

Understanding solid-liquid interfaces through MD simulations



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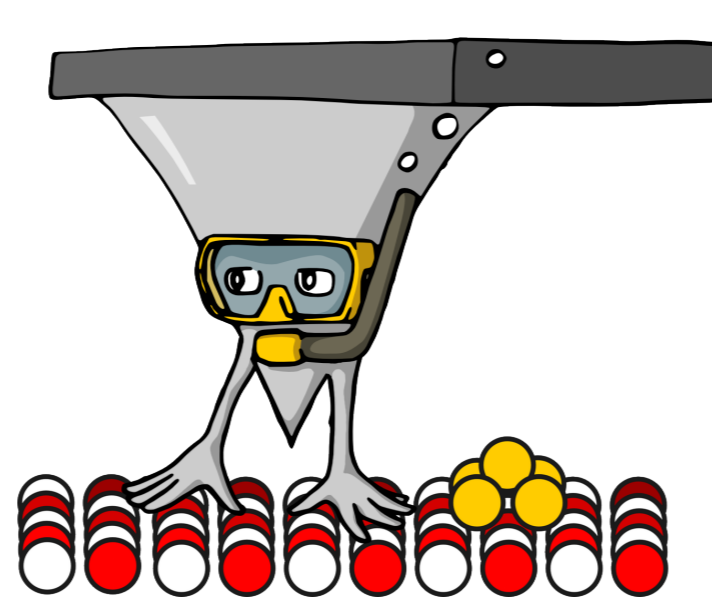
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Introduction

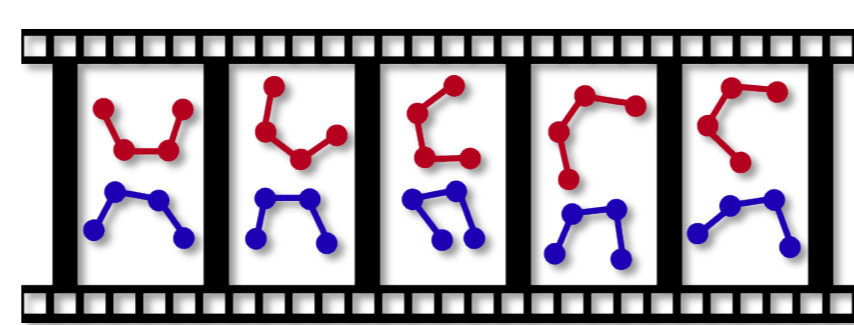
In many nanoscale applications the interface between the solid and the liquid is of crucial importance. But understanding the physics at these solid-liquid interfaces is far from trivial. Although spectroscopy and diffraction techniques can provide very accurate information about such interfaces, atomic force microscopy (AFM) has the advantage of probing the investigated system locally, thus allowing a deeper understanding of these type of interfaces. When using AFM in a liquid environment it allows sub-nanometer studying of the solid-liquid interface, and it is perhaps one of the few tools capable of resolving the nature of the formed hydration layers at the interface [1,2].

Though, from a molecular perspective even AFM experiments, with the tip submerged in the liquid, span a large time scale and individual atomic-level processes cannot be measured. This is exactly where large-scale molecular dynamics (MD) simulations prove extremely useful in elucidating the physical origins of the solid-liquid interfaces.



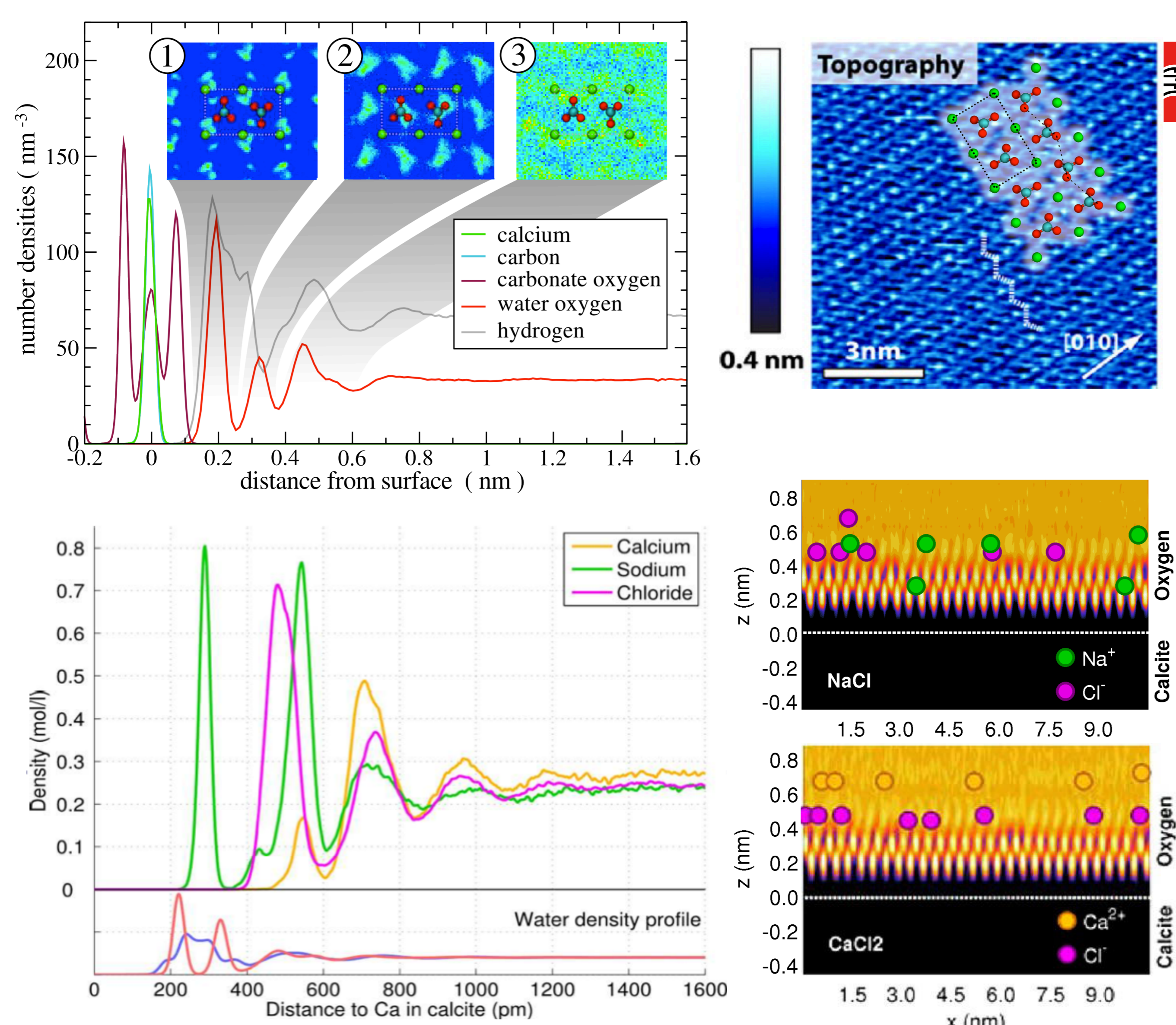
Molecular dynamics simulations

At its core molecular dynamics (MD) simulations solve Newton's equations of motion for each individual atom in the system under consideration, where the interactions between the individual atoms are determined by a potential energy function given by a specific (empirical) force field. Typically such systems contain thousands to millions of atoms and the complexity of coupled equations demand high performance computing. This limits the length and time scale accessible in MD simulations to several nanometers and -seconds. However, the main power of MD simulations is the availability of the time evolution of each atom's position, which can be analyzed by sophisticated algorithms.



$$V_{ij}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

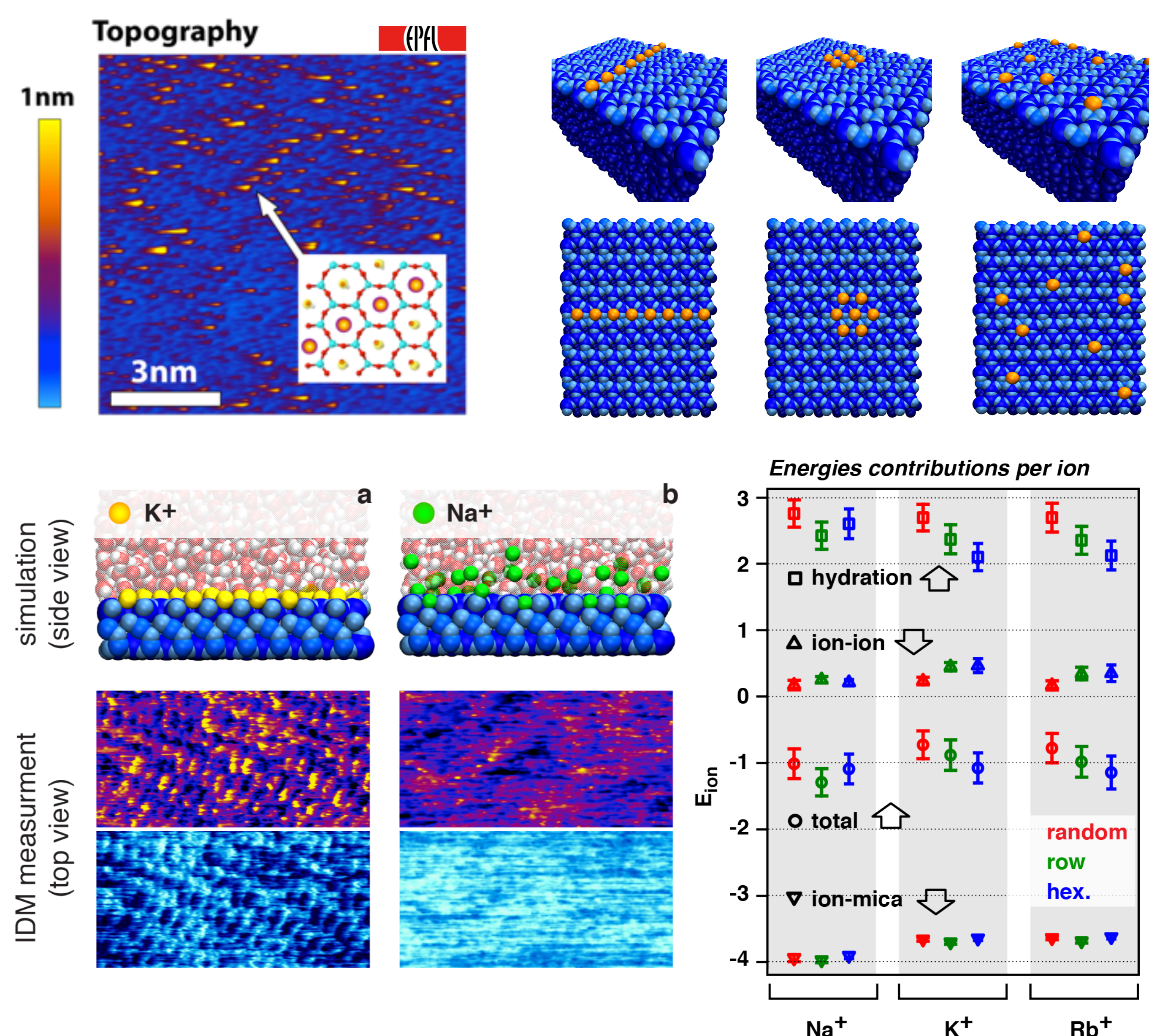
Calcite-water interface (and ions)



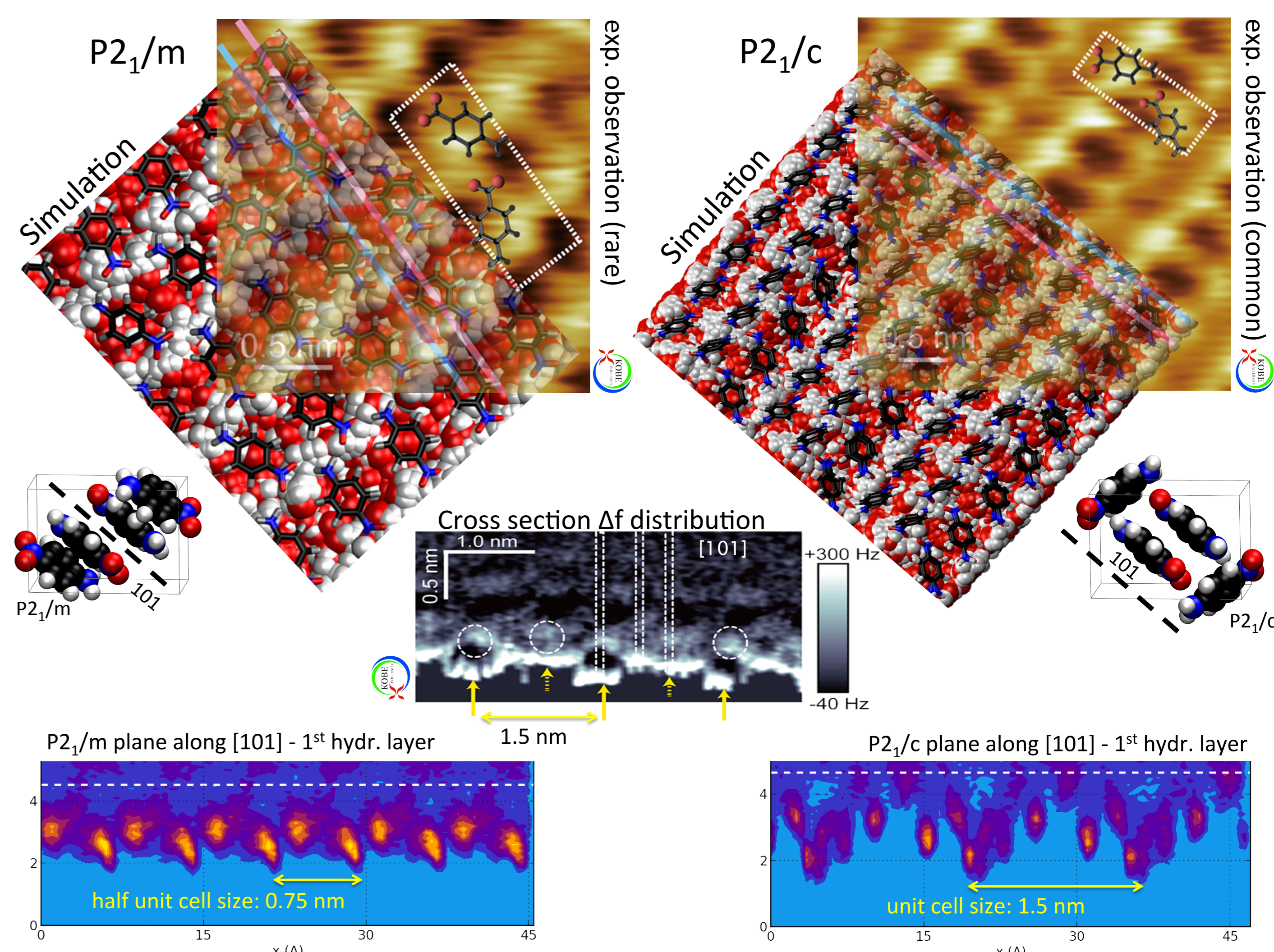
The MD simulations reveal a similar hydration structure as observed in the experiments (top right). But also three distinctive hydration layers are observed [3,4]. The addition of ions (Na⁺/Ca²⁺) show them rarely passing the final hydration layer and their location depends on their hydration state.

Muscovite mica-water interface (and ions too)

Recent AFM experiments on muscovite mica with either Na⁺, K⁺ or Rb⁺ ions in solution show them adsorbing at the surface (coverage depending on the concentration), but preferably in regular patterns (e.g., rows or hexagons) [5].



Interface between p-nitroaniline and water



Comparison of the experimental and MD data suggest a different surface structure than in the bulk, having an increased hydration energy [6].

References

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