Towards first-principles simulations of electrochemical processes at the nanoscale

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Abstract

First principles simulations are crucial in many areas of nanoscience. In electrochemistry, however, the complexity of the electrochemical environment and the presence of the external electrode potential have precluded direct application of first principles methods like DFT. We aim to overcome these barriers by utilizing recent breakthrough advances in modelling techniques that allow us to extend the use of DFT to the complexity of the electrochemistry processes.

We demonstrate how Non-Equilibrium Green's Functions (NEGF) 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 [1,2], implemented in the SIESTA DFT code [2,3], and commonly used to study electronic transport in nanoscale constrictions, is used here to describe the electrified solid/liquid interface, including the electronic charge redistribution induced by the external bias, and the resulting electrostatic profile. This allows us to study the structural and dynamic changes in the liquid (including the electrical double layer) and chemical reactions occurring at the electrified interface.

We will show DFT molecular dynamics simulations of aqueous electrolytes as a proof of concept for future realistic, atomistic first-principles simulations of electrochemical processes. Additionally, we explore the possibility of reaching much larger system sizes and longer simulation times by combining the DFT approach to deal with the electrodes (where the quantum-mechanical description is essential), with a molecular mechanics model for the liquid electrolyte (or part of it, not involved in the electrochemical reactions). This hybrid QM/MM approach is currently fully functional in SIESTA, allowing the simulation of realistic system sizes with a greatly reduced computational workload. The code, which offers parallelism though both OpenMP and MPI, shows an excellent parallel performance in modern HPC platforms.

References

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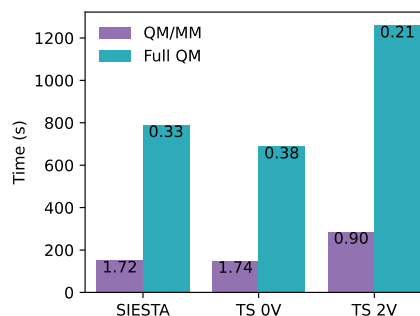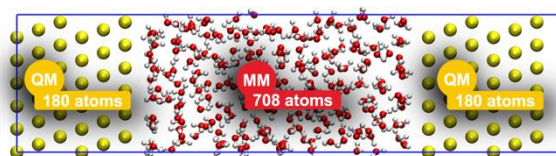
Figures

Figure 1: Left: QM/MM setup for electrode (gold) / electrolyte (water). Right: comparison of timings for QM/MM vs fully QM calculations for three MD steps for SIESTA using diagonalization (left bars), and for TranSIESTA using the NEGF formalism at V=0 Volt (center bars) and V=2 Volt (right bars). The numbers on the bars indicate the number of picoseconds per day. Data are from MareNostrum IV, using 384 cores. For this system size, QM/MM is about five times faster than a fully QM calculation.