

Insights from the modeling of AFM measurements at the calcite–water interface

P. Spijker¹ K. Voïtchovsky² M. Ricci² F. Stellacci² J. F. Molinari¹

¹Computational Solid Mechanics Laboratory (LSMS), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH 1015, Lausanne, Switzerland

²Supramolecular Nanomaterials and Interfaces Laboratory (SUNMIL), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH 1015, Lausanne, Switzerland

Solid–liquid interfaces play a fundamental role in many biomolecular and electrochemical applications at the nanoscale. Although spectroscopy and diffraction techniques can provide very accurate information about such interfaces, atomic force microscopy (AFM) has the advantage of probing the investigated system locally, thus allowing a deeper understanding of interfaces. Recently, a new enhancement of AFM based on small amplitude modulation atomic force microscopy (AM–AFM), has demonstrated the capability to probe the solid–liquid interface quantitatively at with sub-nanometer precision [1]. We have applied this technique to investigate the calcite–water interface with atomic-level resolution. The importance of this study is emphasized by the fact that calcite plays an important role in geochemical and environmental systems [2].

In order to enhance the insight obtained through the AM–AFM experiments on these calcite–water interfaces, we performed large-scale molecular dynamics (MD) simulations of similar systems, in which the 10–14 surface of calcite is exposed to a water-ion solution (Na⁺, Ca²⁺, Rb⁺, or Cl⁻). Our simulations show a strong ordering of water near the interface. For instance, the computed density profiles perpendicular to the surface are in good agreement with comparable X-ray scattering measurements [3]. Furthermore, it is shown that despite the charged calcite surface ions do not get adsorbed at the interface, but tend to be blocked by the strong ordered water layer.

Using the strength of having insight at processes at the atomic scale when using MD simulations it is revealed how a single step in the calcite surface can break the water structure and allows for strong ion adsorption at or near the surface. Finally, based on the data from the MD simulations, topographic images similar to those obtained from AM–AFM measurements are constructed, demonstrating a good agreement between simulations and experiments.

[1] K. Voïtchovsky, J.J. Kuna, S.A. Contera, E. Tosatti, and F. Stellacci, *Nat. Nanotechnol.* **5**, 401 (2010).

[2] F. Heberling, T.P. Trainor, J. Lützenkirchen, P. Eng, M.A. Denecke, and D. Bosbach, *J. Colloid Interface Sci.* **354**, 843 (2011).

- [3] P. Geissbühler, P. Fenter, E. DiMasi, G. Srajer, L.B. Sorensen, and N.C. Sturchio, *Surf. Sci.* 573, 191 (2004).