Dielectric constant at metal/water interfaces

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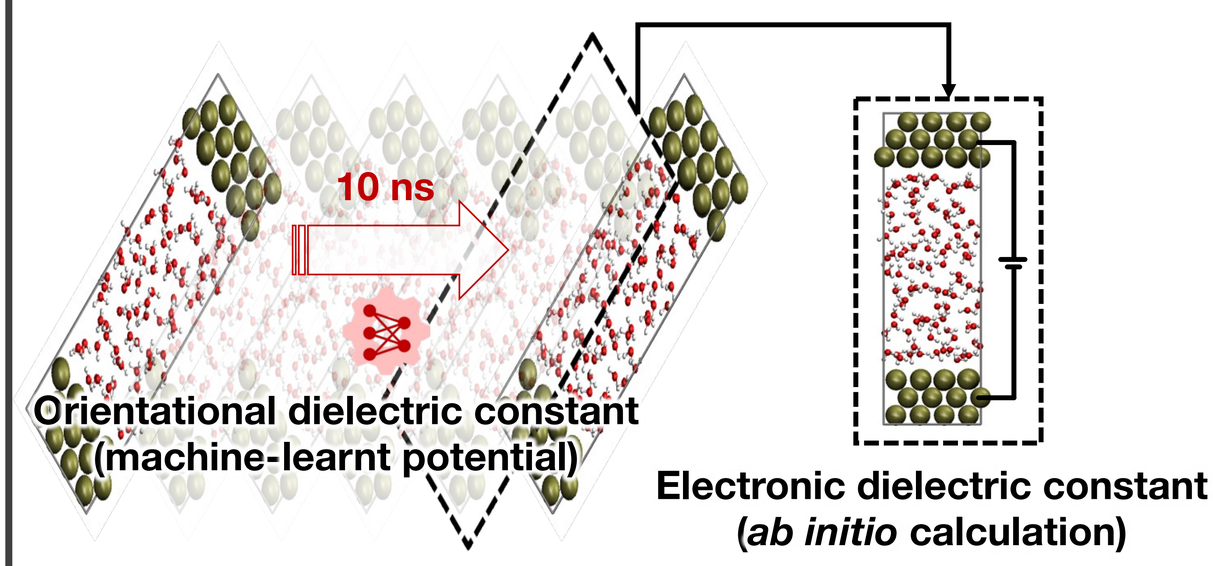
Introduction

The dielectric constant at the interface directly influences the interfacial capacitance and the interfacial electric field. Therewith, it also influences reaction energetics and reaction kinetics. Knowledge of the interfacial dielectric constant is therefore relevant. Unfortunately, relatively little is known about how the dielectric constant changes as we approach the interface. Here, we study the behaviour of two contributions to the dielectric constant, the electronic dielectric constant and the orientational one, by using machine-learnt potential and ab initio calculations.

Project overview

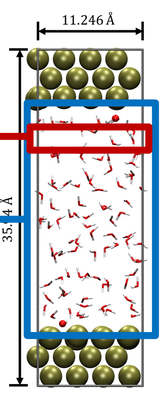


Aiming at **sufficient sampling with *ab initio* accuracy**, we trained a machine-learnt potential (MLP). Based on the trajectories from MLP sampling, we can calculate 1) the orientational dielectric constant from the **dipole fluctuations** and 2) the electronic dielectric constant from the **polarization charges**.

***Model system**: Pt(100)/H_2O interface*

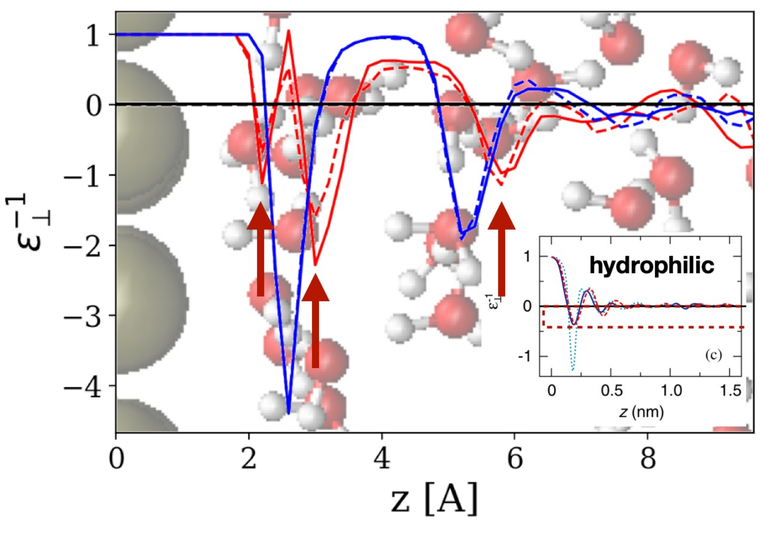
Orientational dielectric constant [1] [2]

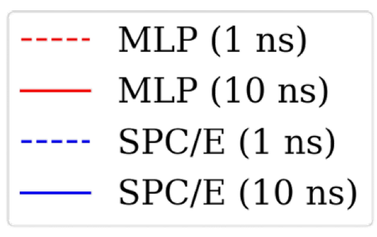
$$\varepsilon_{\perp}^{-1}(z) = 1 - \frac{\langle m_{\perp,0}(z) M_{\perp,0}\rangle - \langle m_{\perp,0}(z)\rangle \langle M_{\perp,0}\rangle}{\varepsilon_0 k_B T + \left(\langle M_{\perp,0}^2\rangle - \langle M_{\perp,0}\rangle^2\right)/V}$$



m(z): local polarization; ***M**: total dipole moment*

*SPC/E water: -0.8476 for O, 0.4238 for H





Open question:
Correlation between water structures and ori. dielectric const.?

Electronic dielectric constant

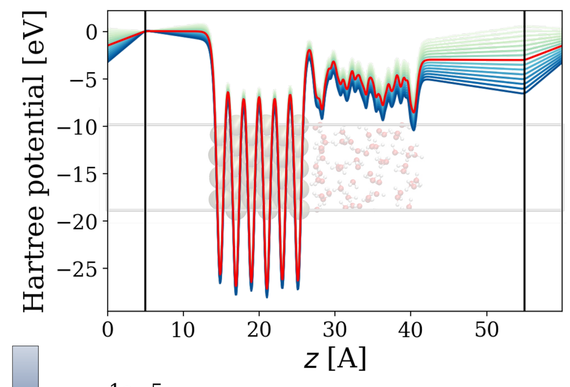
Computational setup:

Basis set: DZVP-SR/GTH

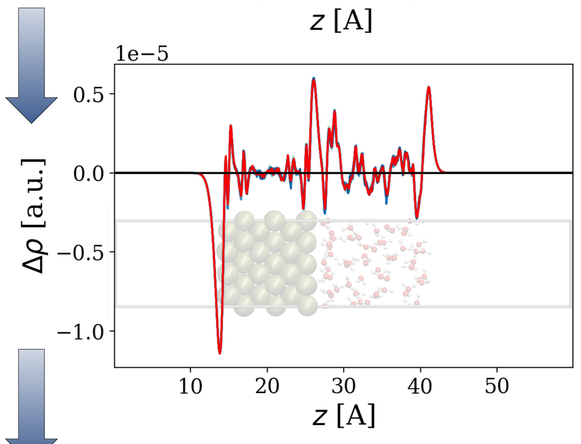
PW CUTOFF: 400 Ry

Functional: PBE+D3

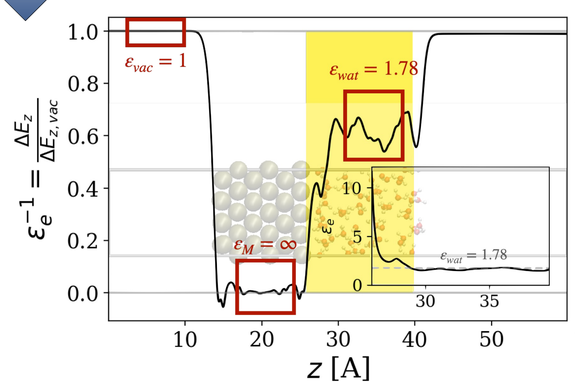
Dirichlet BC in Z and PBC in XY



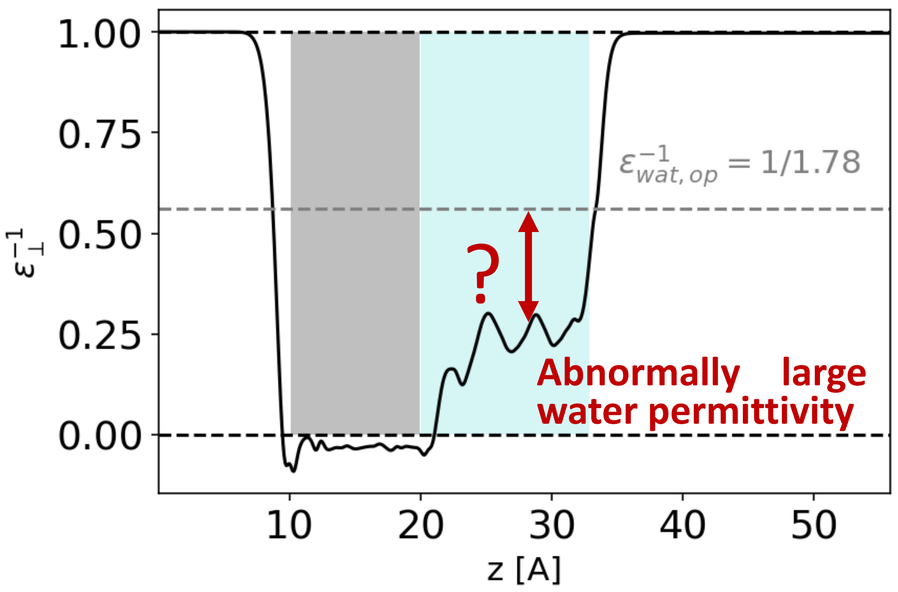
Calculate polarization charges from the electron density changes under various fields[3]



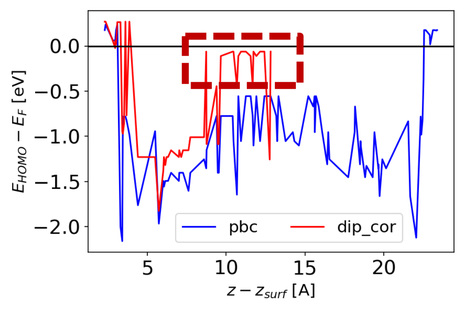
Calculate the electronic dielectric constant from the polarization charge



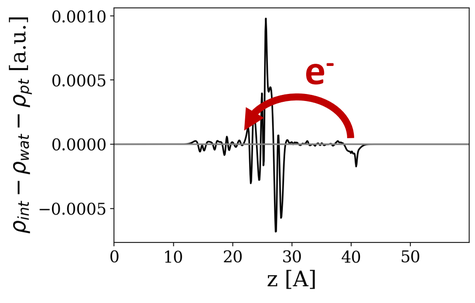
BUT! Level alignment issue?!



lead to



water HOMOs increase



ET from water to metal

References

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[2] Bonthuis, D. J.; Gekle, S.; Netz, R. R. *Phys. Rev. Lett.* **2011**, *107*, 1.
[3] Giustino, F.; Pasquarello, A. *Phys. Rev. B* **2005**, *71*, 144104.

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