## Atomic-scale Investigations of Solid-Liquid Interfaces by Frequency Modulation Atomic Force Microscopy

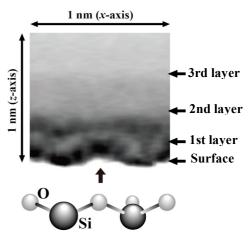
## Hirofumi Yamada

Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan, h-yamada@kuee.kyoto-u.ac.jp

Solid-liquid interfaces play crucial, fundamental roles in a wide variety of physical and chemical processes, such as crystal growth, electrochemical reactions and various biological functions. Investigations of atomic-scale structures and interactions at solid-liquid interfaces are, therefore, essentially important for understanding theses microscopic processes. Force mapping method based on frequency modulation atomic force microscopy (FM-AFM) is a remarkable technique for atomic-scale investigations of interaction forces on a specific site of crystal surfaces. The technique has been used mainly in vacuum environments, where highly sensitive force detection can be performed due to the high Q-factor in the cantilever oscillation. However, since significant progress has been made in FM-AFM in liquids over the past few years [1, 2], the force mapping method can be used for atomic or molecular scale investigations of interaction forces at solid-liquid interfaces, such as solvation forces.

In this study three-dimensional (3D) force (frequency shift:  $\Delta f$ ) mapping method has been applied to the investigations of molecular-scale hydration structures at solid-liquid interfaces as well as those around biomolecules such as proteins and DNA molecules. The 3D visualization of the hydration structures allows us to make a precise comparison of the experimental data with theoretical calculations of water structures, which can provide a molecular scale understanding of the hydration structure. However, there have been several difficulties in the 3D force mapping in

liquids because of a large, linear and nonlinear thermal drift of the tip position relative to the surface in an unstable liquid environment. We have developed a low-thermal-drift FM-AFM working in liquids based on a commercial AFM instrument. A sufficiently low, lateral thermal drift rate of less than 1 nm/min was achieved in liquids by an accurate temperature control of the environment and by a large reduction of the liquid evaporation. We obtained 3D frequency shift  $(\Delta f)$  data on a muscovite mica surface in a 1M KCl solution [3]. Figure 1 shows an example of two-dimensional (2D)  $\Delta f$  mapping data taken out of the  $3D-\Delta f$  data. The result was compared with water density distributions calculated using the 3D reference interaction site model (3D-RISM) theory. In addition, we also discuss a latest result of 3D visualization of hydration structures around biomolecules such as DNA molecules.



**Figure 1** Two-dimensional (*x* and *z* directions) frequency shift mapping (gray contrast) in a KCl aqueous solution on a mica crystal surface.

## References

- [1] T. Fukuma, K. Kobayashi, K. Matsushige and H. Yamada, Appl. Phys Lett. 87, 034101 (2005).
- [2] S. Rode, N. Oyabu, K. Kobayashi, H. Yamada and A. Kuhnle, Langmuir 25, 2850 (2009).
- [3] K. Kimura, S. Ido, N. Oyabu, K. Kobayashi, Y. Hirata, T. Imai, H. Yamada: *J. Chem. Phys.* **132** 194705 (2010).