Simulating Atomic Force Microscopy of Calcite in Water

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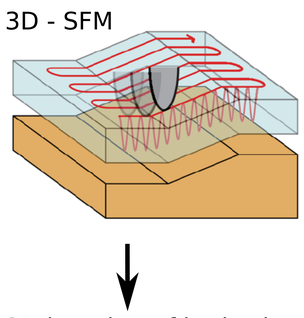
Atomic Force Microscopy in liquids

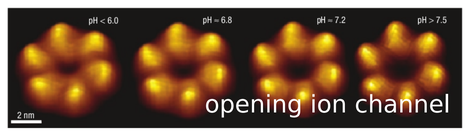
In Atomic Force Microscopy, a sharp tip mounted on a cantilever is used to scan a surface. The changes in the force acting between surface and tip atoms create an image of the surface. On relatively flat surfaces, atomic resolution can be achieved.

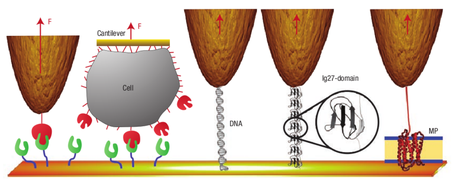
In liquids, the AFM can be used to study and manipulate biological systems [1]. It can also probe and visualize hydration layer structures on top of surfaces [2].

Computer simulations are needed to interpret images and understand the details of interaction mechanisms.

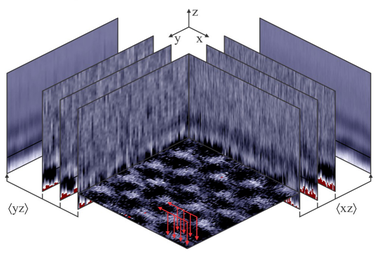


Biological systems can be studied *in vivo* using AFM





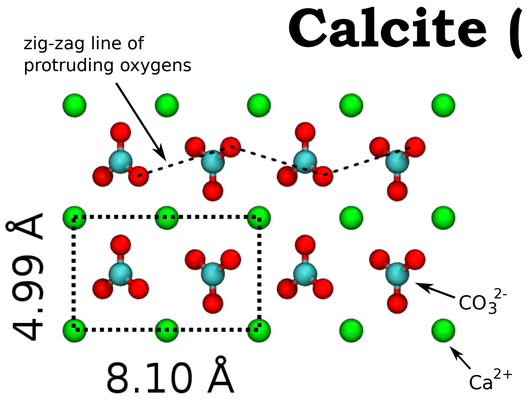
AFM tip functionalized to manipulate biological systems



[1] D. J. Müller and Y. F. Dufrêne, Nature Nanotechnolgy 3 (2008)

[2] T. Fukuma *et al.*, PRL 104 (2010)

Calcite ($10\bar{1}4$) surface



Calcite is a stable polymorph of calcium carbonate. The (1014) surface (left) is charge neutral and stable. FM-AFM images in vacuum show atomic resolution [1]. Images obtained in water at room temperature exhibit a similar level of detail [2].

Although the images in water resemble those in vacuum, the imaging mechanism in liquid is more complicated, due to the presence of hydration layers on the surface and tip [3].

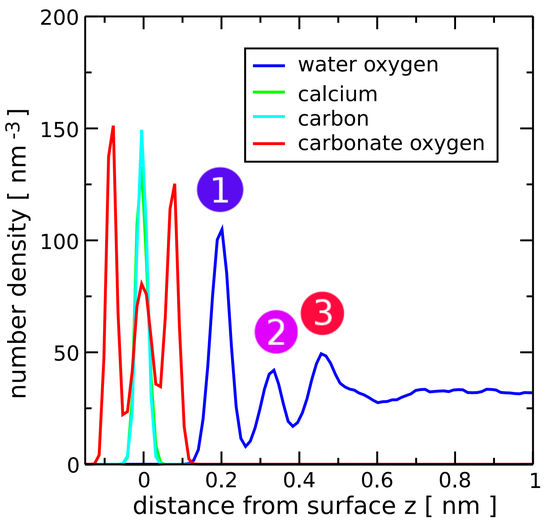
What is the AFM imaging mechanism of Calcite in water?

[1] J. Schütte *et al.*, Langmuir 26, 8295 (2010)

[2] S. Rode *et al.*, Langmuir 25, 2850 (2009)

[3] M. Watkins and A.L. Shluger, PRL 105, 196101 (2010)

Calcite hydration layer structure

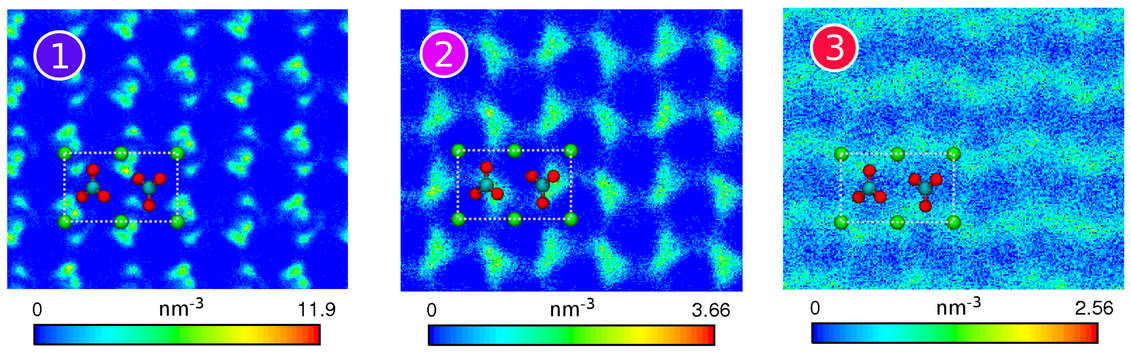


There are are three distinct hydration layers at the calcite-water interface.

Left: Number densities of the different atomic species present at the calcite-water interface from 4 ns (N,V,T) - Molecular Dynamics simulations at T = 300 K.
The empirical interaction potentials [1] were parameterized to reproduce structural and thermodynamic properties of the interface.

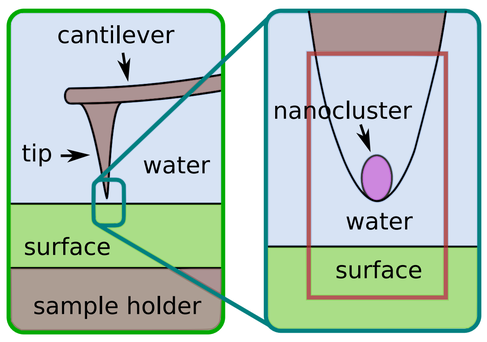
[1] P. Raiteri and J. D. Gale, JACS 132, 17623 (2010)

Below: 2D number density maps of water molecule oxygen atoms within the first (left), second (middle), and third (right) hydration layer.



Above: MD snapshot details showing calcite surface layer and water molecules in the first three hydration layers.

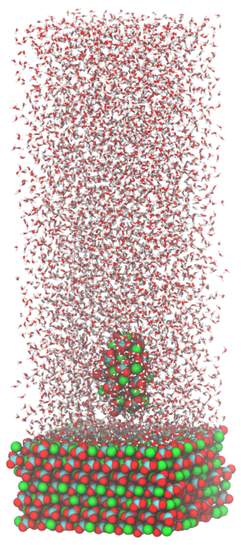
Simulation methodology

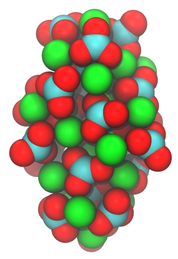


cantilever oscillation has slower timescale than the movements of water molecules, the system is close to equilibrium.

Tip apex region can be modeled by a nanocluster.

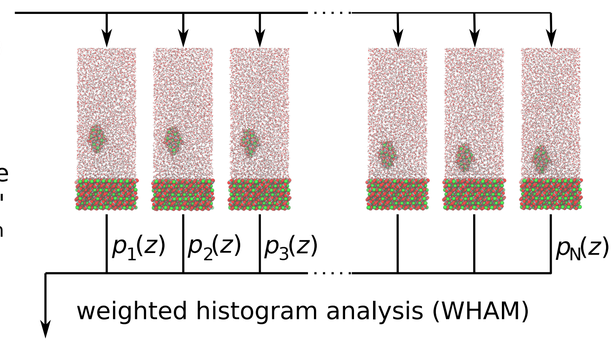
Tip apex likely covered in surface material.





125 atom calcite nanocluster 'tip' annealed in vacuum and equilibrated in water

We compute the free energy of the system as a function of the tip-surface distance, using umbrella sampling.



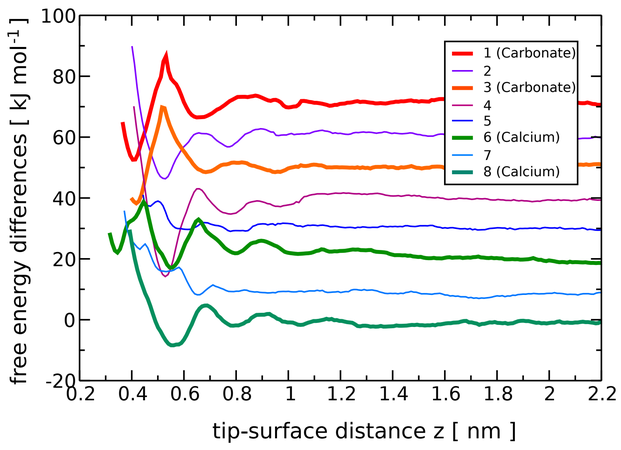
In every umbrella window, 4.5 ns of (N, V, T) - MD are carried out, with the center of mass distance between tip and surface, z, constrained by a harmonic potential.

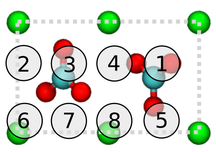
continuous free energy profile $F(z) = -k_B T \ln p(z)$ → force-distance curve $f(z) = -\mathrm{d}F/\mathrm{d}z$ → force-distance map $f\,[x, y, z]$ → virtual AFM, simulated AFM images

CSC

MD simulations were performed with GROMACS on CSC's Murska cluster.

Free energy curves

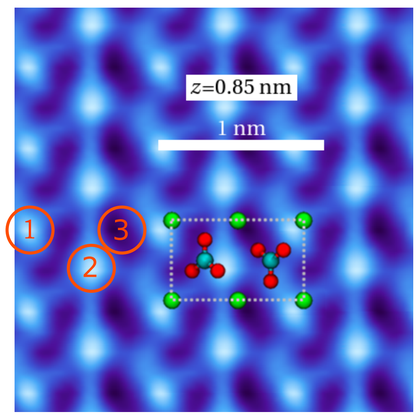




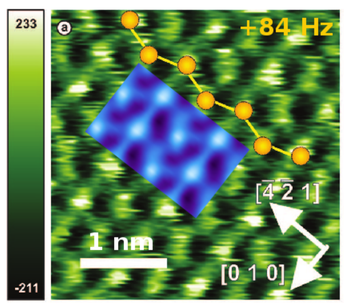
Free energy curves computed over eight points in the surface unit cell (left).

At large tip-surface distances, the free energy curves are flat. When the hydration layers of tip and surface start to interact, free energy barriers appear. At smaller distances, the free energy curves above calcium and carbonate ions differ significantly.

Simulated AFM images



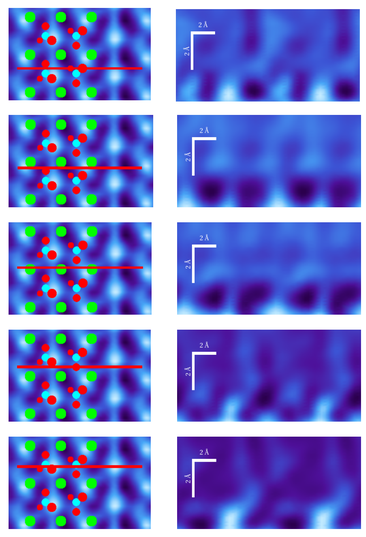
Very good agreement with experiment for A = 0.3 nm and z = 0.85 nm



The AFM image is the result of interactions between hydration layer water molecules and the direct interactions with atoms in the surface.

To explain the contrast, MD trajectories have to be analyzed in detail.

3D force spectroscopy



hydration layer interaction at closest approach