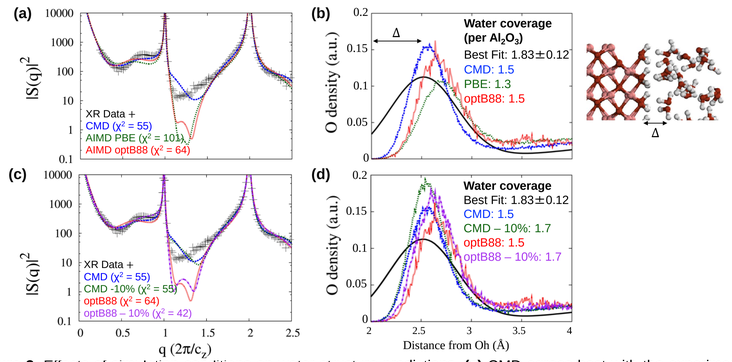


Figure 3. Effects of simulation conditions on water structure predictions. **(a)** CMD agrees best with the experimental XR data resulting from **(b)** water coverage and height closest to those of the experimental best fit. optB88 (AIMD) significantly improves the agreement compared to PBE. **(c)** The compressed optB88 system has the best quality of agreement with the experimental data resulting from **(d)** improved water layer coverage and height.

- CMD and AIMD calculations result in significant differences in the predicted water structure, namely the height and coverage of water in the first hydration layer, which is the main difference in the relative disagreement with experimental data for these two techniques.
- Compressing the AIMD systems further improved the prediction of first adsorbed water layer coverage and height, and resulted in the best χ^2 for the tests performed.
- Effects on quality of agreement with experimental data of structural model (# layers in alumina slab and presence of water), choice of pseudopotential, statistical sampling, and computed observable (electron densities vs. atomic form factors) were less significant.

Water Structure vs. pH

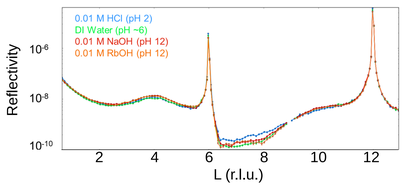


Figure 4. XR data of the alumina(001)/water interface vs. pH. Small changes are seen at L = 6-8 Å.

- PBE water height overestimate is similar to pH-dependent changes on rutile-water [4].
- Substantial pH-dependent changes in vSFG spectra have been attributed to orientational changes of water molecules[1].
- XR data only show weak changes.
- Resonant XR has been done to probe how ions affect the interfacial water structure.

3D Water Structure

Experimental Non-Specular XR

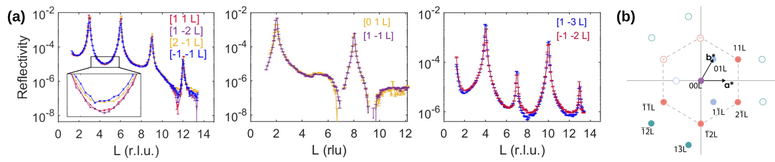


Figure 5. Measured non-specular reflections (vs. reciprocal lattice units, r.l.u.) grouped by symmetry relationships in an ideal alumina crystal. **(a)** *Left:* Nominally 6-fold symmetric reflections display subtle changes (inset), revealing an apparent 3-fold symmetry. *Middle:* [HKL] with first Bragg peak at L = 2. *Right:* [HKL] with first Bragg peak at L = 1. **(b)** Reciprocal space schematic with color-coordinated symmetry equivalent diffractions spots.

Theoretical Non-Specular XR

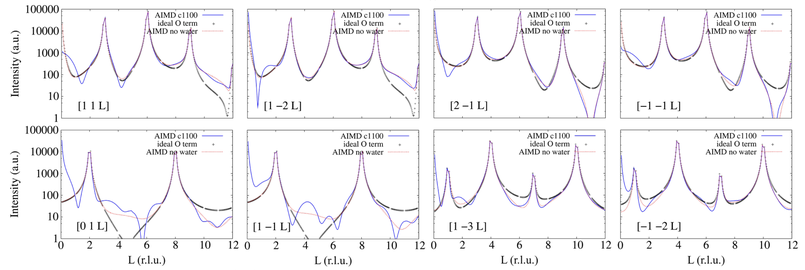


Figure 6. Reflectivity curves calculated from the simulated alumina/water structure with and without water and compared to an ideally-terminated alumina surface.

- The experimental data and simulated reflectivity display equivalent symmetry relationships between the various curves as well as qualitatively similar features.
- Deviations in the ideal symmetry relationships may be due to lateral changes in the alumina surface after relaxation and subsequent ordering of water molecules.

Conclusions and Future Work

- The 10% compressed optB88 exchange correlation functional achieves the best quality of agreement between the predicted structure and the XR data. However, the water height and coverage still exceed those of the XR best fit model, indicating the van der Waals interactions present in optB88 (but not PBE) help but may not fully account for interactions among water molecules and between water and the alumina surface.
- Preliminary comparison between the experimental and calculated non-specular XR indicate qualitative similarities between the two. A direct χ^2 comparison will be done to quantify the accuracy of the predictions.
- Assess structural changes due to pH and compare with results from vSFG studies.

References and Acknowledgements

[1] Catalano, *Geochim. Cosmochim. Acta* (2011); Zhang et. al., *JACS* (2008); Tuladhar et. al., *J. Phys. Chem. C* (2017); [2] Harmon et. al., *submitted* (2018). [3] Letchworth-Weaver et. al., *In preparation*. [4] Zhang et. al., *Surf. Sci.* (2007).

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