Operando Molecular Science in Liquid–Solid Interfaces of Finite Thickness

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Professional Employment
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We are proud of our internationally compatible studies of liquid–solid interfaces; 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.

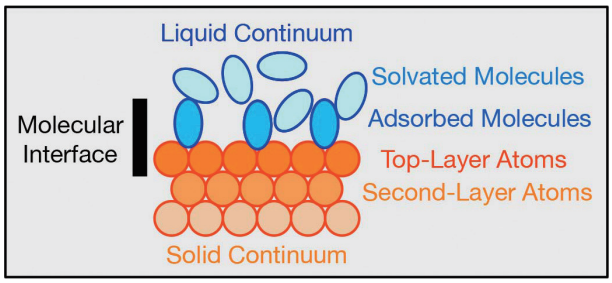

Figure 1. Liquid–Solid Interface of Finite Thickness.

Selected Publications

- Y.-H. Chew, N. Saijo, Y. Kumabe, T. Tachikawa and H. Onishi, "Unravelling the Influence of Major Seawater Salt Ions on the Photogenerated Charge Carriers in a Sr-Doped $NaTaO_3$ Photocatalyst *via* ATR-FTIR," *J. Phys. Chem. C* **129**, 3531–3538 (2025).
- M. Yanagi, J. Casanova-Cháfer, T. Hara, Y.-H. Chew, T. Yoshida, H. Onishi, C. Bittencourt and N. Ichikuni, "Calcination-Driven Co^{4+} Incorporation in Hydrothermally Synthesized $NaTaO_3$," *Chem. Lett.* **54**, upaf053 (2025).
- R. Yanagisawa, T. Ueda, K. Nakamoto, Z. Lu, H. Onishi and T. Minato, "The Iinterface between Ice and Alcohols Analyzed by Atomic Force Microscopy," *J. Chem. Phys.* **161**, 024702 (2024).
- 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. 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. Atomic Force Microscopy (AFM) in Sub-Zero Antifreeze Liquid

Ice in nature is surrounded by liquid most of the time, and therefore it is key to understand how ice and liquid interact. Atomic force microscopy is widely used for topographic imaging and force sensing at liquid–solid interfaces. Operation in antifreeze liquids has been examined at temperatures below the freezing point of water, although most AFM research in liquid is conducted in water at room temperatures. In our recent study,[1] the topographic imaging in the amplitude-modulation mode and force curves in the contact mode were examined on ice films under antifreeze liquid, using a Dimension XR Icon Nano Electrochemical microscope (Bruker).

In the present study,[2] a Shimadzu microscope (SPM-8100FM) capable of imaging and force spectroscopy in the frequency-modulation mode was utilized for probing graphite in 1-octanol ($C_8H_{17}OH$) liquid at temperatures as low as −15 °C. The topography of octanol molecules adsorbed on graphite was resolved, and octanol molecules in the liquid phase exhibited flat layers over graphite as evidenced in force spectroscopy. These results underlined the viability of frequency-modulation atomic force microscopy (FM-AFM) in sub-zero temperature liquids.

The resonance oscillation of the cantilever was mechanically excited with a piezo-actuator. In octanol liquid at RT, the resonant frequency of the cantilevers (f_0) was 100–140 kHz, with the quality factor of resonance ranging from 2 to 4. The oscillation amplitude was regulated at a preset amplitude in topographic imaging. When a conservative force was applied to the tip, the resonance frequency of the cantilever oscillation shifted accordingly. The topography of the object was traced by regulating the frequency shift (Δf) at a predefined setpoint. Figure 2 illustrates the topographic images observed at 27 and −11 °C.

In the images, linear stripes were recognized with trenches between the stripes. The edges of the stripes were presented brighter than the middle. This appearance is consistent to what proposed in earlier studies; the alcohol molecules are paired *via* hydrogen bonding when adsorbed on graphite, and the paired molecules exhibit stripes that are epitaxial to the graphite lattice.

To visualize the local density distribution of octanol liquid, the resonantly oscillating cantilever was scanned vertically from the bulk octanol to the graphite surface. During one such vertical scan, the frequency shift was recorded as a function of vertical coordinate, thereby obtaining one Δf–distance curve. Upon reaching a predetermined Δf threshold, signifying tip-to-solid contact, the cantilever was retracted into octanol by 4–5 nm. Subsequent to this retraction, the cantilever was shifted in the horizontal direction, and an additional vertical scan was conducted. A total of 1024 vertical scans were systematically acquired to construct a Δf map on a plane perpendicular to the graphite surface.

Figure 3 shows two Δf maps observed at 27 °C and −6 °C. The maps are associated with the distribution of the octanol-induced force on the AFM tip apex. Bright color in the Δf maps represent positive frequency shift. The brightest region at the bottom of each map represents the boundary between the liquid and solid. The repulsive force on the tip exhibited a rapid increase when the tip penetrated deeper into this region, signifying tip-to-solid contact. Hence, the envelope of the brightest region delineates the topography of the physisorbed octanol monolayer on graphite.

The frequency shift exhibited an uneven distribution in the proximity of the surface. Alternating dark and bright layers appeared in the maps, suggesting that the surface was covered by five or six liquid octanol layers. The vertical distance between the layers was 0.5 and 0.6 nm at 27 °C and −6 °C, respectively. The octanol liquid layers were suggested to be separated by this distance. The liquid-induced force pushing or pulling the tip apex is contingent on the local liquid density, though force–density relation is not straightforward. Subsequent examination of continuous scanning within a temperature range of −14 °C to 30 °C revealed no substantial structural variation, despite the lowest temperature was close to the freezing point of octanol.

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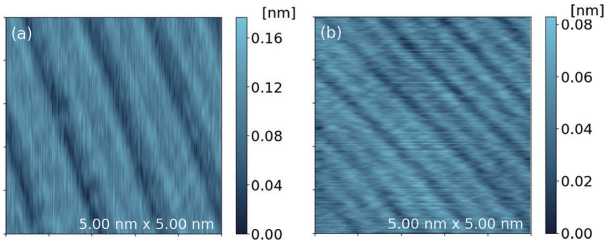

Figure 2. Topographic images of 1-octanol physisorbed on graphite captured at (a) 27 and (b) −11 °C.

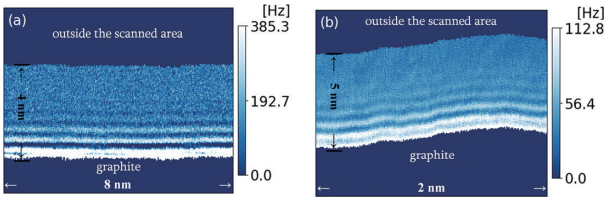

Figure 3. 1-Octanol liquid over a graphite wafer at (a) 27 and (b) −6 °C. The frequency-shift of the cantilever resonance oscillation (Δf) was mapped on a plane that was perpendicular to the wafer. A large (or small) positive frequency-shift is depicted using a bright (or dark) color.

References

1) R. Yanagisawa, T. Ueda, K. Nakamoto, Z. Lu, H. Onishi and T. Minato, *J. Chem. Phys.* **161**, 024702 (2024).
2) Z. Lu, R. Yanagisawa, S. Moriguchi, T. Ueda, K. Nakamoto, T. Minato and H. Onishi, *Jpn. J. Appl. Phys*. **64**, 05SP05 (2025).