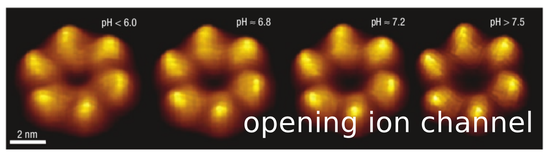
Understanding non-contact atomic force microscopy imaging of insulators in water

B. Reischl[1], P. Spijker[1], M. Watkins[2], N. Kobayashi[3], T. Fukuma[3] and A. S. Foster[1]

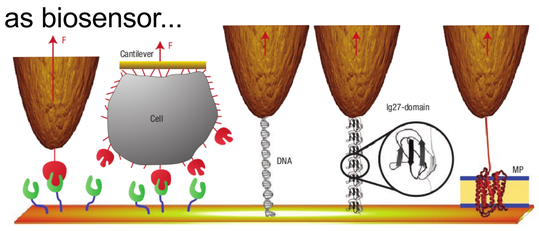
[1]COMP Centre of Excellence, Department of Applied Physics, Aalto University
[2]London Centre for Nanotechnology and Department of Physics and Astronomy, University College London
[3]Bio-AFM Frontier Research Center and Division of Electrical and Computer Engineering, Kanazawa University
email: bernhard.reischl@aalto.fi

Atomic Force Microscopy in liquids

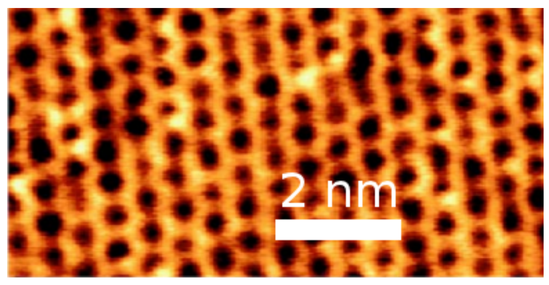
Images and movies of biological systems in physiological environment...



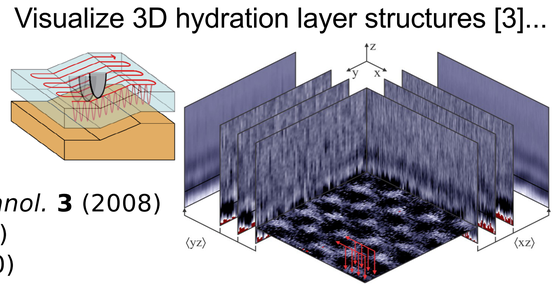
Bio-nanotechnology: Single biomolecule manipulation, functionalized AFM tips, AFM as biosensor...



Atomic resolution images on flat surfaces in liquid, e.g. mica [2],...



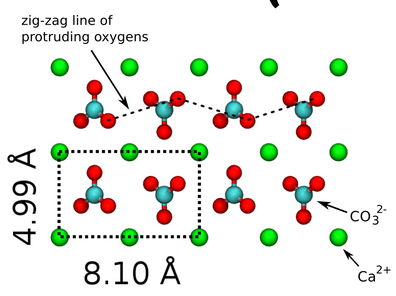
Visualize 3D hydration layer structures [3]...



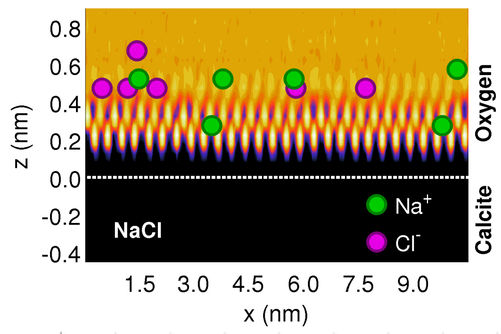
[1] D. J. Müller and Y. F. Dufrêne, *Nat. Nanotechnol.* **3** (2008)
[2] T. Fukuma *et al.*, *Appl. Phys. Lett.* **87** (2005)
[3] T. Fukuma *et al.*, *Phys. Rev. Lett.* **104** (2010)

Imaging mechanism not well understood, but computer simulations can give new insight

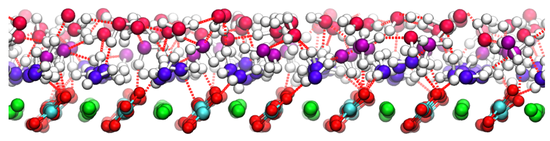
Simulation meets experiment: Calcite ($10\bar{1}4$) surface in water

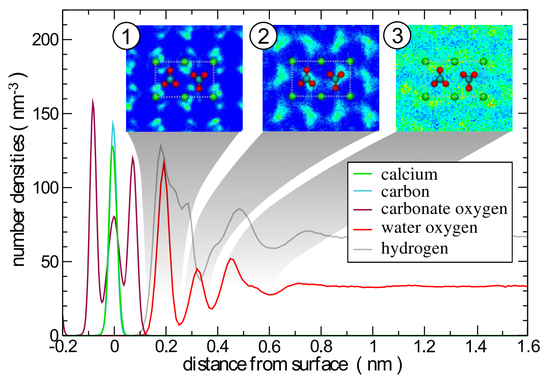


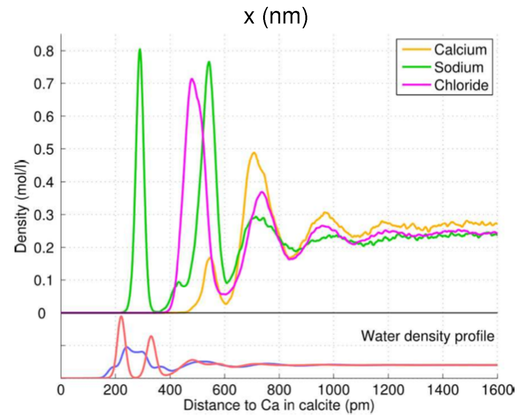
Ions from solution penetrate hydration layers, but do not adsorb on the surface [2]



Hydration layer structure from simulation [1]

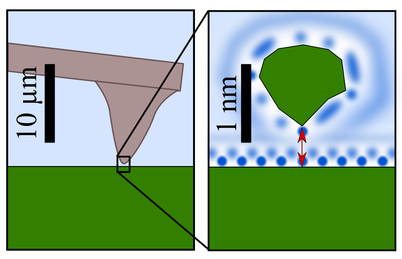






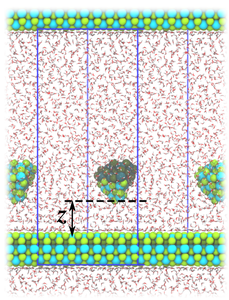
[1] B. Reischl, M. Watkins and A. S. Foster, *J. Chem. Theory Comput.* **9**, 600-608 (2013)
[2] M. Ricci, P. Spijker, F. Stellacci, J.-F. Molinari and K. Voitchovsky, *Langmuir* (accepted 2013)

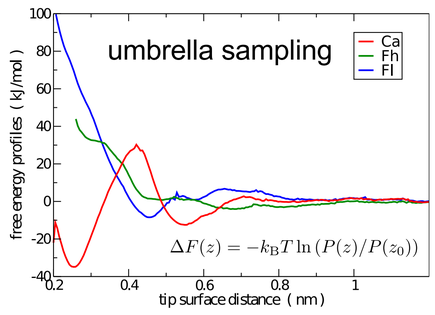
Force from free energy calculations

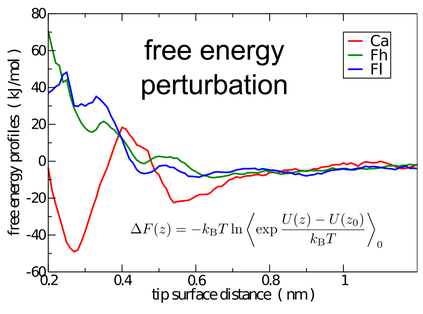


Free energy as function of tip-surface distance z takes into account entropic force contributions from water molecules in hydration layers

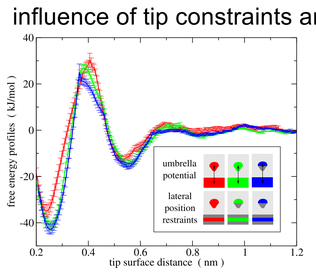
Benchmarking: free energy calculations of a fully solvated CaF_2 nanocluster tip over different sites of the CaF_2 (111) surface in NVT or NpT ensembles at room temperature, using atomistic interaction potentials

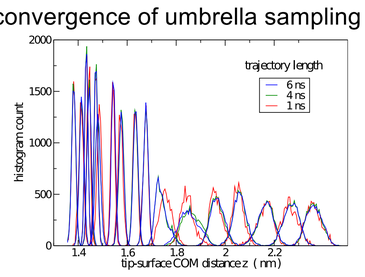




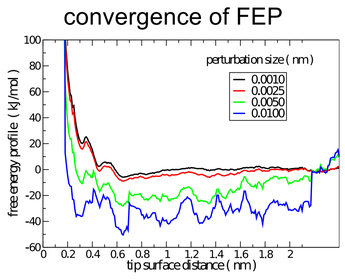


influence of tip constraints and convergence of umbrella sampling





convergence of FEP

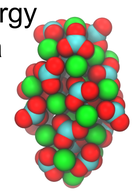


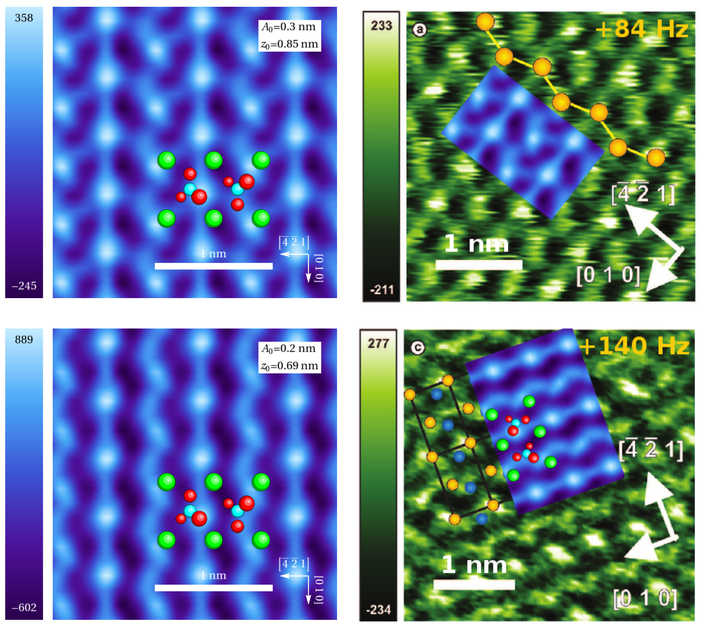
Free energy calculations are accurate, but computationally demanding

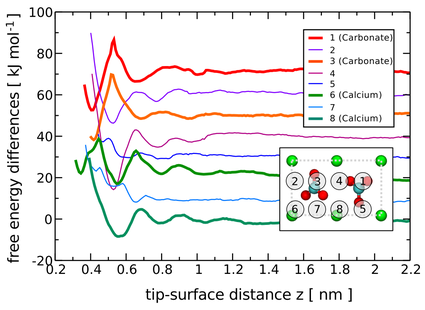
B. Reischl, M. Watkins and A. S. Foster, *J. Chem. Theory Comput.* **9**, 600-608 (2013)

Simulated AFM images

Simulated frequency shift images obtained with our virtual AFM, using a force field derived from the free energy calculations with a calcite tip, agree very well with experimental FM-AFM images [1]





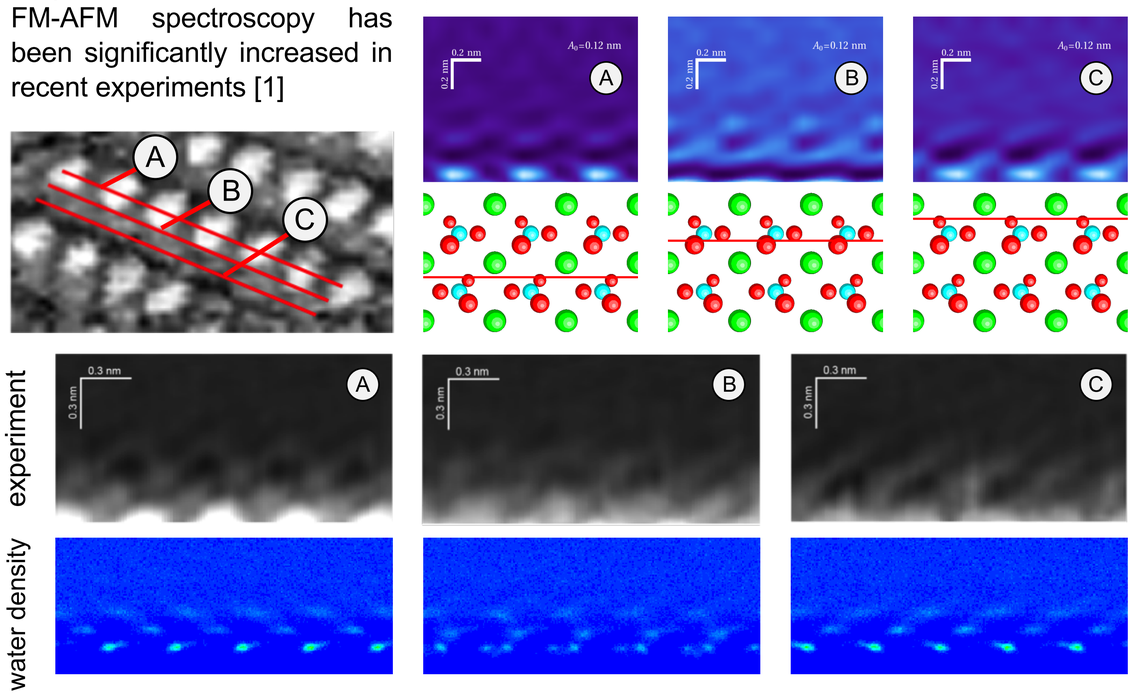


[1] S. Rode, N. Oyabu, K. Kobayashi, H. Yamada and A. Kühnle, *Langmuir* **25**, 2850 (2009)

Simulated spectroscopy images

Using ultra small cantilevers with over 10x higher oscillation frequencies, the resolution in FM-AFM spectroscopy has been significantly increased in recent experiments [1]

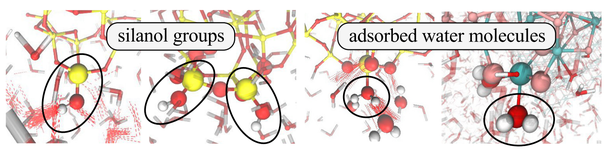
This will help establish the link between the images *seen* by AFM, and the atomistic, as well as collective, processes that can be observed in the simulation

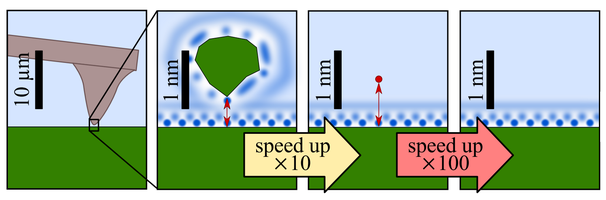


[1] N. Kobayashi, T. Fukuma, B. Reischl, F. Federici Canova and A. S. Foster, in preparation.

Force from local water densities

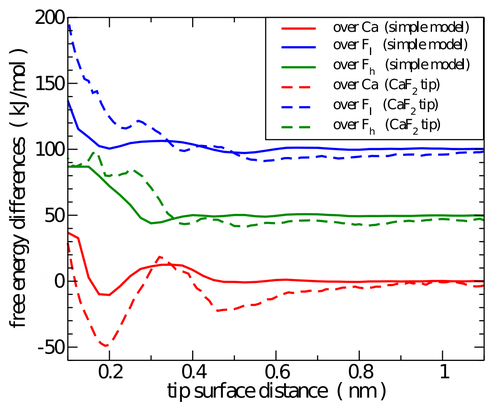
Sharp AFM tips that expose an OH group, or strongly bind a water molecule will interact strongly with individual water molecules in hydration layers.





Then, the free energy profile of a "water molecule tip" can be calculated directly from the local equilibrium water densities:

$$\Delta F(z) = -k_B T \ln(\rho(z)/\rho_0)$$



Simple model is computationally cheap, but not always applicable

M. Watkins and B. Reischl, submitted to *J. Chem. Phys.* (2013)