

Modelling metal electrolyte interfaces from density functional theory based molecular dynamics

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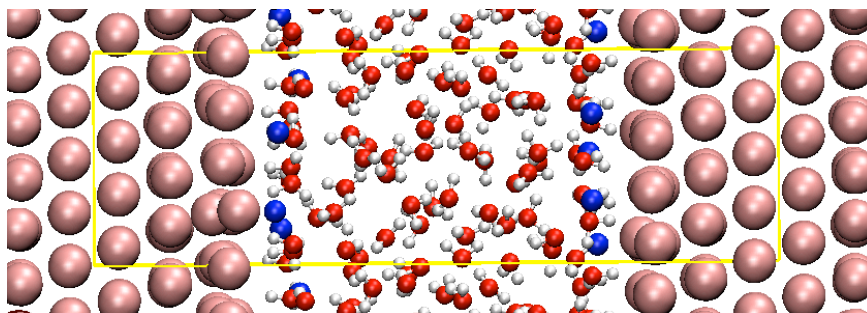
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Metal-electrolyte interfaces are of great importance for electrochemical devices, in which many processes occur. Due to the level of complexity, experiment alone is difficult to reveal the microscopic structures and properties of interfaces. Ab initio modelling, on the other hand, can offer a complementary tool to help gain atomic level understanding of interfaces.

We aim at investigating the properties of transition metal-electrolyte interfaces with density functional theory based molecular dynamics (DFTMD) simulations. Firstly, based on the recently developed DFTMD standard hydrogen electrode (SHE)¹, we've proposed a new computationally efficient scheme for determining the electrode potential of the metal-electrolyte interfaces on the SHE scale.² The reliability of this new scheme has been verified by estimating the potential of zero charge (PZC) for several metal surfaces, namely Pt(111), Au(111), Pd(111) and Ag(111). We've also found that there is an apparent charge transfer between the surface water molecules and the metal electrode, which is the dominant factor for the energy difference between the PZC of a metal surface and its work function.

We then constructed an electric double layer by bringing in counter ions into the Helmholtz layer. The model is shown below. The estimated double layer capacitance of Au(111) from our calculations is $\sim 30 \mu\text{F}/\text{cm}^2$, which is close to the experimental value of $20 \mu\text{F}/\text{cm}^2$. As for Pt(111), we found its double layer capacitance was maximized around PZC, corresponding to the experimental phenomena.³ We attributed it to the pseudo-capacitance caused by surface water chemisorption.



References

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