DFT and QM/MM simulations of nanoconfined water between electrified gold surfaces using Non-Equillibrium Green's Functions

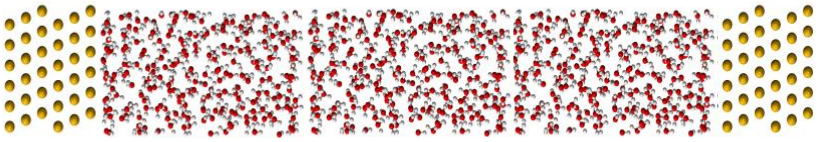
Pablo Ordejón
Ernane de Freitas, Pol Febrer
Catalan Institute of Nanoscience and Nanotechnology - ICN2 (CSIC and BIST), Campus de la UAB, 08193 Cerdanyola del Valles, Barcelona (Spain)
pablo.ordejon@icn2.cat

Albeit water is the most common and best studied solvent, understanding its structure and properties at the surface of materials is still an open problem. Besides, important modifications of its structure and dynamics occur when the surfaces are electrified (as in electrochemical environments), and when the confinement space is nanometric. Density Functional Theory (DFT) simulations can deal with these issues, although imposing the external voltage in the simulation has proven difficult. Non-Equillibrium Greens functions (NEGF) techniques [1,2] as implemented in the SIESTA DFT package [3,4] are used here to address this problem, allowing first-principles molecular dynamics simulations of nanoconfined water in the presence of a finite voltage between the two confining surfaces. We will present proof of concept calculations of water between gold electrodes, showing the potential of our approach. We also show how to increase the size of systems (in terms of number of atoms) and the simulation time which can be addressed by these simulations by using a quantum mechanics/molecular mechanics (QM/MM) approach coupled to the NEGF method, to investigate the metal-water interaction, providing a good balance between accuracy and computational cost. We validated our results against full QM calculations and analysed the performance. This hybrid approach emerges as a viable way of studying way larger systems compared to those currently used to investigate the dynamics of electrified metal-water interfaces using first principles.

References

[1] Brandbyge, Mozos, Ordejón, Taylor, Stokbro, Phys. Rev. B 65, 165401 (2002).
[2] Papior, Lorente, Frederiksen, García, Brandbyge, Comp Physics Comm. 212, 8 (2017).
[3] Soler et al., J. Phys.: Cond. Mat., 14, 2745 (2002).
[4] García et al, J. Chem. Phys. 152, 204108 (2020).

Figures



$Au - (H_2O)_{236 \times n} - Au \qquad (n=3)$

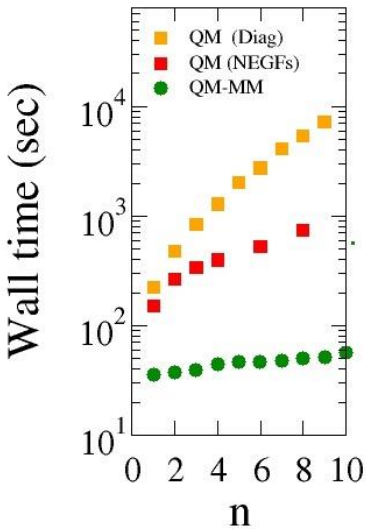


Figure 1: Top: QM/MM setup for nanoconfined water between gold electrodes. Systems containing repetitions of the 236 H_2O molecules were used for timing purposes. Right: CPU time per MD step for n=1 to n=10, showing the wall time needed per Molecular Dynamics step, for the full QM approach using straight diagonalization (yellow points), the NEGF approach (red points) and the QM/MM hybrid method (green points). The calculations were done using 384 Intel Platinum 8160 (2.1GHz) cores of MareNostrum IV at the Barcelona Supercomputing Centre.