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

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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 these 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.

References