Developing realistic models of interfaces from simulation

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I will describe several recent pieces of work focussing on developing an atomistic-level understanding of a range of interfaces. A variety of computational approaches are used, and connected to state-of-the-art experiments, often using the non-contact atomic force microscope (NC-AFM).

(i) Insulator - molecule - metal. In collaboration with NC-AFM experimental researchers at the University of Hamburg, we unambiguously identified the adsorption configurations of a complex molecule on ionic crystals (NaCl, NiO) and the nature of surface ions [1,2]. These systems can provide a sensitive test system to calibrate the accuracy of computational approaches and also act as a tape measure, providing an accurate measure of tip-sample distance, which is extremely hard to estimate independently.

(ii) Insulator - water. High-resolution imaging and force spectroscopy using AFM in solution opens a wide area of possible applications allowing real-time and real-space imaging of surfaces in solution. To obtain full benefit and provide a significant new analytical ability, it is vital to understand the underlying imaging mechanism(s) that can lead to high (atomic or molecular) resolution. Our simulations of solvated nanoparticles near surfaces show several possible mechanisms that lead to measurable force differences and image contrast over surface sites [3]. We used free-energy perturbation theory to calculate the free energies of nanoparticle-surface interaction. Water-mediated interactions can cause significant force differences above different surface sites, and are in most cases larger, and longer ranged, than the direct vacuum-like interactions.

(iii) Water ice - vacuum. Resolving the atomic structure of the surface of ice particles within clouds, over the temperature range encountered in the atmosphere and relevant to understanding heterogeneous catalysis on ice, remains an experimental challenge. By using first-principles calculations, we show that the surface of crystalline ice exhibits a remarkable variance in vacancy formation energies, akin to an amorphous material. We find vacancy formation energies as low as 0.1-0.2 eV, which leads to a higher than expected vacancy concentration. Because a vacancy's reactivity correlates with its formation energy, ice particles may be more reactive than previously thought. We also show that vacancies significantly reduce the formation energy of neighbouring vacancies, thus facilitating pitting and contributing to pre-melting and quasi-liquid layer formation [4]. These surface properties arise from proton disorder and the relaxation of geometric constraints,

which suggests that other frustrated materials may possess unusual surface characteristics.

[1] G. Teobaldi, K. Lammle, T. Trevethan, M. Watkins, A. Schwarz, R. Wiesendanger and A. L. Shluger, Phys. Rev. Lett., 106 (2011) 216102
[2] K. Lämmle, T. Trevethan, A. Schwarz, M. Watkins, A. L. Shluger and R. Wiesendanger, Nano Letters, 10 (2010) 2965
[3] M. Watkins, A. L. Shluger, Phys. Rev. Lett., 105 (2010) 196101
[4] M. Watkins, D. Pan, E. G. Wang, J. VandeVondele, A. M. Michaelides and B. Slater, Nature Materials, 10 (2011) 794