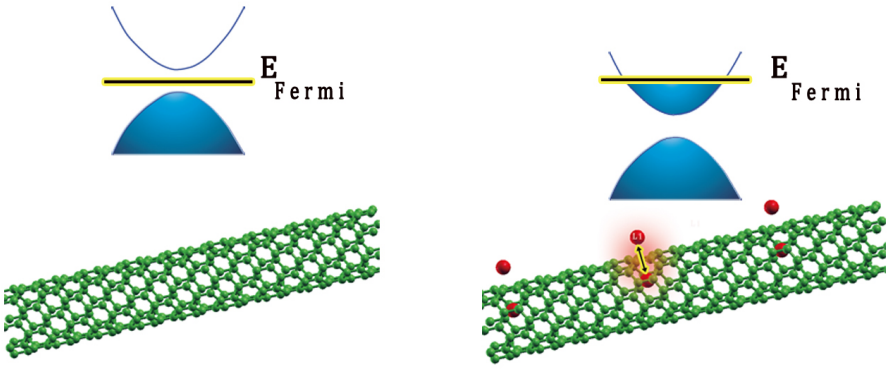
Ions in nanostructures

Wolfgang Schmickler, Ulm University

We have investigated alkali and halide ions in thin nanotubes and -slits by a combination of density functional theory (DFT), statistical mechanics, and grand-canonical Monte Carlo. If we place alkali or halide atoms into these structures and run a DFT program the atoms become ionized, and the transferred charge resides as image charge on the walls. For nanotubes the electrostatic interactions can be characterized by the *effective image radius*, which is the radius of a perfect metallic conductor which would yield the same distribution of the electrostatic potentials; for nanoslits an *effective image plane* is used instead. These concepts make it possible to construct effective Hamiltonians for ensembles of ions, which are solely based on DFT. In the corresponding grand-canonical ensemble both the electrode potential and the charge are well defined.

On this basis we investigate the storage of ions in nanostructures, calculate the the ionic densities and the corresponding capacities as a function of the electrode potential. We compare our results with those of other researchers who have used classical DFT or Ising models.

Finally, we discuss an unexpected result: A Li^+ ion placed inside a semiconducting carbon nanotube and a Li^+ placed outside attract each other. This effect is caused by the shift of the Fermi level caused by the presence of the ions.



References

1. Leila Mohammadzadeh, Aleksej Goduljan, Fernanda Juarez, Paola Quaino, Elizabeth Santos, Wolfgang Schmickler, *On the energetics of ions in carbon and gold nanotubes*, ChemPhysChem **17** (2016) 78.

2. W. Schmickler, *A simple model for charge storage in a nanotube*, Electrochim. Acta **173** (2015) 91.

3. W. Schmickler and D. Henderson, *On the capacitance of narrow nanotubes*, Phys. Chem. Chem. Phys., **19** (2017) 20393