

Dynamics of ionic liquids on graphite electrode surface

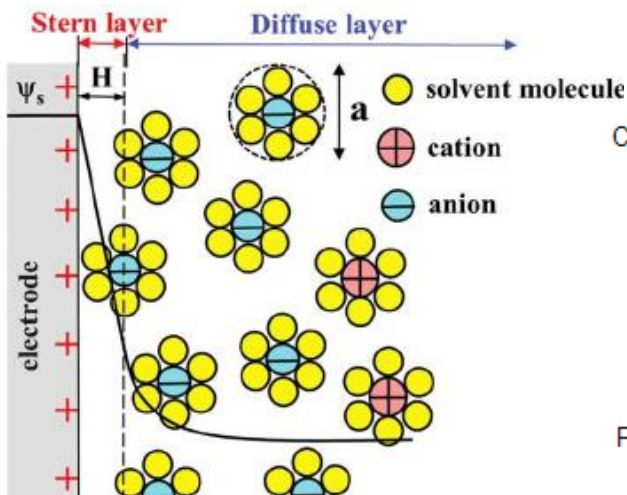
Taichi Inagaki

2018 6/28 CREST Workshop

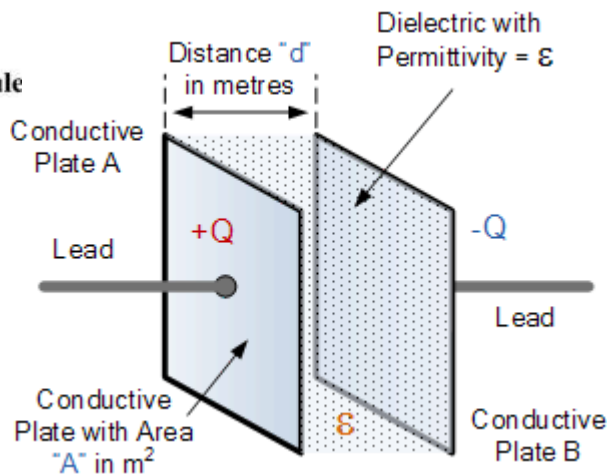
Static Electrochemical Properties

Development of many electric devices (battery, capacitor, electric sensor, ...) is enhanced by understanding of electrochemical properties:

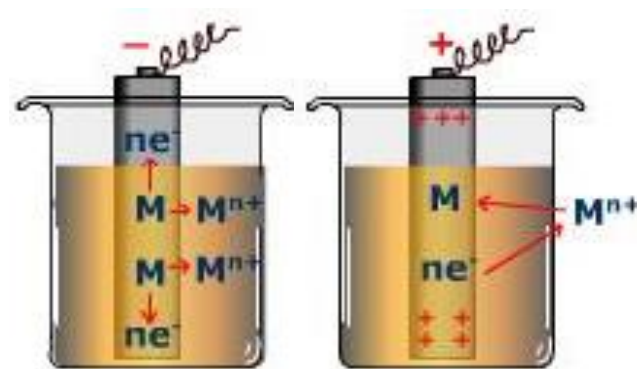
electric double layer capacitance electrode potential



J. Electrochem. Soc.
162, A5158, 2015.



Website "Introduction
to Capacitors".



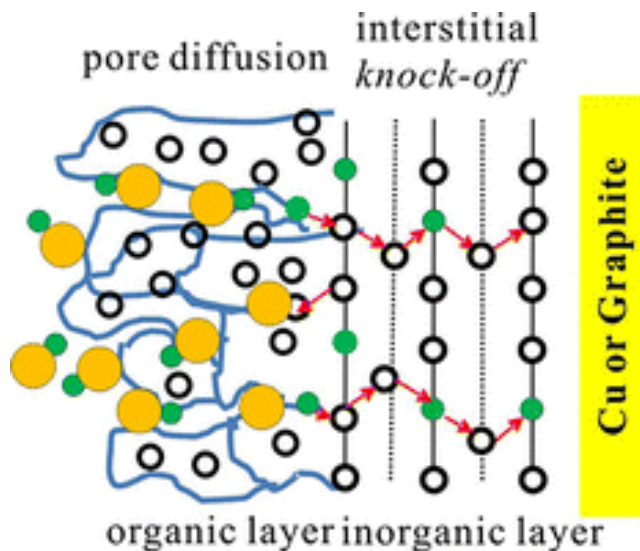
Website "CHEM-GUIDE:
Electrode Potential".

Static properties are essential in electrochemistry.

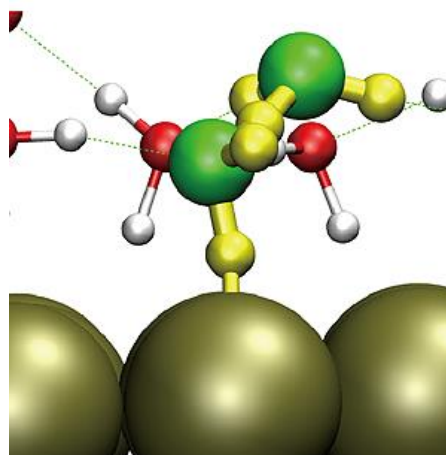
Dynamic Electrochemical Properties

diffusion

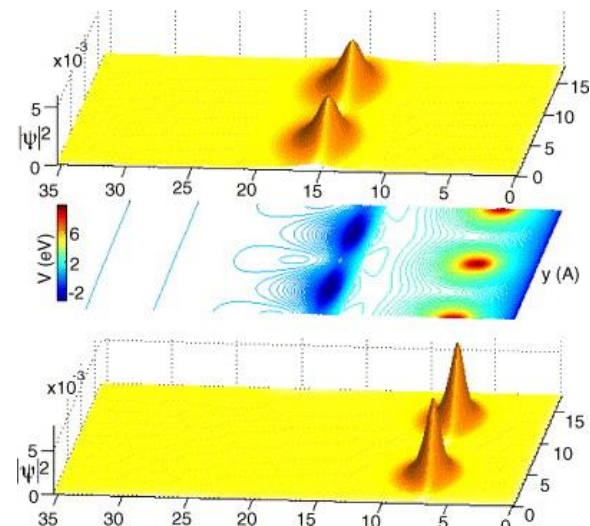
chemical reaction electron dynamics



J. Am. Chem. Soc.,
134, 15476, 2012.



Website: "GREEN
(NIMS)"

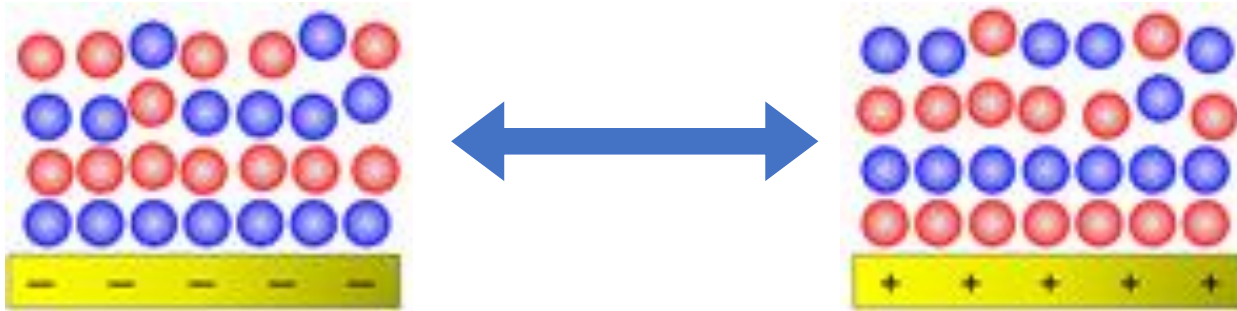


Surf. Sci. Rep.,
56, 1, 2004.

Compared to the statics, dynamics in electrochemistry have many unrevealed issues.

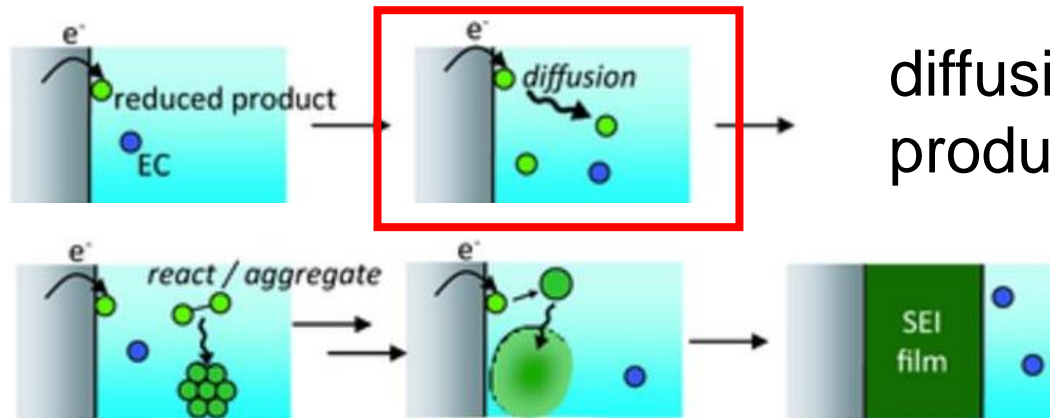
Adsorption/Desorption Process

electric double layer reconstruction



J. Phys. Chem. Lett.,
4, 3110, 2013.

initial formation process of SEI film



diffusion of a reduction
product to bulk solution

J. Electrochem. Soc.,
162, A2670, 2015.

What kind of dynamics and kinetics are there?

Purpose of This Work

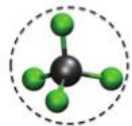
To gain insight into the dynamics of molecules at electrode surface, I performed

1. rate estimate of desorption process of ionic liquid from the graphite surface
2. estimate of time scale of electric double layer reconstruction (i.e., relaxation of surface structure).

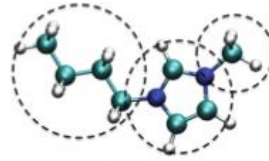
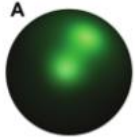
by means of the molecular dynamics (MD) simulation method.

Computational Model

coarse-grained rigid model of ionic liquid (IL)



BF₄ anion

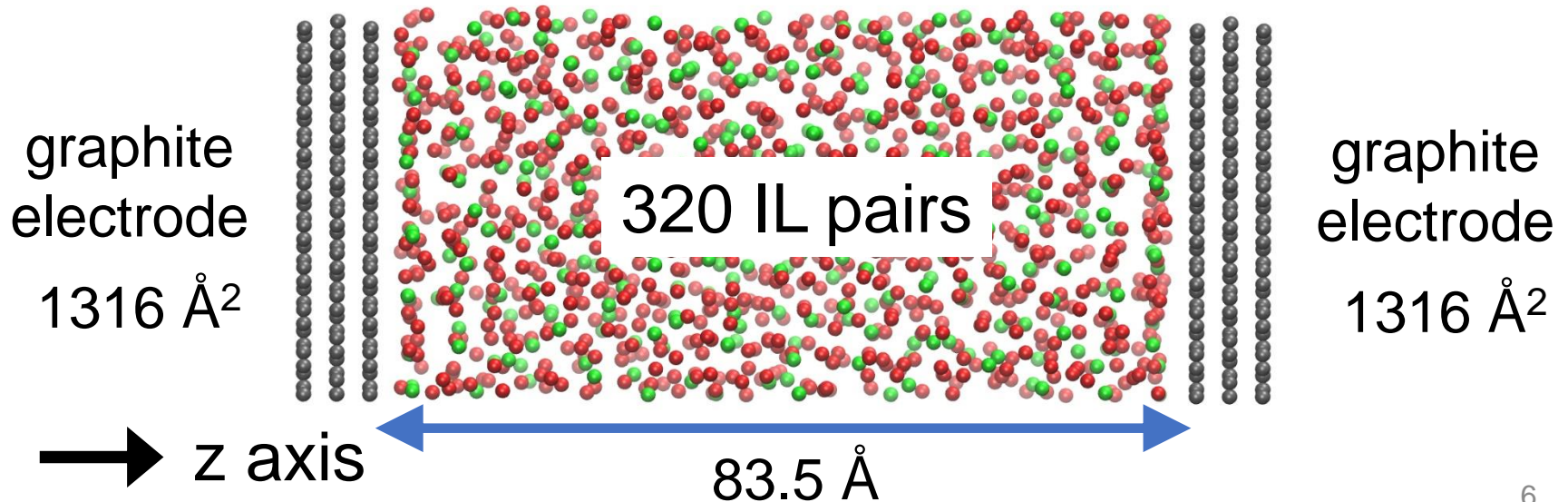


BMIM cation



Lennard-Jones and electrostatic interactions

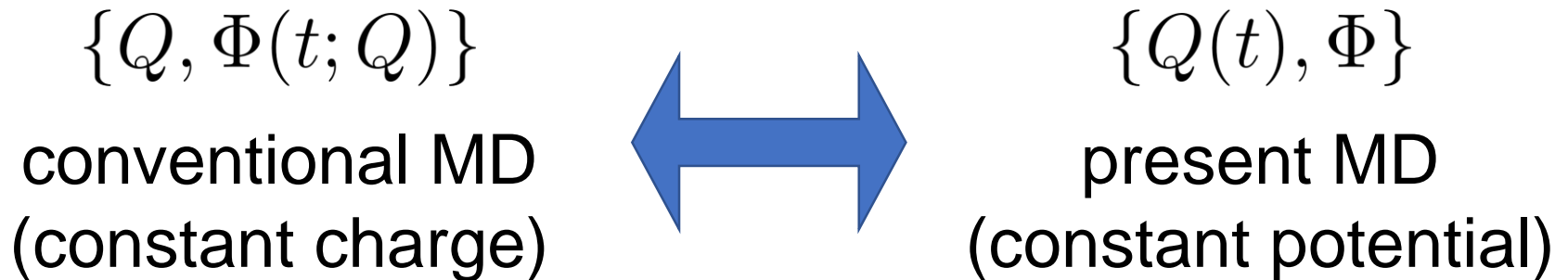
MD simulation system



Constant Potential Method

Control electrostatic potential Φ on electrode by **dynamically changing electrode charges** Q .

Comparison with the conventional MD



Merit

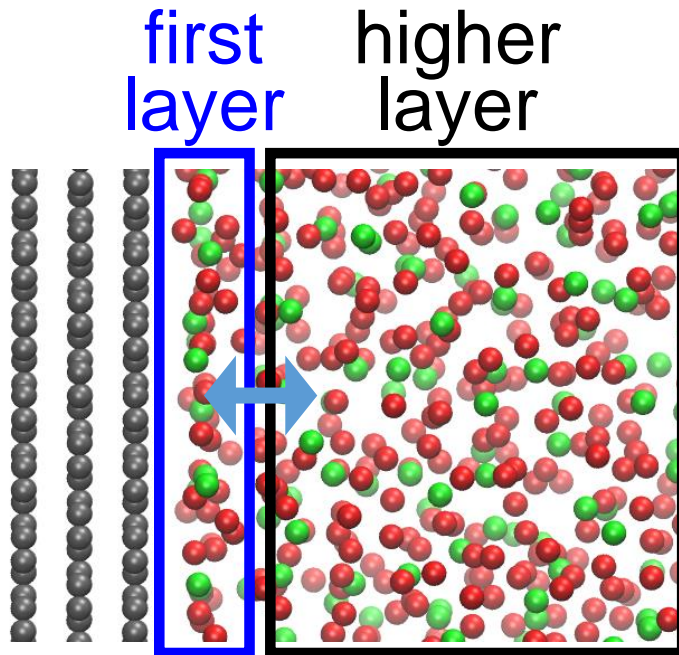
Electronic polarization of electrode is taken into account straightforwardly.

Computational Details

- force field: model proposed by Merlet et al.
(*JPCA*, 116, 7687, 2012)
- long-range interaction: PPPM Ewald method
with Ewald surface term
- short-range cutoff: 10 Å
- geometry: electrode atoms were fixed
- temperature of atoms: 400 K
- time step: 0.1 fs
- temperature of charges: 0.00001 K
- fictitious mass of charge: 25 fs²V/e

Desorption Process of IL

In equilibrium state, molecules go back and forth between the first and higher layers.



first layer:
adsorbed state, **A**

higher layer:
desorbed state, **D**

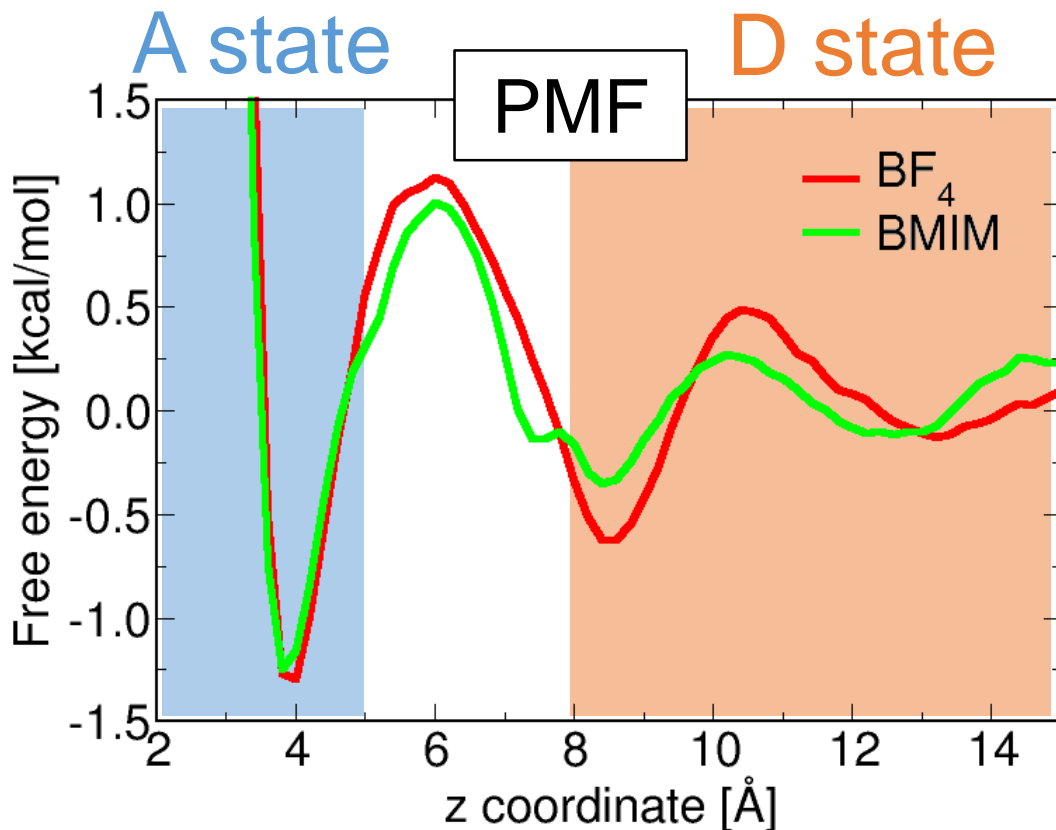


desorption process: $\mathbf{A} \rightarrow \mathbf{D}$

Rate Constant Estimate Method

time correlation function method

$$C(t) = \frac{\langle h_i(z_0)g_i(z_t) \rangle}{\langle h_i(z_0) \rangle} \quad \Rightarrow \quad k = dC(t)/dt$$



A: adsorbed state

$$h_i(z) = \begin{cases} 1 & (z \in A) \\ 0 & (z \notin A) \end{cases}$$

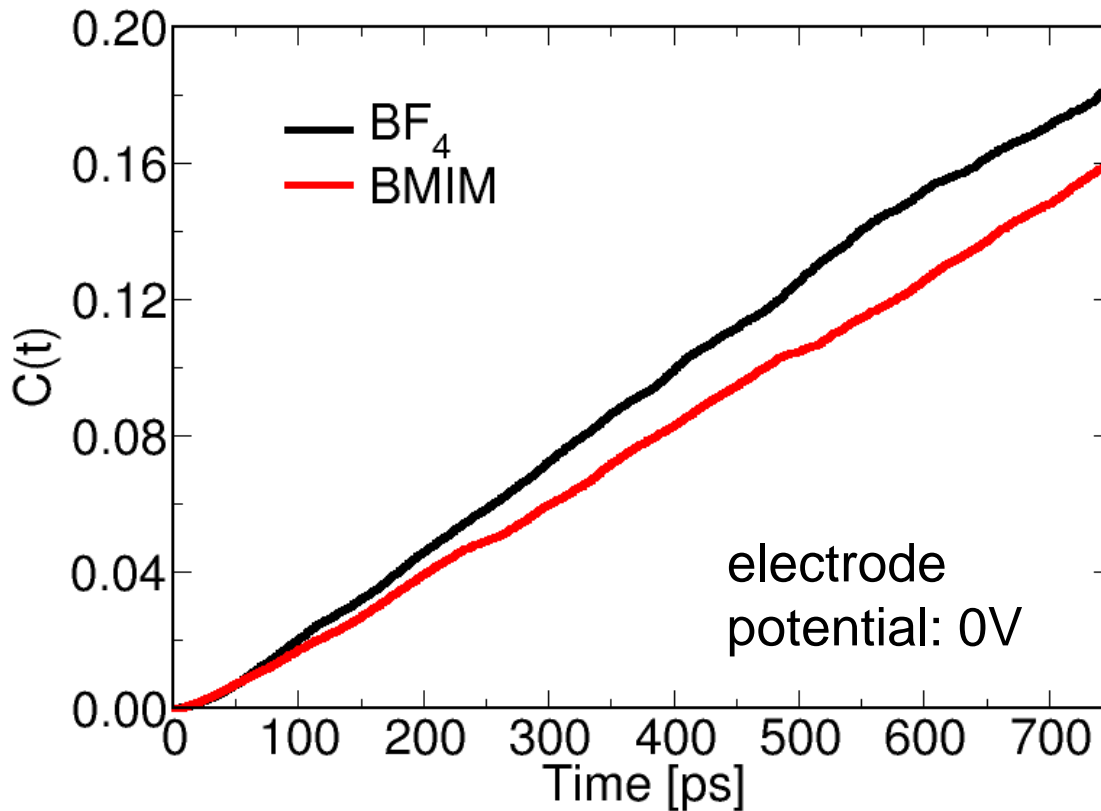
D: desorbed state

$$g_i(z) = \begin{cases} 1 & (z \in D) \\ 0 & (z \notin D) \end{cases}$$

Desorption Rate Constant

$$C(t) = \frac{\langle h_i(z_0)g_i(z_t) \rangle}{\langle h_i(z_0) \rangle}$$

$$k = dC(t)/dt$$



0.22 /ns

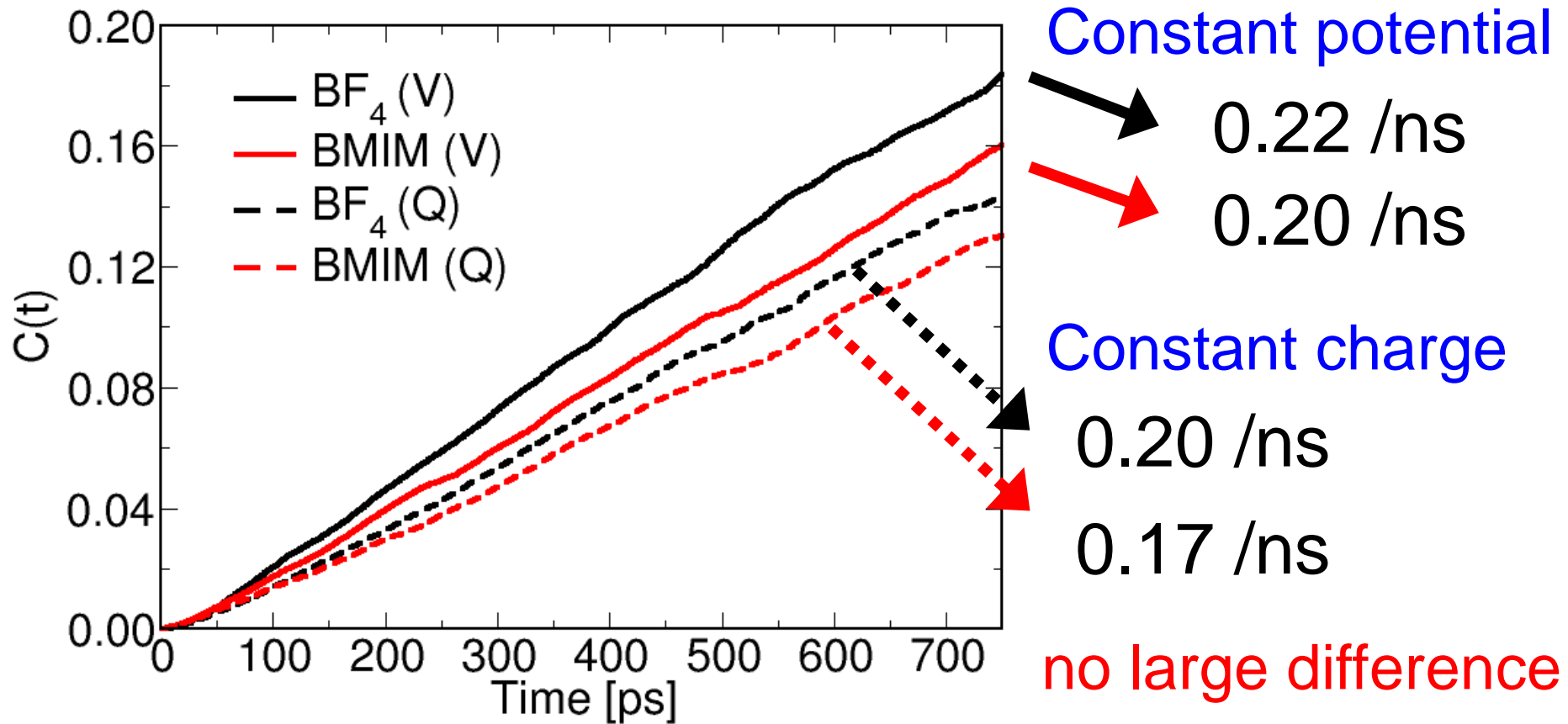


0.20 /ns



It takes ~5 ns to escape from the first layer.

Comparison to Constant Charge MD Calculations



Because the electrostatic interaction between IL's is expected to be larger than between graphite and IL.

Comparison to TST Rate Constant

Time correlation method: 0.22 /ns (BF₄), 0.20 /ns (BMIM)

$$k = d \left(\frac{\langle h_i(z_0)g_i(z_t) \rangle}{\langle h_i(z_0) \rangle} \right) / dt$$

⇒ computationally high cost

Transition state theory (TST) is one of the ways for computationally efficient estimate of rate constant.

This is because TST is based on the statics, rather than dynamics.

However, does TST give the correct estimate of the desorption rate constant?

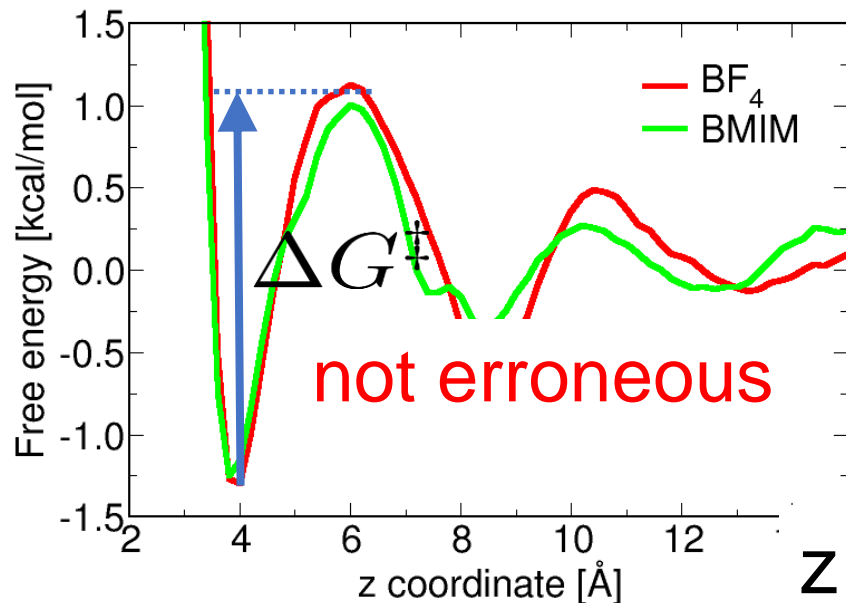
Comparison to TST Rate Constant

Time correlation method: 0.22 /ns (BF₄), 0.20 /ns (BMIM)

$$k = d \left(\frac{\langle h_i(z_0) g_i(z_t) \rangle}{\langle h_i(z_0) \rangle} \right) / dt$$

Transition state theory: 65.1 /ns (BF₄), 68.0 /ns (BMIM)

$$k^{\text{TST}} = \nu \exp(-\beta \Delta G^\ddagger)$$



TST greatly overestimates the rate constants.

Free energy barrier is lower than correct one.

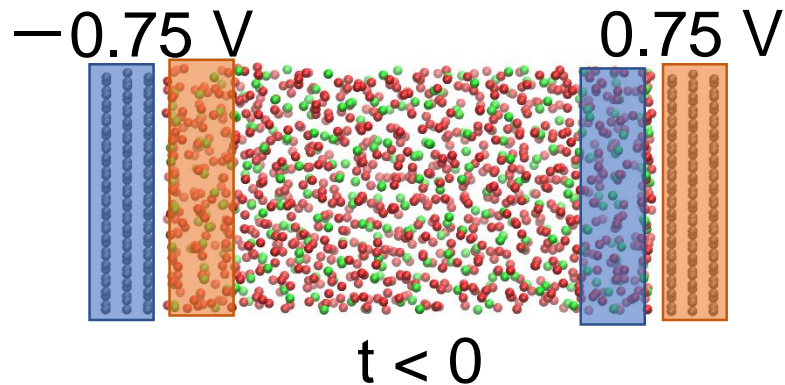


z coordinate \neq good reaction coordinate of the desorption.

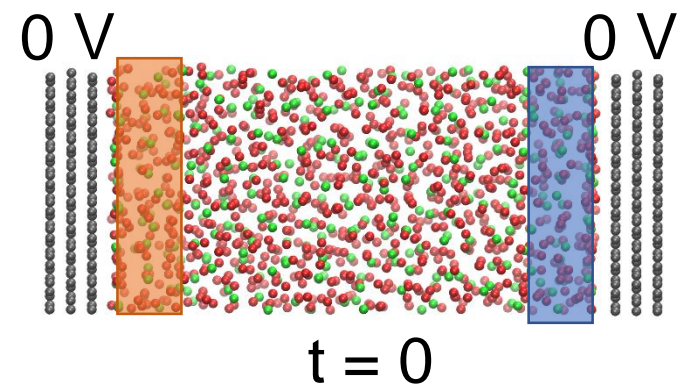


Relaxation of Electric Double Layer

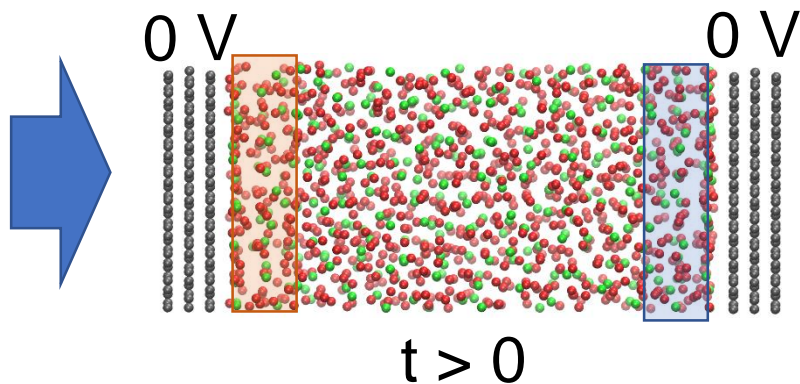
Equilibrium state under the biased electrode



Electrode potentials are suddenly turned off.



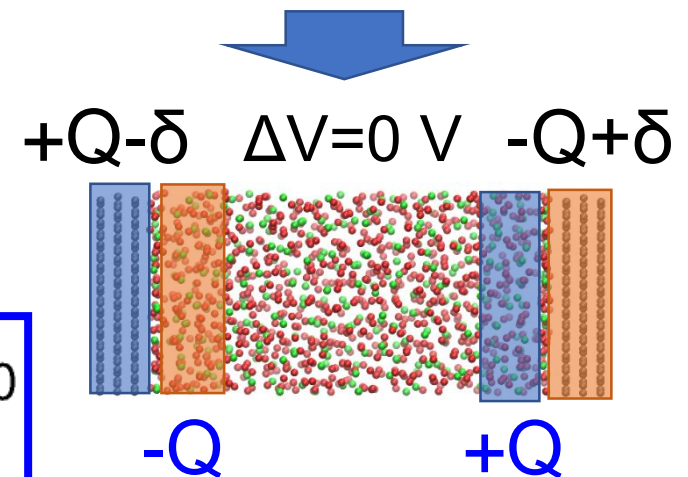
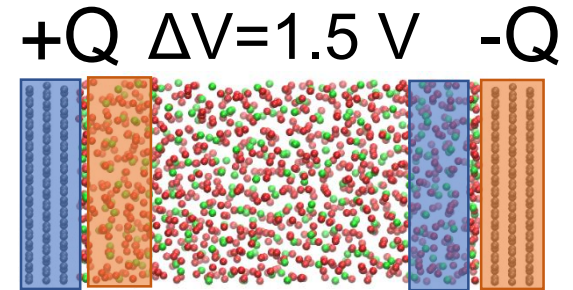
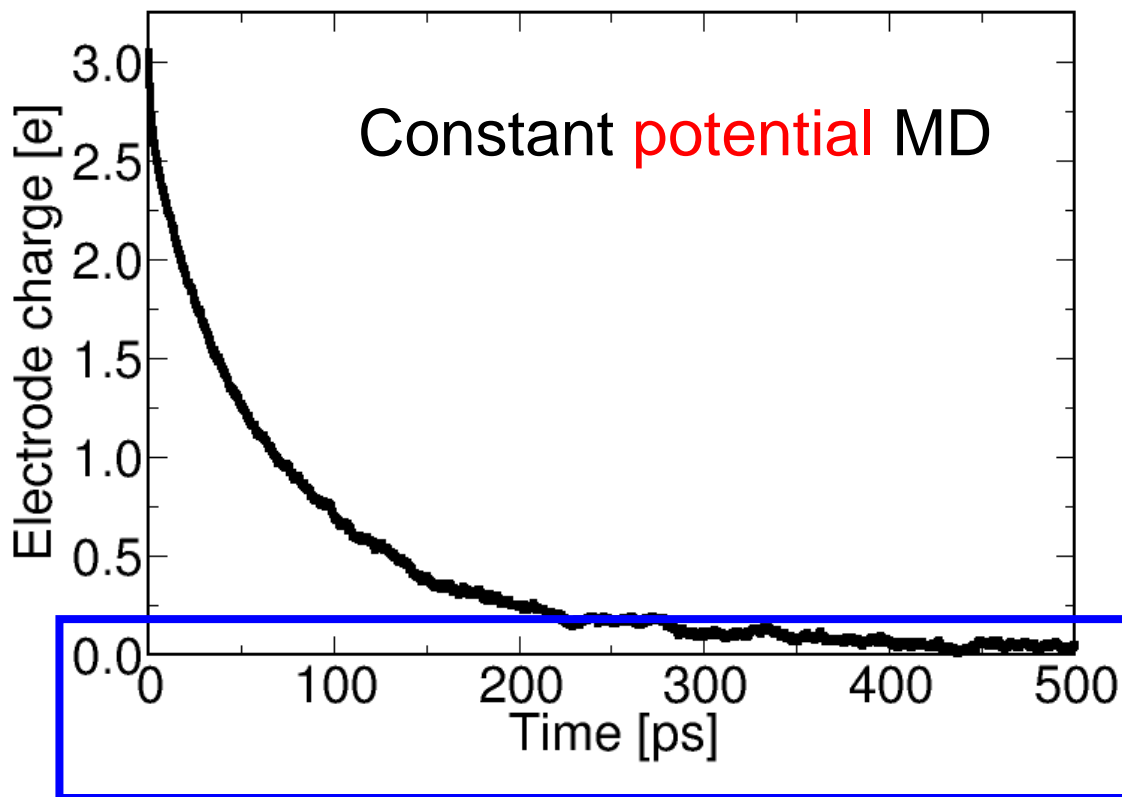
Relax to the zero potential equilibrium



How rapidly will the electric double layer structure relax?

Relaxation of Electrode Charge

time scale: hundreds of pico-seconds

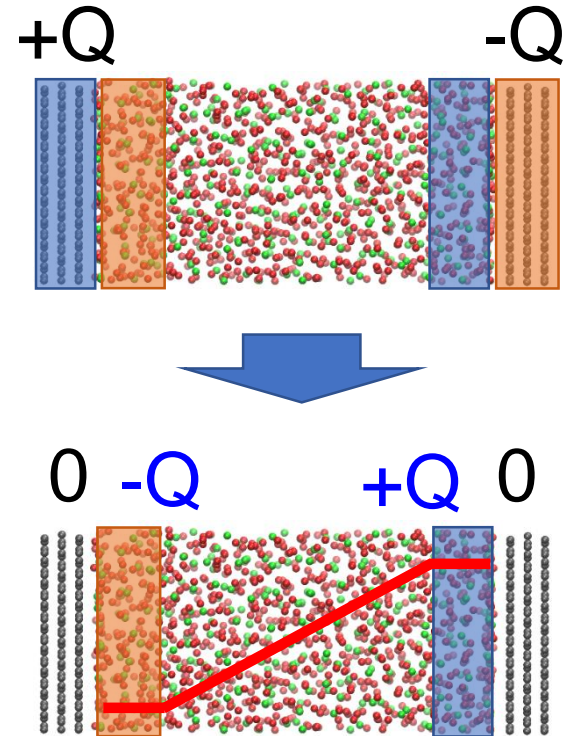
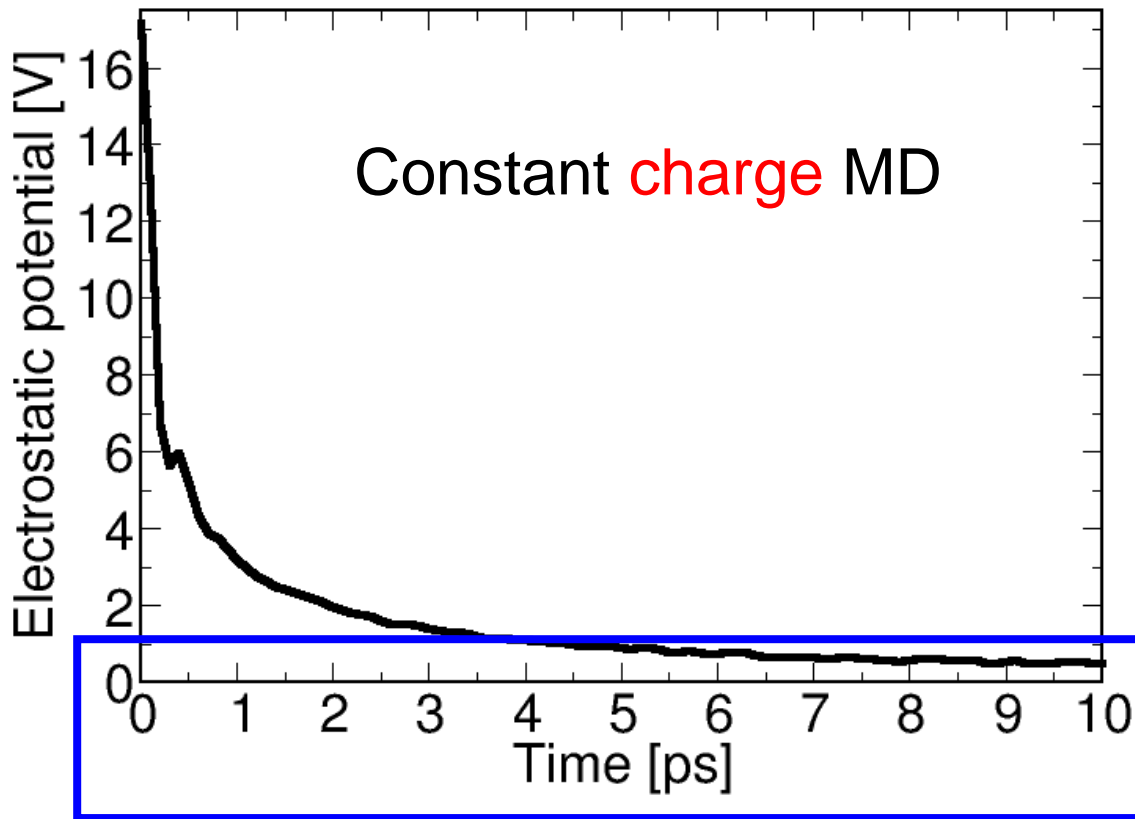


The drop of potential is small perturbation to IL molecules.

$$Q \sim 3.0 e, \delta \sim 0.1 e$$

Constant Charge Case

time scale: several pico-seconds



The drop of charges is large perturbation to IL molecules.

Summary

- Dynamics of ionic liquids on the graphite electrode surface was investigated.
- Desorption time scale was found to be nano-second order in the graphite/ionic liquid case.
- Comparing with the rate constant derived by transition state theory, the reaction coordinate of desorption was found not to be easy to specify.
- Rate of the electric double layer reconstruction was found to be critically affected by the electrode polarization.