First-principles simulation of electrochemical reactions at solid-liquid interface

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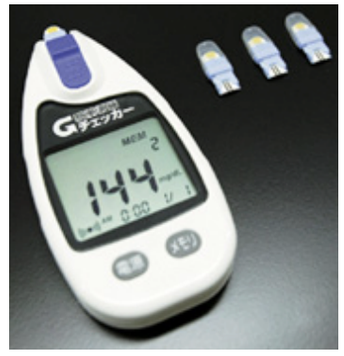
07/03/2018

ISS2018@ISSP

Outline

- Introduction
- Simulation platform for electrochemical interface
  - Effective screening medium (ESM) method
  - Constant bias potential (constant-μ_e) method
  - Hybrid simulation method: DFT+liquid theory (ESM-RISM)
- Applications
  - Lithium Insertion/Desorption Reaction in Li-ion battery
- Summary
- Appendix (How to define the electrode potential from DFT)

Electrochemical devices/engineering



Battery
- Manganese dry cell
- Lead battery
- NiCd, NiH secondary battery
- Fuel cell
- Lithium secondary battery

Capacitor
- Electrolytic condenser
- Double layer condenser
- Supercapacitor

Photovoltaic cell
- c-Si, a-Si solar cell
- Dye sensitized solar cell
- photoelectrochemical hydrogen production

Sensor
- pH meter
- ion selective concentration meter
- glucose, etc. (using enzyme) gas (oxygen, etc.)

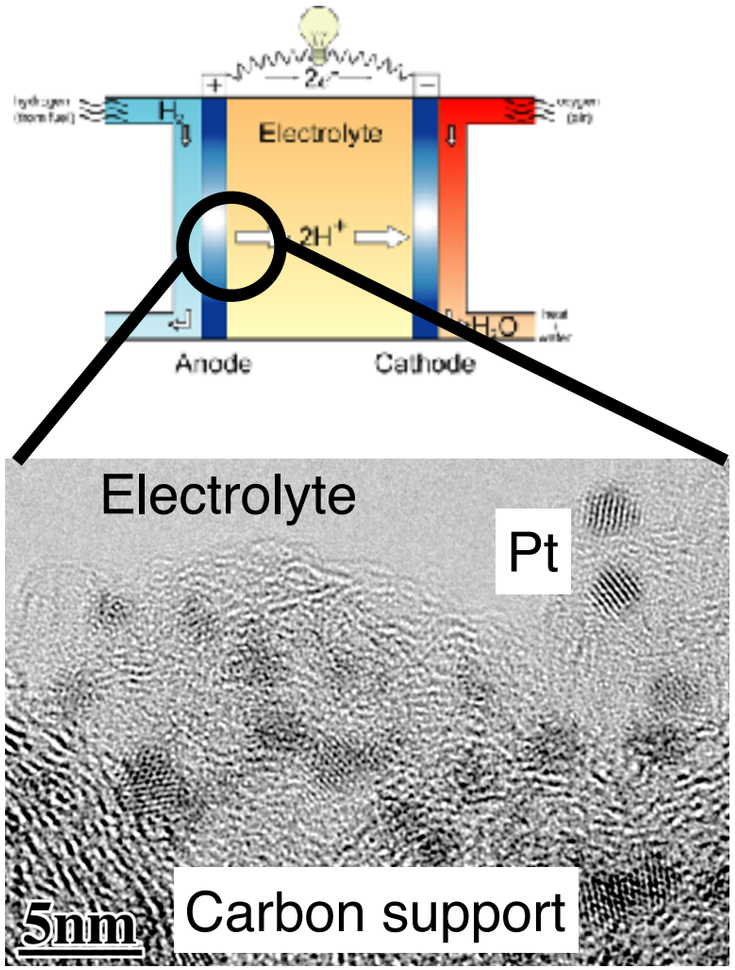
Electroplating

Cathodic protection
- Fe → Fe_2O_3

Electrolysis
- Aluminum, Copper, etc.
- Water, salt, etc.
- Organic chemicals
- tetraethyl lead

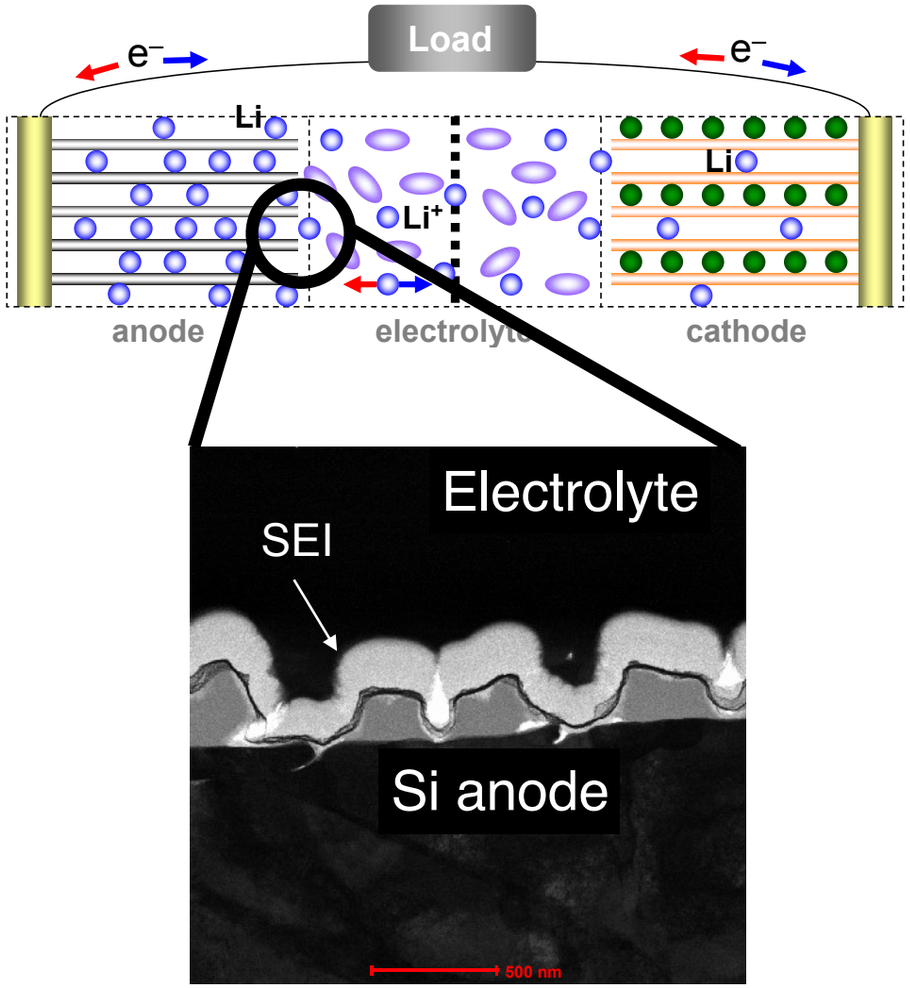
Target systems

Energy generation
(Fuel cell)



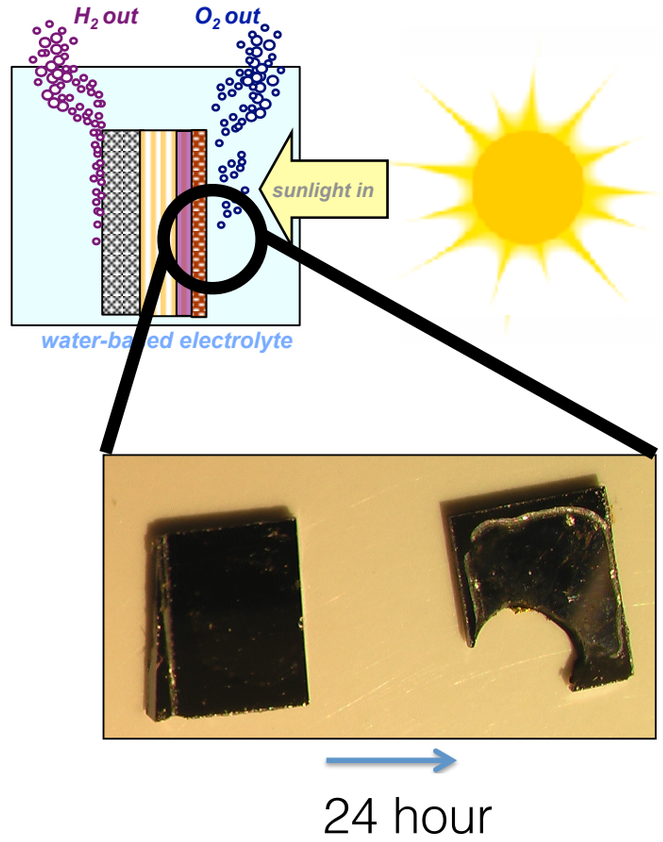
- overpotential
- a cheaper alternative to Pt

Energy storage
(Secondary battery)



- formation mechanism of SEI
- interface resistance

Energy harvesting
(PV, PEC)



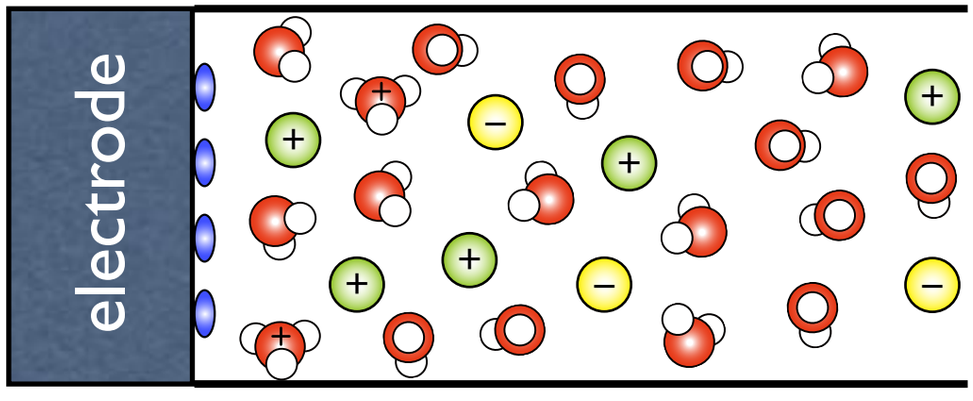
- corrosion mechanism
- surface modification

Electrochemical interface

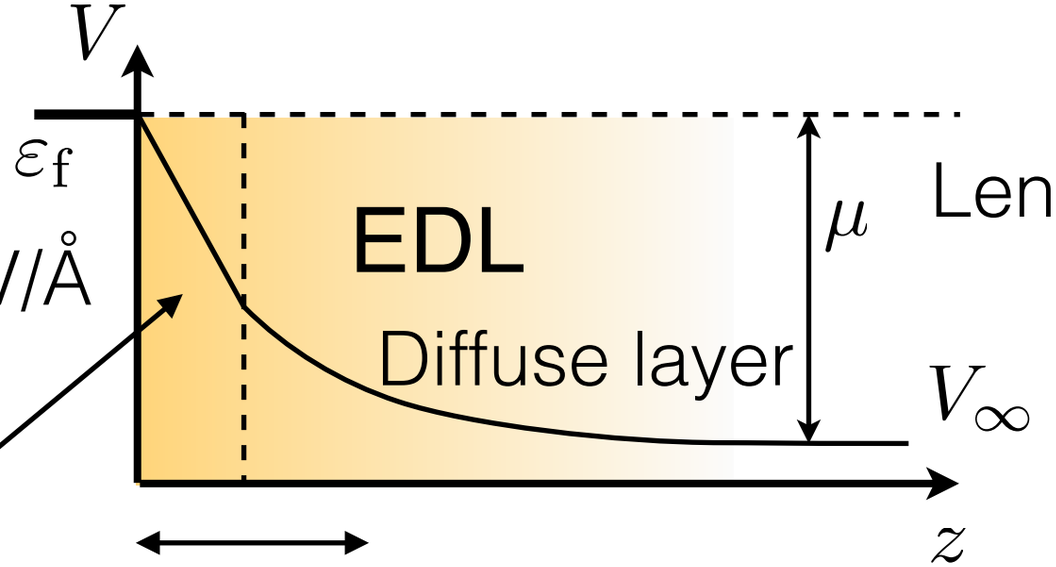
25°C, 1.0M NaCl, Electrode: Pt

4 nm^2 surface area

3-layer Pt(111):
460Pt atoms



1 NaCl / 50 H_2O



Electric field: 0.1~0.5 V/Å

Helmholtz layer: ~Å

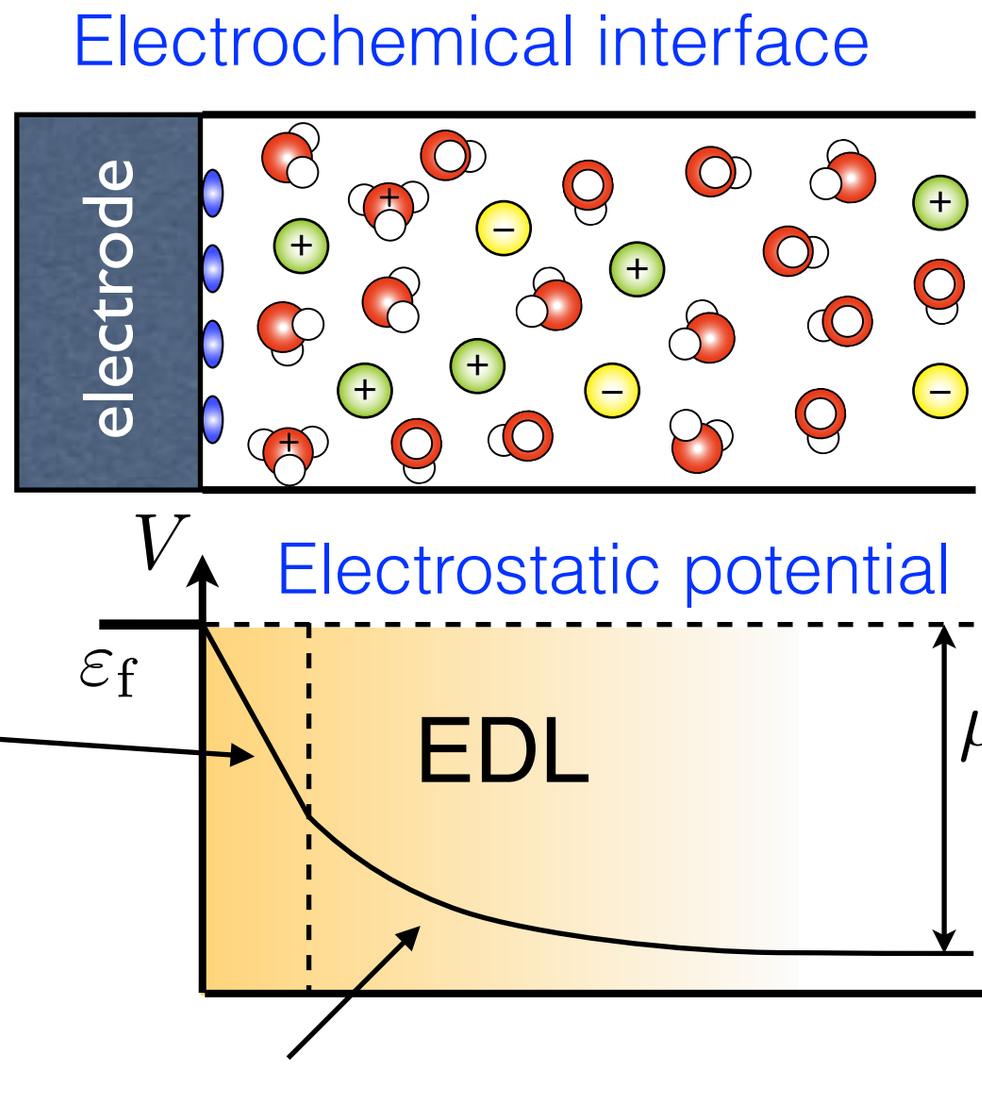
Length scale of EDL:
nm ~ μm

Depth

2 nm: 800 atoms (264 H_2O, 5 NaCl)
10 nm: 5000 atoms (1320 H_2O, 25 NaCl)
0.1 μm: 50000 atoms (13200 H_2O, 250 NaCl)

4 Challenges in modeling an electrochemical reaction for DFT-MD

1.Strong electric field in Helmholtz layer



2.Bias potential control

3.Screening in diffuse layer

4.Origin of electrostatic potential

4 Challenges in modeling an electrochemical reaction for DFT-MD

1. Strong electric field in Helmholtz layer

ESM method

Effective Screening Medium method

Phys. Rev. B **73**, 115407 (2006)

2. Bias potential control

Constant-μ_e method

Phys. Rev. Lett. **109**, 266101 (2012)

3. Screening in diffuse layer

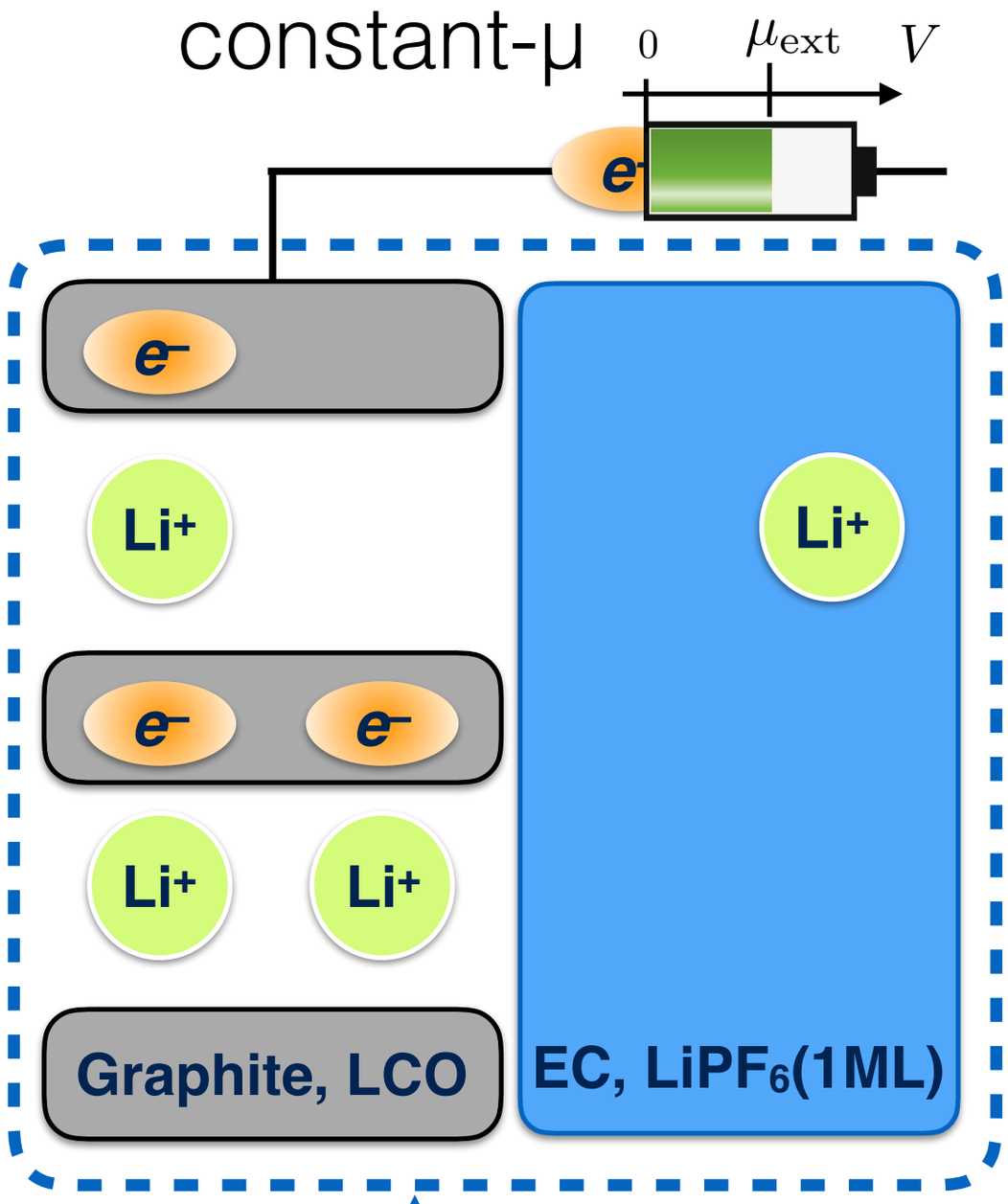
4. Origin of electrostatic potential

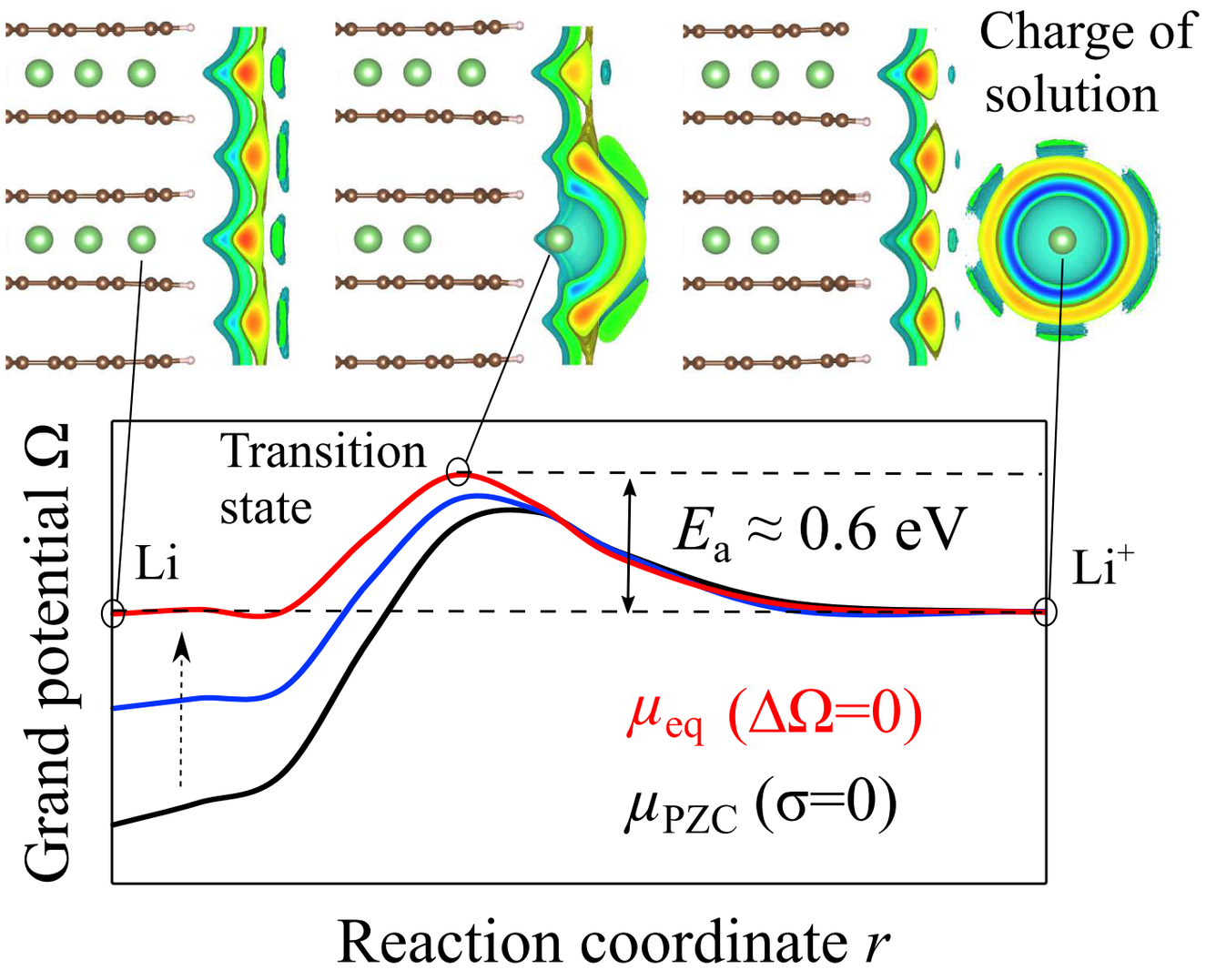
ESM-RISM method

Reference Interaction Site Model

Phys. Rev. B **96**,115429 (2017)

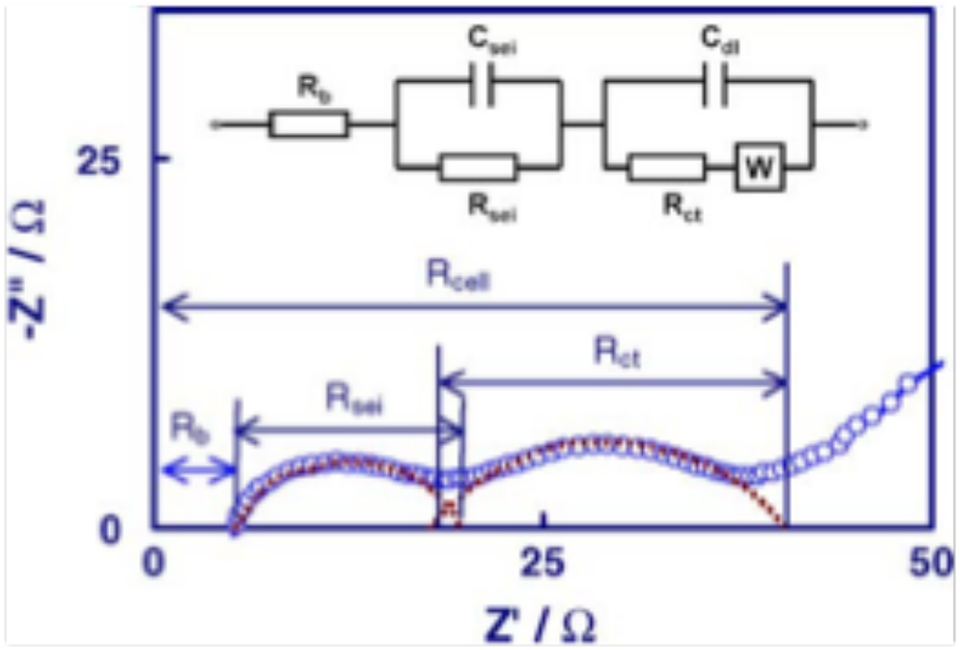
Solvation process of Li-ion





J. Haruyama, et. al., MO, J. Phys. Chem. C, 122, 9804(2018)

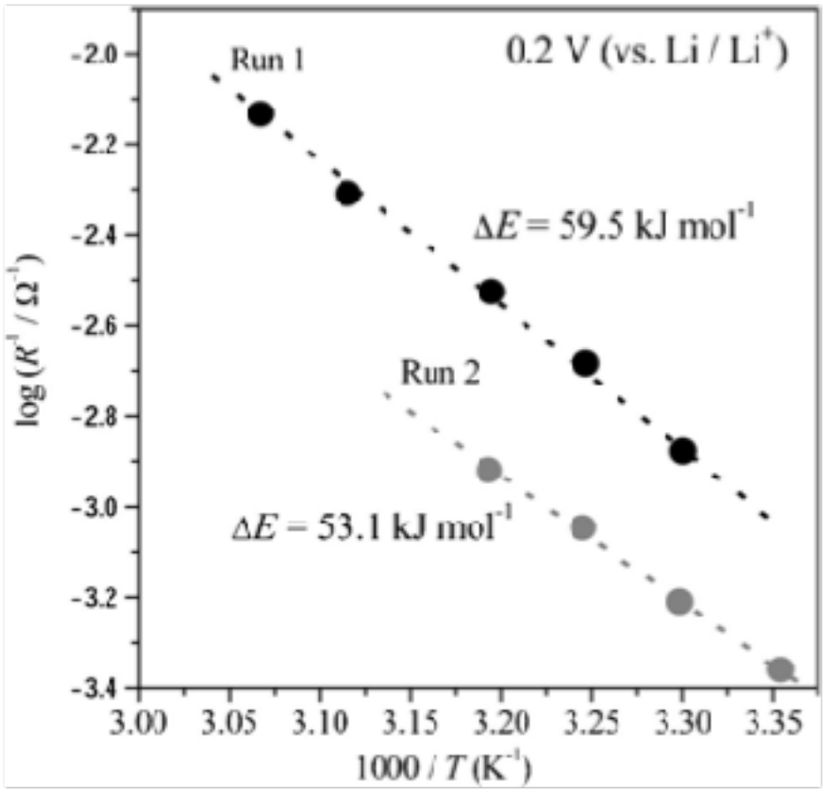
Electrochemical impedance spectroscopy (EIS) measurements



Typical EIS of Conventional LIB cell
LiCoO2|EC3:EMC7 LiPF6 1M|Graphite

In the fully charged and discharged states as well as at the low temperatures (≤20◦C), the R_{cell} of the Li-ion cells is predominated by the R_{ct}.

S. S. Zhang, K. Xu, and T. R. Jow, Electrochemica Acta **49**, 1057 (2004).



Temperature-dependence of R_{ct} @0.2 V *vs*. Li/Li+

The activation energies were evaluated to be around 50-60 kJ/mol (0.5-0.6 eV). These values are very large compared to lithium ion conduction in active materials.

T. Abe, H. Fukuda, Y. Iriyama, and Z. Ogumi, J. Electrochem. Soc. **151**, A1120 (2004).

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Total energy functional in conventional method

Total energy functional

$$E[\rho_{\mathrm{e}}] = T[\rho_{\mathrm{e}}] + E_{\mathrm{xc}}[\rho_{\mathrm{e}}] + \frac{1}{2}\iint \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \frac{\rho_{\mathrm{e}}(\boldsymbol{r})\rho_{\mathrm{e}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \int \mathrm{d}\boldsymbol{r} v_{\mathrm{ext}}(\boldsymbol{r})\rho_{\mathrm{e}}(\boldsymbol{r}) + E_{\mathrm{II}}$$

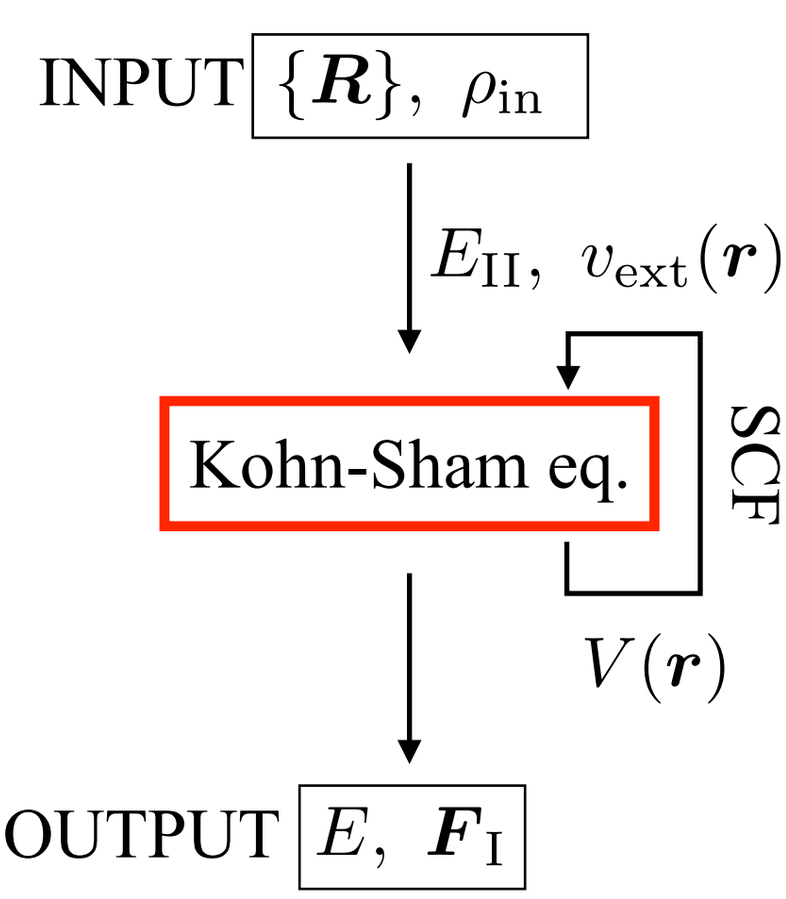
$\frac{\delta E}{\delta \rho_{\mathrm{e}}} = 0$ ↓ Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \hat{V}_{\mathrm{NL}} + V_{\mathrm{xc}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i \psi_i(\boldsymbol{r})$$

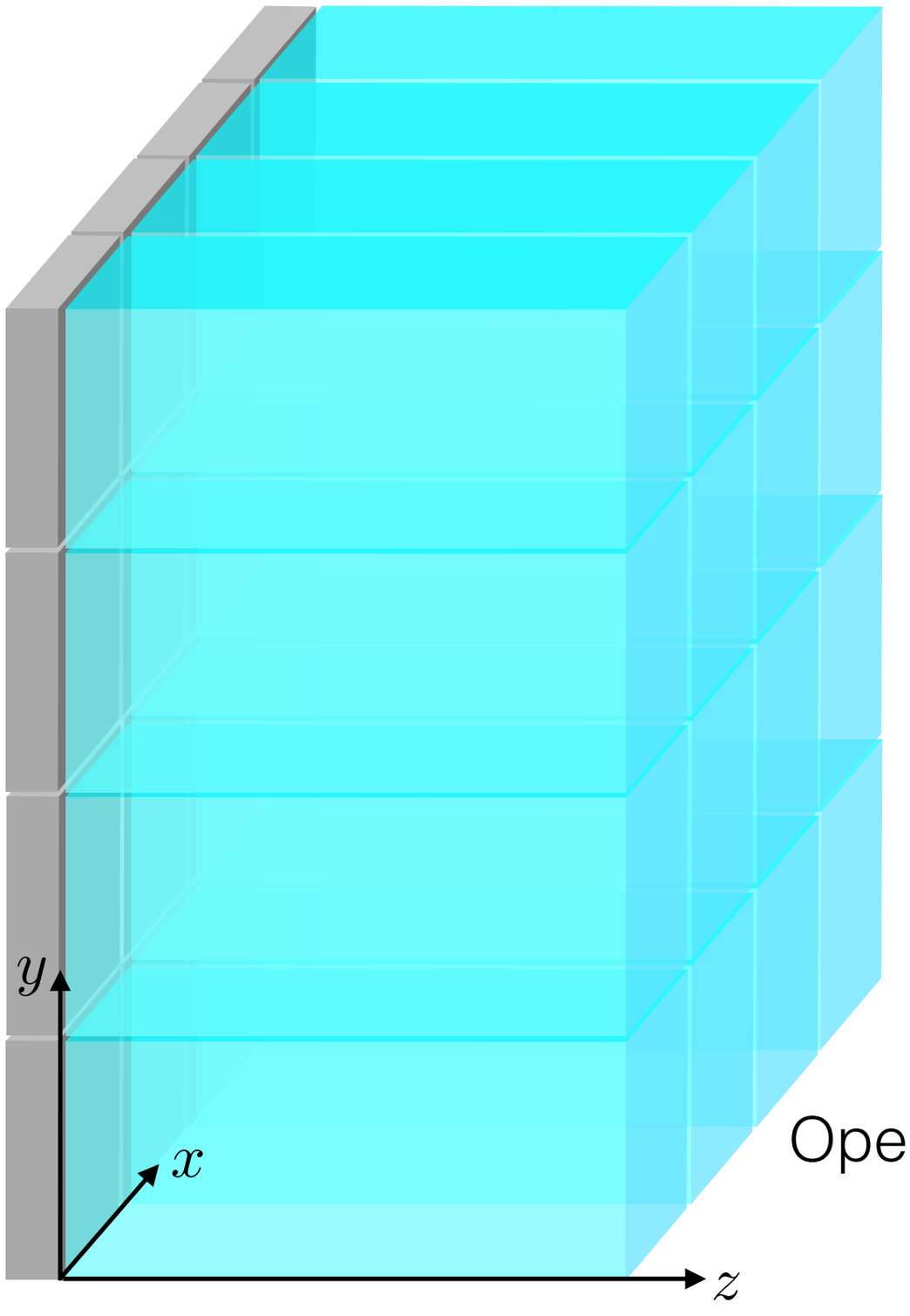
Poisson equation is solved with periodic boundary condition in advance and use the following expression

$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' \frac{\rho_{\mathrm{tot}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} = \int \mathrm{d}\boldsymbol{r}' G^{\mathrm{PBC}}(\boldsymbol{r},\boldsymbol{r}')\rho_{\mathrm{tot}}(\boldsymbol{r}')$$

Need to solve Poisson eq. with different BC.



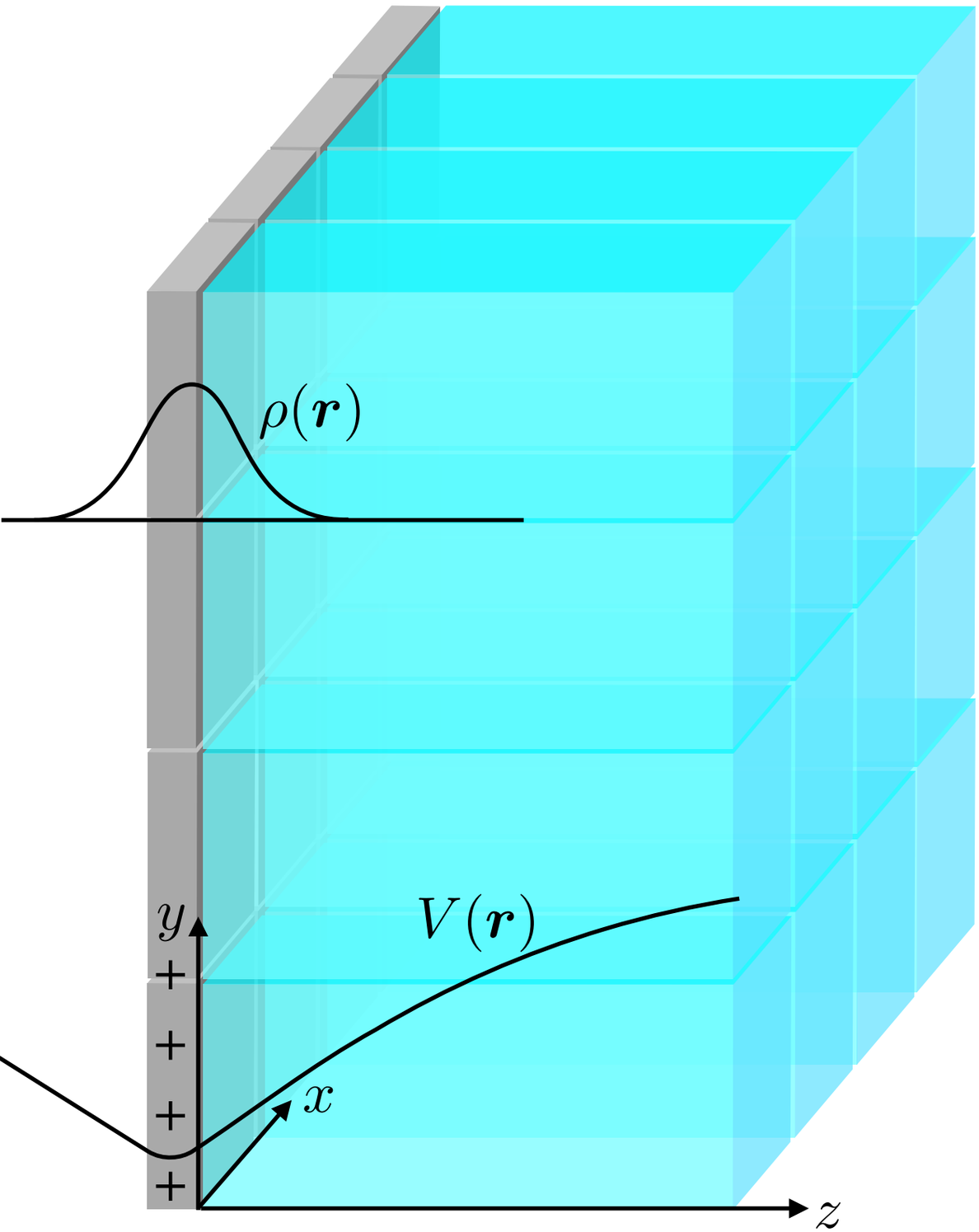
Boundary condition at the interface



2D periodic boundary condition (2D PBC)

Open boundary condition (OBC)

Boundary condition at the interface



- In the density functional theory (DFT), we need to solve two equations.

<u>Kohn-Sham equation</u>

$$\left[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \hat{V}_{\mathrm{NL}} + V_{\mathrm{xc}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

→3D PBC

<u>Poisson equation</u>

$$\nabla[\epsilon(\boldsymbol{r})\nabla]V(\boldsymbol{r}) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{r})$$

→2D PBC + OBC

↓

Mixed boundary condition (MBC)

Effective screening medium (ESM)

M.O. and O. Sugino, PRB 73, 115407 (2006)

How to solve the poisson equation under MBC?

$$\nabla[\epsilon(\boldsymbol{r})\nabla]V(\boldsymbol{r}) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{r})$$

Laue representation

$$[\partial_z\{\epsilon(z)\partial\} - \epsilon(z)g_{||}^2]V(\boldsymbol{g}_{||}, z) = -4\pi\rho(\boldsymbol{g}_{||}, z)$$

$$[\partial_z\{\epsilon(z)\partial\} - \epsilon(z)g_{||}^2]G(\boldsymbol{g}_{||}, z, z') = -4\pi\delta(\boldsymbol{g}_{||}, z - z')$$

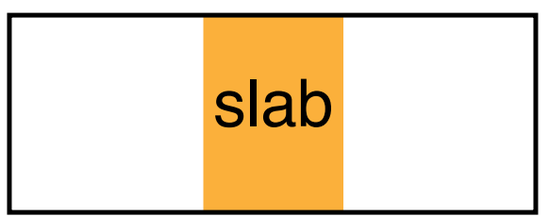
We can get Green's function analytically with each boundary conditions.

Effective screening medium (ESM)

M.O. and O. Sugino, PRB 73, 115407 (2006)

(i)

$$\partial_z V(g_\parallel, z)\big|_{z=\pm\infty} = 0, \quad \epsilon(z) = 1$$

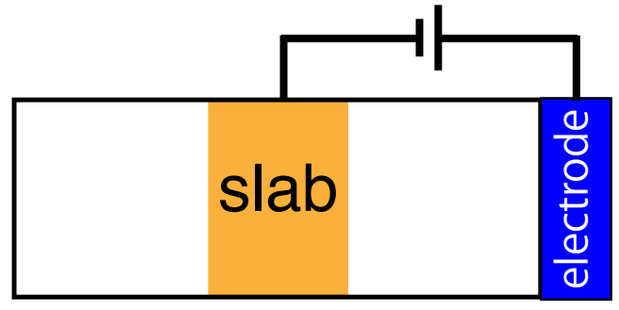


neutral surface, polarized surface...

(ii)

$$\begin{cases} V(g_\parallel, z_1) = 0 \\ \partial_z V(g_\parallel, z)\big|_{z=-\infty} = 0 \end{cases}$$

$$\epsilon(z) = \begin{cases} 1 & \text{if} \quad z \geq z_1 \\ \infty & \text{if} \quad z \leq z_1 \end{cases}$$

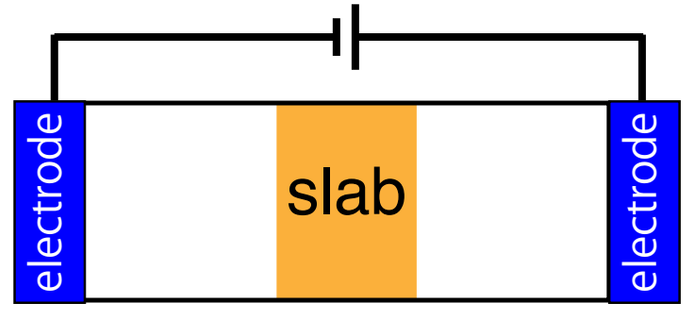


STM, gate electrode...

(iii)

$$\begin{cases} V(g_\parallel, z_1) = 0 \\ V(g_\parallel, -z_1) = V_0 \end{cases}$$

$$\epsilon(z) = \infty \quad \text{if} \quad |z| \geq z_1$$

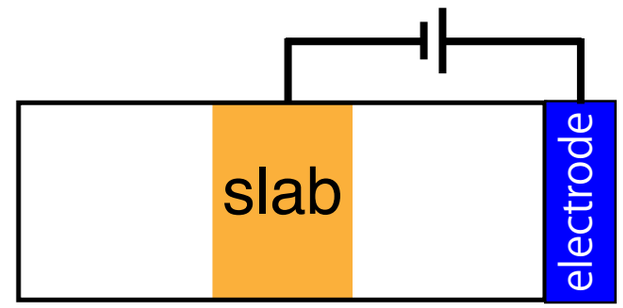


nano-structure in capacitor, zigzag pot.

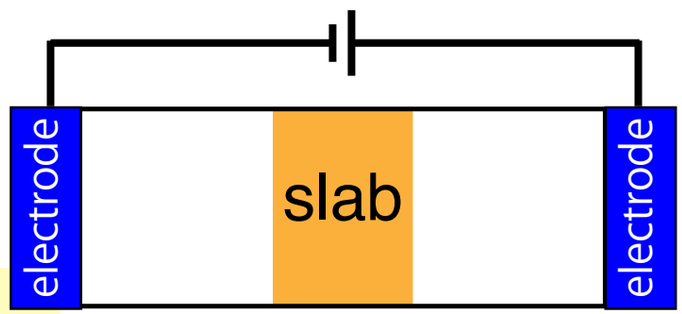
Effective screening medium (ESM)

M.O. and O. Sugino, PRB 73, 115407 (2006)

$$G^{(\mathrm{i})}(g_\parallel, z, z') = \frac{4\pi}{2g_\parallel}\mathrm{e}^{-g_\parallel|z-z'|}$$



$$G^{(\mathrm{ii})}(g_\parallel, z, z') = \frac{4\pi}{2g_\parallel}\mathrm{e}^{-g_\parallel|z-z'|} - \frac{4\pi}{2g_\parallel}\mathrm{e}^{-g_\parallel(2z_1-z-z')}$$



$$G^{(\mathrm{iii})}(g_\parallel, z, z') = \frac{4\pi}{2g_\parallel}\mathrm{e}^{-g_\parallel|z-z'|} + \frac{4\pi}{2g_\parallel}\frac{\mathrm{e}^{-2g_\parallel z_1}\cosh\{g_\parallel(z-z')\} - \cosh\{g_\parallel(z+z')\}}{\sinh(2g_\parallel z_1)}$$

Total energy functional of the ESM method

Total energy functional

$$E[\rho] = T[\rho] + E_{\mathrm{xc}}[\rho] + \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \int d\boldsymbol{r}v_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r}) + E_{\mathrm{ion}}$$

V ➠ variable

$$E[\rho_{\mathrm{e}}, V] = T[\rho_{\mathrm{e}}] + E_{\mathrm{xc}}[\rho_{\mathrm{e}}] + \int d\boldsymbol{r}\left[+\frac{\epsilon(\boldsymbol{r})}{8\pi}|\nabla V(\boldsymbol{r})|^2 + \rho_{\mathrm{tot}}(\boldsymbol{r})V(\boldsymbol{r})\right]$$

$\frac{\delta E}{\delta V} = 0$ → Generalized Poisson equation

$$\nabla[\epsilon(\boldsymbol{r})\nabla]V(\boldsymbol{r}) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{r})$$

conventional

$$\epsilon(\boldsymbol{r}) = 1$$

$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}\frac{\rho_{\mathrm{tot}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

ESM

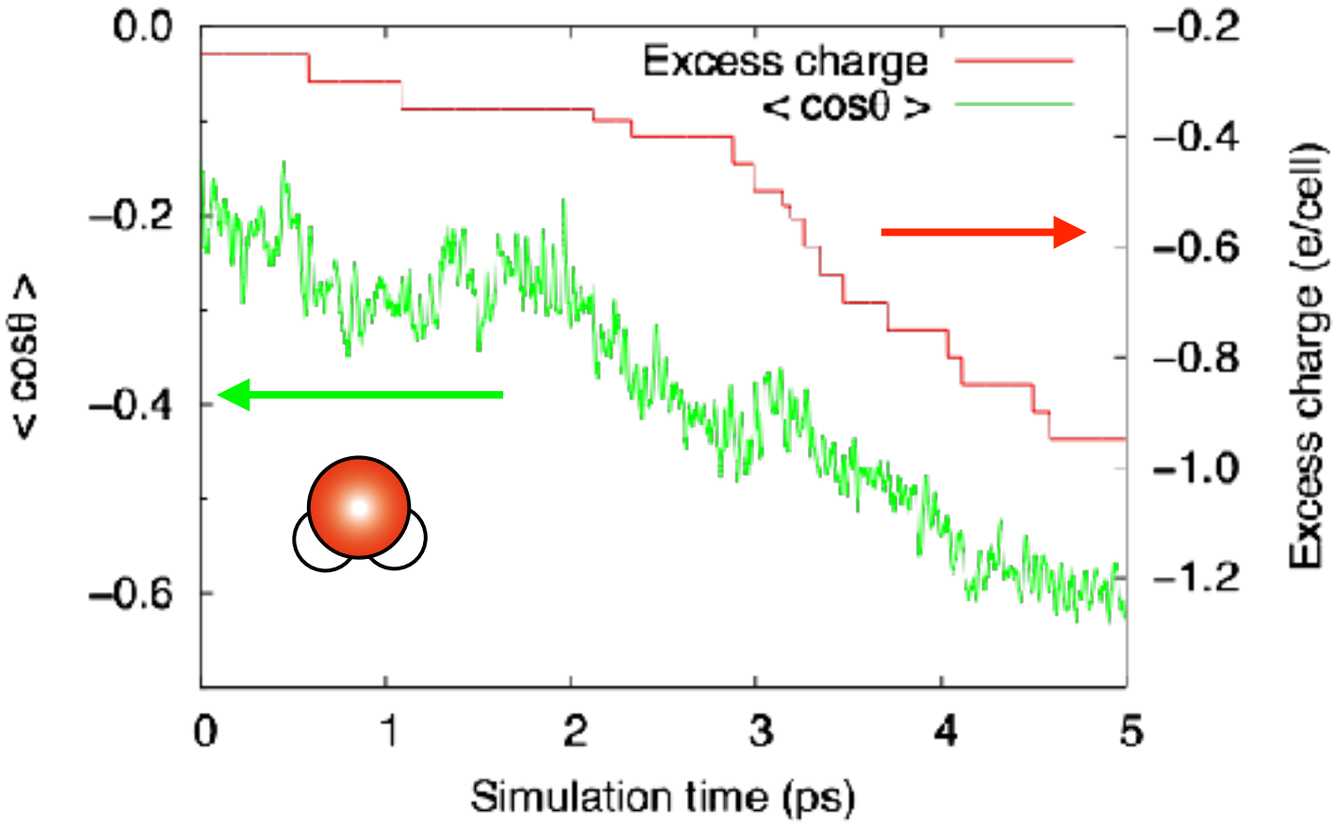
$\epsilon(\boldsymbol{r})$: **model dependent**

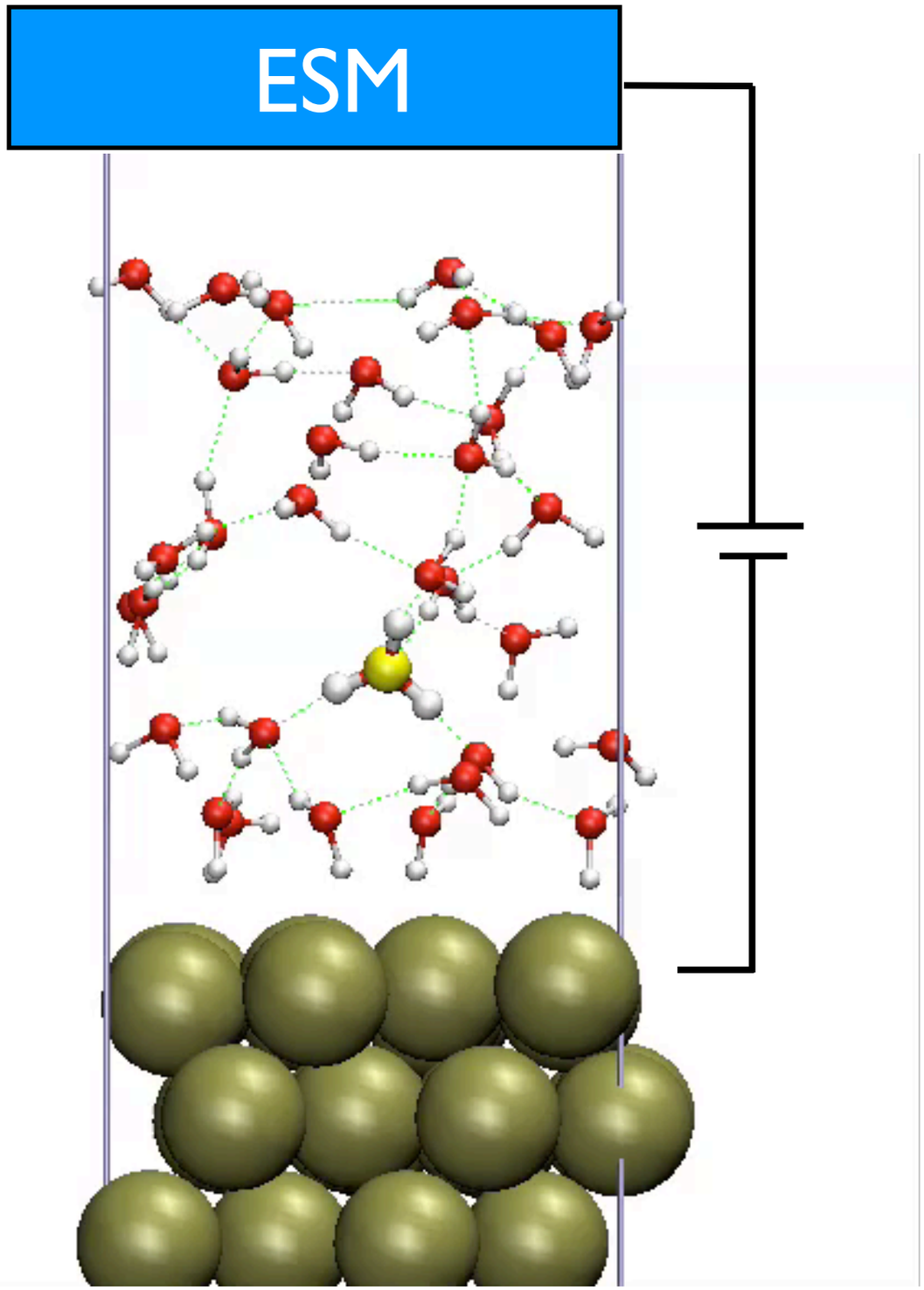
$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}G(\boldsymbol{r},\boldsymbol{r}')\rho_{\mathrm{tot}}(\boldsymbol{r}')$$

$\frac{\delta E}{\delta \rho_{\mathrm{e}}} = 0$ → Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \hat{V}_{\mathrm{NL}} + V_{\mathrm{xc}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

Schematic animation of electrochemical interface simulation



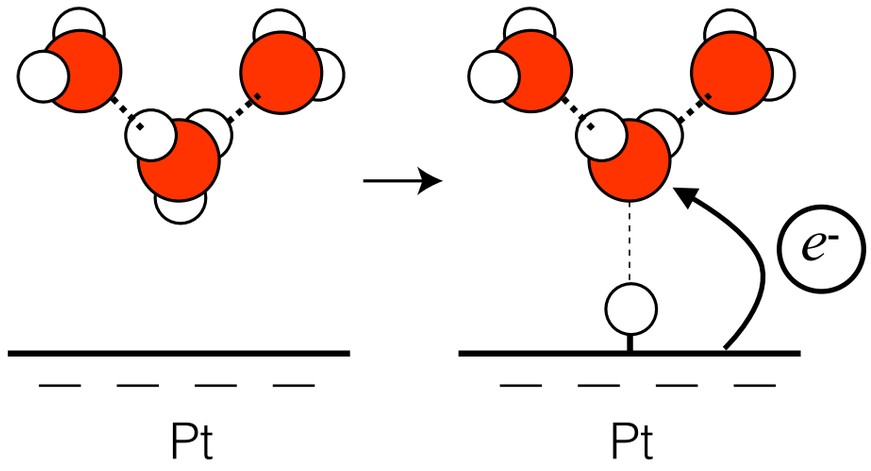


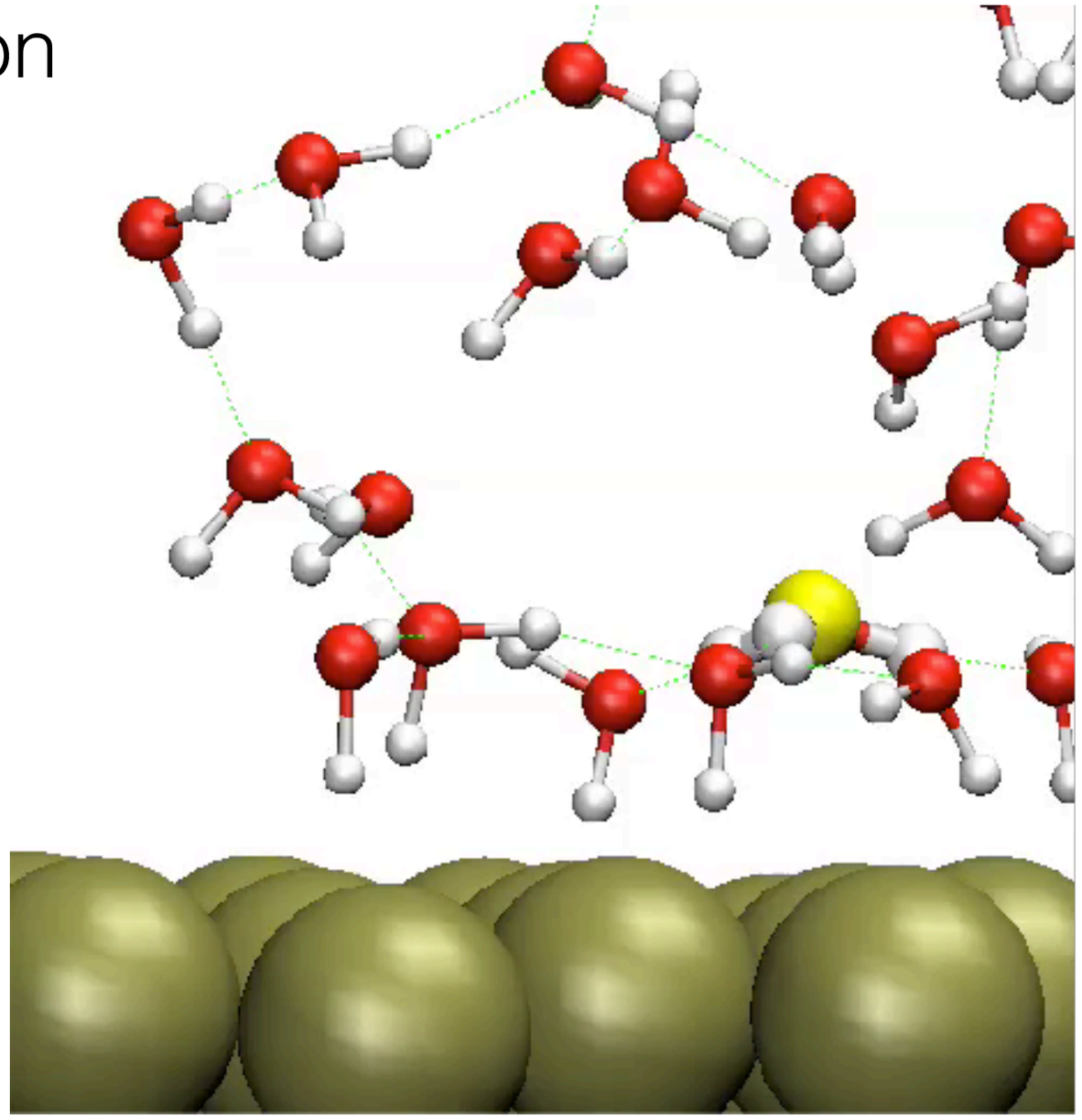
J. Phys. Soc. Jpn **77**, 024802 (2008)

Electrochemical reaction

Hydrogen adsorption reaction

$$\mathrm{H_3O^+} + e^- \rightarrow \mathrm{H_2O} + \mathrm{H_{ad}}$$





J. Phys. Soc. Jpn **77**, 024802 (2008)

Q=-0.95 (e/cell)

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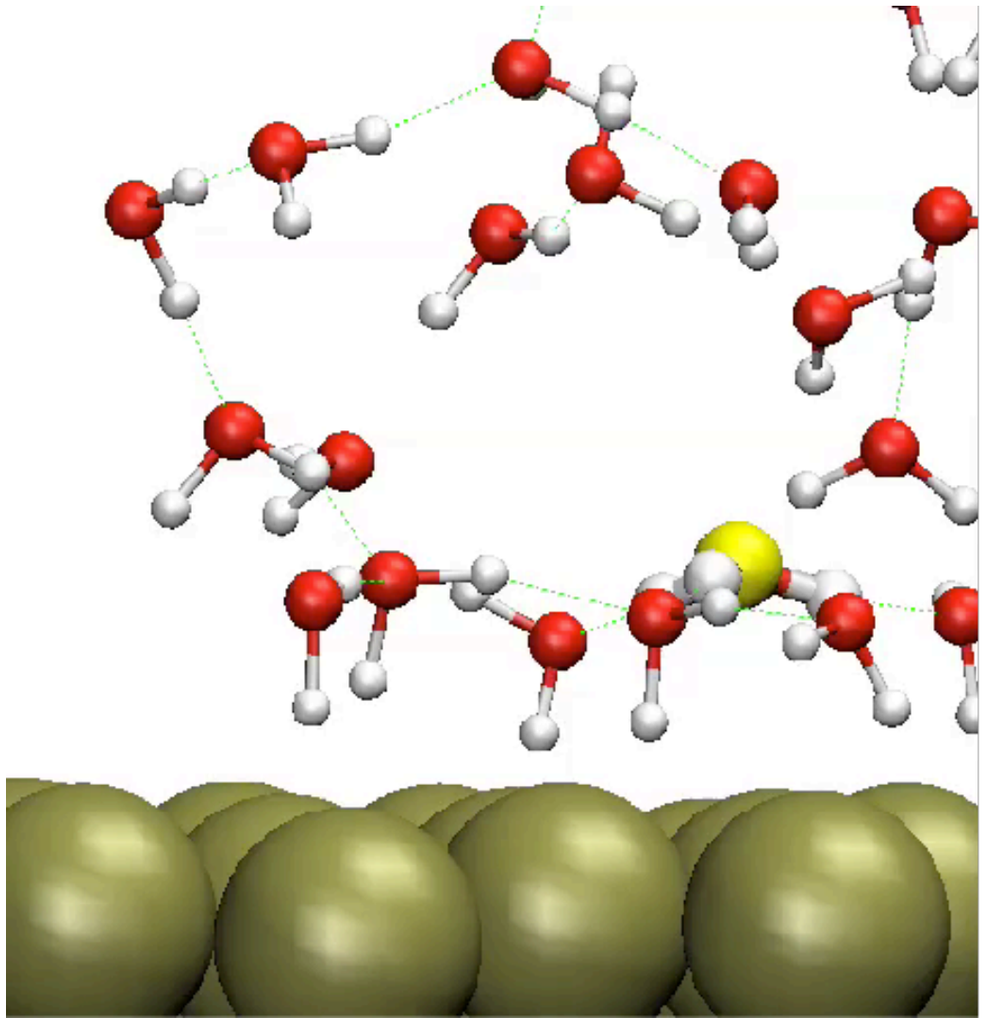
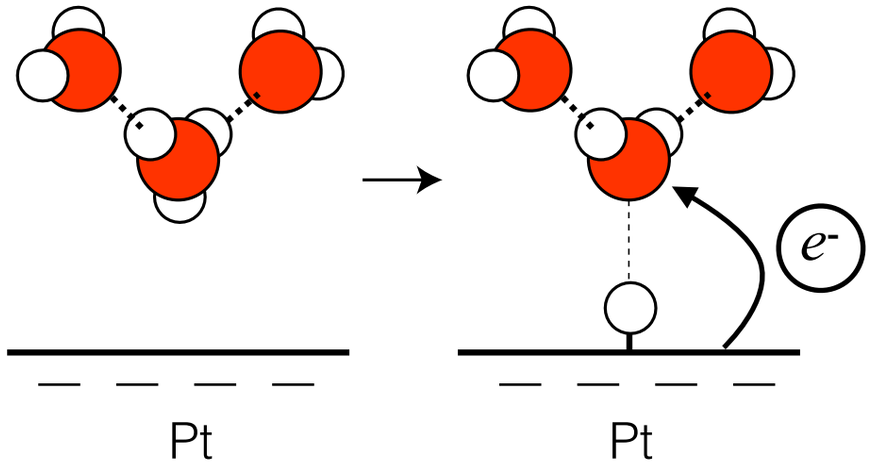
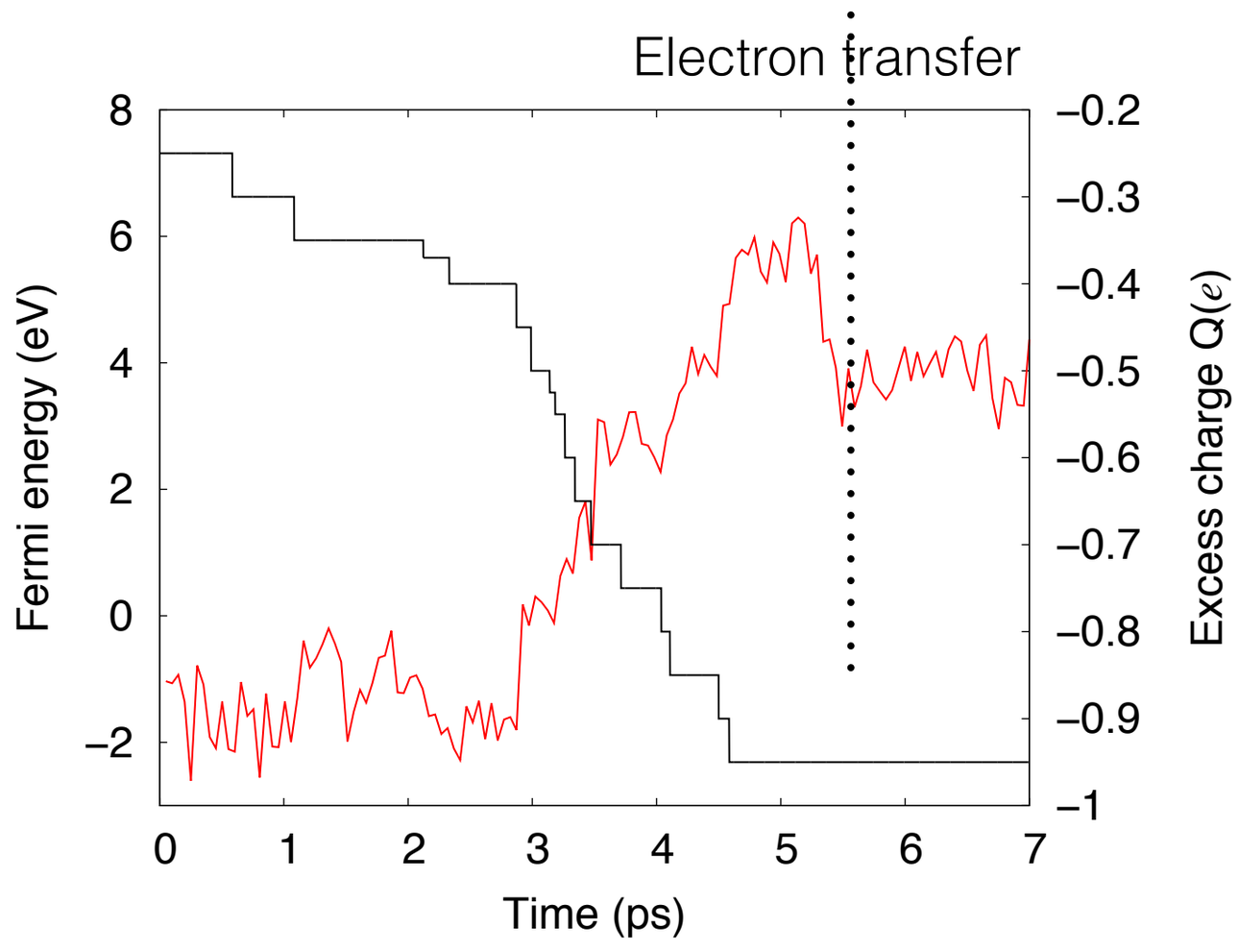
Why we need a bias control?

Hydrogen adsorption reaction

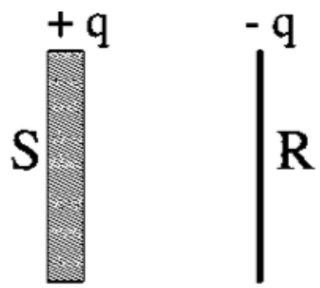
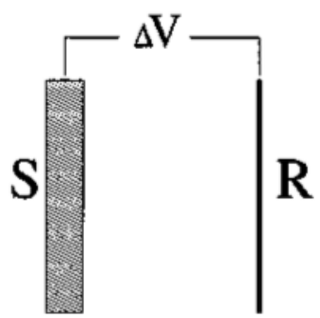


Q=-0.95 (e/cell)



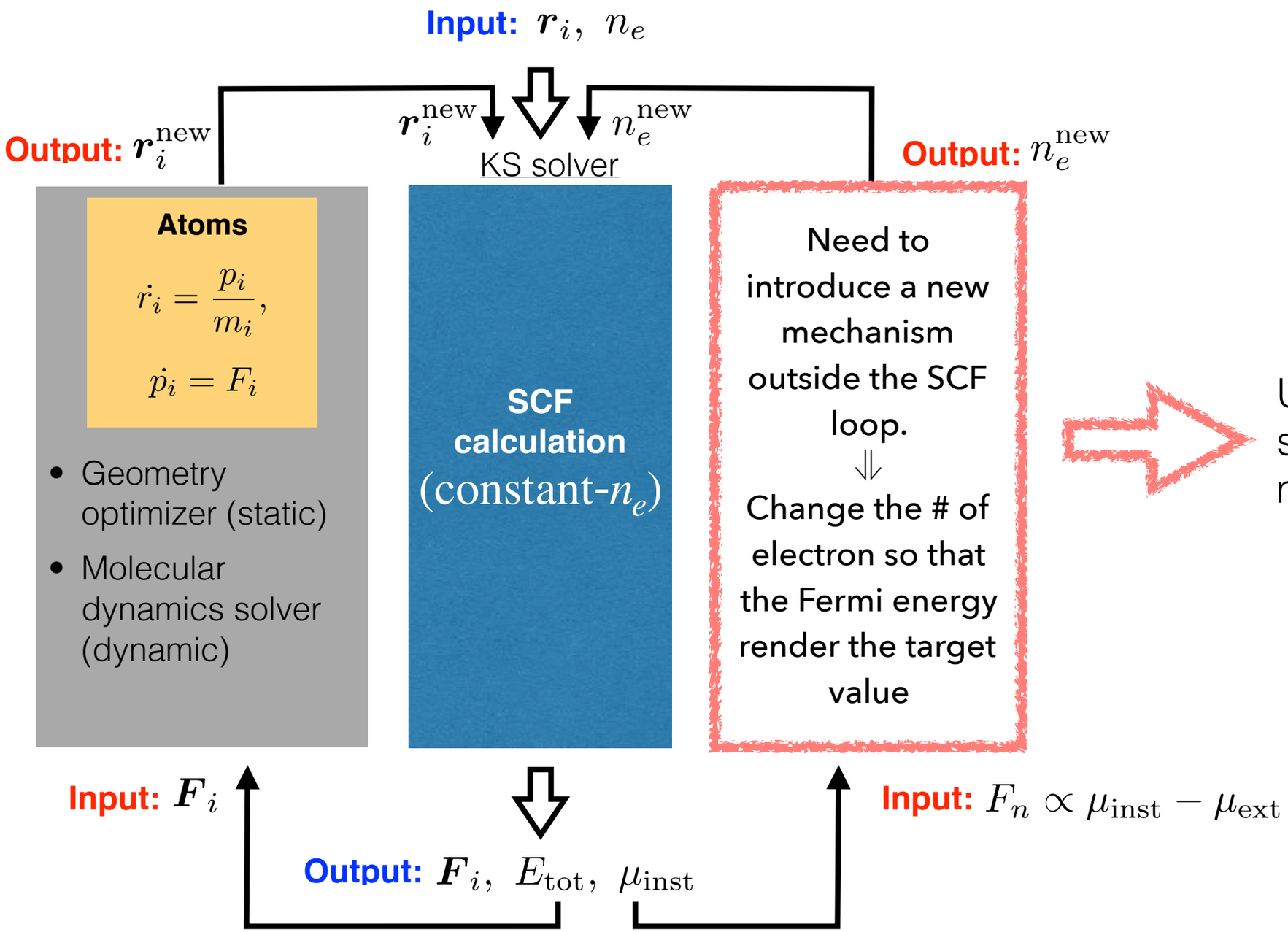


Limitation of the original conventional DFT-MD

Mode	Scheme	Thermodynamic potential	Experimental realization	
$N_e = \text{const}$		$F(T, V, N_e)$	Isolated capacitor	conventional simulation
$\mu = \text{const}$		$\Omega(T, V, \mu)$	Electrochemistry (STM)	experimental simulation

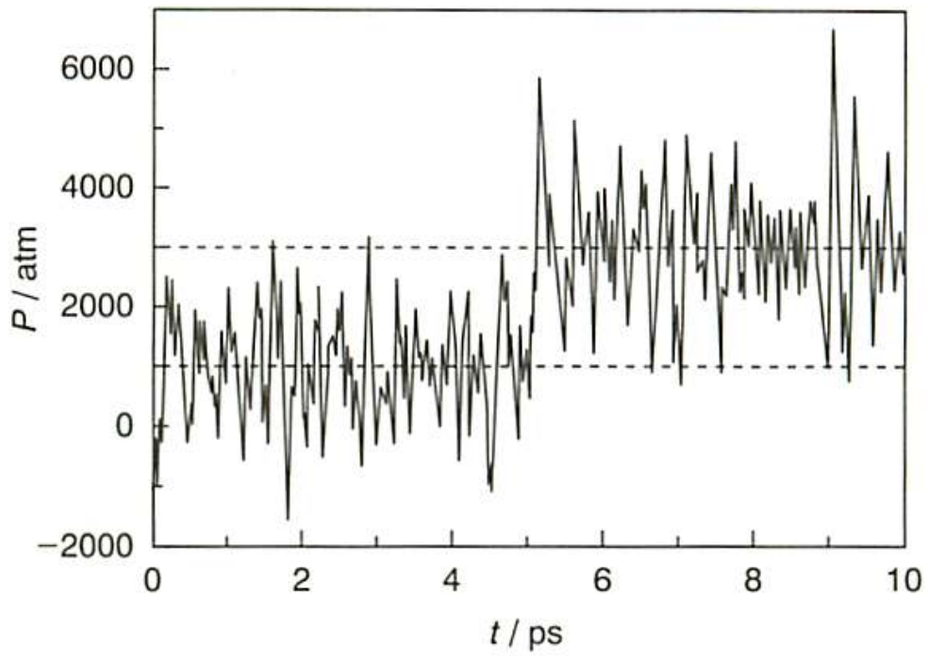
A. Lozovoi et al., JCP 115, 1661 (2001)

How to realize constant-μ_e system



Grand canonical ensemble in electronic system

Conventional NPT MD simulation



v_{cell} : Cell volume

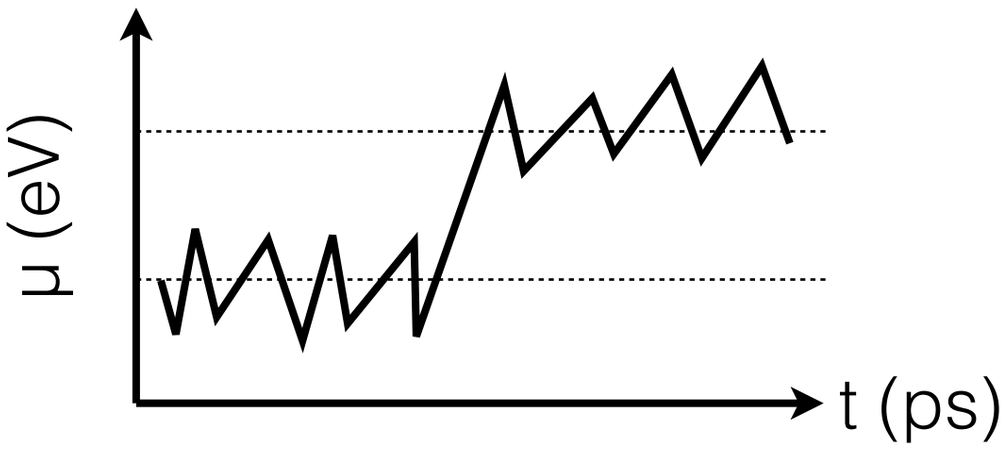
$M_{v_{\mathrm{cell}}}$: Fictitious mass for variable cell

$$\dot{v}_{\mathrm{cell}} = \frac{P_{v_{\mathrm{cell}}}}{M_{v_{\mathrm{cell}}}}$$

$$\dot{P}_{v_{\mathrm{cell}}} = P - P_{\mathrm{ext}}$$

from Virial theorem

If we can introduce a fictitious motion for amount of charge n_e, we can realize NVTμe MD simulation

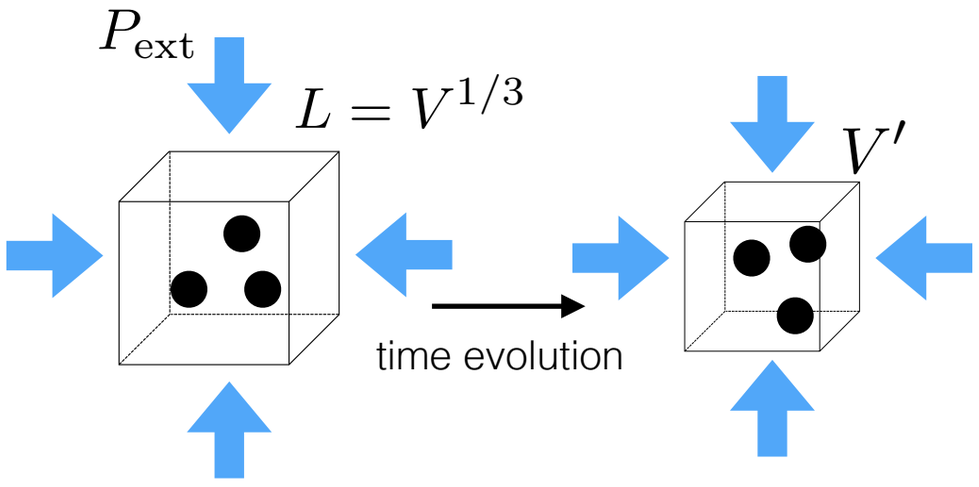


$$\dot{n}_{\mathrm{cell}} = \frac{P_{n_{\mathrm{cell}}}}{M_{n_{\mathrm{cell}}}}$$

$$\dot{P}_{n_{\mathrm{cell}}} = \mu - \mu_{\mathrm{ext}}$$

Constant pressure MD (Andersen method)

H. C. Andersen, J. Chem. Phys. 72, 2384 (1980)



- Consider the volume as a dynamics variable
- Replace the coordinates $\boldsymbol{r}_i$ by scaled coordinates $\tilde{\boldsymbol{r}}_i$,

$$\boldsymbol{r}_i = V^{\frac{1}{3}}\tilde{\boldsymbol{r}}_i, \quad (0 \leq \tilde{r}_i \leq 1)$$

and the time derivative of $\tilde{\boldsymbol{r}}_i$ is defined as

$$\dot{\boldsymbol{r}}_i = V^{\frac{1}{3}}\dot{\tilde{\boldsymbol{r}}}_i$$

Lagrangian for extended system

$$L_P = \frac{1}{2}\sum_i^N m_i V^{\frac{2}{3}}\dot{\tilde{\boldsymbol{r}}}_i^2 - E(\{V^{\frac{1}{3}}\tilde{\boldsymbol{r}}\};\psi) + \frac{1}{2}W\dot{V}^2 - P_{\text{ext}}V$$

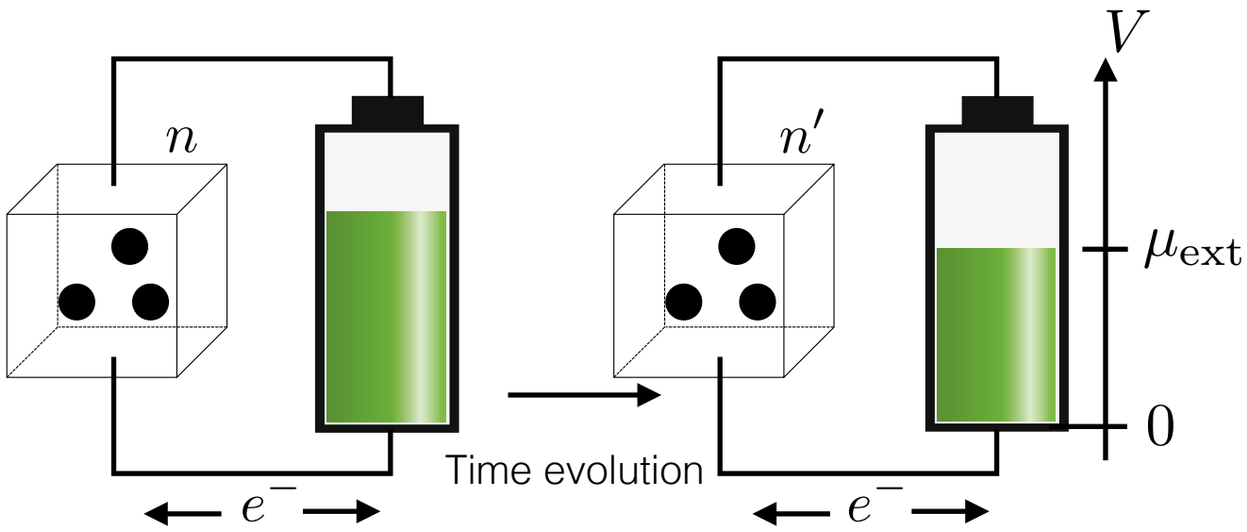
where, W is the fictitious mass of the cell. The Euler-Lagrange equation becomes

$$\begin{cases} m_i\ddot{\tilde{\boldsymbol{r}}}_i = -V^{-\frac{2}{3}}\dfrac{\partial E(\{V^{\frac{1}{3}}\tilde{\boldsymbol{r}}\};\psi)}{\partial\tilde{\boldsymbol{r}}_i} - \dfrac{2\dot{V}}{3V}\dot{\tilde{\boldsymbol{r}}} \\ W\ddot{V} = \dfrac{1}{3V}\left[\displaystyle\sum_i^N m_i V^{\frac{2}{3}}\dot{\tilde{\boldsymbol{r}}}_i^2 - \sum_i^N \boldsymbol{r}_i\cdot\frac{\partial E(\{\boldsymbol{r}\};\psi)}{\partial\boldsymbol{r}_i}\right] - P_{\text{ext}} \end{cases}$$

Instantaneous pressure (Virial theorem)

Constant-μ MD

N. Bonnet et al., Phys. Rev. Lett. 109, 266101 (2012)



- Consider FCP as a dynamical variable
- Connecting the system to a potentiostat to keep the Fermi energy of the system as target Fermi energy μ_{ext}.

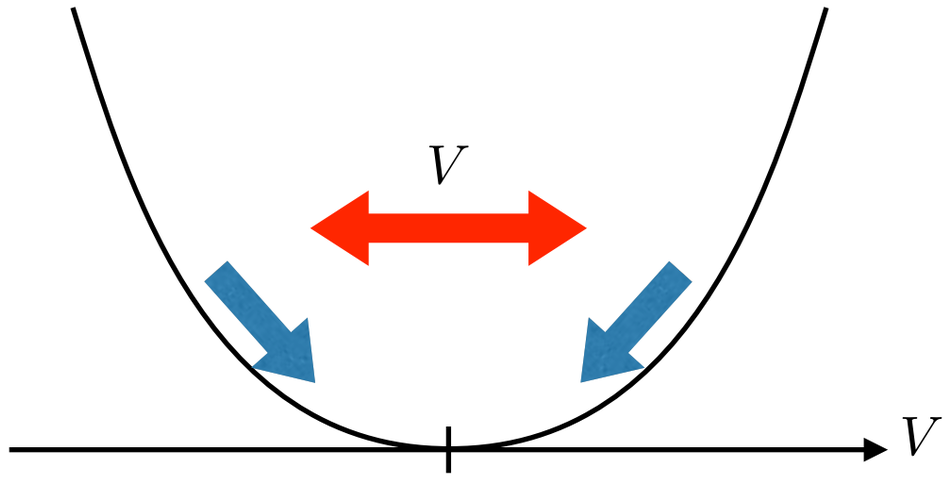
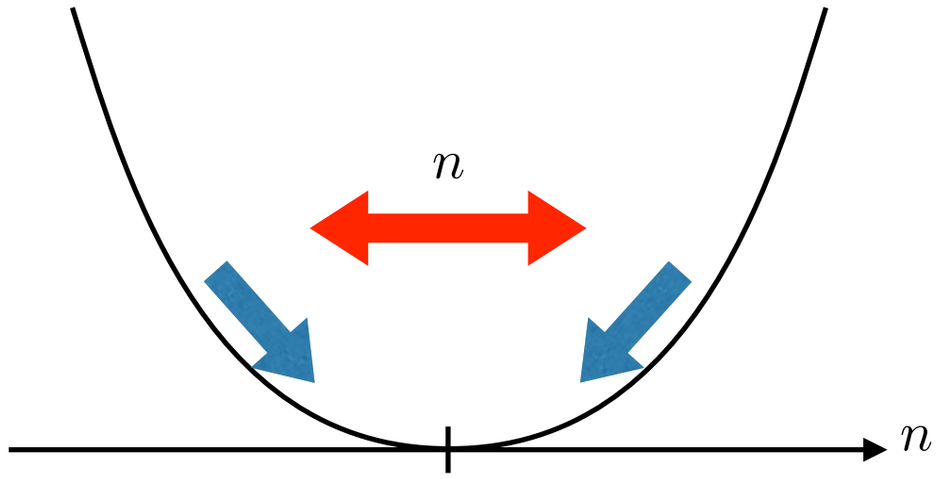
Lagrangian for extended system

$$L_\mu = \frac{1}{2}\sum_i^N m_i \dot{\boldsymbol{r}}_i^2 - E(\{\boldsymbol{r}\};\psi) + \frac{1}{2}M\dot{n}^2 - (-\mu_{\mathrm{ext}} n)$$

where, M is the fictitious mass of FCP. The Euler-Lagrange equation becomes

$$\begin{cases} m_i \ddot{\boldsymbol{r}}_i = -\dfrac{\partial E(\{\boldsymbol{r}_i\};\psi)}{\partial \boldsymbol{r}_i} \\ M\ddot{n} = -\left(\dfrac{\partial E(\{\boldsymbol{r}_i\};\psi)}{\partial n} - \mu_{\mathrm{ext}}\right) \end{cases}$$

Instantaneous Fermi energy

	Constant pressure	Constant chemical potential
		
Extensive var.	$-\delta V$ V_0 δV	$-\delta n$ n_0 δn
Intensive var.	$P_{\rm in} > P_{\rm ext}$ $P_{\rm in} = P_{\rm ext}$ $P_{\rm in} < P_{\rm ext}$	$\mu_{\rm in} < \mu_{\rm ext}$ $\mu_{\rm in} = \mu_{\rm ext}$ $\mu_{\rm in} > \mu_{\rm ext}$
Mean value	$P_{\rm ext} = \langle P_{\rm in} \rangle$	$\mu_{\rm ext} = \langle \mu_{\rm in} \rangle$
Linearization at equilibrium	$W\ddot{V} = P_{\rm in} - P_{\rm ext}$ $\to W\delta\ddot{V} \simeq -\frac{B}{V_0}\delta V$	$M\ddot{n} = \mu_{\rm in} - \mu_{\rm ext}$ $\to M\delta\ddot{n} \simeq -\frac{1}{C}\delta n$

Restoring force yields the oscillation around the bottom

Bulk modulus: $B = -V_0 \dfrac{\partial P}{\partial V}$

Capacitance: $\dfrac{1}{C} = \dfrac{\partial \mu}{\partial n}$

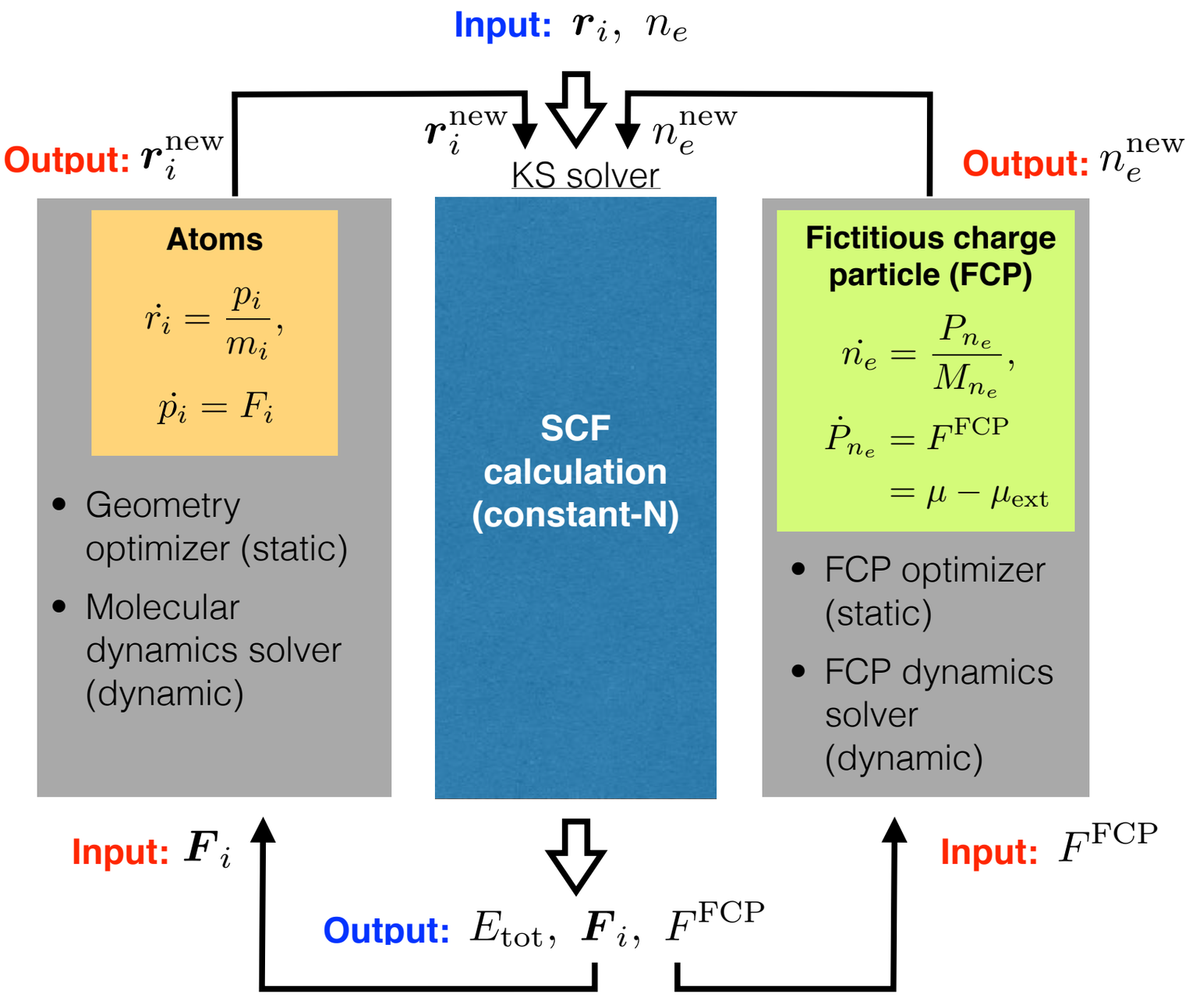
Statistical ensemble

By connecting an appropriate thermostat, e.g. Nosé thermostat, scaling method…, we can realize an isobaric and grand canonical ensembles.

	Isobaric	**Grand canonical (for electron)**
Partition function	$Y = \iiint \exp\left[-(\mathcal{H} + P_{\mathrm{ext}}V)/k_BT\right] \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{q}\mathrm{d}V$ $\mathcal{H} = \frac{1}{2}\sum_i^N m_i \boldsymbol{r}_i^2 + E(\{\boldsymbol{r}\};\psi)$	$\Xi_\mu = \iiint \exp\left[-(\mathcal{H} - \mu_{\mathrm{ext}}n)/k_BT\right] \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{q}\mathrm{d}n$ $\mathcal{H} = \frac{1}{2}\sum_i^N m_i \boldsymbol{r}_i^2 + E(\{\boldsymbol{r}\};\psi)$
Fluctuation of extensive variable	Compressibility $\kappa = -\frac{1}{\langle V\rangle}\frac{\partial\langle V\rangle}{\partial P_{\mathrm{ext}}} = \frac{\langle \delta V^2\rangle}{k_BT\langle V\rangle}$	Capacitance $C = \frac{\partial\langle n\rangle}{\partial \mu_{\mathrm{ext}}} = \frac{\langle \delta n^2\rangle}{k_BT}$

Johnson-Nyquist noise

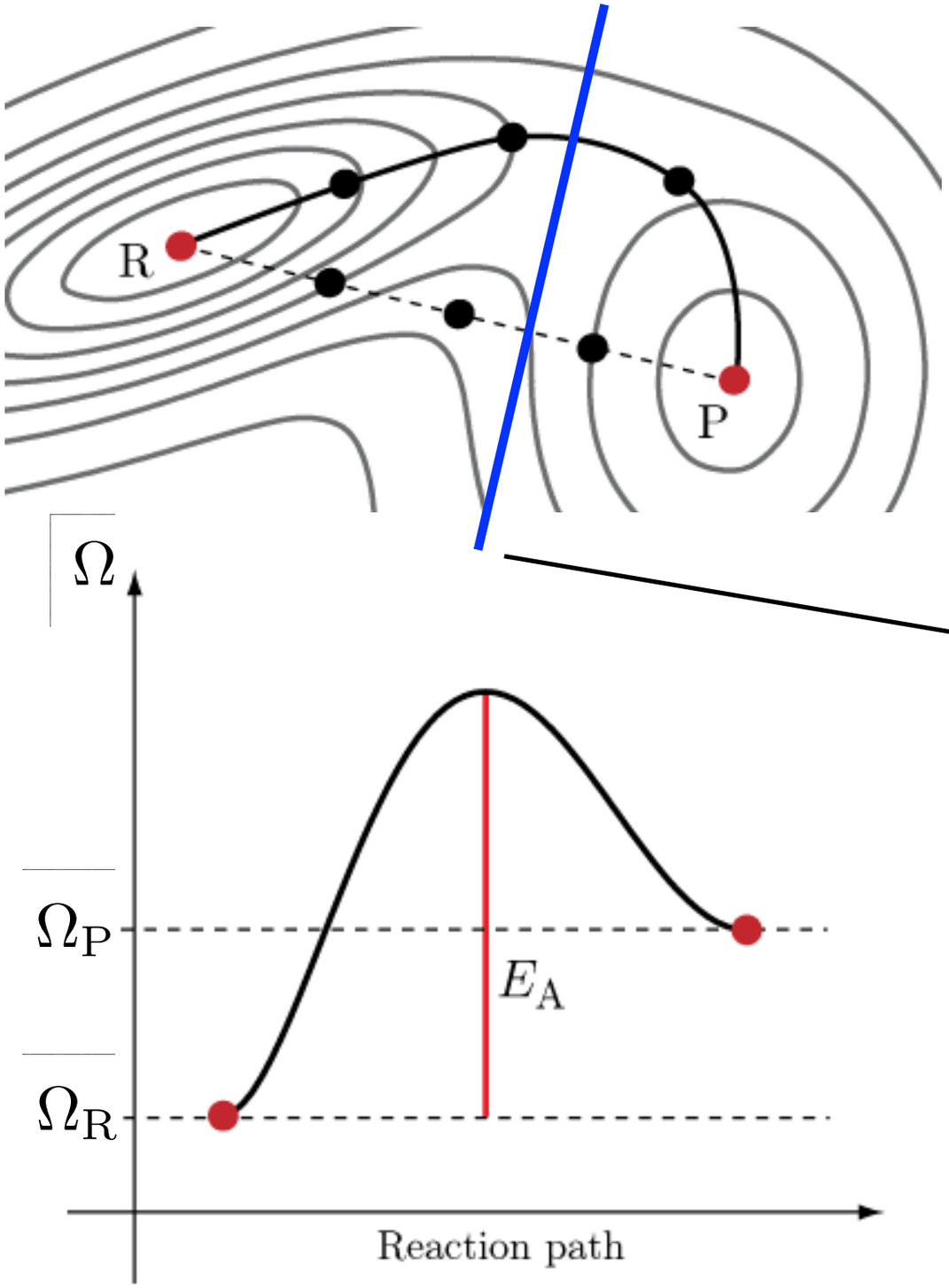
How to realize constant-μ system



- Fictitious charge particle (FCP) is introduced with fictitious mass.
- For static calculation, FCP is optimized by line minimization scheme. We can obtain the grand potential.
- For MD simulation, FCP is evolved by equation of motion for FCP. We can obtain the grand canonical ensemble.
- FCP is updated at each atomic step. (e.g., Geometry optimization step, MD step)

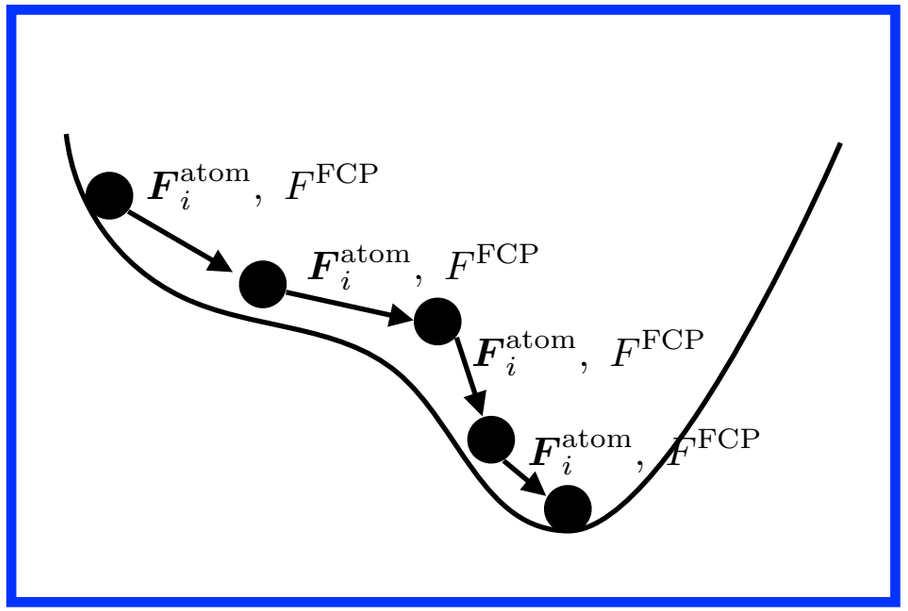
Phys. Rev. Lett. **109**, 266101 (2012)

NEB method in Ω-space



Searching the minimum energy path (MEP) using NEB with constant-μ

Constrained geometry optimisation on hyperplane in $\tilde{E}$-space



FCP is also updated at each atomic step.
⇒no additional calculation cost

Generalized force acting on atoms & FCP

Minimize Ω instead of the total energy E

$$\Omega = E - \mu_{\mathrm{ext}} n$$

$\tilde{E}$ includes the potential $\mu_{\mathrm{ext}} n$ derived from an external potentiostat.
Force acting on atoms

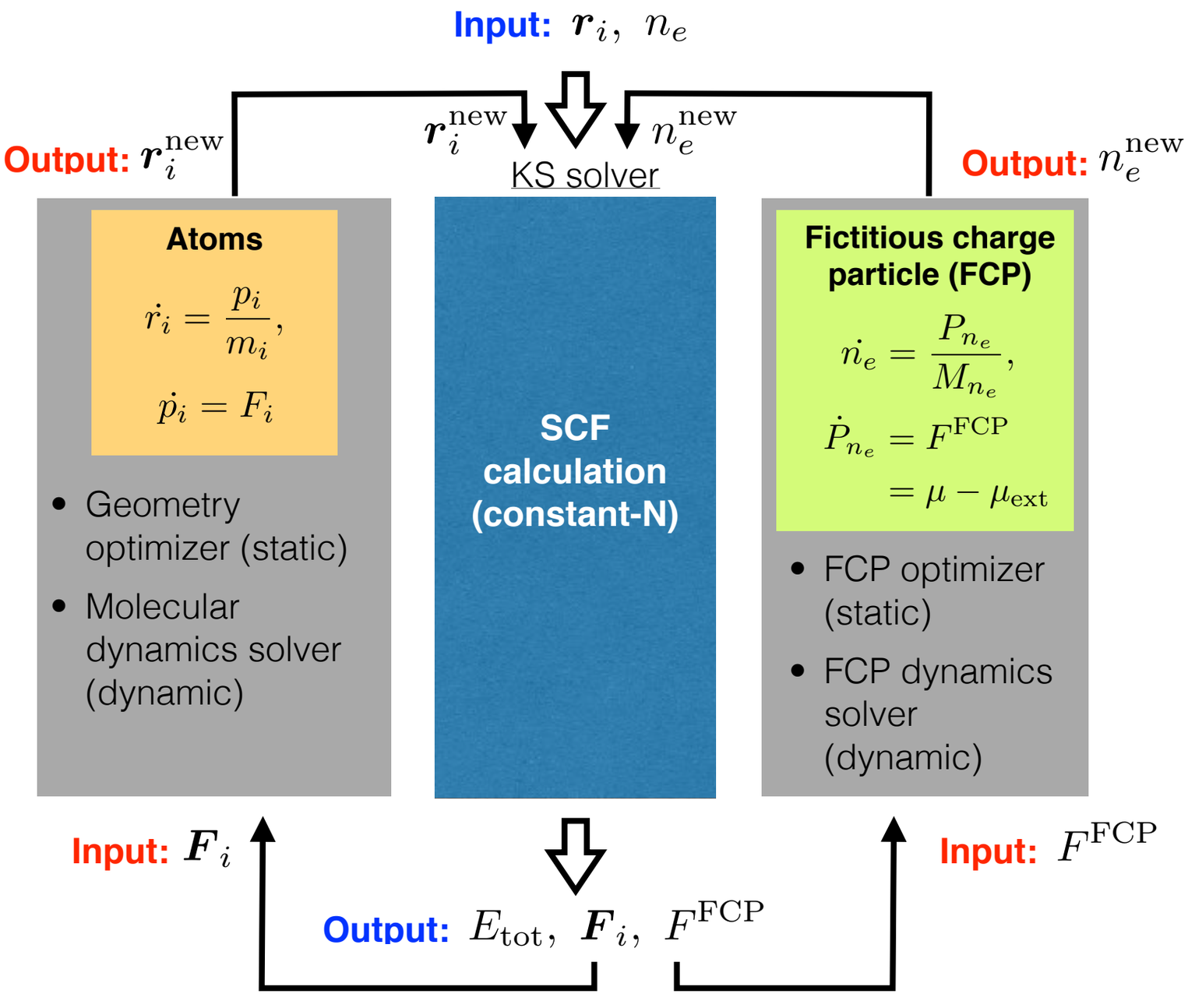
$$\boldsymbol{F}_i = -\frac{\partial \Omega}{\partial \boldsymbol{r}_i} = -\frac{\partial E}{\partial \boldsymbol{r}_i}$$

Force acting on FCP

$$F^{\mathrm{FCP}} = -\frac{\partial \Omega}{\partial n} = -(\mu - \mu_{\mathrm{ext}})$$

We need to consider the generalized force acting on atoms & FCP to optimize the geometry and μ.

How to realize constant-μ system



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Phys. Rev. Lett. **109**, 266101 (2012)

Test calculation (Pt-H_2O interface)

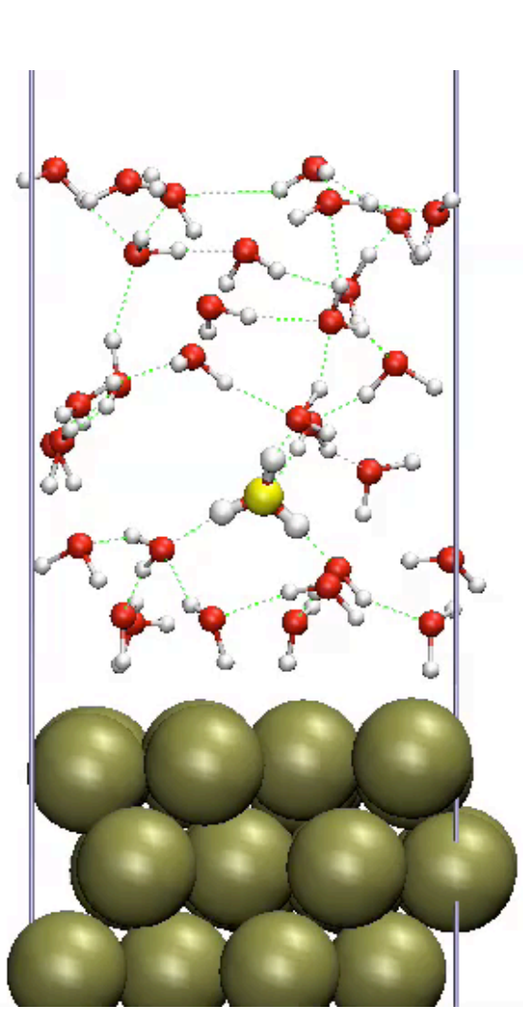
constant-N

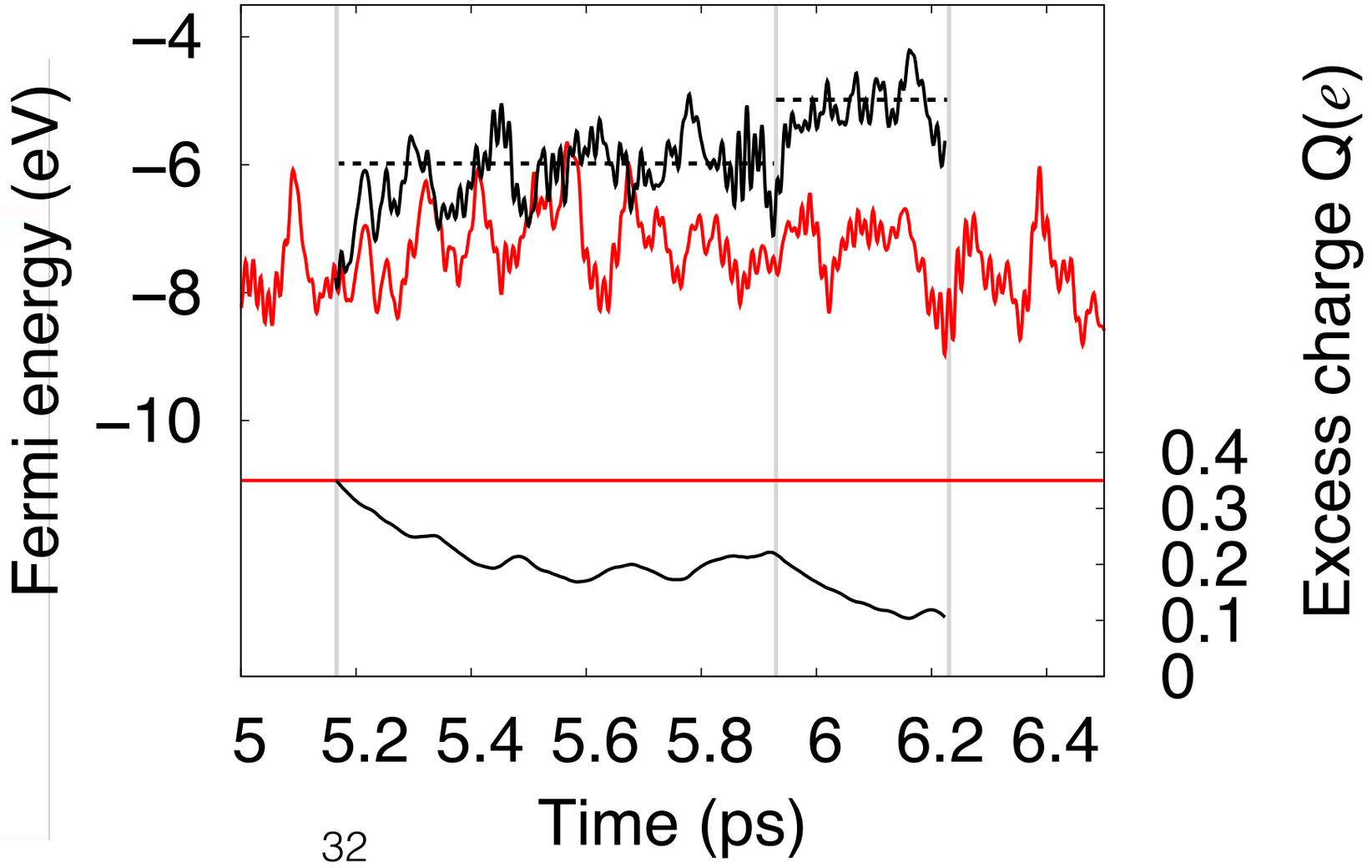
$T_{\mathrm{atom}} = 353$ K
$Q = 0.35$ (e/cell)

constant-μ

$\mu_{\mathrm{ext}} = -6.0$ eV
$T = 300$ K
$M_{n_e} = 300$ cm^{-1}
$M_{\xi_e} = 100$ cm^{-1}

$\mu_{\mathrm{ext}} = -4.9$ eV
$T = 300$ K
$M_{n_e} = 300$ cm^{-1}
$M_{\xi_e} = 100$ cm^{-1}





Outline

- Introduction
- Simulation platform for electrochemical interface
  - Effective screening medium (ESM) method
  - Constant bias potential (constant-μ_e) method
  - Hybrid simulation method: DFT+liquid theory (ESM-RISM)
- Applications
  - Lithium Insertion/Desorption Reaction in Li-ion battery
- Summary
- Appendix (How to define the electrode potential from DFT)

Simulation platform for electrochemical interfaces

1. Strong electric field in Helmholtz layer

ESM method

Effective Screening Medium method

Phys. Rev. B **73**, 115407 (2006)

2. Bias potential control

Constant-μ method

Phys. Rev. Lett. **109**, 266101 (2012)

3. Screening in diffuse layer

4. Origin of electrostatic potential

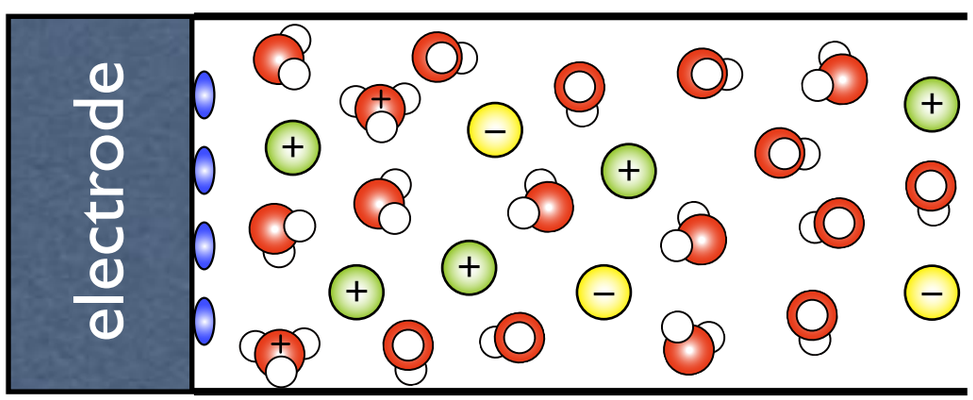
ESM-RISM method

Reference Interaction Site Model

Phys. Rev. B **96**,115429 (2017)

Simulation platform for electrochemical interfaces

- Explicit solvation model



  - All atom calculation
  - BOMD, CPMD, …

- Implicit solvation model

  - Classical liquid theory
  - JDFTx, ENVIRON, PCM,…

3. Screening in diffuse layer

4. Origin of electrostatic potential

ESM-RISM method

Reference Interaction Site Model

Phys. Rev. B **96**,115429 (2017)

Concept of DFT+continuum medium hybrid method

Total energy functional

$$E[\rho] = T[\rho] + E_{\mathrm{xc}}[\rho] + \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \int d\boldsymbol{r}v_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r}) + E_{\mathrm{ion}}$$

V ➠ variable

$$E[\rho_{\mathrm{e}}, V] = T[\rho_{\mathrm{e}}] + E_{\mathrm{xc}}[\rho_{\mathrm{e}}] + \int d\boldsymbol{r}\left[+\frac{\epsilon(\boldsymbol{r})}{8\pi}|\nabla V(\boldsymbol{r})|^2 + \rho_{\mathrm{tot}}(\boldsymbol{r})V(\boldsymbol{r})\right]$$

$\frac{\delta E}{\delta V} = 0$ → Generalized Poisson equation

$$\nabla[\epsilon(\boldsymbol{r})\nabla]V(\boldsymbol{r}) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{r}) \longleftarrow \rho_{\mathrm{tot}} = \rho_{\mathrm{DFT}} + \rho_{\mathrm{solv}}$$

PCM: Environ
RISM: ESM-RISM
CDFT: JDFT

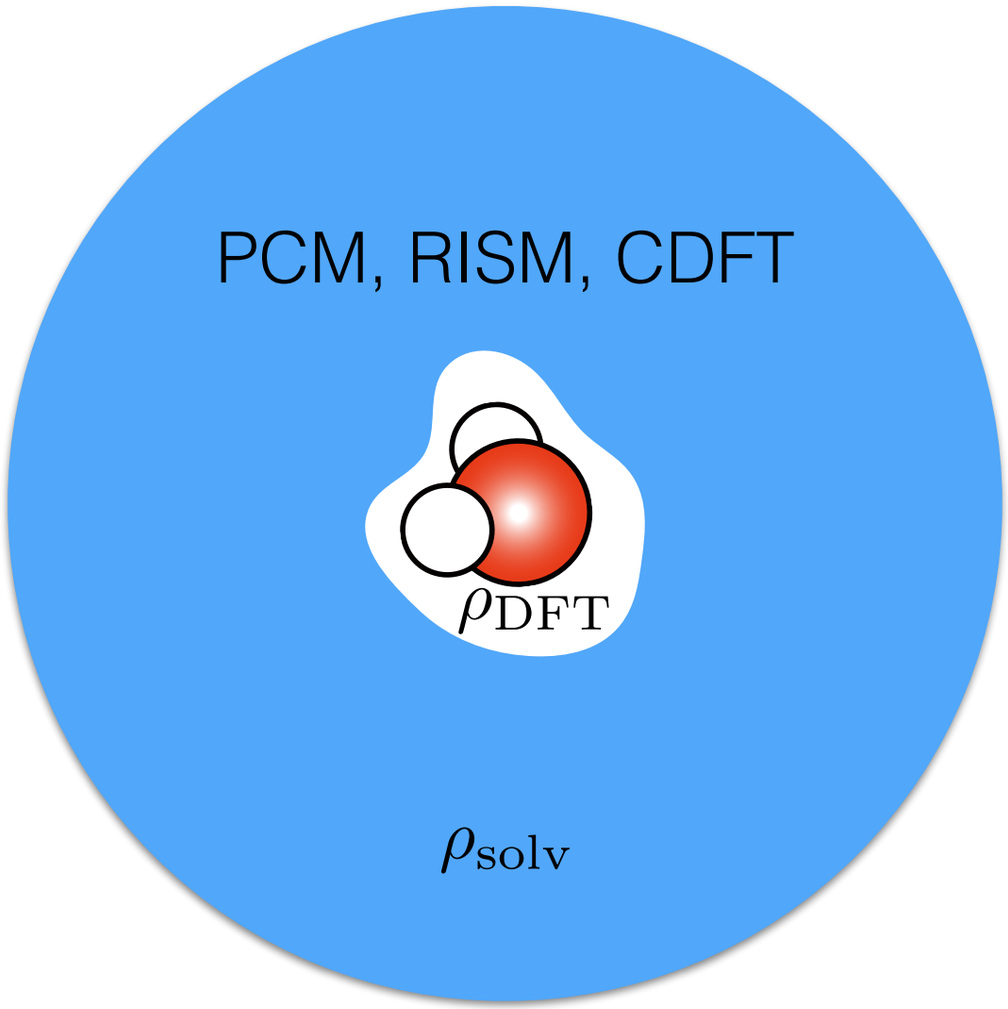
$\frac{\delta E}{\delta \rho_{\mathrm{e}}} = 0$ → Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \hat{V}_{\mathrm{NL}} + V_{\mathrm{xc}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

Concept of DFT+continuum medium hybrid method

Generalized Poisson equation

$$\nabla[\epsilon(\boldsymbol{r})\nabla]V(\boldsymbol{r}) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{r}) \longleftarrow \rho_{\mathrm{tot}} = \rho_{\mathrm{DFT}} + \rho_{\mathrm{solv}}$$



Concept of DFT+continuum medium hybrid method

Generalized Poisson equation

$$\nabla[\epsilon(\boldsymbol{r})\nabla]V(\boldsymbol{r}) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{r}) \longleftarrow \rho_{\mathrm{tot}} = \rho_{\mathrm{DFT}} + \rho_{\mathrm{solv}}$$

PCM, JDFT

$$\epsilon(\boldsymbol{r}) = 1$$

$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}\frac{\rho_{\mathrm{tot}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

ESM

$\epsilon(\boldsymbol{r})$: **model dependent**

$$V(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' G^{\mathrm{MBC}}(\boldsymbol{r},\boldsymbol{r}')\rho_{\mathrm{tot}}(\boldsymbol{r}')$$

Laue representation

$$\left[\partial_z\{\epsilon(z)\partial_z\} - \epsilon(z)g_{\parallel}^2\right] V(\boldsymbol{g}_{\parallel}, z) = -4\pi\rho_{\mathrm{tot}}(\boldsymbol{g}_{\parallel}, z)$$

Open boundary condition

$$\partial_z V(\boldsymbol{g}_{\parallel}, z)\Big|_{z=\pm\infty} = 0, \quad \epsilon(z) = 1$$

$$\begin{cases} G^{\mathrm{MBC}}(\boldsymbol{g}_{\parallel}, z, z') = \dfrac{4\pi}{2g_{\parallel}}\mathrm{e}^{-g_{\parallel}|z-z'|} \\ G^{\mathrm{MBC}}(\boldsymbol{r}_{\parallel}-\boldsymbol{r}'_{\parallel}, z, z') = \dfrac{1}{\sqrt{|\boldsymbol{r}_{\parallel}-\boldsymbol{r}'_{\parallel}|^2 + (z-z')^2}} \end{cases}$$

Concept of DFT+continuum medium hybrid method

Total energy functional

$$E[\rho] = T[\rho] + E_{\mathrm{xc}}[\rho] + \frac{1}{2}\iint d\boldsymbol{r}d\boldsymbol{r}'\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \int d\boldsymbol{r}v_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r}) + E_{\mathrm{ion}}$$

V ➠ variable

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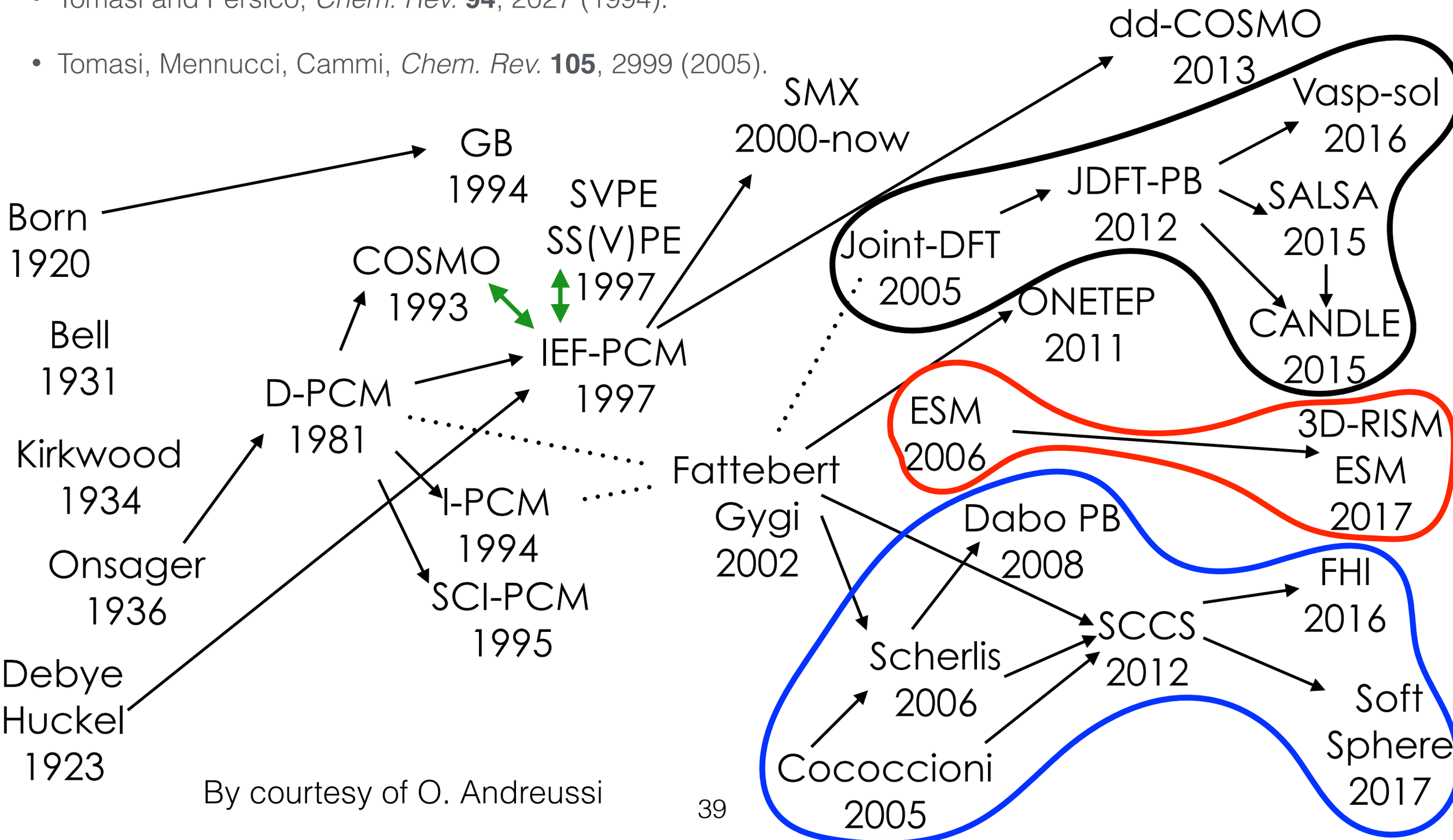
$\frac{\delta E}{\delta \rho_{\mathrm{e}}} = 0$ → Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \hat{V}_{\mathrm{NL}} + V_{\mathrm{xc}}(\boldsymbol{r})\right]\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r})$$

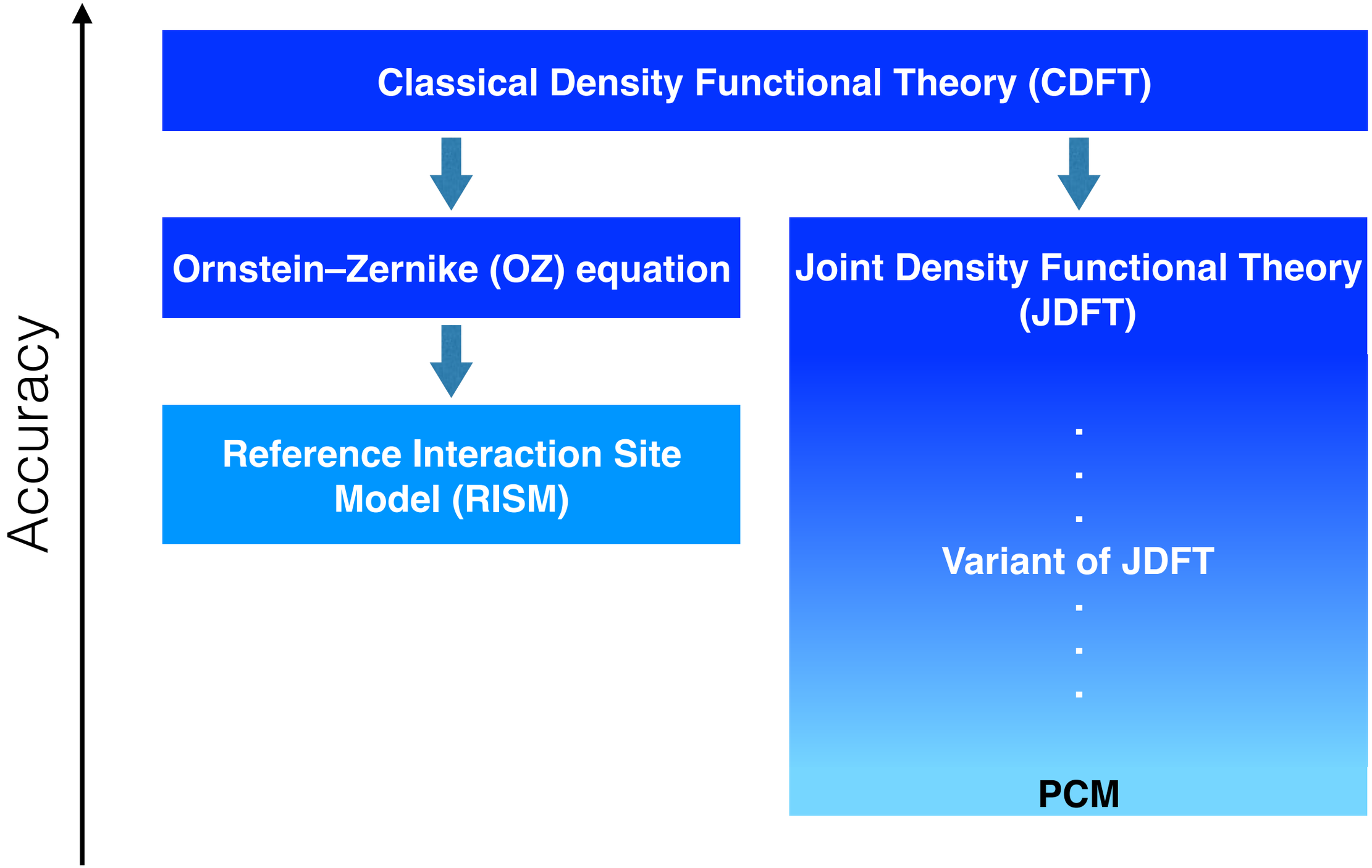
Continuum Genealogy

- Tomasi and Persico, *Chem. Rev.* **94**, 2027 (1994).
- Tomasi, Mennucci, Cammi, *Chem. Rev.* **105**, 2999 (2005).



By courtesy of O. Andreussi

Implicit solvation models



What is the RISM theory?

Ornstein-Zernike equation

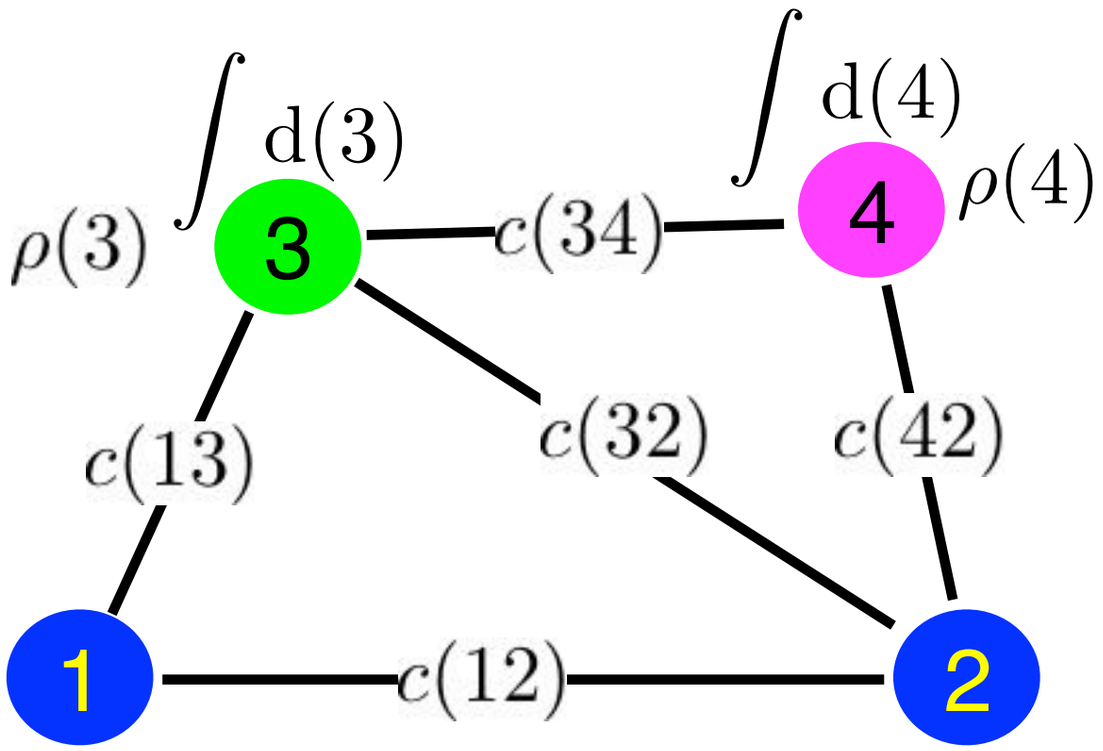
Direct correlation function

Total correlation function

$$\begin{cases} h(\boldsymbol{r}_1, \boldsymbol{r}_2) = c(\boldsymbol{r}_1, \boldsymbol{r}_2) + \int \mathrm{d}\boldsymbol{r}_3 c(\boldsymbol{r}_1, \boldsymbol{r}_3)\rho(\boldsymbol{r}_3)h(\boldsymbol{r}_3, \boldsymbol{r}_2) \\ h(\boldsymbol{r}_1, \boldsymbol{r}_2) = g(\boldsymbol{r}_1, \boldsymbol{r}_2) - 1 \end{cases}$$

Pair distribution function

$$h(12) = c(12) + \int \mathrm{d}(3)c(13)\rho(3)c(32) + \int \mathrm{d}(3)\mathrm{d}(4)c(13)\rho(3)c(34)\rho(4)c(42)\cdots$$



1D-RISM

1D-RISM equation

$$\begin{cases} h_{\alpha\gamma}(r) = \sum_{\mu\nu} \int \mathrm{d}\boldsymbol{r}' \int \mathrm{d}\boldsymbol{r}'' \omega_{\alpha\mu}(|\boldsymbol{r} - \boldsymbol{r}'|) c_{\mu\nu}(|\boldsymbol{r}' - \boldsymbol{r}''|) \chi_{\nu\gamma}(r'') \\ \omega_{\alpha\mu}(r) = \dfrac{1}{4\pi r^2} \delta(r - l_{\alpha\mu}) \\ \chi_{\nu\gamma}(r) = \omega_{\nu\gamma}(r) + \rho_\gamma h_{\nu\gamma}(r) \end{cases}$$

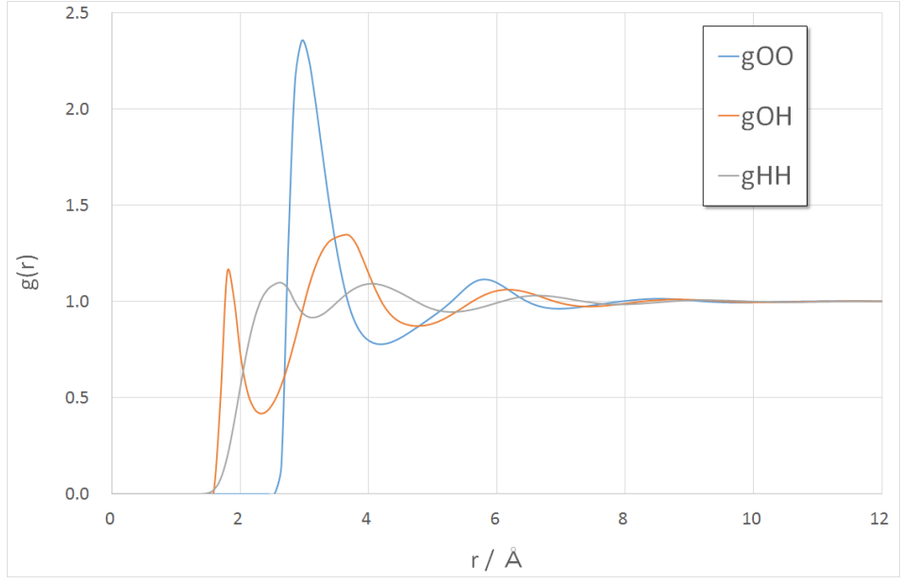
Closure relation (Kovalenco-Hirata)

$$g_{\alpha\gamma}(r) = \begin{cases} \exp\left[-\beta u_{\alpha\gamma}(r) + h_{\alpha\gamma}(r) - c_{\alpha\gamma}(r)\right] & \text{for} \quad g_{\alpha\gamma} \leq 1 \\ 1 - \beta u_{\alpha\gamma}(r) + h_{\alpha\gamma}(r) - c_{\alpha\gamma}(r) & \text{for} \quad g_{\alpha\gamma} > 1 \end{cases}$$

Bulk liquid
ex) 1ML NaCl@Water

Interaction between atomic sites (Lennard-Jones + Coulomb)

$$\begin{cases} u_{\alpha\gamma}(r) = 4\epsilon_{\alpha\beta} \left[\left(\dfrac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\dfrac{\sigma_{\alpha\beta}}{r} \right)^{6} \right] + \dfrac{q_\alpha q_\gamma}{r} \\ \epsilon_{\alpha\beta} = \sqrt{\epsilon_\alpha \epsilon_\gamma} \\ \sigma_{\alpha\gamma} = \dfrac{\sigma_\alpha + \sigma_\gamma}{2} \end{cases}$$

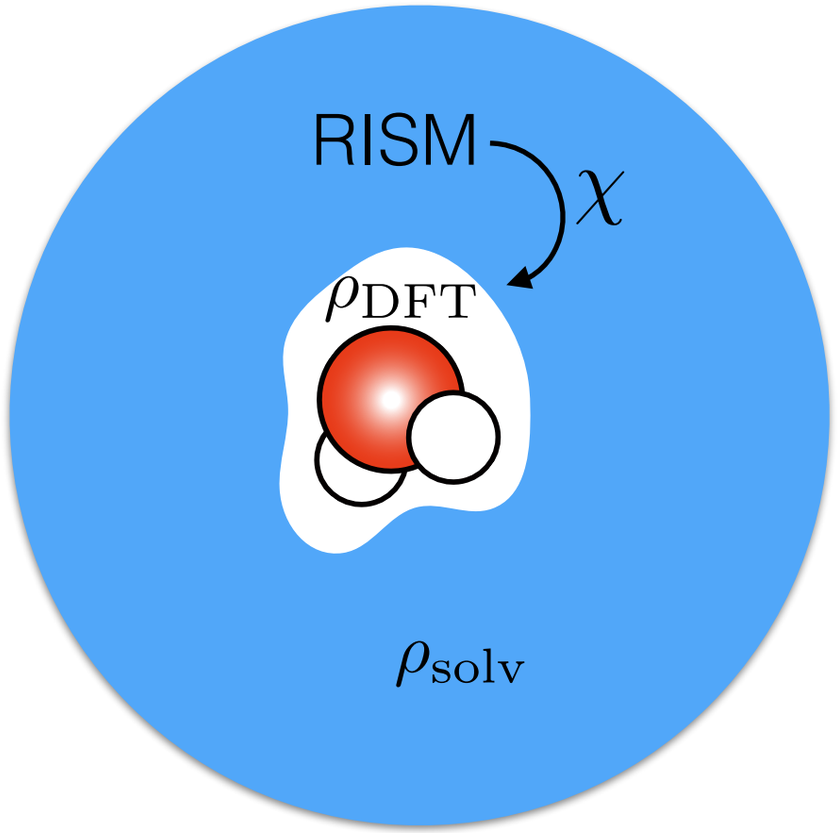


3D-RISM

3D-RISM equation

From 1D-RISM

$$\begin{cases} \chi_{\nu\gamma}(\boldsymbol{r}) = \sum_{\boldsymbol{g}} \chi_{\nu\gamma}(g) \mathrm{e}^{\mathrm{i}\boldsymbol{g}\cdot\boldsymbol{r}} \\ h_\gamma(\boldsymbol{r}) = \sum_\nu \int \mathrm{d}\boldsymbol{r}' c_\nu(\boldsymbol{r}') \chi_{\nu\gamma}(\boldsymbol{r}' - \boldsymbol{r}) \end{cases}$$



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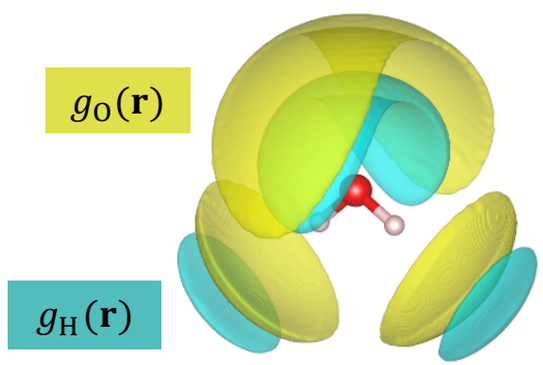
Interaction between atomic sites
(Lennard-Jones + Coulomb)



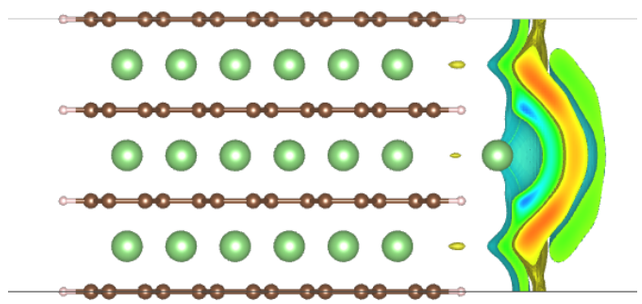
$$u_\gamma(\boldsymbol{r}) = \sum_A 4\epsilon_{\gamma A} \left[\left(\frac{\sigma_{\gamma A}}{|\boldsymbol{r} - \boldsymbol{R}_A|} \right)^{12} - \left(\frac{\sigma_{\gamma A}}{|\boldsymbol{r} - \boldsymbol{R}_A|} \right)^{6} \right] + \int \mathrm{d}\boldsymbol{r}' \frac{q_\gamma \rho_{DFT}}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

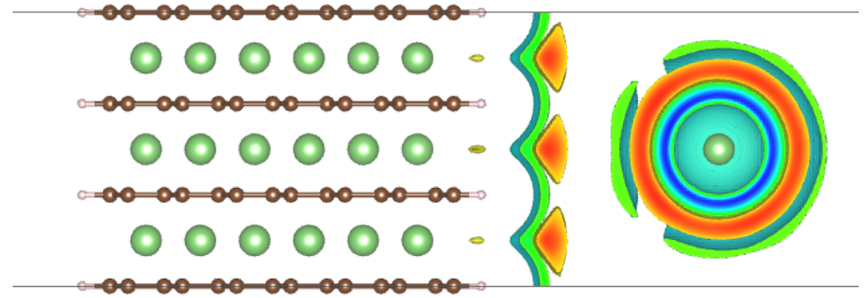
Laue-RISM

Laue-RISM equation

From 1D-RISM

$$\begin{cases} \chi_{\nu\gamma}(\boldsymbol{g}_{\parallel}, z'-z) = \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{\infty} \mathrm{d}g_z \chi_{\nu\gamma}(g)\mathrm{e}^{\mathrm{i}g_z(z'-z)} \\ h_\gamma(\boldsymbol{g}_{\parallel}, z) = \displaystyle\sum_{\nu}\int \mathrm{d}z' c_\nu(\boldsymbol{g}_{\parallel}, z')\chi_{\nu\gamma}(\boldsymbol{g}_{\parallel}, z'-z) \end{cases}$$





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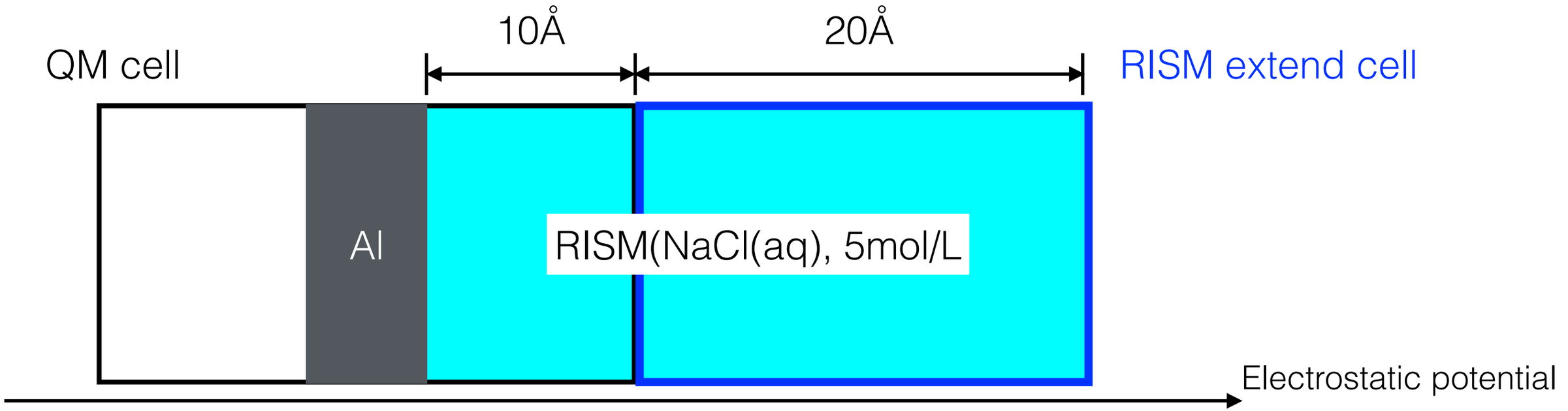
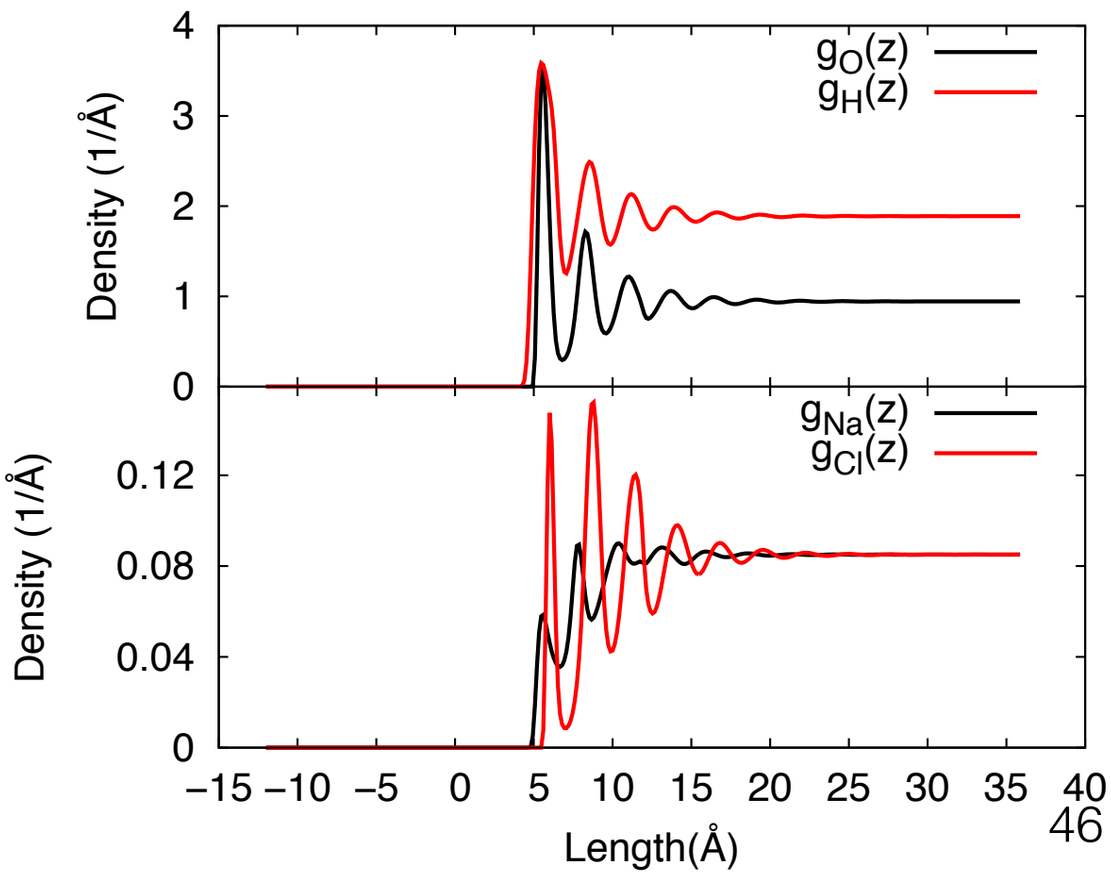
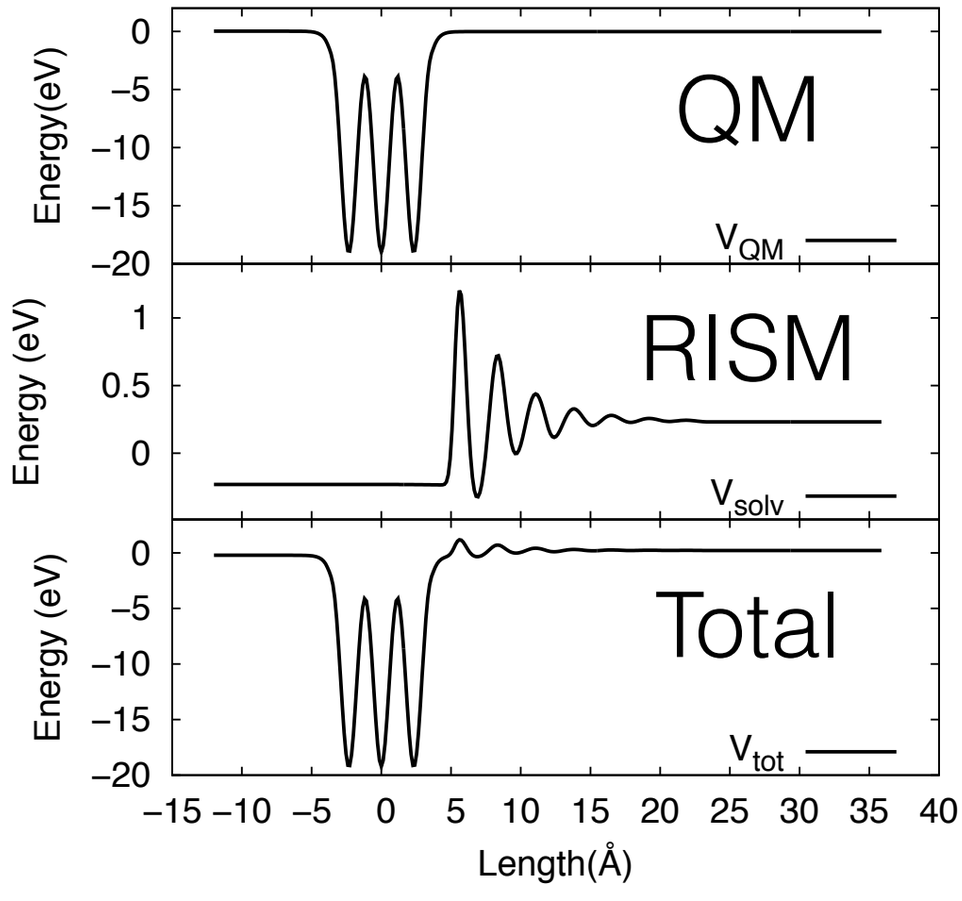
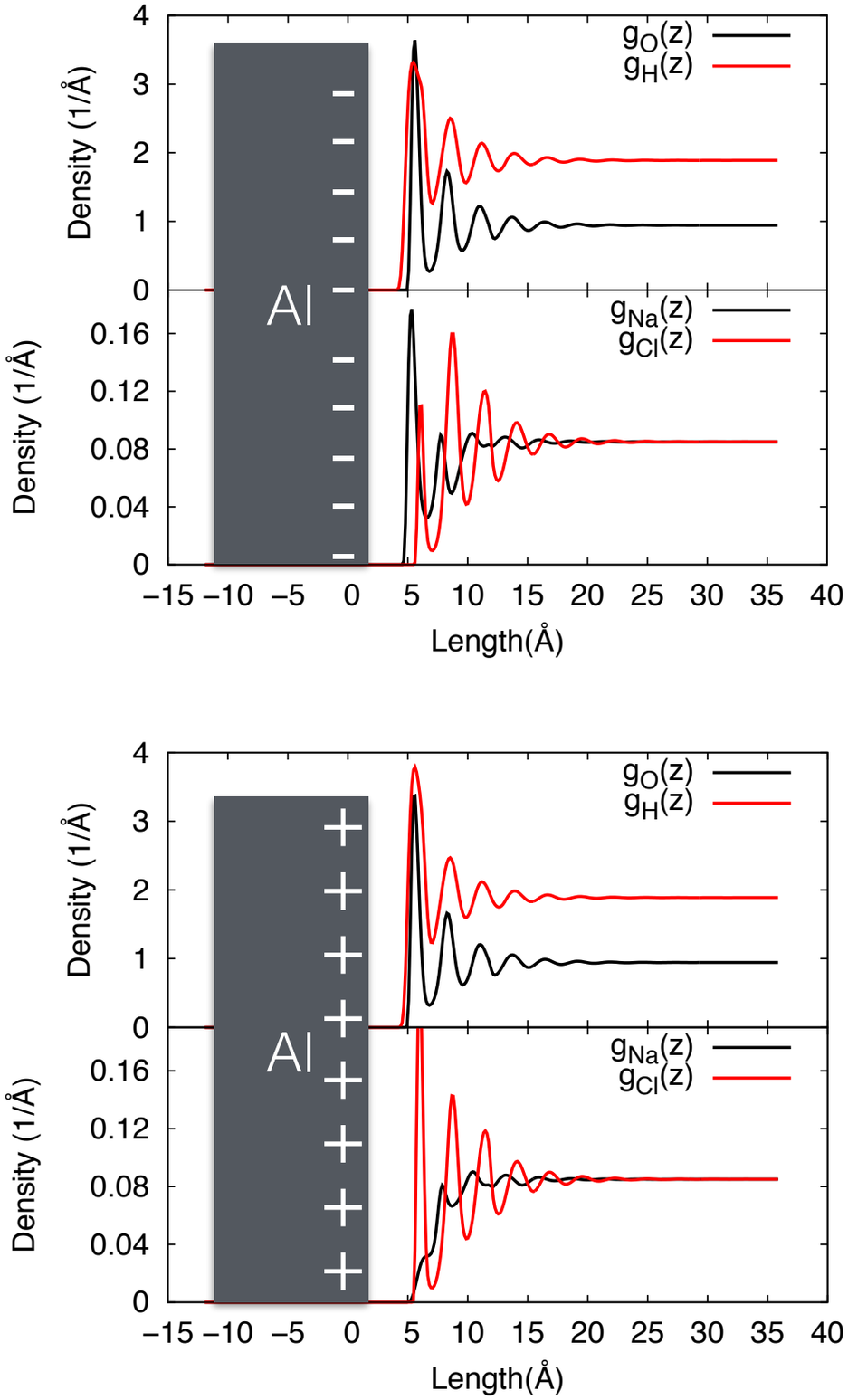
Al - NaCl aqueous interface

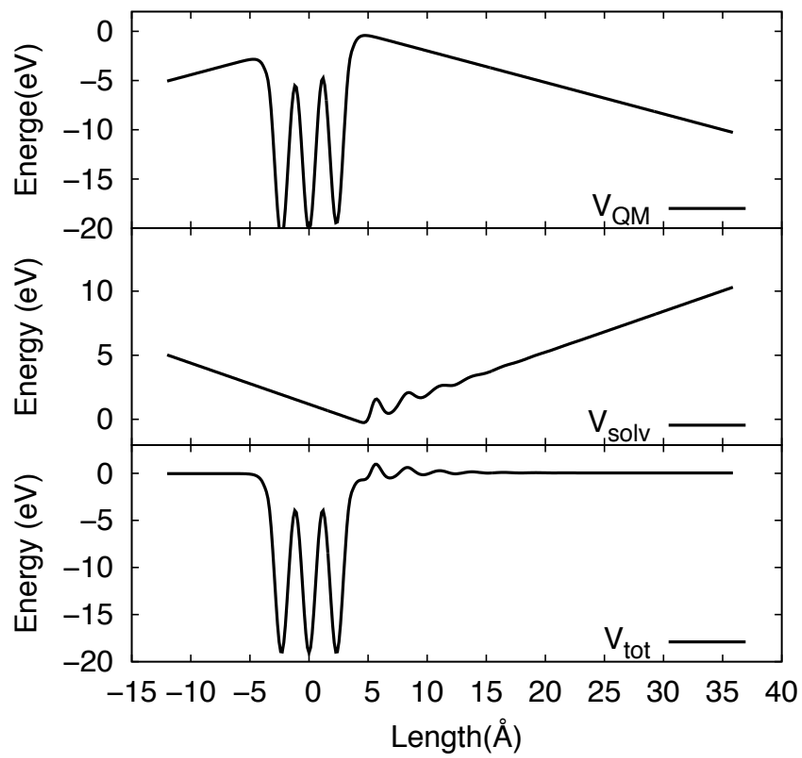






Al/NaCl溶液界面(電気二重層)

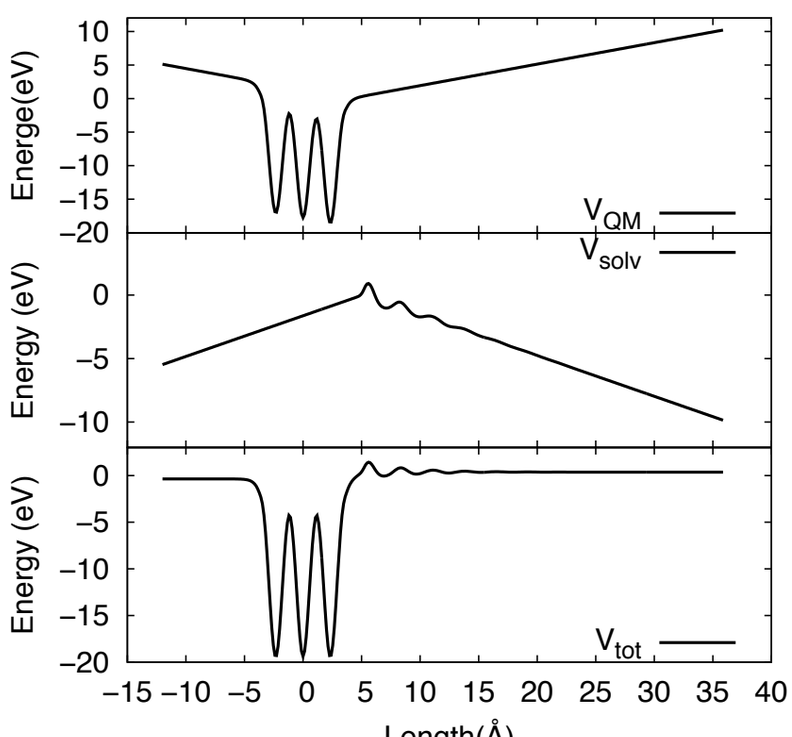




QM

RISM

Total

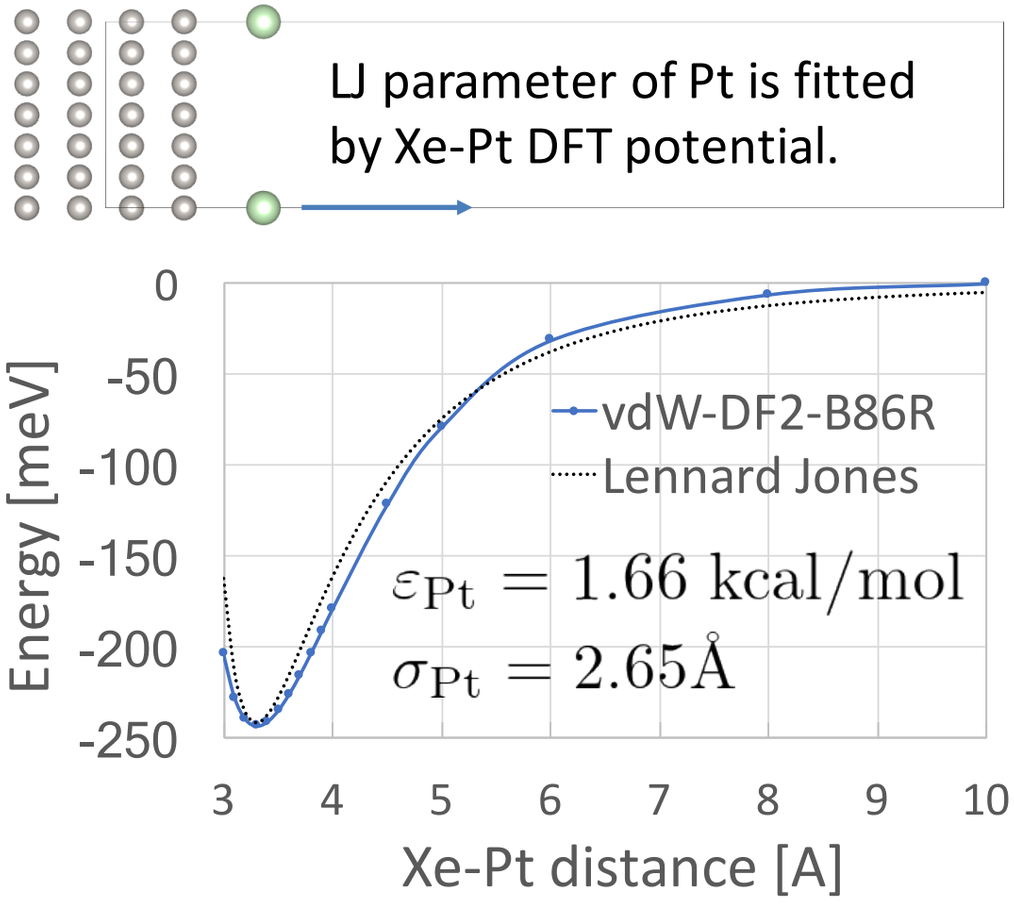


QM

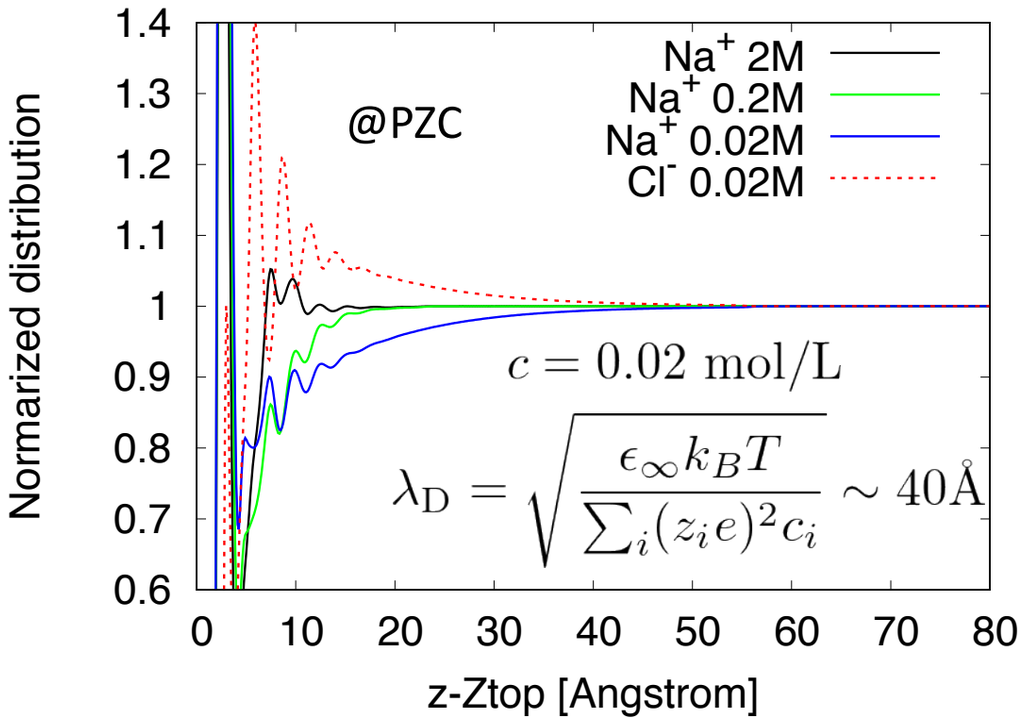
RISM

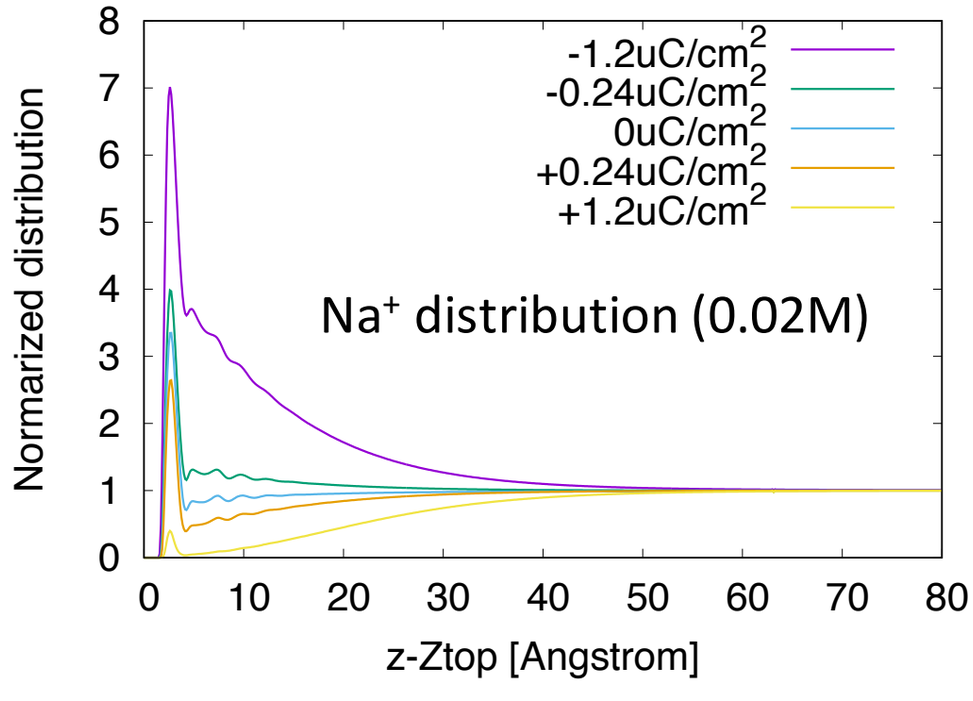
Total

RISM vs. Debye Hückel



Double layer distance

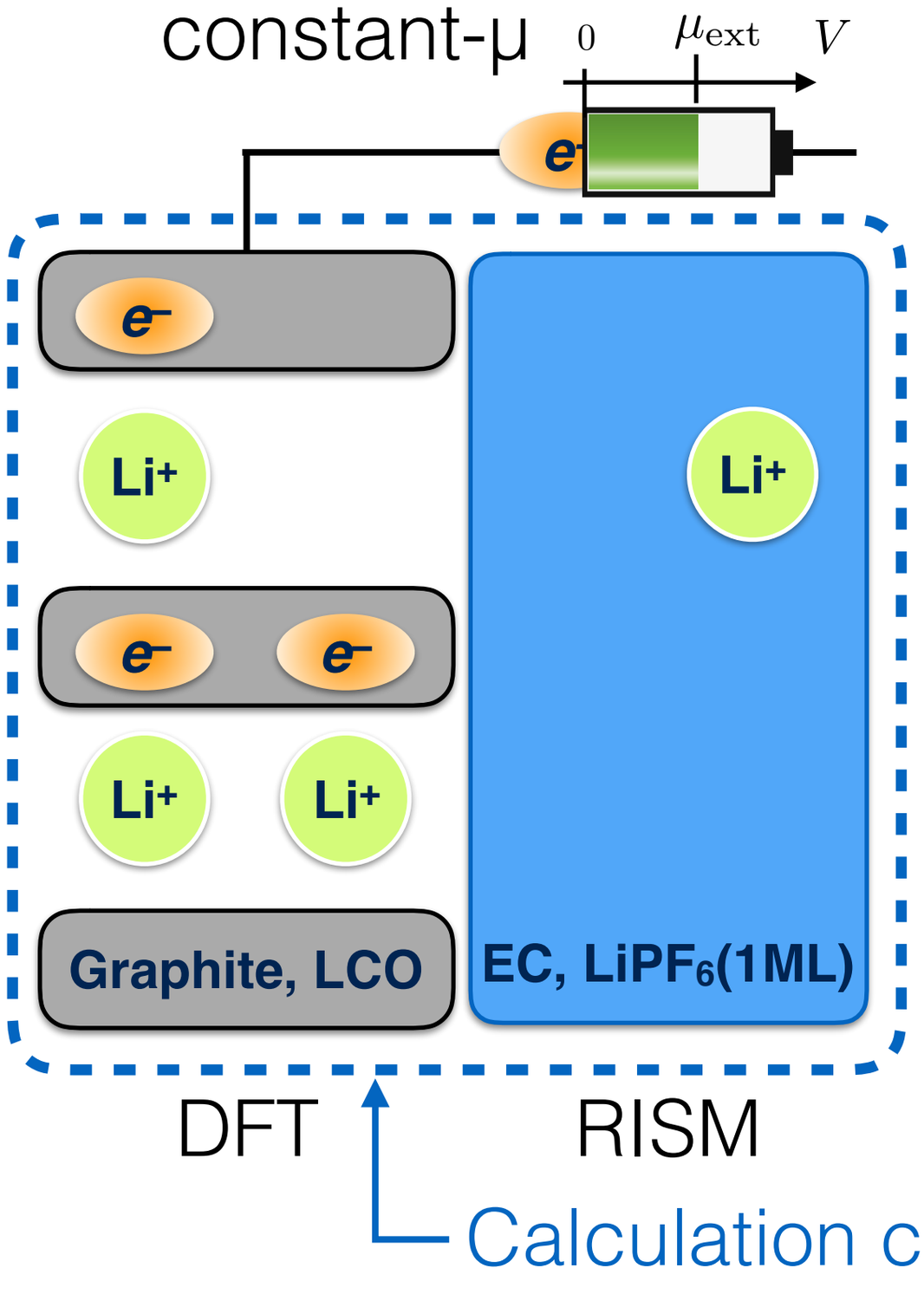


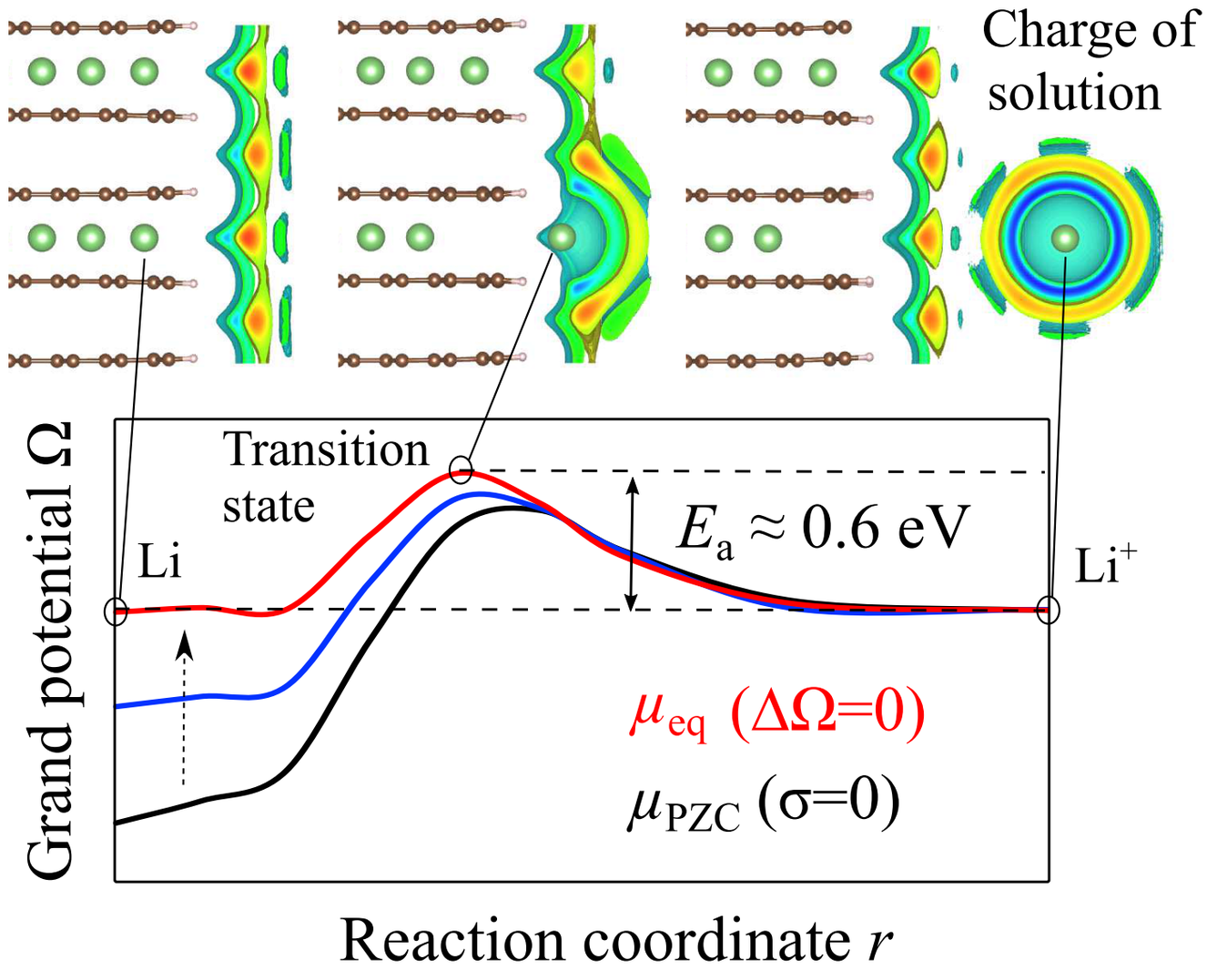


Outline

- Introduction
- Simulation platform for electrochemical interface
  - Effective screening medium (ESM) method
  - Constant bias potential (constant-μ_e) method
  - Hybrid simulation method: DFT+liquid theory (ESM-RISM)
- Applications
  - Lithium Insertion/Desorption Reaction in Li-ion battery
- Summary
- Appendix (How to define the electrode potential from DFT)

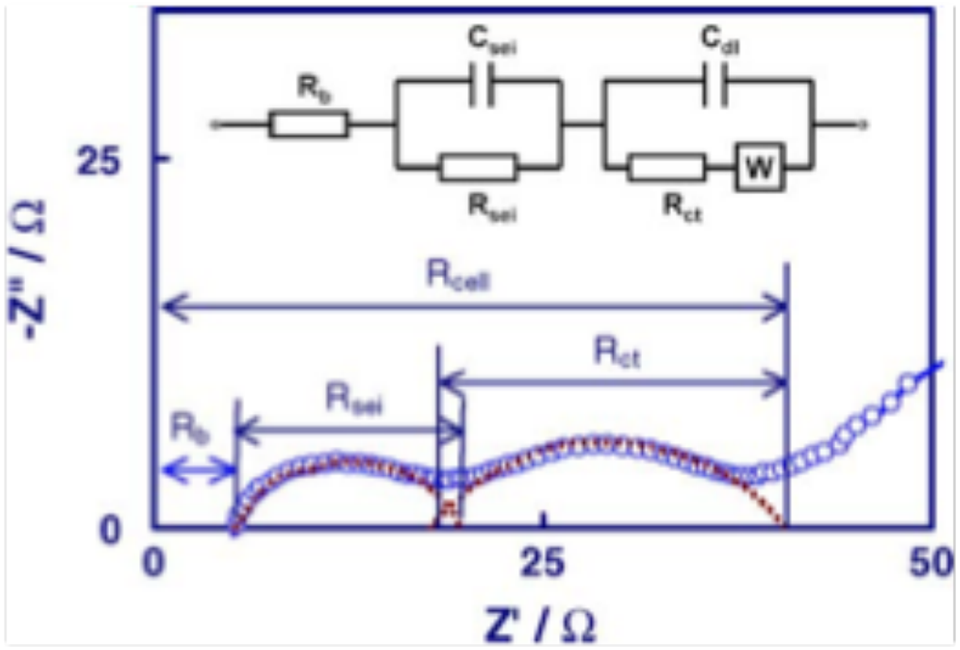
Solvation process of Li-ion





J. Haruyama, et. al., MO, J. Phys. Chem. C, 122, 9804(2018)

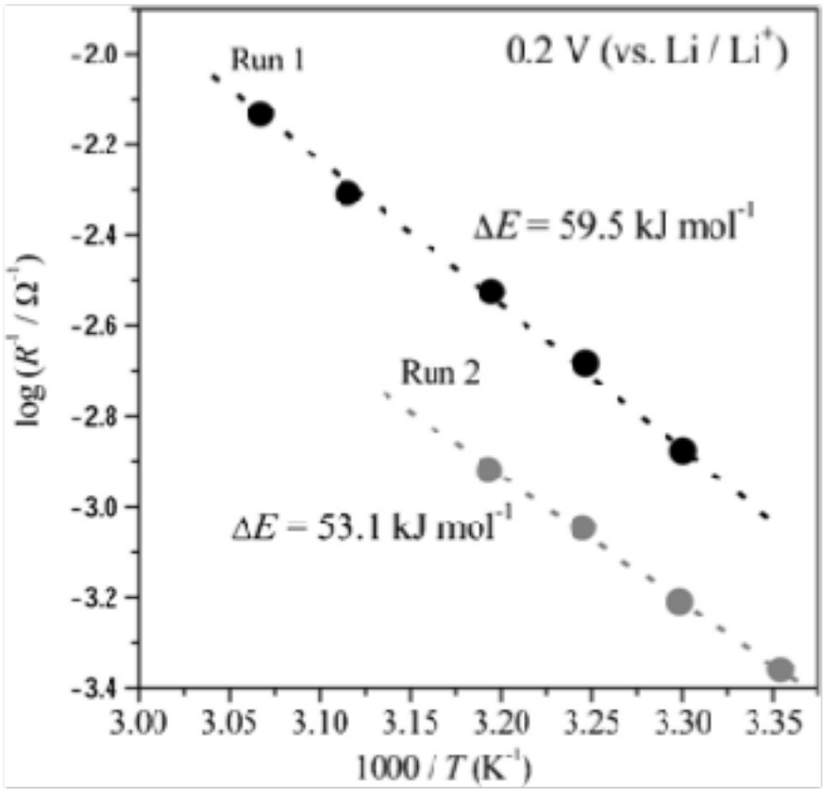
Electrochemical impedance spectroscopy (EIS) measurements



Typical EIS of Conventional LIB cell
LiCoO2|EC3:EMC7 LiPF6 1M|Graphite

In the fully charged and discharged states as well as at the low temperatures (≤20◦C), the R_{cell} of the Li-ion cells is predominated by the R_{ct}.

S. S. Zhang, K. Xu, and T. R. Jow, Electrochemica Acta **49**, 1057 (2004).

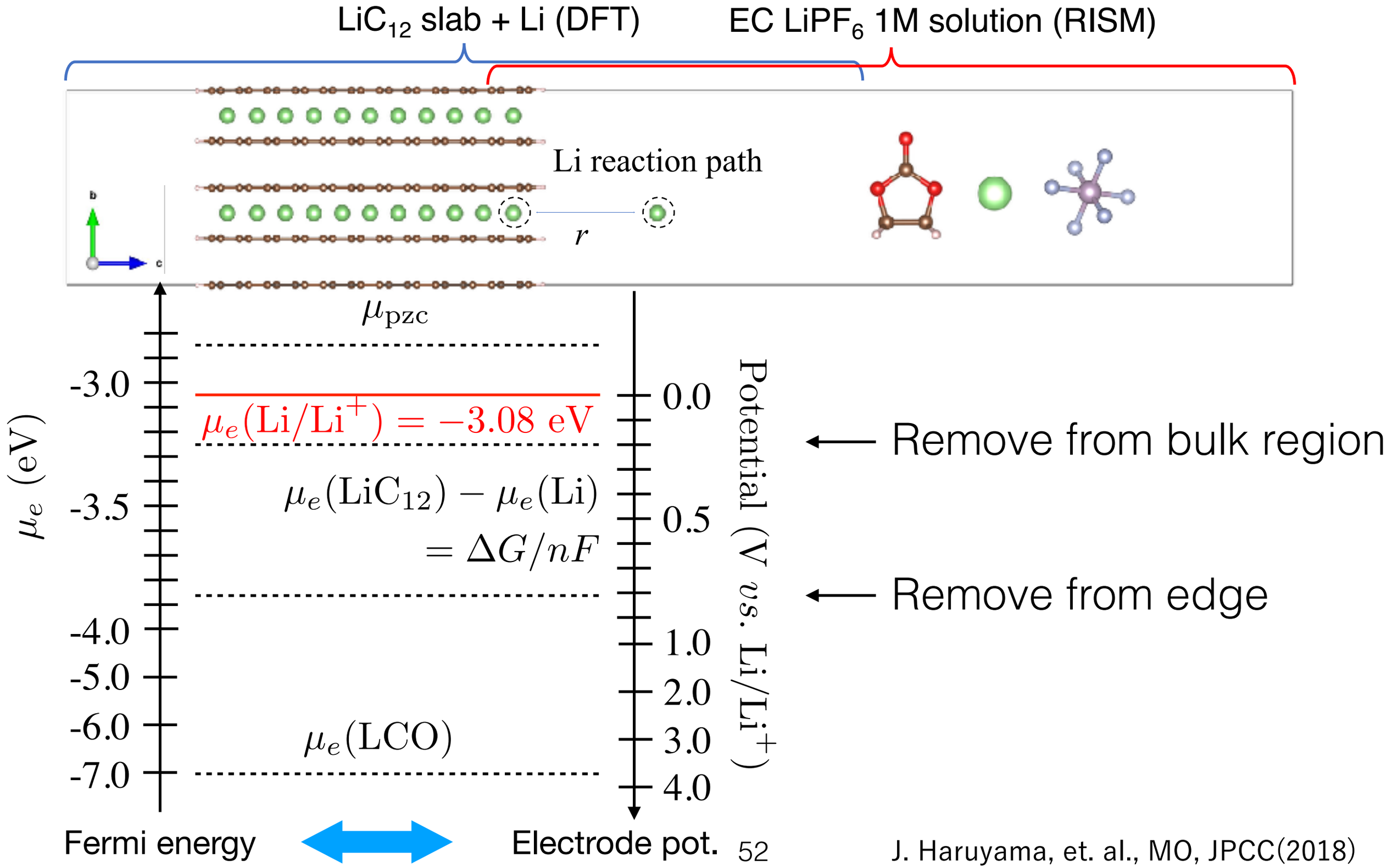


Temperature-dependence of R_{ct} @0.2 V *vs*. Li/Li+

The activation energies were evaluated to be around 50-60 kJ/mol (0.5-0.6 eV). These values are very large compared to lithium ion conduction in active materials.

T. Abe, H. Fukuda, Y. Iriyama, and Z. Ogumi, J. Electrochem. Soc. **151**, A1120 (2004).

Definition of the electrode potential (Calculation)



J. Haruyama, et. al., MO, JPCC(2018)

Summary

- We have developed a series of simulations methods to simulate the electrode/electrolyte interface.

- We can define the reference electrode potential which is consistent with thermodynamics and electrochemistry.

- Our simulation technique is applicable many electrochemical systems, such as secondary ion batteries, fuel cells, collision, electroplating, ion exchange membrane