Molecular dynamics simulation at a constant electrode electrostatic potential

Taichi Inagaki

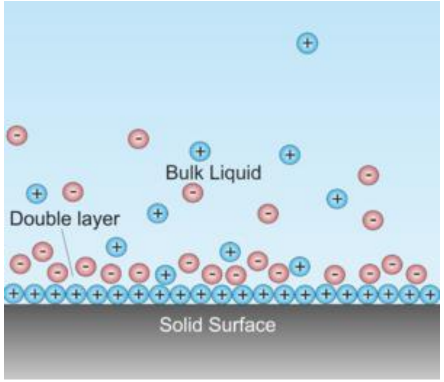
2017 7/24 CREST Workshop

Electrochemistry

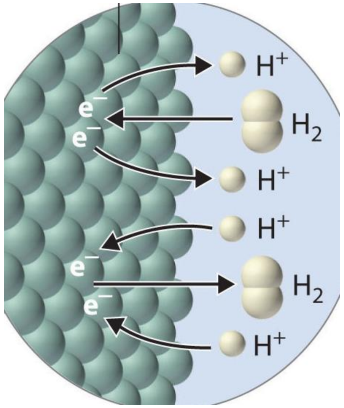
surface physics

chemical reaction at electrode surface

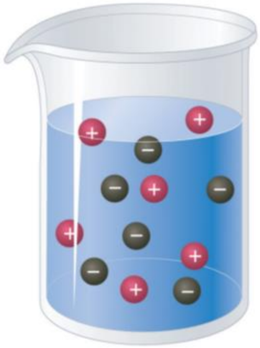
electrolyte solution



Wikipedia “Double layer (surface science)”



“The Chemistry LibreTexts library” web page

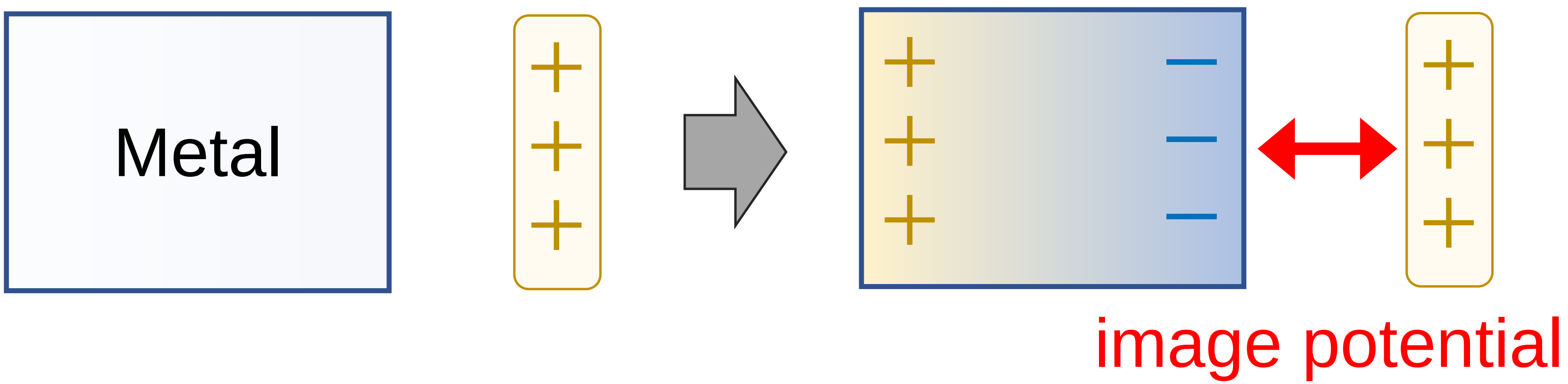


“Aqueous Solutions”, section 4.1 from the book Principles of General Chemistry

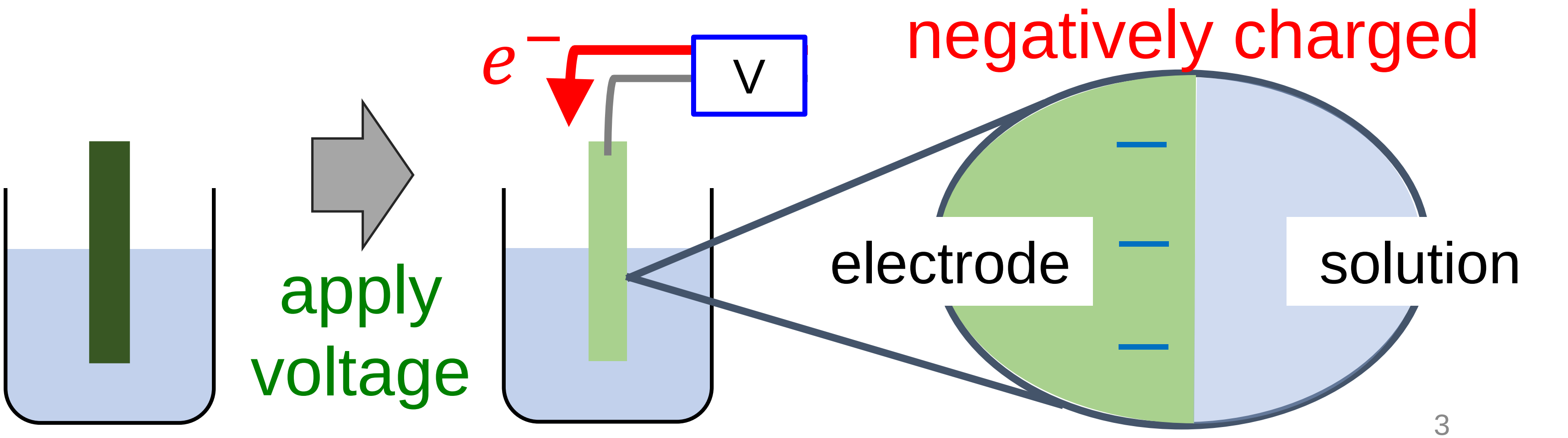
Battery, Capacitor, Electric sensor, Corrosion, …

Metal Electrode Surface

1. Polarization of metal surface

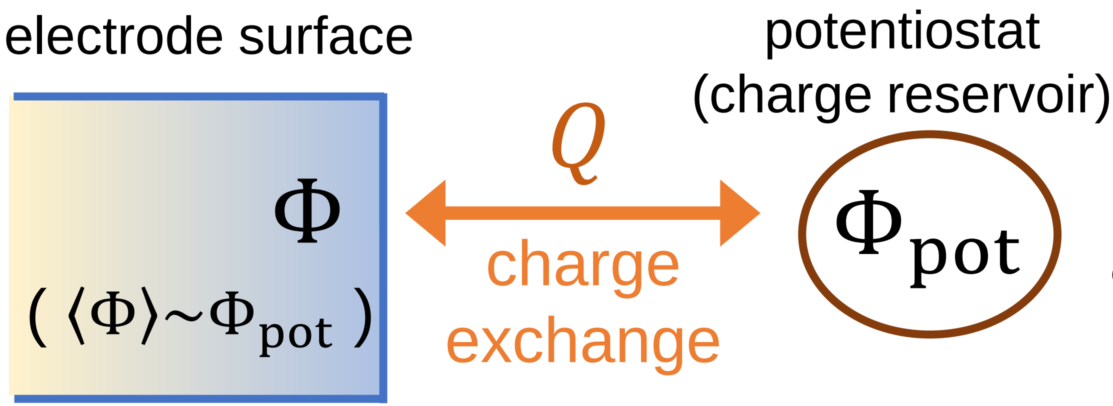


2. Electrode potential (voltage)



Modeling of Electrode Metal

- External potentiostat method



control Φ to be constant

Φ: electrostatic potential (ESP) at electrode

a kind of extended system method

cf. Andersen's constant pressure method

constant pressure (P, V) ⟺ external potentiostat (Φ, Q)

Siepmann and Sprik (*J. Chem. Phys.*, **102**, 511, 1995)

Reed and coworkers (*J. Chem. Phys.*, **126**, 084704, 2007)

Modeling of Electrode Metal

➢ Image charge method

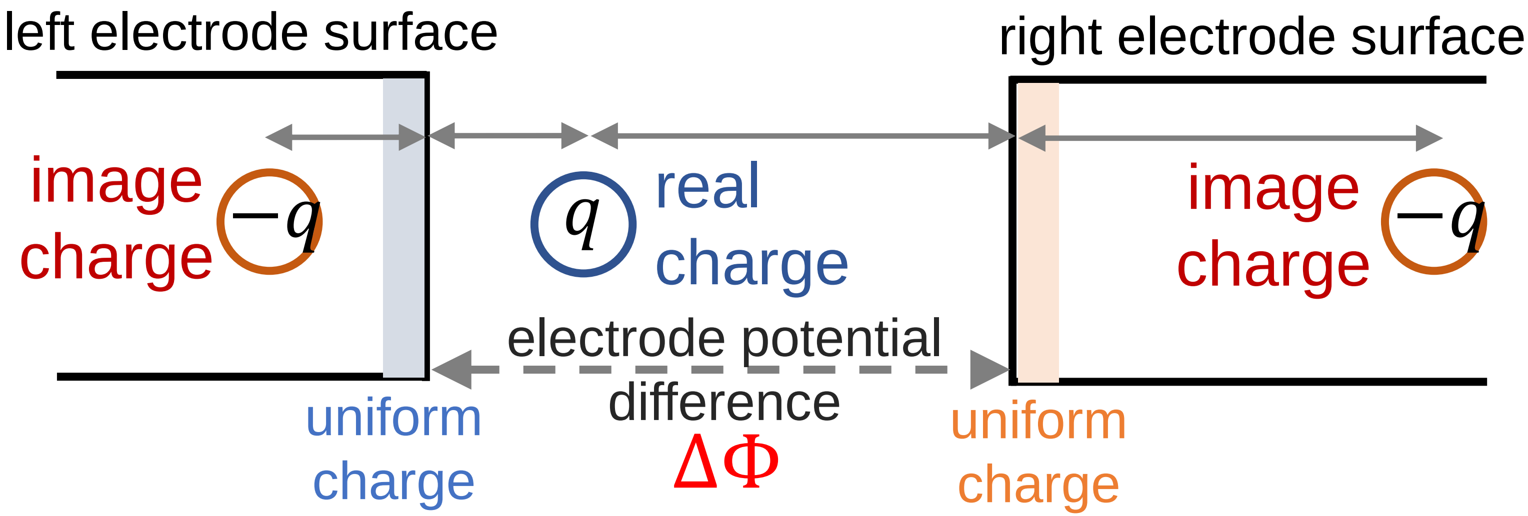


image charges in the interior of the electrode

⇒ polarization of electrode surface

uniform charges at the electrode surfaces

⇒ electrode potential difference $\Delta\Phi$

Petersen and coworkers (*J. Phys. Chem. C*, **117**, 3747, 2013)

Features of the two methods

External potentiostat method		Image charge method
✓	inhomogeneous surface	✗
✓	half cell model	✗
✓ ✗	computational cost	✓
✗	implementation	✓

Constant Electrode Potential Model

Hamiltonian for my external potentiostat method

$$H_{\mathrm{NVE\Phi}}\left(\boldsymbol{r},\boldsymbol{p},\boldsymbol{Q},\boldsymbol{P}_Q;\boldsymbol{\Phi}_{\mathrm{pot}}\right)=\sum_{j}^{N}\frac{\boldsymbol{p}_j}{2m_j}+\sum_{i}^{n}\frac{\boldsymbol{P}_{Q,i}}{2M_{Q,i}}+U(\boldsymbol{r},\boldsymbol{Q})-\boldsymbol{Q}\boldsymbol{\Phi}_{\mathrm{pot}}+E_{\mathrm{self}}$$

$\boldsymbol{Q}$: electrode atomic point charges

$\boldsymbol{P}_Q, \boldsymbol{M}_Q$: fictitious momenta and masses associated with $\boldsymbol{Q}$

$\boldsymbol{\Phi}_{\mathrm{pot}}$: potentiostat potential (parameter)

With this Hamiltonian, equations of motions for $\boldsymbol{r}$ and $\boldsymbol{Q}$ are constructed, and solved.

- ✓ 3D periodic boundary condition
- ✓ Point charge model (E_{self} is introduced for this model)
- ✓ Electrode charge as dynamical variable

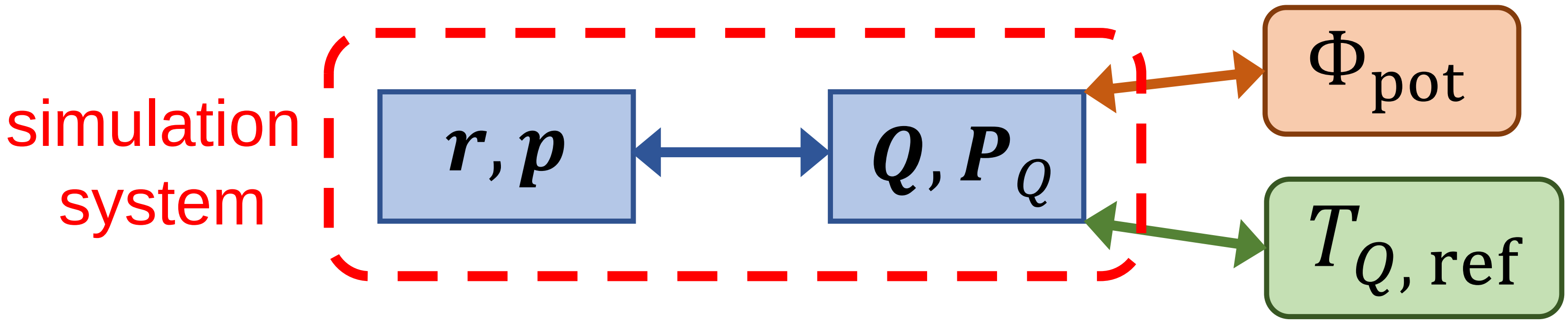
Thermostated Electrode Charge

Electrode charges mimic electrons in the electrode.

~ Adiabaticity between atomic and charge dynamics should be achieved.

Thermostat for electrode charges should be attached.

$$H'_{\mathrm{NVE\Phi T_\Phi}}(\boldsymbol{\Gamma}) = \sum_{j}^{N} \frac{\boldsymbol{p}_j}{2m_j} + \sum_{i}^{n} \frac{\boldsymbol{P}_{Q,i}}{2M_{Q,i}} + \sum_{k}^{n_k} \frac{\boldsymbol{p}_{\xi,k}}{2M_{\xi,k}} + U'(r,Q) + kT_{Q,\mathrm{ref}} \sum_{k}^{n_k} g_k \xi_k$$



Computational Details

- Long-range electrostatic interaction:

  Particle-Particle Particle Mesh Ewald method

- Ewald surface term:

  included

- Electrode atom coordinates:

  fixed

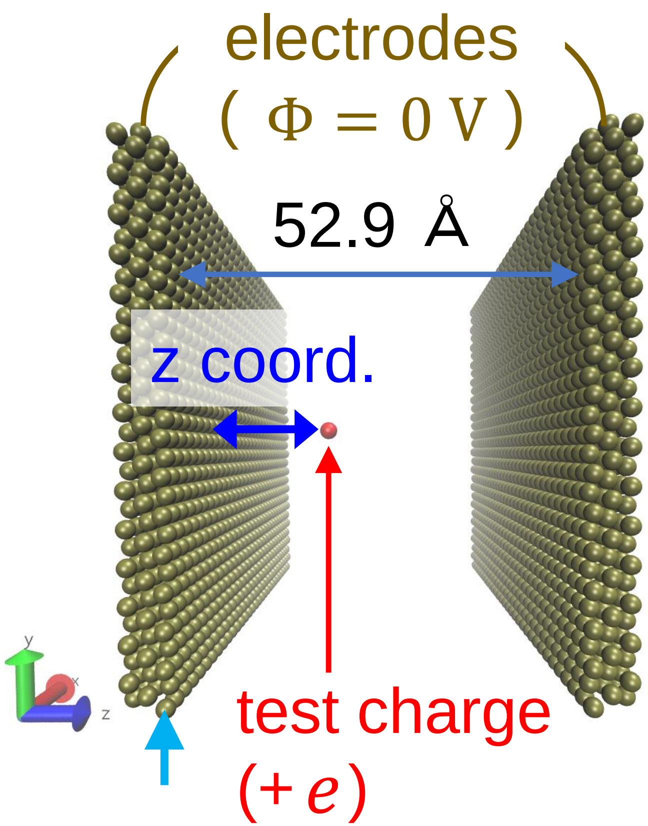
- MD program package:

  modified LAMMPS program package

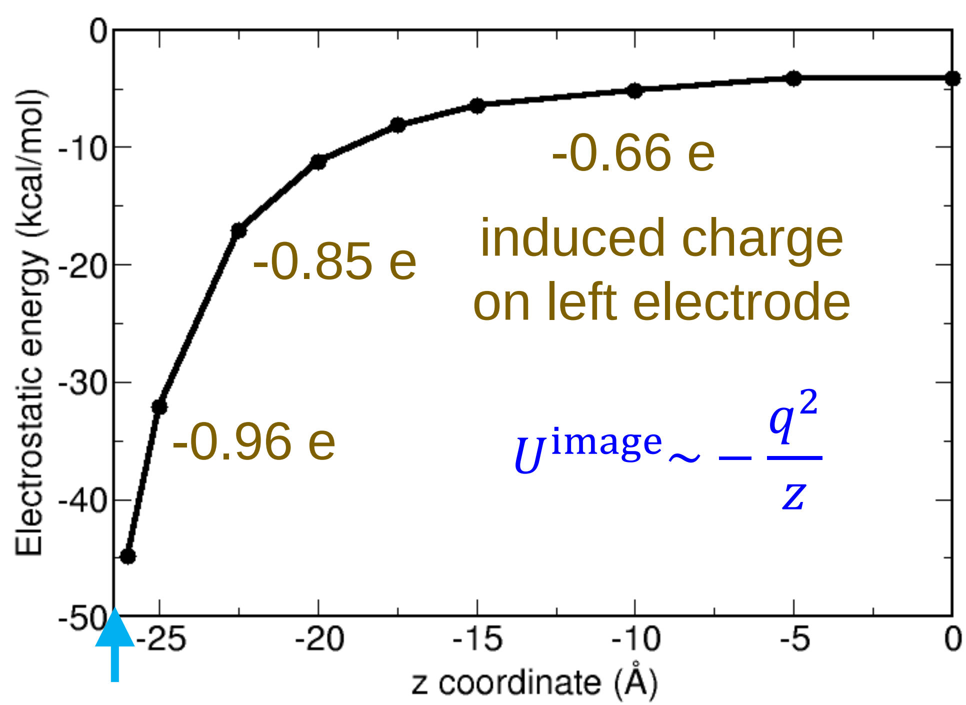
Other parameters and conditions are described below.

Polarization of Electrode

system (fixed)

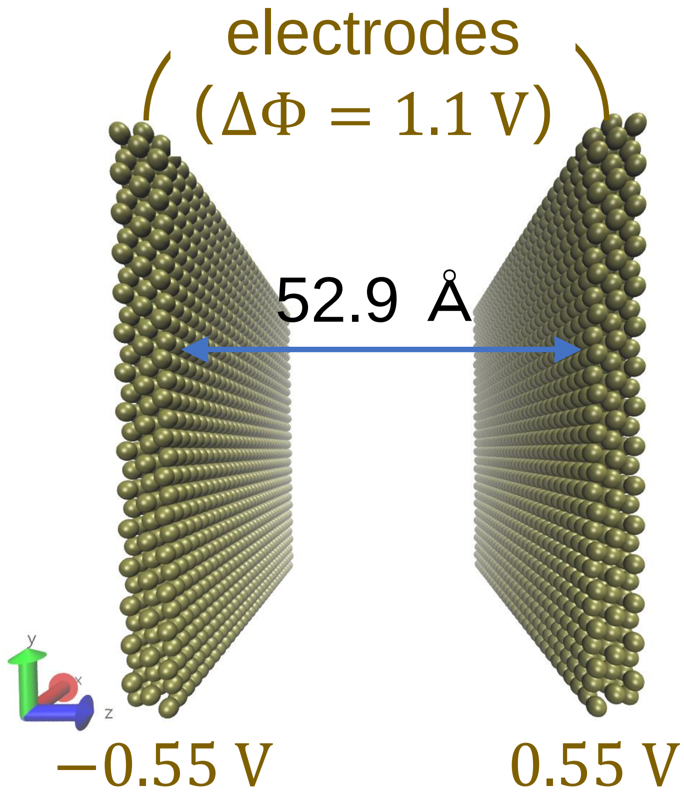


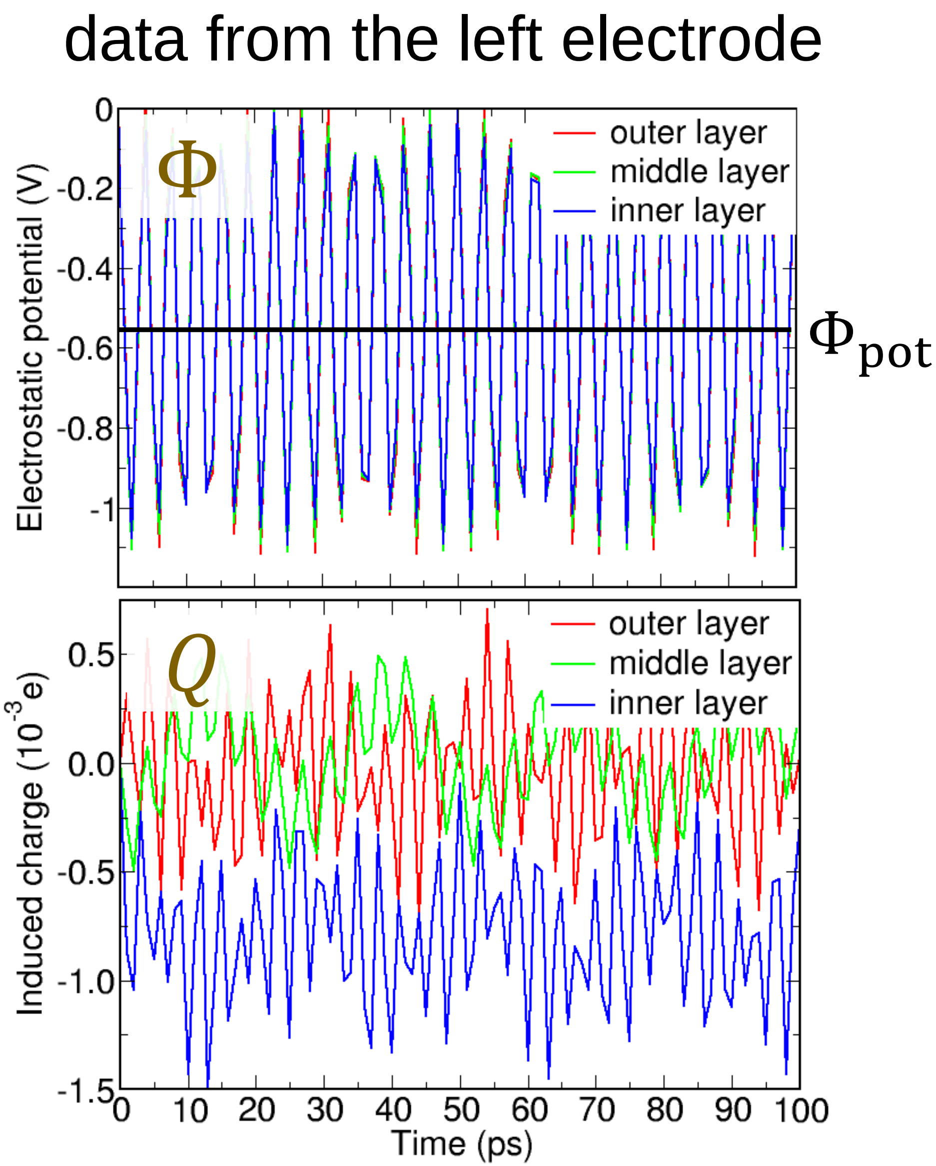
electrostatic energy
vs z coord. of a test charge



Electrodes are certainly polarized by a test charge.

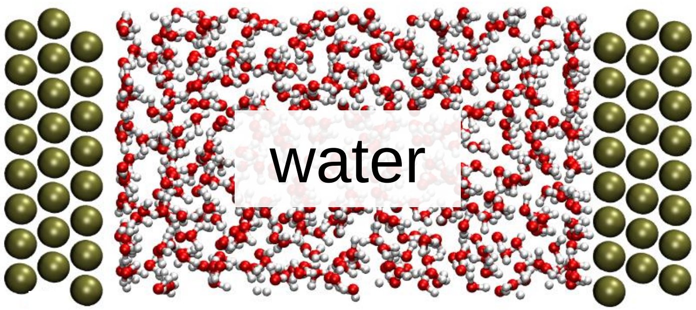
Control of Electrode ES Potential





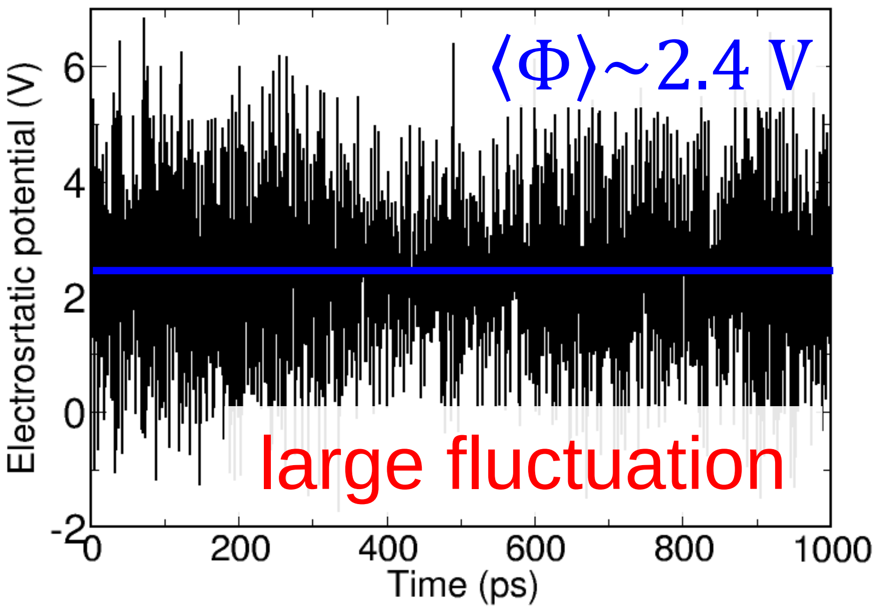
- ESP (Φ) is well controlled.
- Induced charges are mainly localized near the surface.

Adiabaticity between r and Q

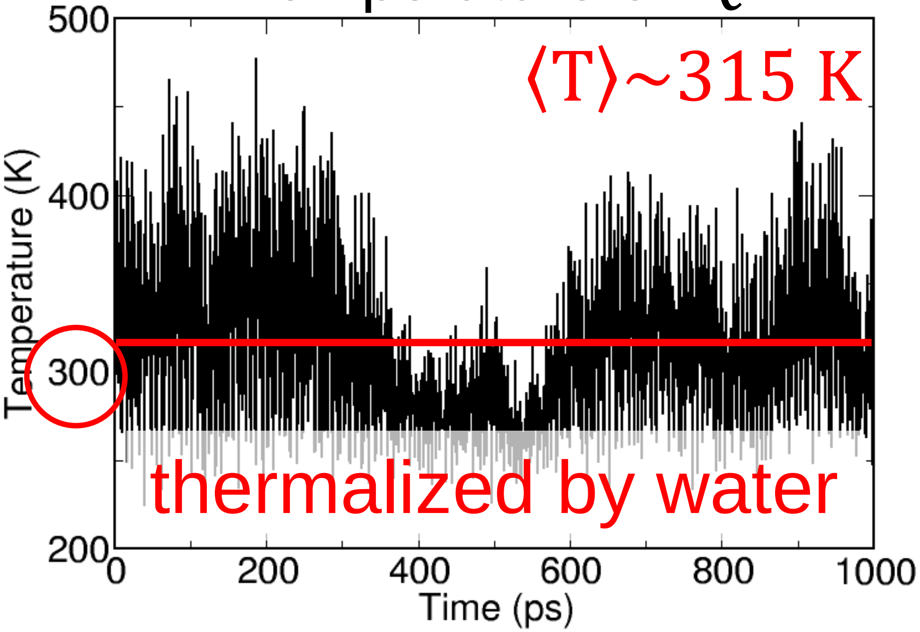


Φ_{pot} at left electrode: 2.4 V
temperature (water): 300 K

Φ at left electrode

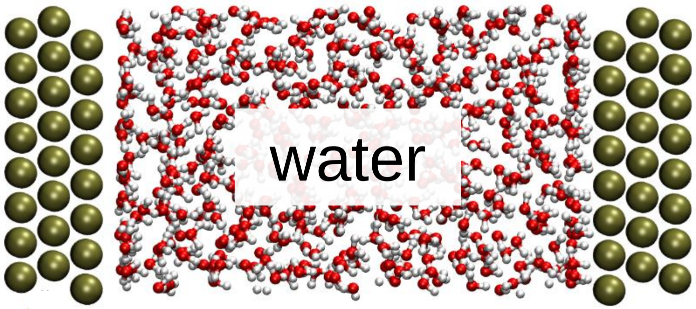


Temperature of Q



Heat flows from water to electrode charges.

Addition of Thermostat for Q

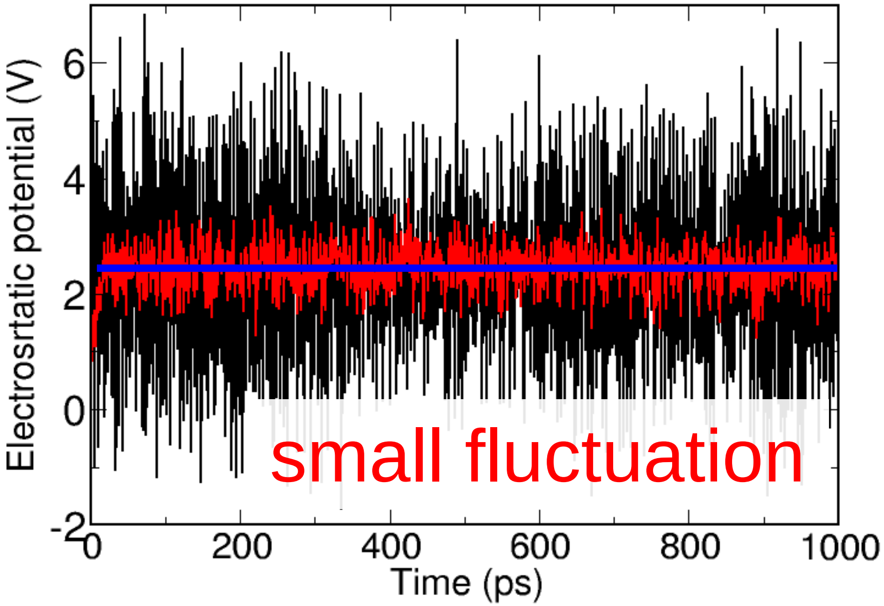


Φ_{pot} at left electrode: 2.4 V

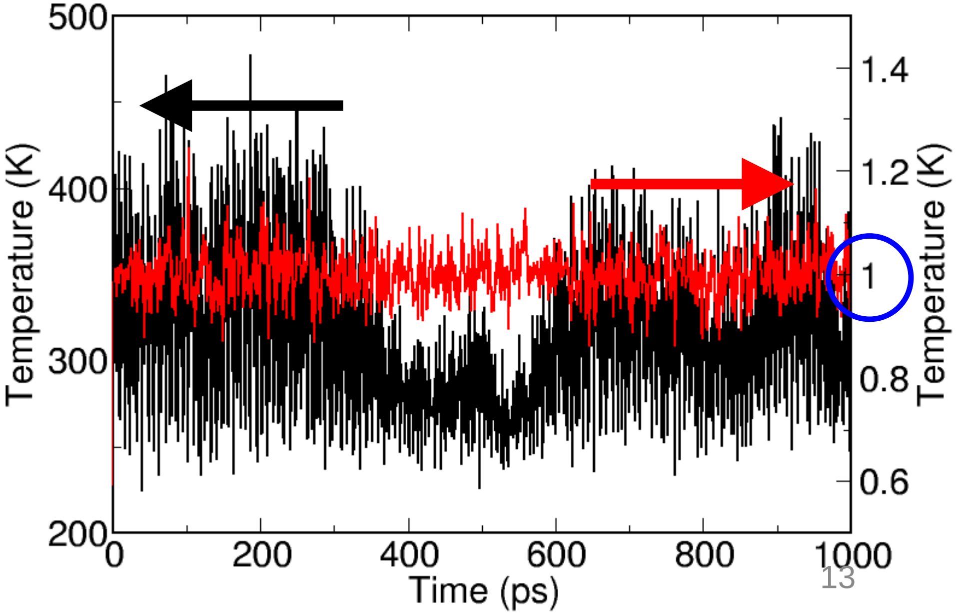
temperature (water): 300 K

temperature (Q): 1 K

Φ at left electrode



Temperature of Q



Adiabaticity was achieved by thermostat for Q.

Summary

- New method accounting for the electrode polarization and ESP was developed.
  - ✓ Image charge and image potential can be calculated reasonably.
  - ✓ ESP on electrode was well controlled.
  - ✓ Adiabaticity was correctly achieved.
- Long time simulations which are infeasible in the first-principles MD are expected to be performed to investigate molecular behaviors near a surface in the more realistic level.