Ab initio simulations of charged surfaces

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Charged surfaces and interfaces play a key role in a variety of fields, ranging from electrochemistry over electronic devices and electronic sensors to electric field evaporation in atom-probe tomography. Surface charging may occur through different mechanisms, such as Fermi level pinning at surface states or point defect creation in semiconductors and insulators, intrinsic charging in heavily doped semiconductors and metals, or ion adsorption in either case. Understanding the relevant phaenomena at the surface based on electronic-structure calculations is hampered by the fact that the energetics of charged species at the atomic (nm) length scale cannot be separated from the electric potentials building up over much larger distances (10-10000 nm), depending on the origin of the compensating charges. Reversely, simulations with typically a few 100 atoms only will imply significant artifacts because electrostatic interactions and screening effects are unrealistically strong in such simulations.

In my talk, I will first discuss the link between mesoscopic screening mechanisms and atomistic simulations via electrostatic boundary conditions, highlighting a meaningful definition of the electric reference potential and its spatial dependence needed for a thermodynamic treatment of surface charging. I will demonstrate that the use of 3D periodic boundary condition in the repeated-slab-approach, that is typically combined with an implicit constant compensating background for nominally charged systems, gives rise to electric boundary conditions that cannot be linked directly to experiment. Recovering the energetics in the dilute limit, i.e., at vanishing surface charge densities or equivalently isolated charged centers require corrections that can be derived from continuum electrostatics. The connection between continuum picture and the „macroscopic“ limit of linear-response properties of the quantum system are highlighted.

In contrast, extremely high fields (10^{10} V/m) occuring for instance in field-induced ion desorption as the fundamental process in atom-probe tomography require the incorporation of such fields directly in the simulation. I will introduce a simple scheme in analogy to the well-known „dipole correction“ in neutral repeated-slab calculations to achieve this, and present preliminary results for the charging of Al surfaces.