

Modelling electrochemical processes through constant Fermi-level molecular dynamics

Assil Bouzid and Alfredo Pasquarello

Chaire de Simulation à l'Échelle Atomique (CSEA),
École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Electrochemical processes such as electron/proton transfers take place in many important research areas such as solar cells, energy storage devices, biological environments, and many technological devices. Quantitative modelling of electrochemical processes is then important to monitor and enhance device engineering. Several methods have been developed to study the thermodynamical and chemical properties of redox half reactions as well as electrode/electrolyte interfaces under constant bias potential.¹⁻⁴

In this contribution, we will focus on two main aspects of electrochemical processes through the recently developed constant Fermi-level molecular dynamics. This technique allows one to simulate systems evolving at constant Fermi energy and models the effect of an electrode by controlling the charge transfer between the single-particle energy levels of the system and an electron reservoir set at a given potential during the dynamics.⁵⁻⁷

First, we benchmark this technique in the case of redox potentials of aqueous species. Like the thermodynamic integration method, our scheme does not require *a priori* knowledge of the products of the reaction, which can simply be obtained by driving the reaction through the variation of the Fermi level. The simulations are performed subject to periodic boundary conditions, in absence of any counterelectrode. We extract the redox level from the evolution of the Kohn-Sham energies upon charging (or discharging) the system. This approach is illustrated for the redox couples $\text{Fe}^{+2}/\text{Fe}^{+3}$, $\text{HO}_2^\bullet/\text{HO}_2^-$, and $\text{MnO}_4^-/\text{MnO}_4^{2-}$ in aqueous solution, and yields redox potentials differing by less than 0.1 eV from respective ones achieved with the thermodynamic integration method.

Second, based on the constant Fermi-level molecular dynamics and a proper band alignment scheme, we present a new technique to simulate the metal/water interface under variable bias potential referenced to the standard hydrogen electrode (SHE). Our band alignment scheme yields an accurate SHE level to which the bias potential is referenced. Based on this alignment scheme, we find a potential of zero charge $\mu_{\text{pzc}} \cong 0.22$ eV relative to the SHE and a double layer capacitance $C_{\text{dl}} \sim 24 \mu\text{Fcm}^{-2}$ in excellent agreement with experimental measurements at the Pt electrode. In addition, we will present results related to the Volmer reaction mechanism and the water organization at the Pt(111)/water interface as a function of the bias potential.

¹ F. Ambrosio, G. Miceli, and A. Pasquarello, J. Chem. Phys. **143**, 244508 (2015).

² R. Jono, Y. Tateyama, and K. Yamashita, Phys. Chem. Chem. Phys. **17**, 27103 (2015).

³ J. Cheng, X. Liu, J. VandeVondele, M. Sulpizi, and M. Sprik, Acc. Chem. Res. **47**, 3522 (2014).

⁴ M. Otani, I. Hamada, O. Sugino, Y. Morikawa, Y. Okamoto, and T. Ikeshoji, J. Phys. Soc. Jpn. **77**, 024802 (2008).

⁵ A. Bouzid and A. Pasquarello, J. Chem. Theory Comput. **13**, 1769 (2017).

⁶ A. Bouzid and A. Pasquarello, Phys. Rev. Appl. **8**, 014010 (2017).

⁷ A. Bouzid and A. Pasquarello, J. Phys.: Condens. Matter **29**, 505702 (2017).