

Towards first-principles electrochemistry: Addressing electrified metal-electrolyte interfaces with DFT-NEGF

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First principles simulations are crucial in many areas of materials science. However, this approach has not been used in the field of electrochemistry, where the complexity of the electrochemical environment and the presence of the external electrode potential have precluded direct application of usual first principles methods like Density Functional Theory (DFT). We aim to overcome these barriers by utilizing recent breakthrough advances in modelling techniques that will allow us to extend the use of DFT to the complexity of the electrochemistry processes.

We demonstrate how Non-Equilibrium Green's Functions techniques can be used to address, from first principles, the atomistic description of metal-electrolyte interfaces in the presence of an external bias applied to the electrodes. The NEGF method allows to deal with open, non-periodic systems driven out of equilibrium by the external applied bias. We use the TranSIESTA method and code [1,2], developed within the SIESTA project [3]) to study problems involving steady-state non-equilibrium situations in nanoscale constrictions, where an external electric bias is applied between the two sides of the constriction, establishing a steady electric current. We show how this computational machinery can be also used to study electrified solid/liquid interfaces [4], where an external bias is applied to the solid electrode. Here, one is not concerned with the quantum electronic transport, but with the effect of the external bias on the structural changes, dynamics and chemical reactions induced at the metal/liquid interface. We will show molecular dynamic simulations of aqueous electrolytes as a proof of concept for future realistic, atomistic first-principles simulations of electrochemical processes.

References

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Figures

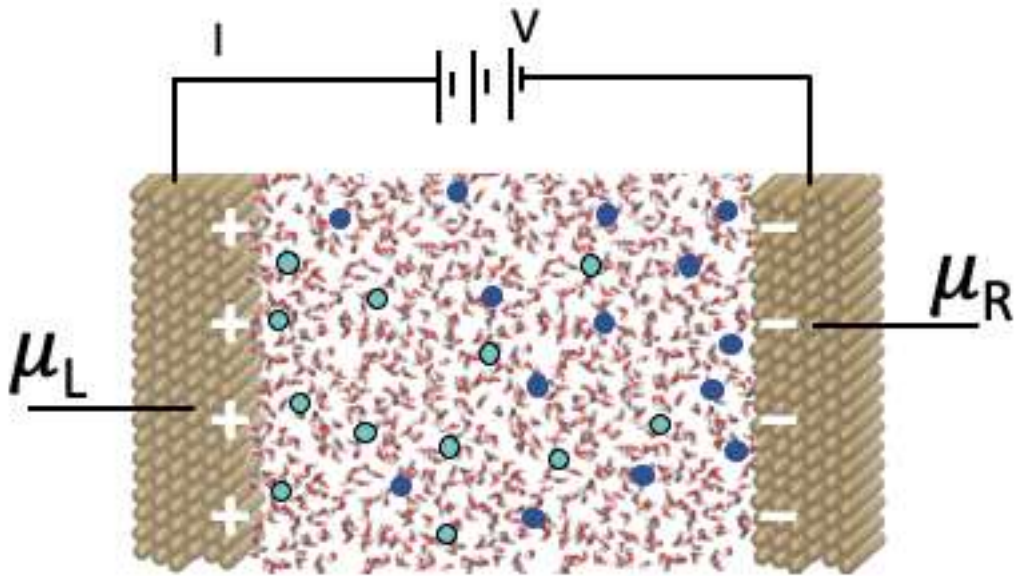


Figure 1. Scheme of the simulation setup for the study of the interface between an electrolyte (water with a salt in solution) and the electrified metallic surface.

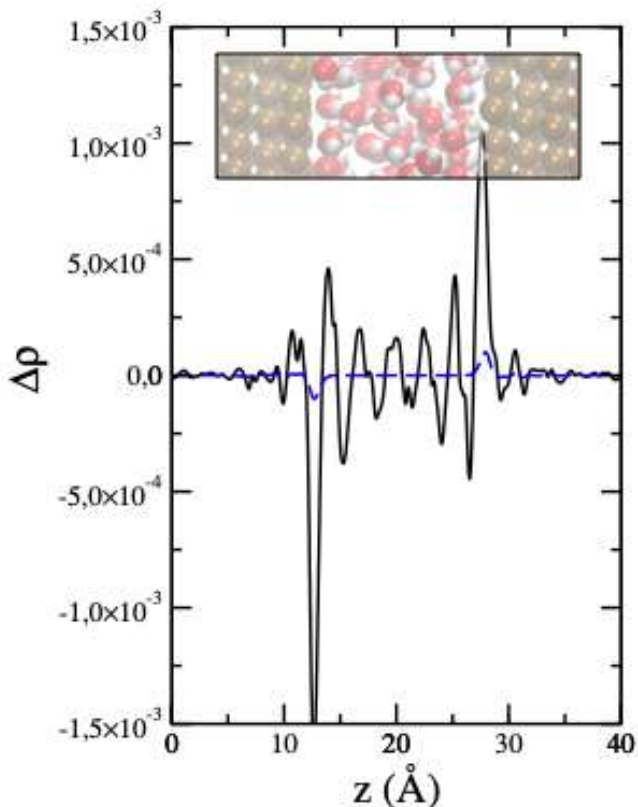


Figure 2. Charges induced by the application of a bias voltage between the two metallic electrodes. Full black and dashed blue lines show the results of the simulation with and without water between the electrodes, respectively. Surface charges accumulate on the metallic surfaces, while the electronic cloud of the water molecules is also polarized, and the water molecules rotate to (partially) align their dipoles along the bias field. The charges induced on the surface are much larger in the presence of water, as the water polarization leads to interface charges that must be screened by free charges in the metallic lead.