

Free energy of adsorption evaluation at the metal/liquid interface

Paul Clabaut^a, Carine Michel^a and Stephan N. Steinmann^a

^a*ENS de Lyon*

paul.clabaut@ens-lyon.fr

Metal/liquid interfaces stand out by their increasing importance in catalysis and their computational complexity. One of the biggest challenge of this domain is to be able to evaluate the adsorption free energy of a given compound at a metal/liquid interface. Two key ingredients are necessary to reach this goal. The first is a methodology to tackle the problem of the sampling of the water dynamics at the interface while dealing with the costly simulation of the metallic phase. We propose, herein, a computational package that is a refined implementation of the scheme proposed by Steinmann *et al.*[1]. It can be used to compute the adsorption free energy of any molecule at a metal/liquid interface. But this methodology also implies the need of a classical force-field that can accurately describe metal/liquid interactions. This force-field is therefore the second key element needed to address this challenge. Here, we propose the use of a previously published force-field: GAL17 [2] as a first description of the interaction, but also a new currently developed force-field to improve its performances and applicability.

The computation package relies on both quantum and classical calculation, currently performed in VASP and AMBER, respectively. Indeed, the free energy difference is separated in two terms. The first can be evaluated *in vacuo*, at a DFT level and consists in a simple adsorption energy of the molecule on the free metallic surface. The second accounts for the reorganization of the solvent structure that is due to this adsorption and is computed thanks to the Thermodynamic integration method. It relies a sufficient sampling of the reorganization of the water phase, induced by the adsorption of the molecule. Once combined, these two terms provide the desired complete adsorption free energy from the bulk liquid to the water/metal interface.

The chosen force-field is, therefore, the GAL17 force-field that has shown some promising results on Pt (111)/water interfaces. But in this work, we also introduce a novel description based on locally defined metallic surfaces. The extended force-field has been parametrized for 10 noble metal surfaces, i.e., the 100 and 111 facets of Cu, Ag, Au, Pd and Pt. The structuration of the interface obtained with this force field is illustrated in comparison to the METAL force-field which only relies on Lennard-Jones parameters for the interaction between water and metal surfaces.[3]

The combination of this method and force-field could therefore finally achieve the difficult task to provide a physically sound and easy-to-use tool to evaluate any kind a adsorption free energy. Thus, it could be of a tremendous help in the development of numerous catalyst and materials.

References

1. S. N. Steinmann *et al*, *Phys. Chem. Chem. Phys.* **18**, no **46** (2016), 3185061.
2. S. N. Steinmann *et al*, *J. Theor. Comput. Chem.* **14**, no **6** (2018), 323851.
3. H. Heinz *et al*, *J. Phys. Chem. C* **112** no **44** (2008), 17281-17290.