

## Equilibrium and non-equilibrium effects on the local order of water at metallic electrode surfaces

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### INTRODUCTION

The study of liquid/solid interfaces is fundamental in the understanding of electrocatalysis, photocatalysis among other processes associated to new sources of energy. Understanding liquid ordering at the interface involves a detailed study of the nature of the interactions between water-water and water-substrate. A first principles description of all components of the system is the most appropriate methodology in order to advance the understanding of electrochemical processes. In this work we analyze in detail the structural, dynamic and energetic properties of liquid-water interacting with (111) Au and Pd surfaces, with and without the presence of an external potential.

### METHODS

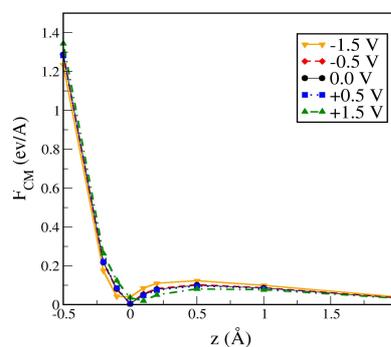
We have performed DFT-based ab initio molecular dynamics (AIMD) using the SIESTA code. The simulations were done at ambient temperature, with and without van der Waals interactions. We also present a methodology to study an electrochemical cell in the presence of an external voltage applied to the electrodes. We combine density functional theory (DFT) and non-equilibrium Green's functions methods (NEGF) to provide a more quantitative connection between the macroscopic voltage and the microscopic interfacial charge distribution.

### RESULTS AND DISCUSSION

Our results show that the order of water at the interface strongly depends on the metal under consideration. And charge transfer at the interface can affect the local order of the water<sup>1</sup>.

We also investigate the adsorption of the water molecule at different orientations on top of Au(111) surface as a function of the applied bias. We find that the position of the most stable configuration changes depending on the absolute

value as well as the sign of the applied voltage, as shown in Fig. 1.



**Figure 1.** (Au-H<sub>2</sub>O) Force at the center of mass as a function of the vertical displacement, for different bias at the electrodes.

### CONCLUSIONS

Our results show that the inclusion of the electronic degrees of freedom (in this case, via DFT) is essential to properly describe the interaction of water and metal surfaces in general. We also show that the external potential plays an important role on the structural properties of the water-solid interface and thus in the simulation of electrochemical processes.

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<sup>1</sup> L. S. Pedroza, A. Poissier, M.V. Fernández-Serra, *J. Chem. Phys.*, **142**, 034706, (2015).