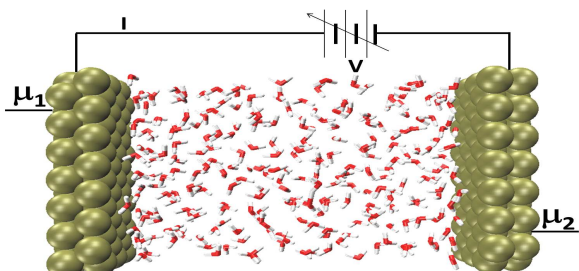


The electrostatic double layer of Pt/water interfaces from first principles molecular dynamics.

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The formation of the electrostatic double layer arguably 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 (water) 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. This simple approach allows us 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 has been 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. The point of zero charge has been identified by the fit of the potential energy drop as a function of the surface charge density.

From a computational point of view, the project represents a challenging, massive computation, requiring the efficiency of the CP2K package¹, and exploiting in full the power of present supercomputers.

¹ www.cp2k.org