Operando Molecular Science in Liquid–Solid Interfaces of Finite Thickness

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Education

1985	B.S. The University of Tokyo
1993	Ph.D. The University of Tokyo

Professional Employment

1989	Assistant Professor, The University of Tokyo
1997	Associate Professor, The University of Tokyo
1999	Project Leader, Kanagawa Academy of Science and Technology
2004	Professor, Kobe University
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Awards

2001	Young Scientist Award , Catalysis Society of Japan
2002	Nano-Probe Technology Award, Nano-Probe Technology Committee, JSPS
2003	Technical Award, Surface Science Society of Japan
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2019	Society Award, Japan Society of Vacuum and Surface Science

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We are proud of our internationally compatible studies of liquid–solid interfacess; photocatalysts for artificial photosynthesis, lubricants for smooth tribology, and ice in antifreeze liquids. Characterization with advanced AFM, time-resolved ATR-IR spectroscopy, soft X-ray absorption and microelectrode-based amperometry are being developed. We look forward to collaborating with researchers in academic and industrial organizations to unravel the science behind material conversion and energy dissipation at liquid–solid interfaces.

A new era of molecular science will be revealed at liquid-solid interfaces of finite thickness (Figure 1). The molecular interface is the site of reaction where molecules of interest collide or interact with other molecules. We need to observe individual molecules there. On the other hand, the molecular interface is connected to the liquid and solid. Materials and energy come from/to the two condensed phases, since functional interfaces are always open to the environment. Operando characterization is absolutely necessary to study the interface in its working state.

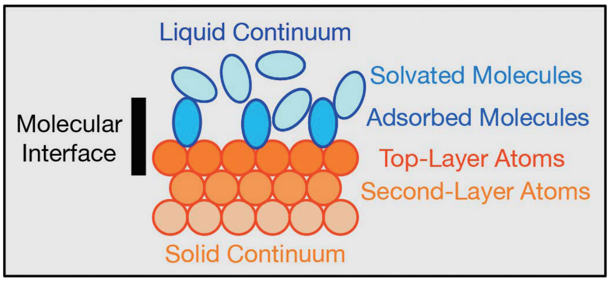

Figure 1. Liquid–Solid Interface of Finite Thickness.

Selected Publications

- Y.-H. Chew and H. Onishi, "Infrared Absorption of $Zn_{0.5}Cd_{0.5}S$ Photocatalyst Bandgap-Excited under an Aqueous Environment," *J. Phys. Chem. C* **128**, 4535–4543 (2024).
- M. Buessler, S. Maruyama, M. Zelenka, H. Onishi and E. H. G. Backus, "Unravelling the Interfacial Water Structure at the Photocatalyst Strontium Titanate by Sum Frequency Generation Spectroscopy," *Phys. Chem. Chem. Phys.* **25**, 31471–31480 (2023).
- Z. Fu, T. Hirai and H. Onishi, "Long-Life Electrons in Metal-Doped Alkali-Metal Tantalate Photocatalysts Excited under Water," *J. Phys. Chem. C* **125**, 26398–26405 (2021).
- T. Kosaka, Y. Teduka, T. Ogura, Y. Zhou, T. Hisatomi, H. Nishiyama, K. Domen, Y. Takahashi and H. Onishi, "Transient Kinetics of O_2 Evolution in Photocatalytic Water-Splitting Reaction," *ACS Catal.* **10**, 13159–13164 (2020).
- S. Xue, A. Sasahara and H. Onishi, "Atom-Scale Imaging of $TiO_2(110)$ Surface in Water by Frequency-Modulation Atomic Force Microscopy," *J. Chem. Phys.* **152**, 054703 (7 pages) (2020).
- S. Moriguchi, T. Tsujimoto, A. Sasahara, R. Kokawa and H. Onishi, "Nanometer-Scale Distribution of Lubricant Modifier on Iron Films: A Frequency-Modulation Atomic Force Microscopy Study Combined with Friction Test," *ACS Omega* **4**, 17593–17599 (2019).

1. Ice in Antifreeze Liquids Characterized by Atomic Force Microscopy

Ice in nature is surrounded by liquid most of the time, and therefore it is key to understand how ice and liquid interact. We could now directly observe the precise shape of ice at the interface between ice and liquid, by using antifreeze and a refrigerated microscope.

Ice provides the most important crystalline molecules in our lives. Because of its critical role in science and engineering, a number of experimental studies have been conducted in bulk ice and also on ice–vacuum interfaces. On the other hand, molecular-scale knowledge of the ice–water interface is still quite limited. The problem is that an ice–water interface fluctuates in space, even when the interface is held exactly at the freezing point.

Here we performed atomic force microscopy (AFM) imaging of ice surfaces immersed in antifreeze organic solvents. Ice in contact with liquid 1-octanol, for example, is stable at temperatures lower than 0 °C and higher than the freezing point of 1-octanol (−16 °C). We expect to have a good chance of mimicking some features, hopefully important features, of the ice–water interface, even though antifreeze solvents are not equivalent to water.

We did some preliminary research in 2022 to find a way to keep the ice–liquid interface below 0 °C on a Bruker AFM (Dimension XR Icon Nano Electrochemical Microscope). The best way we found was to cool the entire microscope in a soundproof box. A liquid nitrogen vessel was pressurized to provide a steady flow of cold nitrogen vapor, and the vapor flow was introduced into the box equipped with copper pipe works cooled with antifreeze fluid (Figure 2). The temperature inside the box was controlled to a desired temperature in a range from RT to −10 °C, stable enough to record topographic images of ice under antifreeze liquids.[1]

Figure 2. The Bruker microscope at the Instrument Center devised for operation at −10 °C.

Ice films were prepared from ultrapure water. After eliminating residual gases by heating to 100 °C, 100 µl of the water was dropped onto a cleaved mica substrate on the microscope cooled in the nitrogen vapor environment. After the water was dropped on mica, the water spread on the surface. This was followed by a gradual phase change of the water from liquid to solid. After waiting about 30 minutes from the initial drop, the ice surface could be scanned using a cantilever in amplitude modulation mode. The images obtained showed that the ice surface is not atomically flat, but rather has a rough structure such as nanometer-scale frost pillars.

The imaging liquid, 1-octanol for the results shown in Figure 3, was then applied to the ice film. The thickness of the octanol layer was about 1 mm. Panel (a) in Figure 3 shows a topographic image obtained at the ice–octanol interface. Two flat terraces were separated by a straight step. A cross section was constructed along the light blue line and shown in panel (b). The height of the step was 0.10 nm, as shown in the cross section. The change of the ice surface in octanol liquid from the rough surface in N_2 vapor would be caused by the partial dissolution of the surface in octanol. A limited concentration of water dissolves in octanol (the solubility of water in 1-octanol is 2 mol l^{-1} at 25 °C in ref. 2).

Considering the various roles of ice, this study concludes that it opens up new possibilities for the study of surface and interfacial phenomena associated with ice in liquids. In addition, the microscope devised in this study is functional for imaging ice and also other materials cooled at −10 °C. It is available for use at the Instrument Center through the Advanced Research Infrastructure for Materials and Nanotechnology (ARIM).

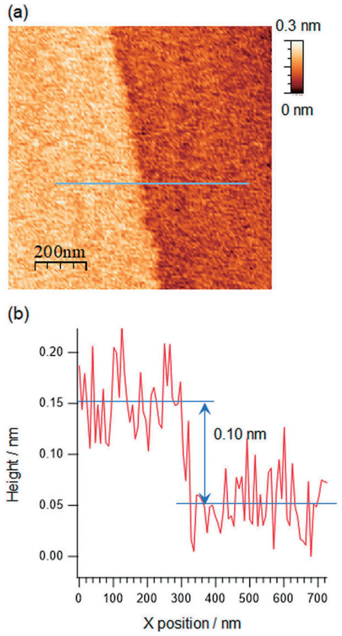

Figure 3. A topographic image of an ice film in 1-octanol liquid at −7 °C. A cross section determined along the line in panel (a) is shown in panel (b).

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