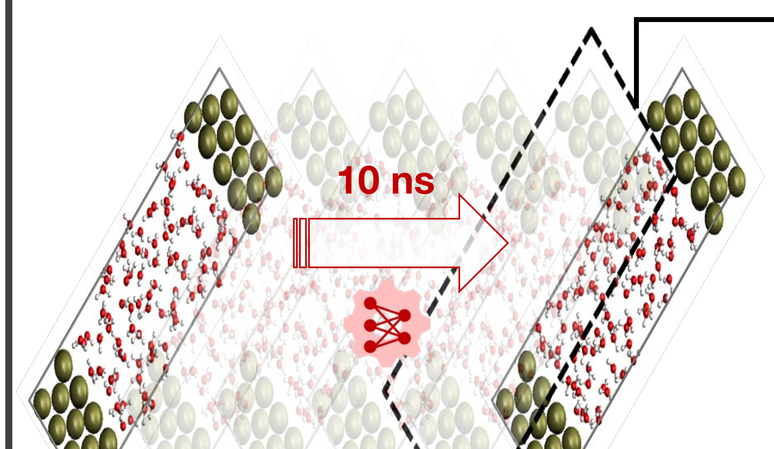
Dielectric constant at metal/water interfaces

Jia-Xin Zhu[1], Marc T.M. Koper[2], Jun Cheng[1], Katharina Doblhoff-Dier[2]

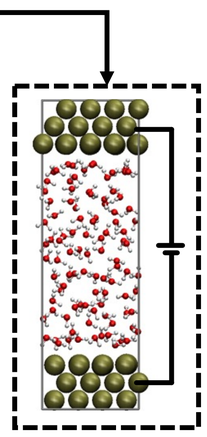
1. *State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*
2. *Leiden Institute of Chemistry, Leiden University, Leiden 2300RA, The Netherlands*

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. **Under high field conditions, water rotation has been saturated and the electronic polarization plays an important role.** Unfortunately, relatively little is known about how the electronic dielectric constant changes as we approach the interface. In this study, we investigate the electronic dielectric as a function of distance from the surface by using molecular dynamics and *ab initio* calculations.



Molecular dynamics sampling (machine-learnt potential)



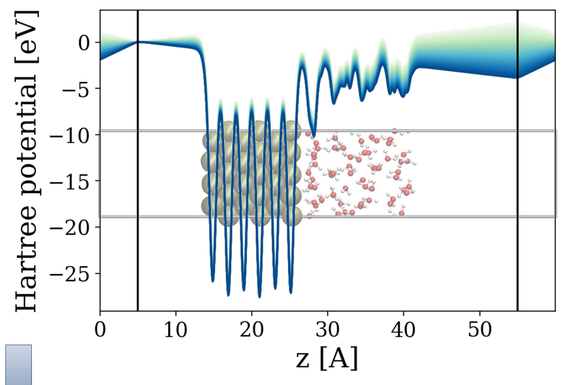
Electronic dielectric constant (*ab initio* calculation)

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

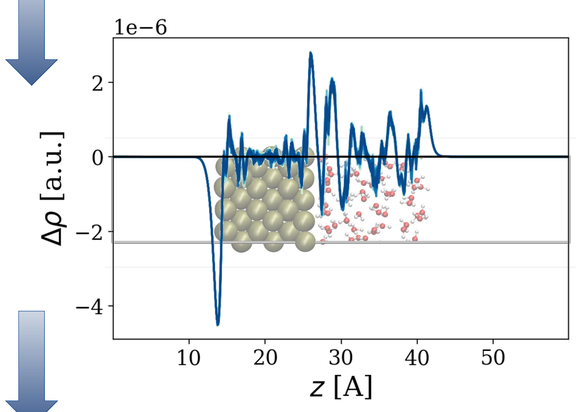
Extracting electronic dielectric constant

Apply an electric field using Dirichlet boundary conditions in Z and PBC in XY

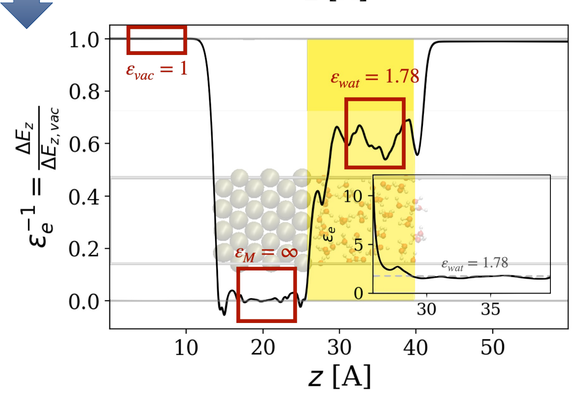
CP2K



Calculate polarization charges from the electron density changes under various fields

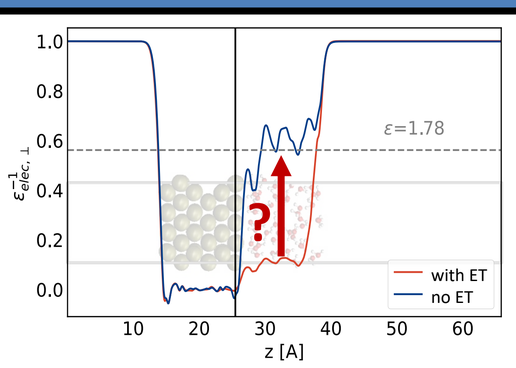


Calculate the electronic dielectric constant from the polarization charge

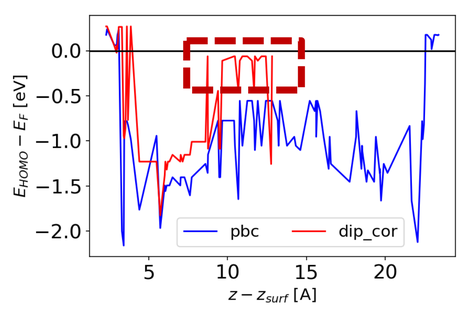


Technical details: avoiding level alignment issue issue

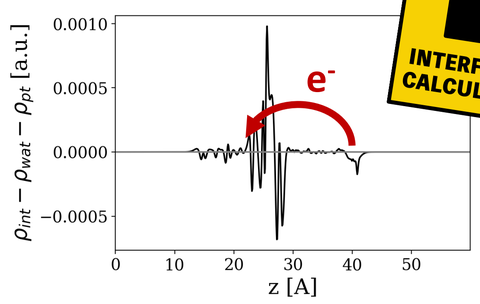
For some snapshots, deviating results are obtained suggesting a very **high permittivity of water**.



These deviations are caused by **level alignment issues** and electron transfer from the water to the metal.



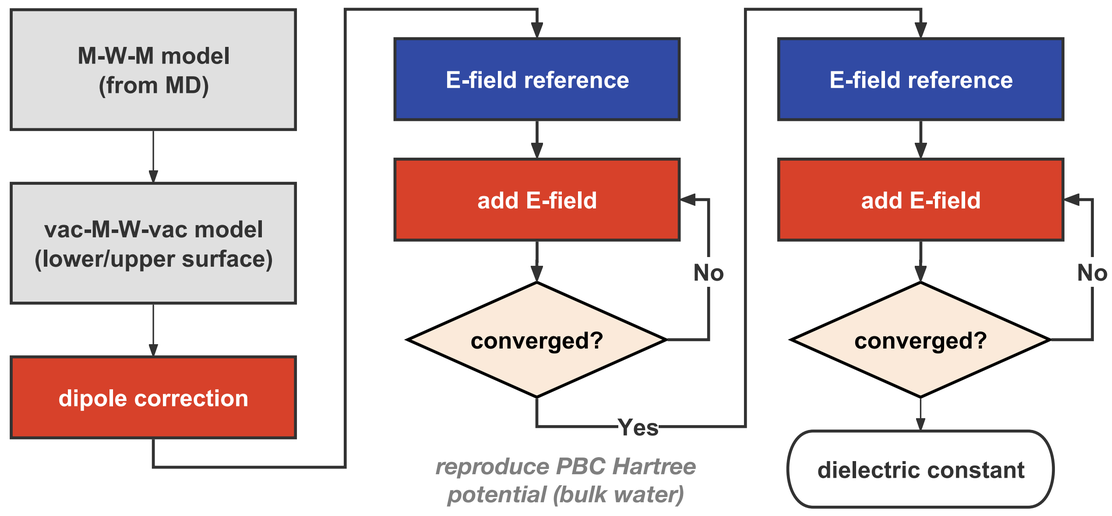
water HOMOs increase



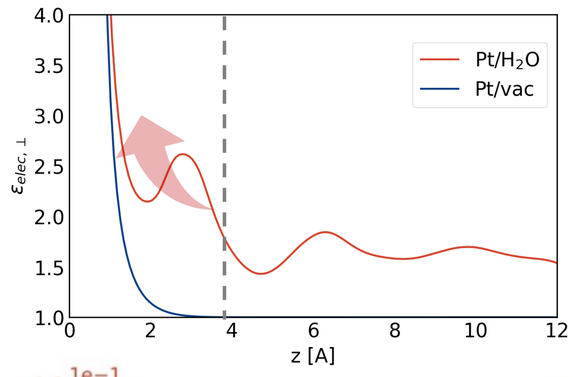
ET from water to metal

CAUTION
INTERFACE IN CALCULATION

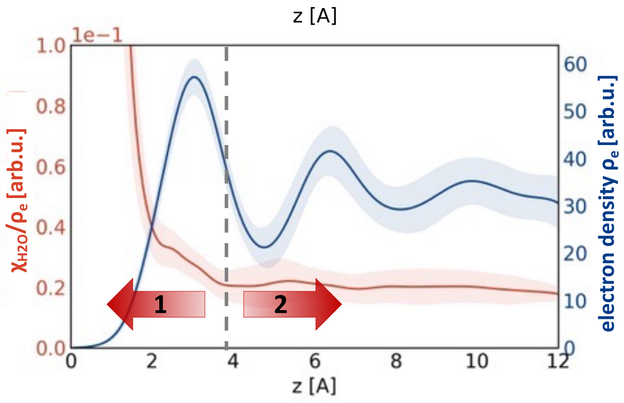
An **iterative workflow** in which we add a bias potential allows us to alleviate these issues and to obtain reliable estimates for the electronic dielectric constant.



Results



Close to the surface, the dielectric constant is **significantly enhanced** compared to the bulk. **Strong oscillations** in the dielectric response are also observed.



1. At and below the first water layer, the dielectric constant is further enhanced.
2. From the second water layer onwards, dielectric constant scales mainly with the water density.

- **Electronic dielectric response is strongly dependant on the distance from the surface.**
- **Electronic dielectric response of water is strongly enhanced at the interface due to a) water density oscillations and b) the water-metal interaction.**

E-mail: jiaxinzhu@stu.xmu.edu.cn; k.doblhoff-dier@lic.leidenuniv.nl

Field Response Machine-Learnt Potential

Jia-Xin Zhu[1], Yong-Bin Zhuang[1], Jun Cheng[1,2,3,*]

1. *State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*
2. *Laboratory of AI for Electrochemistry (AI4EC), IKKEM, Xiamen 361005, China*
3. *Institute of Artificial Intelligence, Xiamen University, Xiamen 361005, China*

Introduction

Simulating electrochemical interfaces with all-atom models can provide microscopic sight, which is crucial for further understanding the electrochemical reaction mechanism. However, this simulation is still challenging. On the one hand, appropriate descriptions of electrochemical interfaces require electronic structure calculation. On the other hand, some processes at the electrochemical interfaces might have a long timescale and cannot be described by brute-force ab initio simulation. In order to simulate the electrochemical interfaces with decent accuracy and efficiency, the machine-learnt potentials with electric field response are built in this project. Considering the distinct dielectric response behaviours, the charge equilibrium method and the Wannier-based method are implemented for the metal and the insulator, respectively. In general, both machine-learnt potentials reproduce the dielectric response decently, building a firm foundation for the further model for the electrochemical interfaces.

Metal: Charge equilibrium method

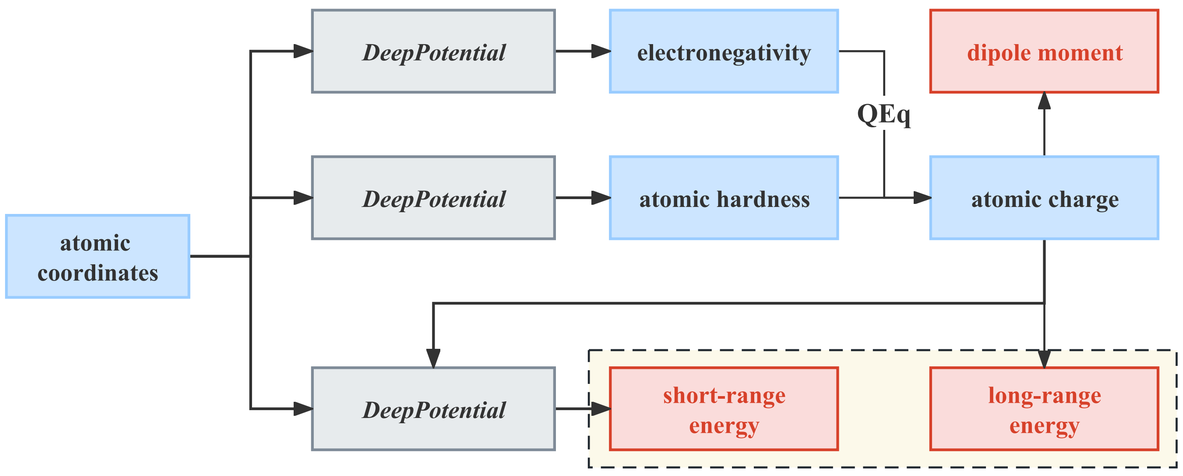
Charge equilibrium (QEq) method

- Reduced density functional theory (DFT)
- Energy minimization under total charge conservation

$$E[\rho,\mathcal{E}] = E_0 + \sum_{i=1}^{N}\left(\chi_i q_i + \frac{1}{2}\eta_i q_i^2\right) + \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r-r'|}drdr' - \mathcal{E}\cdot\sum_{i=1}^{N} q_i r_i$$

QEq method under DP framework

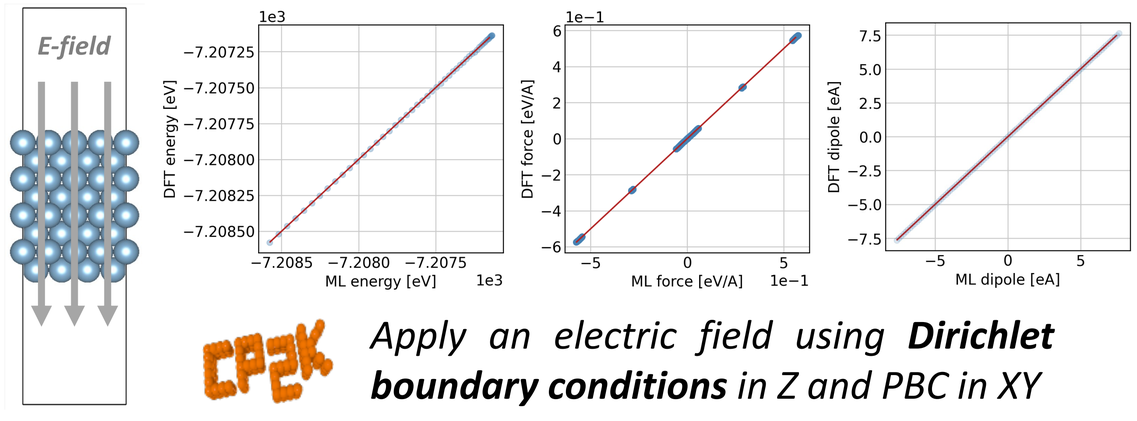
- Electronegativity and atomic hardness from local descriptors[1-2]
- Fit dipole moments rather than atomic charges



[1] T. W. Ko, *et al. Nat. Commun.* **2021**, *12*, 1. [2] C. G. Staacke, *et al. Mach. Learn. Sci. Technol.* **2022**, *3*, 015032.

Model system: Al(100)

✓ Reproduce dielectric response (E-field: 0 to 0.4 V/Å)



*Apply an electric field using **Dirichlet boundary conditions** in Z and PBC in XY*

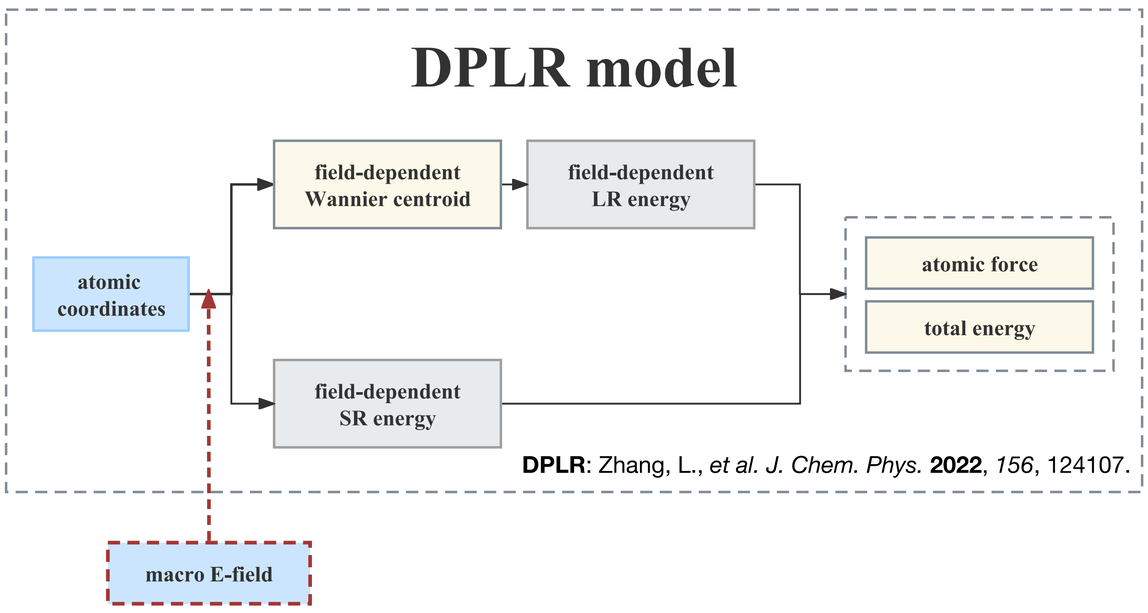
Insulator: Wannier-based method

Wannier-based method

- Wannier centers/centroids: equivalent electron positions
- Works for localized systems (i.e., insulators) only

Wannier-based method under DP framework

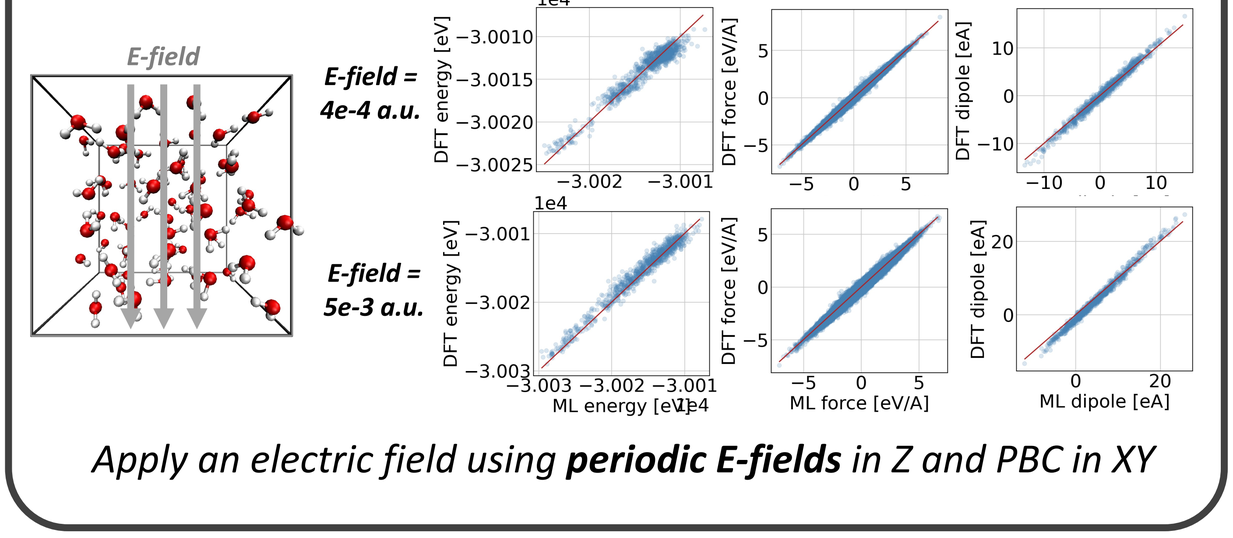
- Add macroscopic E-fields as variables into DPLR model



DPLR: Zhang, L., *et al. J. Chem. Phys.* **2022**, *156*, 124107.

Model system: bulk water

✓ Reproduce dielectric response (E-field: 0.02 to 0.25 V/Å)



*Apply an electric field using **periodic E-fields** in Z and PBC in XY*

Electrochemical interface: how to all-in-one?

Under the DP framework, the machine-learnt potentials with E-field response for either the metal or the insulator systems have been built. Despite the progress in describing the dielectric response, it is still challenging to find a uniform framework applicable to both the (non-local) electrodes and the (local) electrolyte. In the next step, we will try to find the solution by using the machine-learning models with more information, e.g., electron densities.