

## Realistic models of nc-afm tips in solution

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It is well known that the structure of the tip apex is critical in determining a microscopes resolution and the mechanism of image contrast. In UHV there has been extensive work developing plausible tip models for insulating, semiconducting and metallic systems. The situation is at least as complex when the measurements are to be carried out in solution. Conventional silicon AFM cantilevers immersed in water acquire an oxide coating, whose properties can vary significantly. Here we use density functional theory based molecular dynamics simulations to construct silica particles to use as models of scanning probe microscope tips in solution. We will then show results demonstrating how the tip structure, nature of chemical termination, and interaction with aqueous solution, affects simulated force curves.

Characterization of the surface of silica is complicated due to the amorphous nature of the material and a consequent lack of probes that can reveal surface structure in atomistic detail. A further complication is the ready hydroxylation of the material under many environmental conditions. Surface hydroxylation is extremely important, providing the anchoring points for further functionalization and determining the interaction of the material with water – bare siloxane groups (O-Si-O) are strongly hydrophobic, forming almost no hydrogen bonds with adsorbed water, whilst silanol groups (Si-OH) lead to strong hydrophilic interactions. We expect that AFM tips with these different terminations could exhibit strong differences in image contrast mechanism.

Three model silica nanoparticles with diameter of  $\sim 1$  nm were generated by simulated annealing of an initial structure developed by Ya and Foster[1], representing clusters of increasing stability in vacuum. In addition a smaller cluster, believed to be the global minima in vacuum[2], was considered. These four models were fully solvated by hundreds of water molecules and, using a highly efficient implementation of DFT based molecular dynamics[3], their change in structure with time during exposure to water was studied. We identify a variety of surface reactions, similar to those observed by Garofolini and other studies[4], but also note that through the motion of generated hydronium ions, correlated reactions occur at surface sites with large separations. Metastable particles are found after only ca. 5 ps of simulation and we have examined the functional groups present at their surface. The tip models were then used to generate simulated force curves over CaF<sub>2</sub> and CaCO<sub>3</sub> surfaces using the methods we proposed in [5].

### References

- [1] Y. Ma, A.S. Foster, and R.M. Nieminen, *J Chem. Phys.*, 122 144709 (2005)
- [2] E. Flikkema, and S.T. Bromley, *J. Phys. Chem. B*, 108 9638-9645 (2004)
- [3] J. Vandevondele, et al., *Comput. Phys. Comm.*, 167 103-128 (2005)
- [4] T.S. Mahadevan and S.H. Garofalini, *J. Phys. Chem. C*, 112 1507-1515 (2008)
- [5] M. Watkins and A.L. Shluger, *Phys. Rev. Lett.*, 105 196101 (2010)