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

Katherine Harmon1, Kendra Letchworth-Weaver2,3*, Alex Gaiduk3, Federico Giberti3, Francois Gygi4, Giulia Galli3, Maria Chan2, and Paul Fenter5

1Applied Physics Graduate Program, Northwestern University, Evanston, IL 60208; 2Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL 60439; 3Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637; 4Department of Computer Science, University of California, Davis, CA 95616; 5Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439

Introduction

The Al2O3(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 dataset, 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 X-ray 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.

Validation Protocol

Simulation

Methodology: Full interactive molecular dynamics (AIMD) and ab initio molecular dynamics (AIMD) implemented in Qbox

Experiment

Methods

Specular XR Comparison3

Ab-initio Molecular Dynamics vs. XR Data

Origin of χ² Disagreement

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.

3D Water Structure

Experimental Non-Specular XR

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 between 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 χ² comparison will be done to quantify the accuracy of the predictions.

Assess structural changes due to pH and compare with results from vSFG studies.

Water Structure vs. pH

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 orientation 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.

References and Acknowledgements


This work was supported by the MidWest Integrated Center for Computational Materials (MICCoM) Department of Energy, Office of Basic Energy Sciences; K.H. gratefully acknowledges support from the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program and from the Ryan Fellowship and the Northwestern University International Institute for Nanotechnology. X-ray reflectivity measurements were performed at Sector 33-ID-D at the Advanced Photon Source (APS) at ANL, a U.S. DOE Office of Science User Facility operated by ANL under Contract No. DE-AC02-06CH11357.

*Current address: Department of Physics and Astronomy, James Madison University, Harrisonburg, VA 22807