Simulating NC-AFM imaging of Calcite in water

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As a first step towards understanding AFM imaging of complex biosystems in water, we study calcite as a model system. The calcite surface has been studied extensively because of its important role in biomineralization, industrial applications, and as substrate for biomolecule growth and manipulation. Although recent atomically resolved non-contact AFM images of calcite in water [1] resemble those obtained in UHV [2], the imaging mechanism in liquid is more complicated [3], due to the presence of hydration layers around the tip and surface: at room temperature, there is an entropic contribution to the force on the AFM tip from displacing water molecules.

In this work, we use molecular dynamics simulations with empirical interaction potentials to study the AFM imaging mechanism in water. We present two different methods of computing force-distance curves. First, in a quasi-static tip approach, the tip is fixed at a certain position above the surface and the force is obtained from a time average. Second, we use umbrella sampling to calculate the free energy of the system as a continuous function of the tip-surface separation. The force on the tip is then obtained by deriving this free energy profile. In our simulations, we model the AFM tip as a nanocluster composed either of silica, or calcite (Fig. 1), to re-create an oxidized Silicon tip apex, or a tip covered in surface material after initial surface contact. In a final step, the force-distance curves can be used to compute AFM images that can be compared to experimental results.

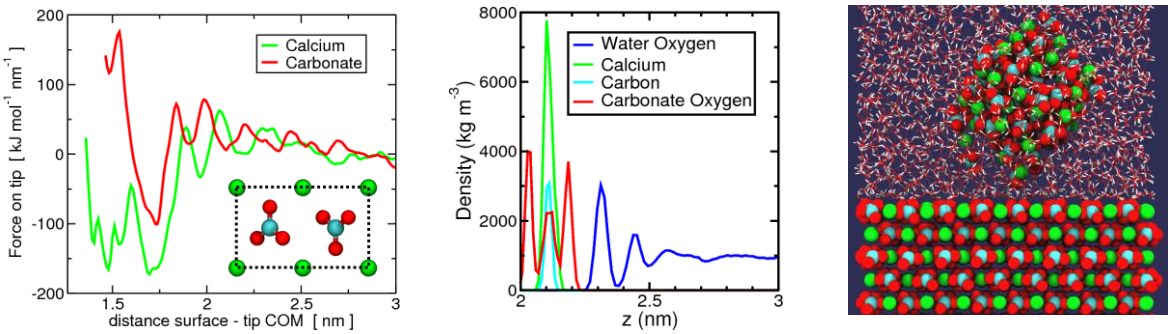

Figure 1: Calcite tip. Force-distance curves over calcium and carbonate groups (left), hydration layers at the calcite-water interface (middle), and snapshot of the simulation (right).

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[3] M. Watkins and A. L. Shluger, Phys. Rev. Lett. 105 (2010).