Understanding contrast in nc-AFM imaging of insulators in water

Bernhard Reischl[1], Adam S. Foster[2], Matthew Watkins[3], Naritaka Kobayashi[4] and Takeshi Fukuma[4]

[1]*Dept. of Physics, Tampere University of Technology, Tampere, FI 33101, Finland;*
[2]*Dept. of Applied Physics, Aalto University School of Science, Aalto, FI 00076, Finland;*
[3]*London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, United Kingdom;*
[4]*Dept. of Electric Eng. and Computer Sci., Kanazawa University, Kanazawa 920-1192, Japan.*
E-mail: bernhard.reischl@tut.fi

We study the AFM imaging mechanism of insulators in water, using the examples of calcite and calcium fluoride. The system, consisting of several layers of surface material, water, and the tip apex represented by a nanocluster, is simulated at room temperature, using molecular dynamics simulations with empirical atomistic interaction potentials. We use umbrella sampling to compute a continuous free energy profile of the system, as a function of the tip-surface separation, for different lateral tip positions. The derivative of this free energy with respect to the tip-surface distance is the best estimate for the force acting on the AFM tip, as the important entropic contributions from interactions with hydration layer water molecules are correctly taken into account in the free energy calculation [1, 2]. We also compare different approaches to simulate the free energy for each system, and comment on the advantages and disadvantages for general simulations of AFM in liquids. With the *virtual AFM* developed in our group, we use the calculated 3D force field to simulate the oscillation of a cantilever with the same resonance frequency, amplitude, force constant, and Q-factor as in the experiment. The frequency shift images and spectroscopy data obtained agree well with the experimental results. Analysis of the molecular dynamics trajectories gives insight into the atomistic details responsible for the contrast observed in the images, and establishes the relation between the real water-insulator interface and that *seen* by AFM.

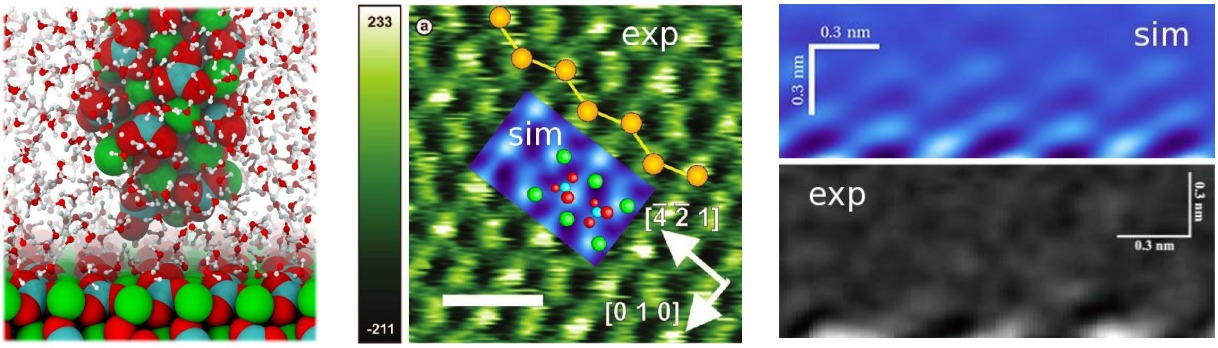

Figure 1: Detail of the molecular dynamics simulation of calcite in water (left). Simulated frequency shift images (center) are in good agreement with experimental results in Ref. [3]. Comparison between simulated and recent experimental 3D force spectroscopy data (right).

References

[1] Watkins M, and Shluger A L, Phys. Rev. Lett. **105**, 196101 (2010).
[2] Watkins M, Berkowitz M L, and Shluger A L, Phys. Chem. Chem. Phys. **13**, 12584 (2011).
[3] Rode S, Oyabu N, Kobayashi K, Yamada H, and Kühnle A, Langmuir **25**, 2850 (2009).