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The electrostatic double layer of Pt/water interfaces from first principles molecular dynamics CLOTILDE CUCINOTTA, Trinity College Dublin, PIETRO BALLONE, University of Rome, STEFANO SANVITO, Trinity College Dublin — The formation of the electrostatic double layer is the most basic phenomenon taking place at electrified interfaces. However, even in the relatively simple case of a Pt/water interface, none of the current theoretical approaches provides a realistic microscopic view of this double layer, accounting for electronic, polarization and solvent re-organization effects. Here we provide for the first time a comprehensive description of the electrostatic double layer of a Pt-water interface, based on ab initio computations, including charge polarization effects at both sides of the interface, explicit solvent and its rearrangements upon changing the electrode polarization. This interface has been modeled with up to 1000 atoms. A simple, fully dissociated salt in solution has been explicitly included. Varying the relative number of cations and anions provides a way to control the charge on the electrode, controlling, in turn, the applied potential. The proposed approach allows to provide a detailed description of the structure of the Pt/water double layer reproducing the localization of electric field and potential energy drop within a microscopic distance from the metal surface. An a posteriori calibration of the relation between charge and potential is performed, analyzing the potential energy profile vs. the distance from the electrode for any given charge, providing for the first time a realistic ab initio determination of the interface capacitance and the point of zero charge.

Clotilde Cucinotta
Trinity College Dublin

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