



# UNDERSTANDING COMPLEX SOLID-LIQUID INTERFACES AT THE ATOMIC SCALE

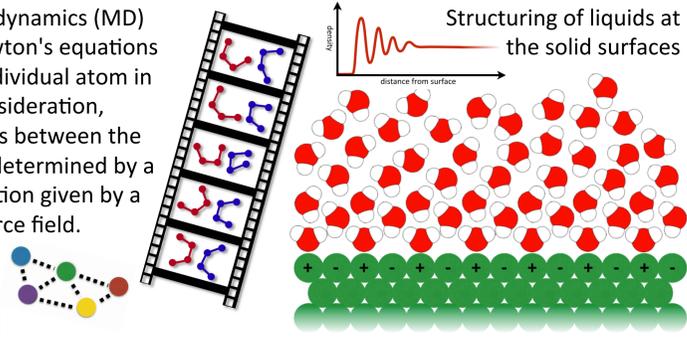
PETER SPIJKER KISLON VOÏTCHOVSKY KEI KOBAYASHI HIROSHI ONISHI ANGELIKA KÜHNLE ADAM FOSTER

## MOLECULAR DYNAMICS SIMULATIONS

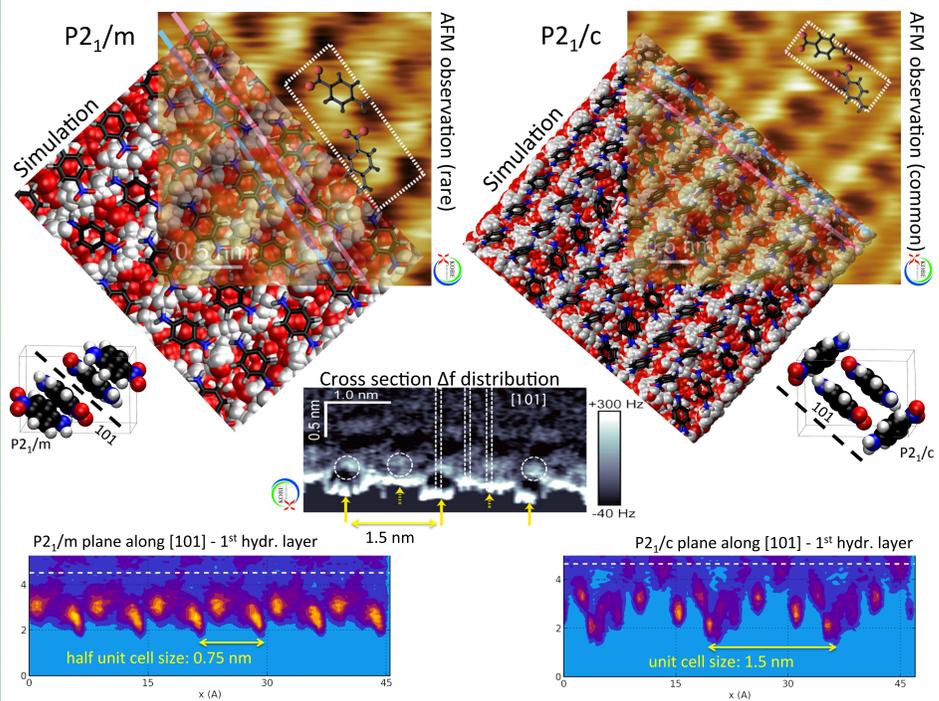
At its core molecular dynamics (MD) simulations solve Newton's equations of motion for each individual atom in the system under consideration, where the interactions between the individual atoms are determined by a potential energy function given by a specific (empirical) force field.

$$V_E(r) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_R r}$$

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

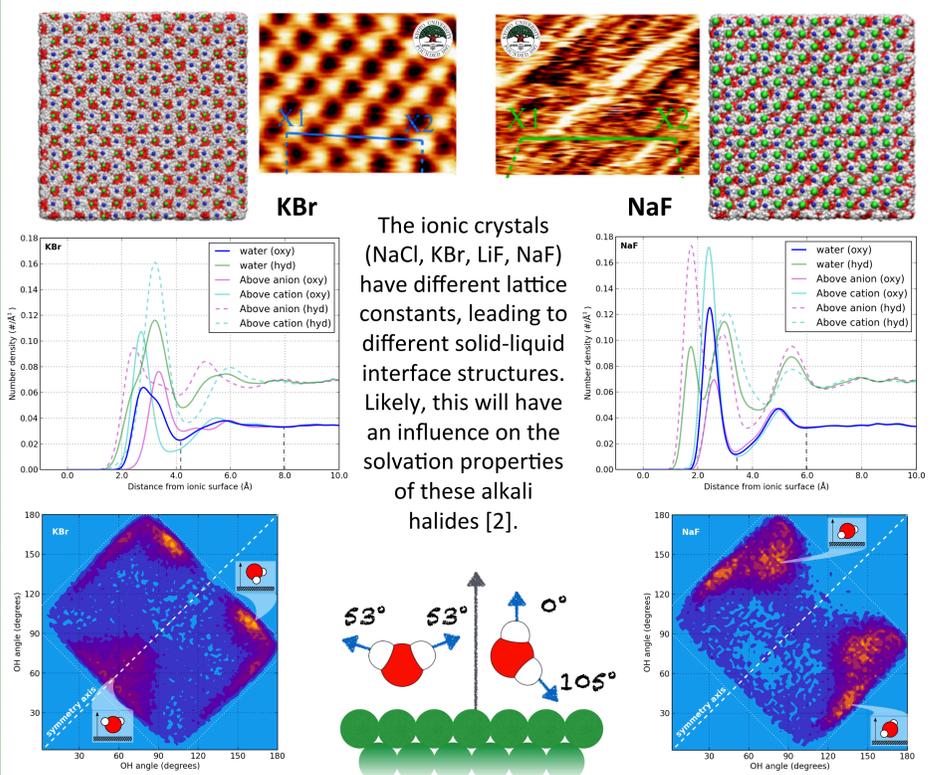


## P-NITROANILINE



AFM experiments and the MD simulations agree very well, and detailed analysis of the MD data and comparison with the experiments, suggests the presence of a different surface structure (compared to the bulk), which has an increased hydration energy [1].

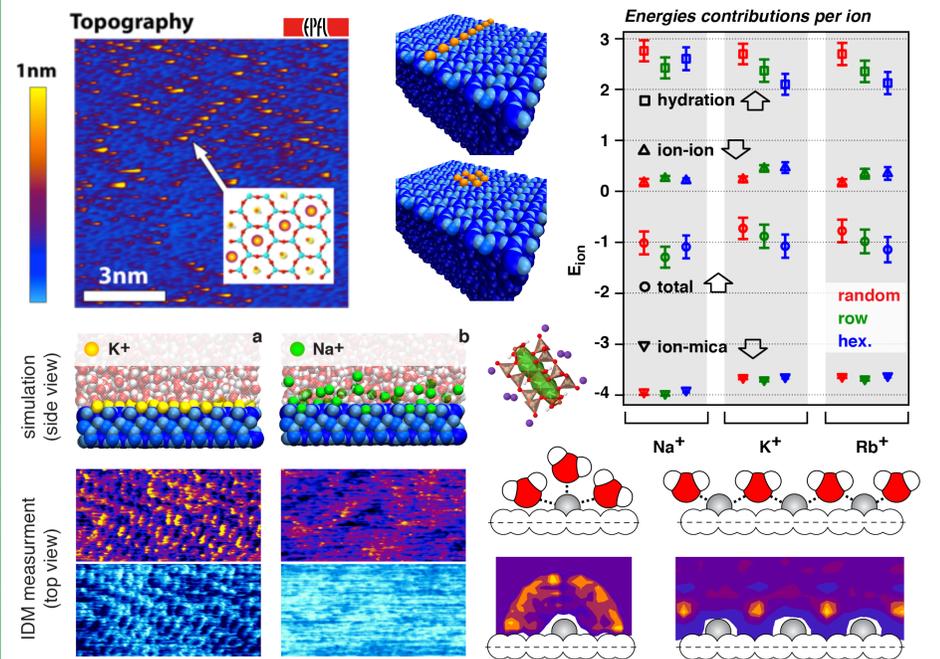
## IONIC CRYSTALS



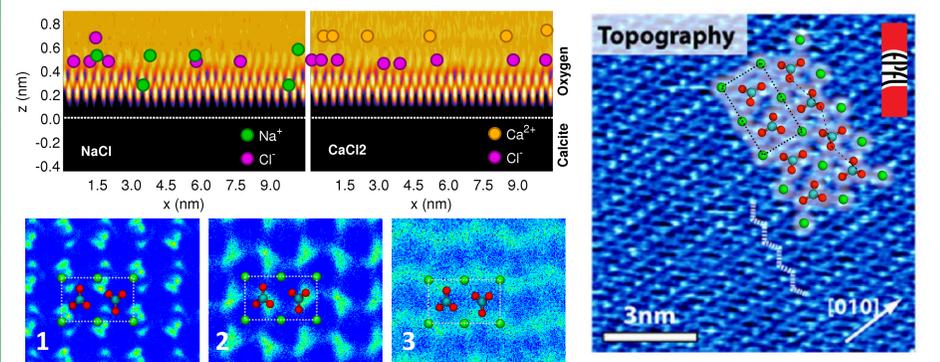
The ionic crystals (NaCl, KBr, LiF, NaF) have different lattice constants, leading to different solid-liquid interface structures. Likely, this will have an influence on the solvation properties of these alkali halides [2].

## MUSCOVITE MICA AND IONS

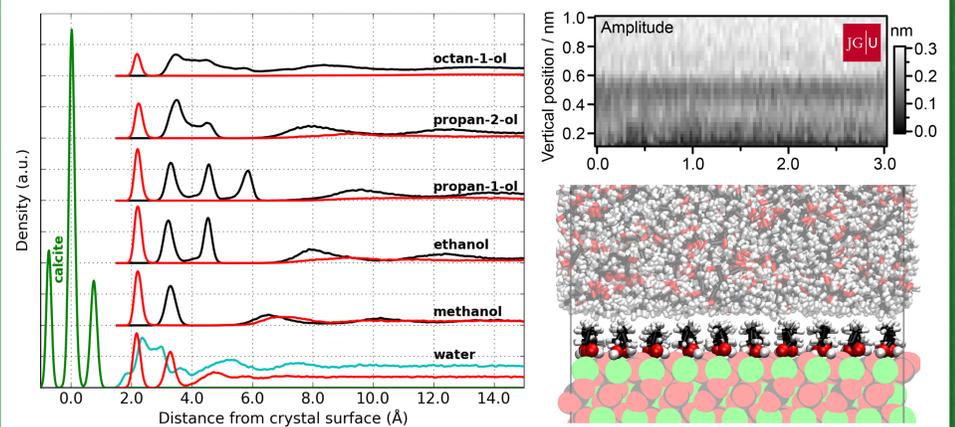
Recent AM-AFM experiments on muscovite mica with either Na<sup>+</sup>, K<sup>+</sup> or Rb<sup>+</sup> ions in solution show them adsorbing at the surface, preferably in regular patterns (e.g., rows or hexagons). Using MD simulations this structuring is shown to be water-induced [3].



## CALCITE – WATER AND ALCOHOLS



MD simulations reveal a similar hydration structure as in the experiments, and at least 3 distinctive hydration layers are observed [4]. Ions (Na<sup>+</sup>/Ca<sup>2+</sup>) rarely pass the final hydration layer [5]. In alcohol solvents strong structuring is also observed, leading to a bilayer-like interface [6].



## FURTHER READING

- [1] P. Spijker, *et al.*, J. Phys. Chem. C, 118:2058 (2014)
- [2] K. Kobayashi, P. Spijker, *et al.*, in preparation (2014)
- [3] M. Ricci, P. Spijker, *et al.*, Nature Communications, in press (2014)
- [4] B. Reischl, *et al.*, J. Chem. Theory Comput., 9:600 (2013)
- [5] M. Ricci, P. Spijker, *et al.*, Langmuir, 29:2207 (2013)
- [6] P. Spijker, *et al.*, in preparation (2014)

