Tutorial: Using ReaxFF to Model Electrochemical Interfaces

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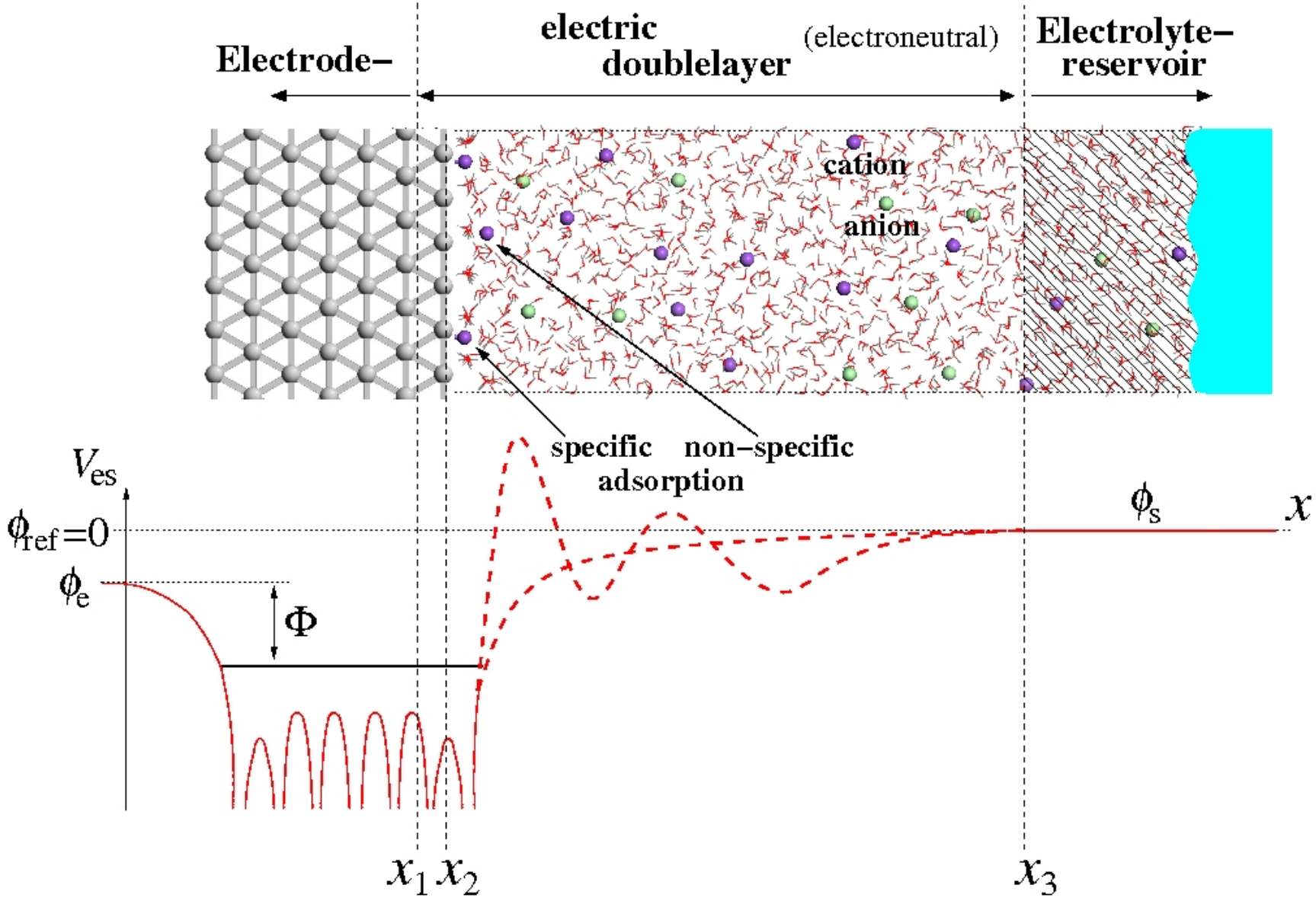
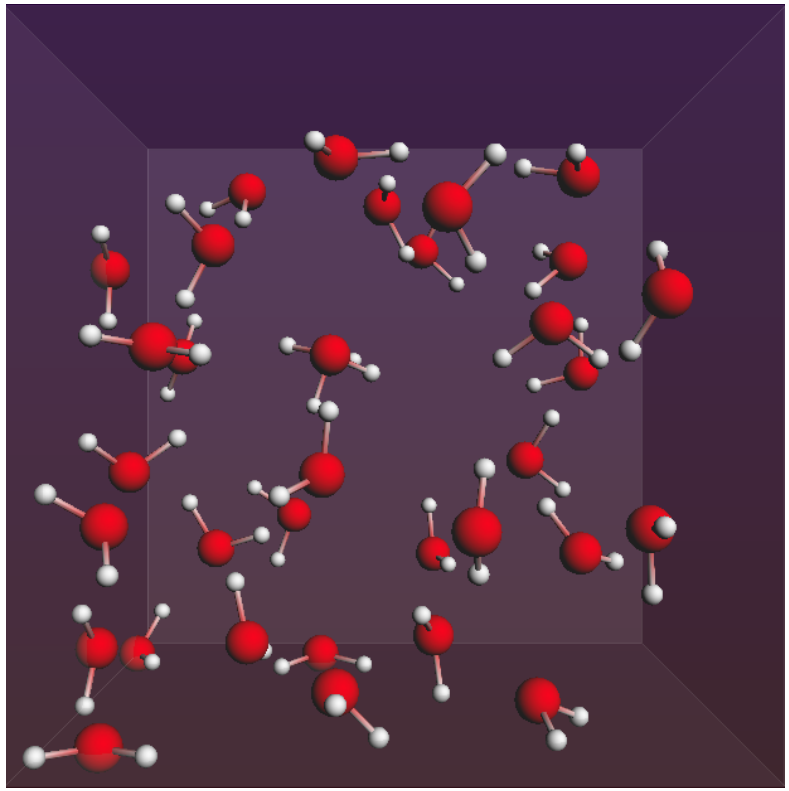
Helmholtz Institute Ulm
Electrochemical Energy Storage

The Problem


Electrode–
electric
doublelayer
(electroneutral)
Electrolyte–
reservoir
cation
anion
specific
adsorption
non–specific
V_{es}
$\phi_{ref}=0$
ϕ_e
Φ
ϕ_s
x
x_1
x_2
x_3

Electrolyte calculation

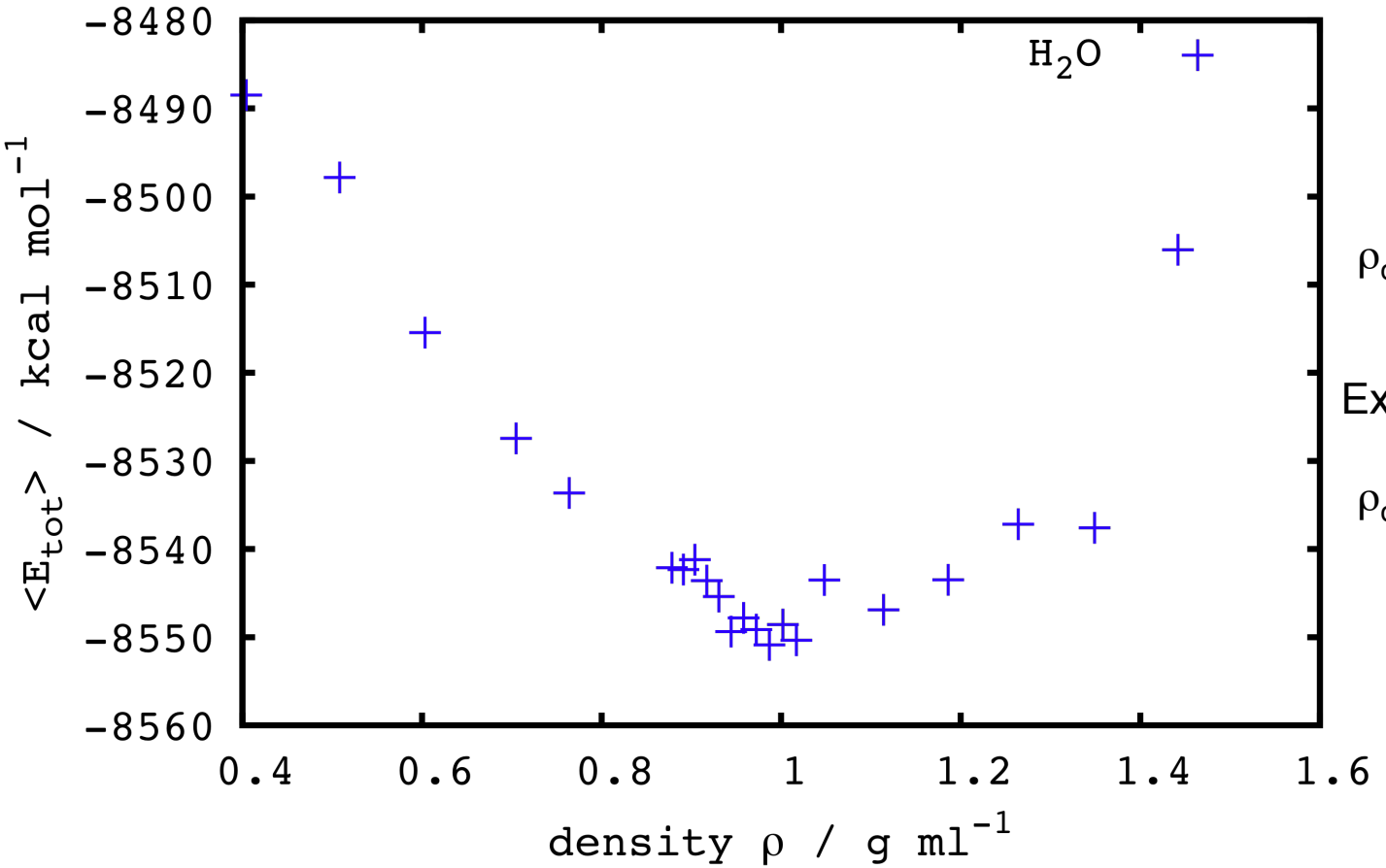
Tasks



1. Build a rectangular box
2. Fill the box with 34 water molecules
3. Adjust the box size to match the density of liquid water (1 g/cm^3)
4. Run MD simulations
   - Use cu-cl.ff forcefield
   - NVT dynamics
   - T=298.15K
   - Method: VV+Berendsen
   - Damping=10fs
   - Non-reactive iterations=40000
   - Reactive iterations=40000
   - Simulation time: each 10ps
   - Δt=0.25fs
5. Vary the cell volume in $\Delta\rho$=0.01 ($0.8 < \rho < 1.2$ g/cm^3)
6. Plot $E_{average}$ vs. ρ

Electrolyte calculation

Results



$\rho_{opt} \approx 1$ g ml^{-1}

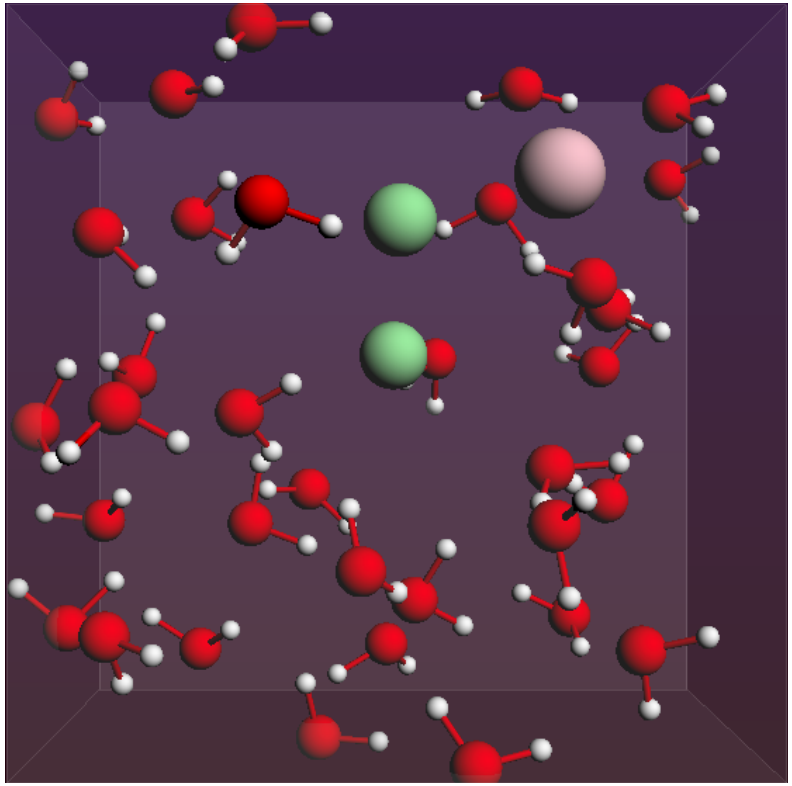
Exp. value at 298.15 K:

$\rho_{opt} = 0.997$ g ml^{-1}[a]

[a] *CRC Handbook of Chemistry and Physics, 88th edition. Boca Raton, Florida: Taylor & Francis Group,* **2008**.

Electrolyte calculation

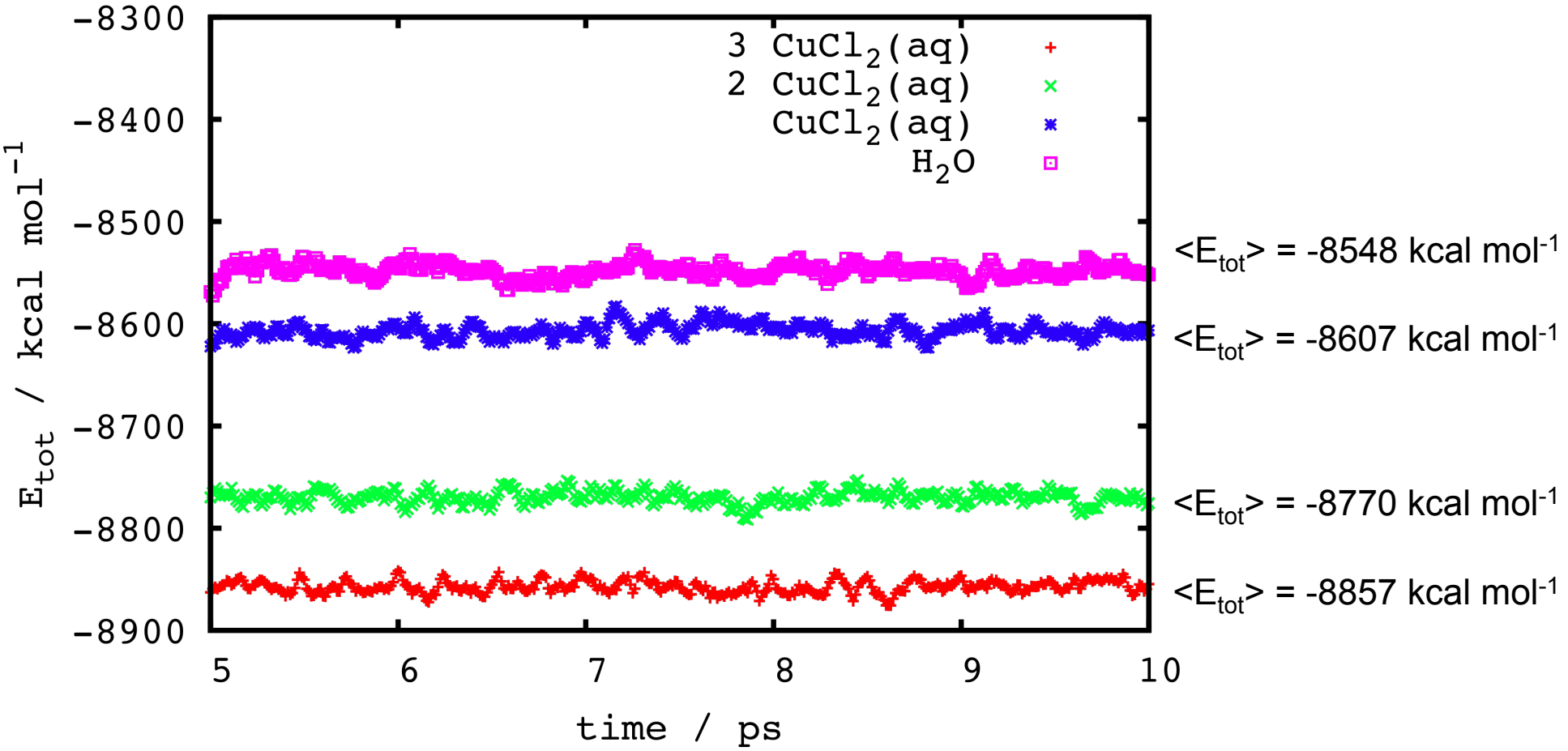
2) Solvation energy of $CuCl_2$



1. Use optimum box size $a=b=c=10.7$Å
2. Add one Cu and 2 Cl atoms
3. Assign charges: Cu 2+, Cl 1−
4. Run MD simulations
   - Use cu-cl.ff forcefield
   - NVT dynamics
   - $T=298.15$K
   - Method: VV+Berendsen
   - Damping=10fs
   - Non-reactive iterations=40000
   - Reactive iterations=40000
   - Simulation time: each 10ps
   - $\Delta t=0.25$fs
5. Plot E_{total} vs. t
   and average properly
6. Do the same for two and three
   $CuCl_2$(aq) molecules

Electrolyte calculation

Results



Electrolyte calculation

Comparison

Solvation energy for $CuCl_2$ based on experimental thermodynamic data.[a]

$\Delta H_f\ Cl_g$	=	29.08 kcal mol^{-1}
$\Delta H_f\ Cl^-_{aq}$	=	−39.95 kcal mol^{-1}
$\Delta H_f\ Cu_g$	=	80.86 kcal mol^{-1}
$\Delta H_f\ Cu^{2+}_{aq}$	=	15.48 kcal mol^{-1}

Therefore:

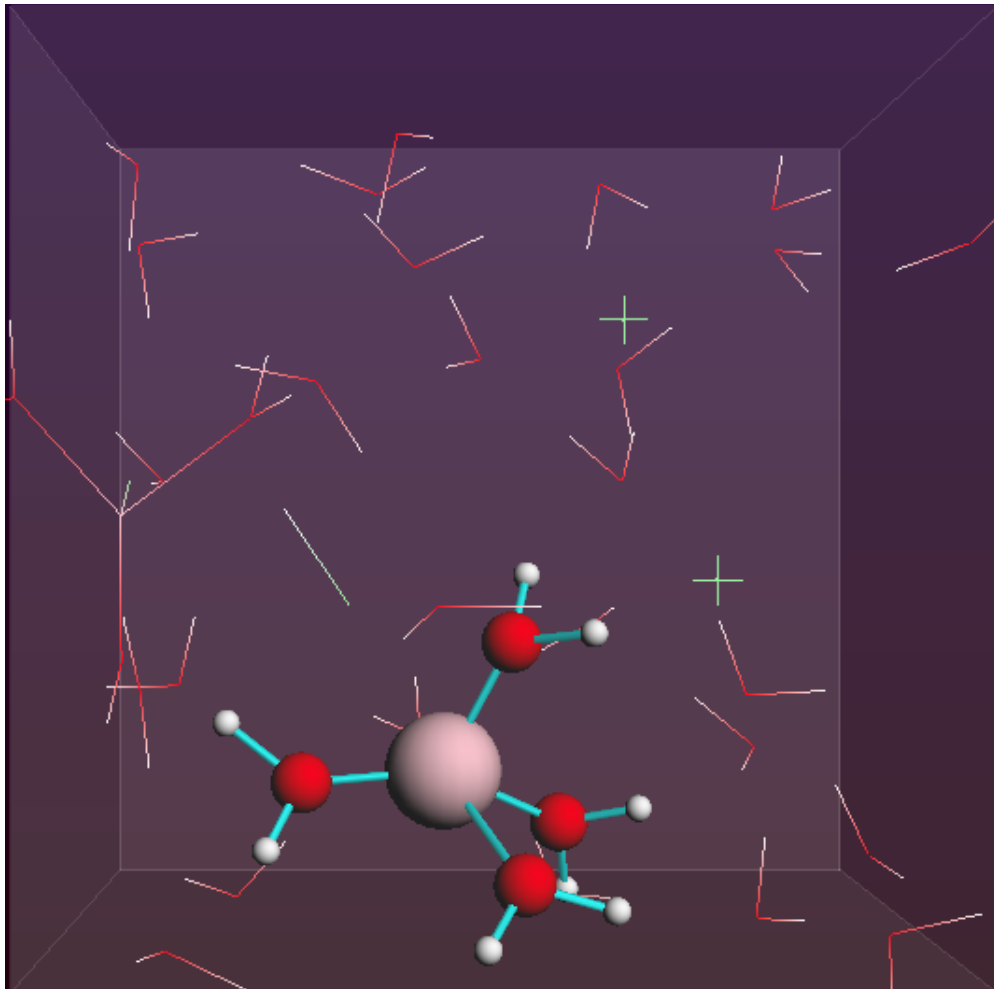
$\Delta H\ \ Cu_g + 2Cl_g \rightarrow CuCl_{2,\ aq} = -203.45$ kcal/mol

Simulation: $\Delta H = -59$ kcal mol^{-1} → too small unitcell

[a] Calculated from ΔH_f values for 1 molar aqueous Cl^-, 1 molar aqueous Cu^{2+}, 1 atm. of gaseous Cu atoms and 1 atm. of gaseous Cl atoms all 298.15 K from *CRC Handbook of Chemistry and Physics, 71st Edition*.

Electrolyte calculation

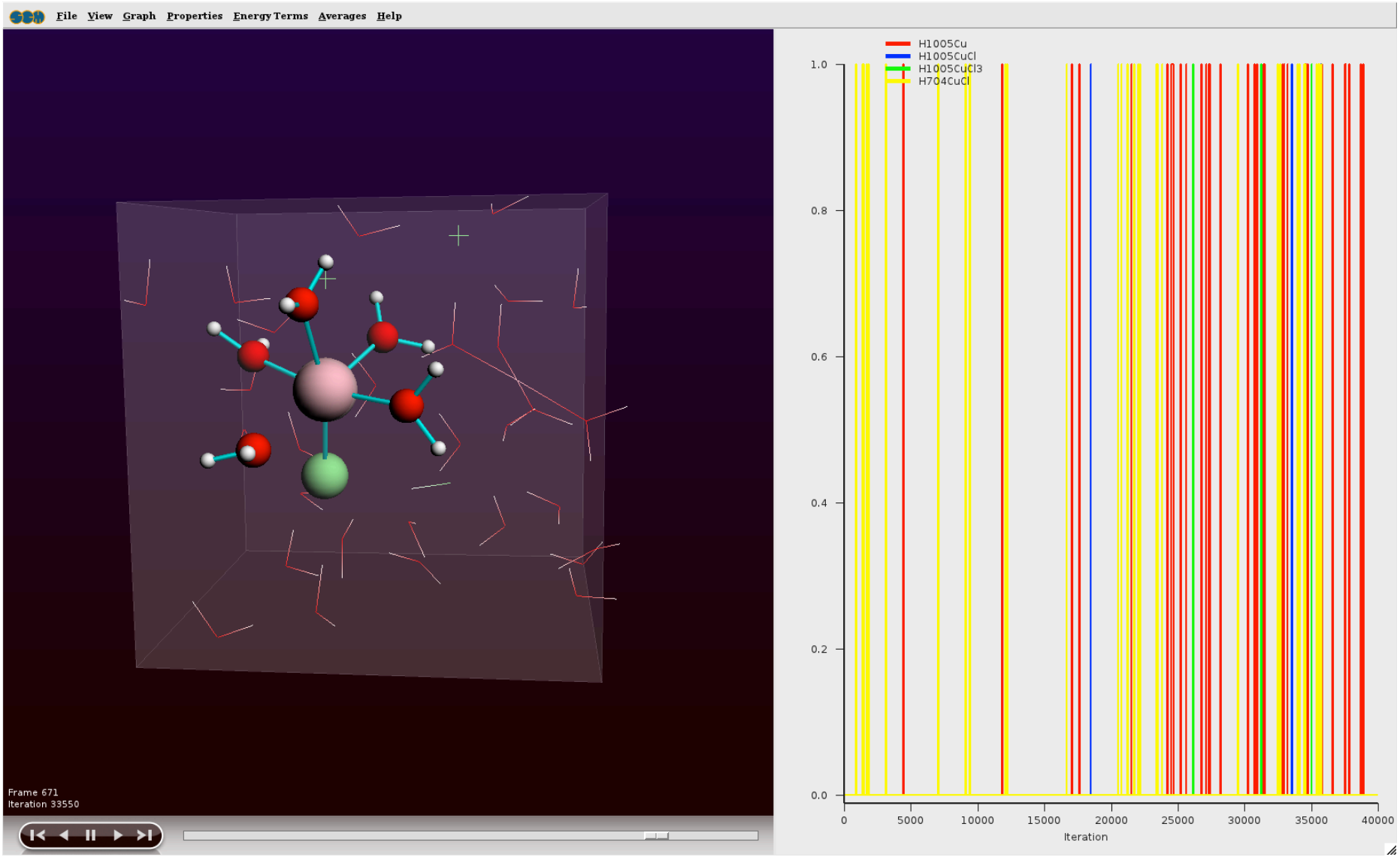
3) Solvation energy of $CuCl_2$ (**reactive simulation**)



1. Use cell with 2 $CuCl_2$(aq)
2. Run reactive MD
   - Use cu-cl.ff forcefield
   - NVT dynamics
   - T=298.15K
   - Method: VV+Berendsen
   - Damping=10fs
   - Non-reactive iterations=0
   - Reactive iterations=40000
   - Simulation time: each 10ps
   - Δt=0.25fs
3. Plot molecule fractions

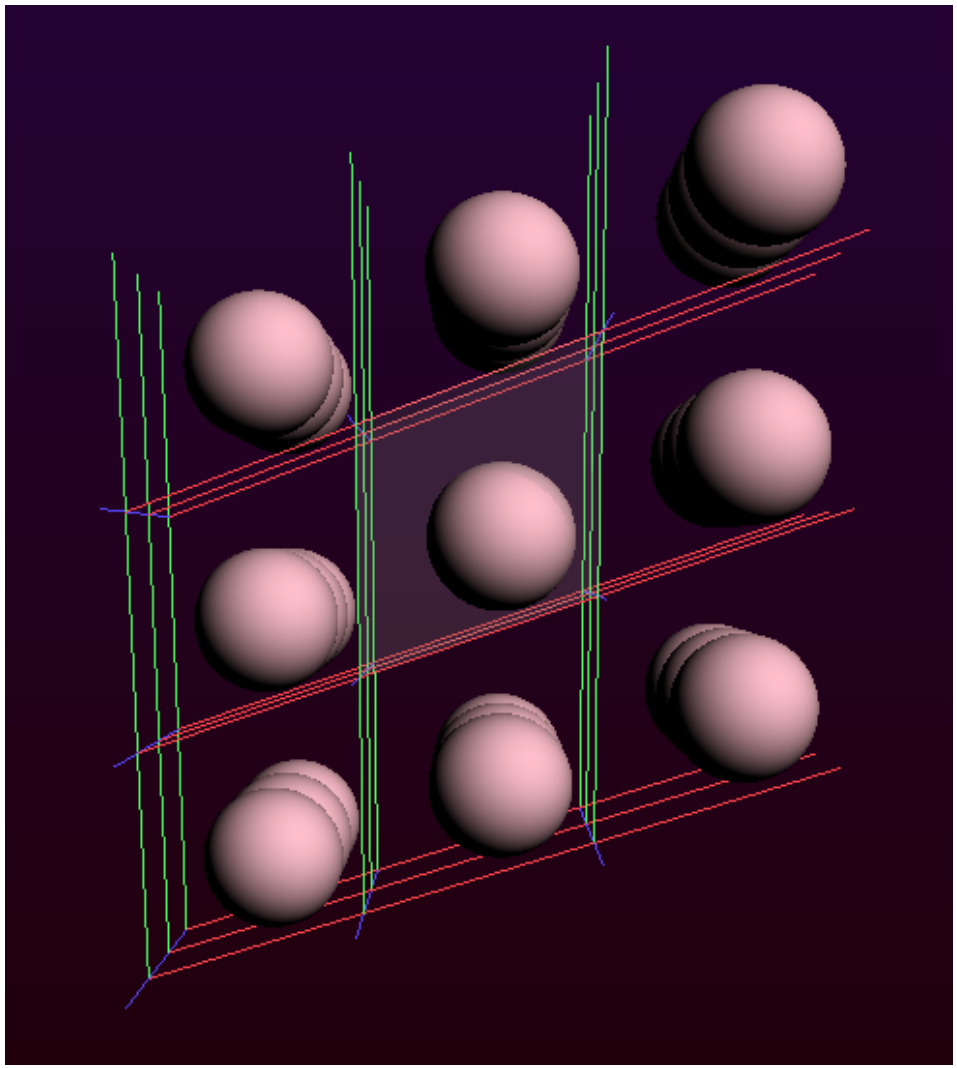
Electrolyte calculation

Analysis of the different species in solution



Bulk calculation

4) Cell optimization/Equation of state (EOS) of solids



1. Build Cu-fcc crystal
2. Do cell optimization
   - Cell optimization
   - Convergence criteria=0.005
3. Vary volume (single-point calc)

4. Plot E_{total} vs. V (Cu-EOS)

   lat. const. 3.5 < a/b/c < 3.9 Å

→ Do fitting to Rose-equation

Bulk calculation

Equation of state (EOS) of solids

Response of the bulk crystal to uniform compression and expansion

Four-parameter equation of state of solids[1]:

$$E = -E_C(1 + \tilde{a} + \delta\tilde{a}^3)e^{-\tilde{a}}$$

$$\tilde{a} = \eta\left(\frac{a_{WS}}{a_{0-WS}} - 1\right)$$

$$B_0 = \frac{\eta^2 E_C}{9V_0}$$

$$\alpha = \frac{1 + 3\delta}{\eta E_C} \cdot 2.459 \cdot 10^{-4}$$

Linear thermal expansion coefficent

$$T_M = 372.3 \cdot (1 - 2\delta)E_C$$

Melting point

For comparison:

Rose equation:

$$E = -E_C(1 + \tilde{a} + 0.005\tilde{a}^3)e^{-\tilde{a}}$$

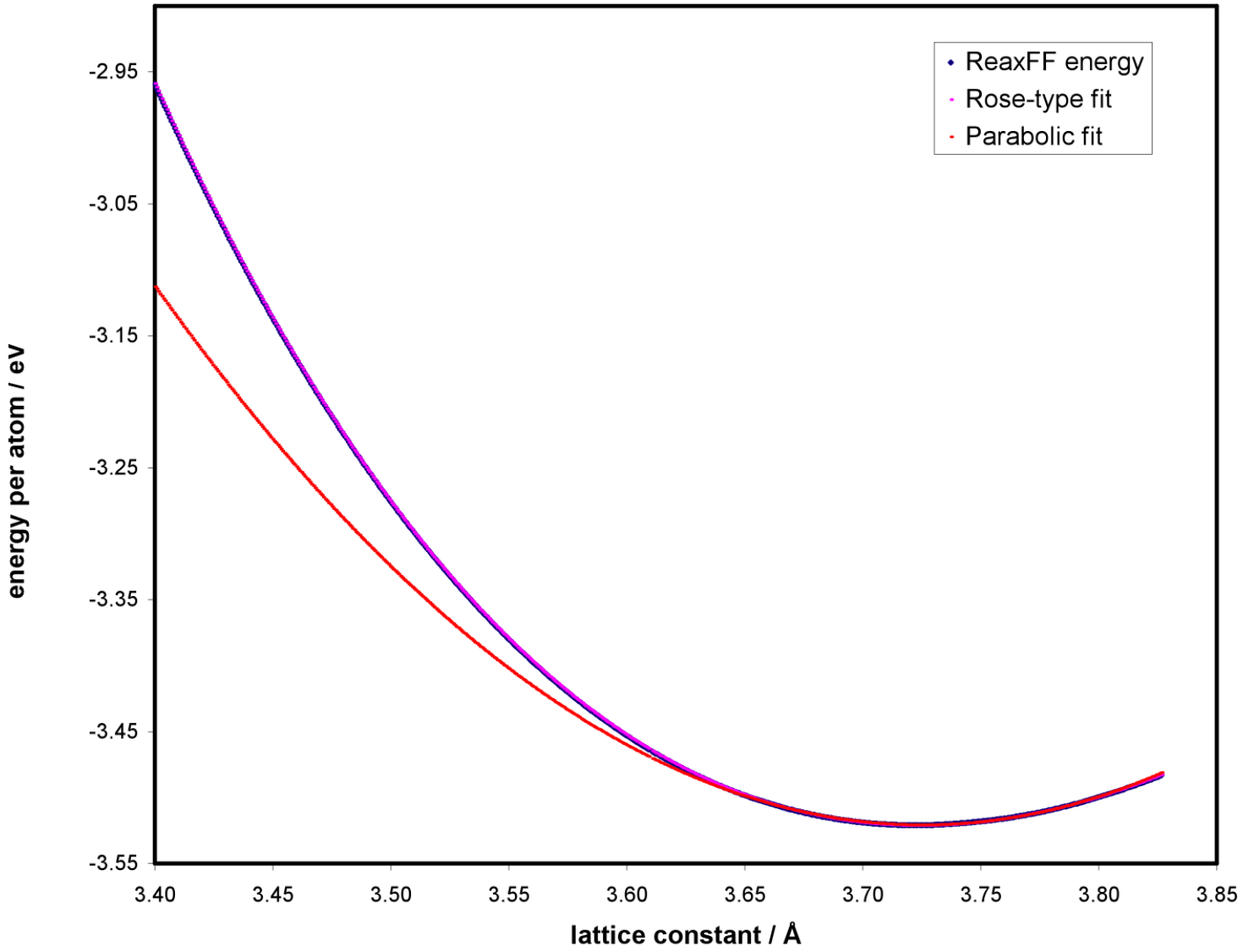
Vinet equation:

$$E = -E_C(1 + \tilde{a})e^{-\tilde{a}}$$

[1] J. H. Li, S. H. Liang, H. B. Guo, and B. X. Liu, *Appl. Phys. Lett.* **87, 194111 (2005).**

Bulk calculation

ReaxFF: EOS



Bulk calculation

Results

	E_C / eV	B / 10^{11} N m^{-2}	a_0 / Å	T_m / K	α / K^{-1}
Rose type fit	3.52	1.53	3.72	1400	$1.12*10^{-5}$
Parabolic fit			3.73		
Exp.*	3.49 [a]	1.37 [a]	3.615 [b]	1357.77 [c]	$1.65*10^{-5}$ [c]

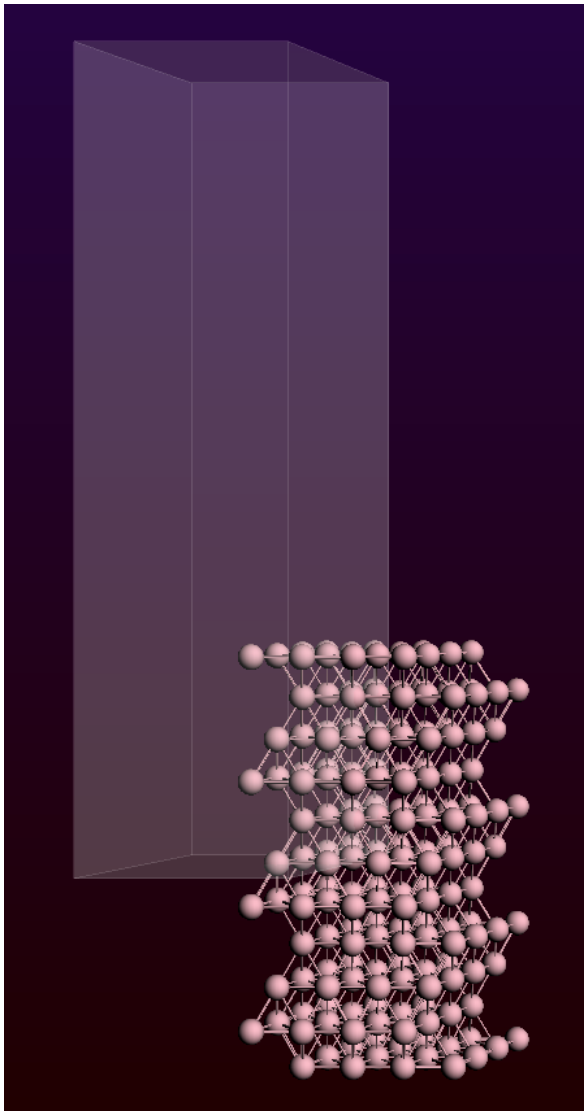
* **all exp. values are quantities for standard conditions**

[a] Charles Kittel. *Introduction to Solid State Physics, 8th edition. Hoboken, NJ: John Wiley & Sons, Inc,* **2005**.

[b] N. W. Ashcroft, N. D. Mermin, *Solid State Physics*, New York, **1976**.

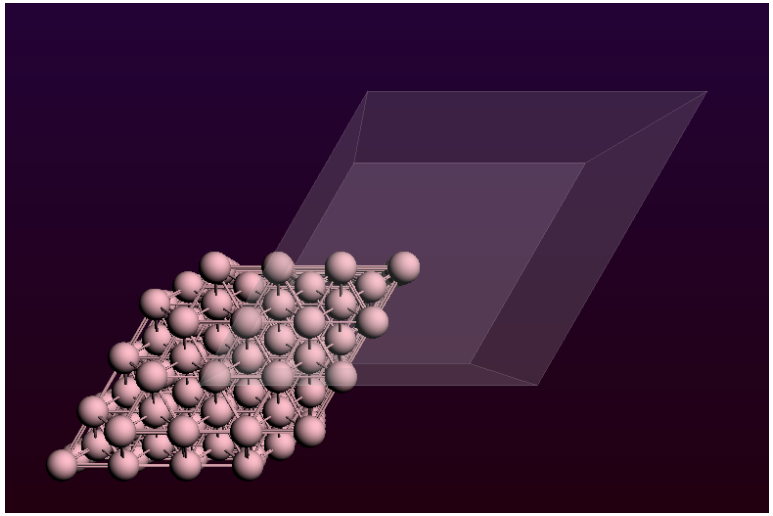
[c] *CRC Handbook of Chemistry and Physics, 88th edition. Boca Raton, Florida: Taylor & Francis Group,* **2008**.

Surface calculation



Side view of a Cu(111) surface

1. Build Cu(111), Cu(100), and Cu(110) slabs with 11 layers (optimized lat. const.)
2. Fix central three layers
3. Energy minimization
   - Convergence criteria=0.005
4. Calculate surface energies
5. Do the same with 4 layer slabs



Top view of a Cu(111) surface

Surface calculation

Calculation of surface free energies

Energy needed to create a surface out of a bulk crystal

Determination of the surface free energy of a pure metal
in the supercell approach:

$$\gamma = \frac{1}{2A}[E_{tot} - N_x E_C]$$

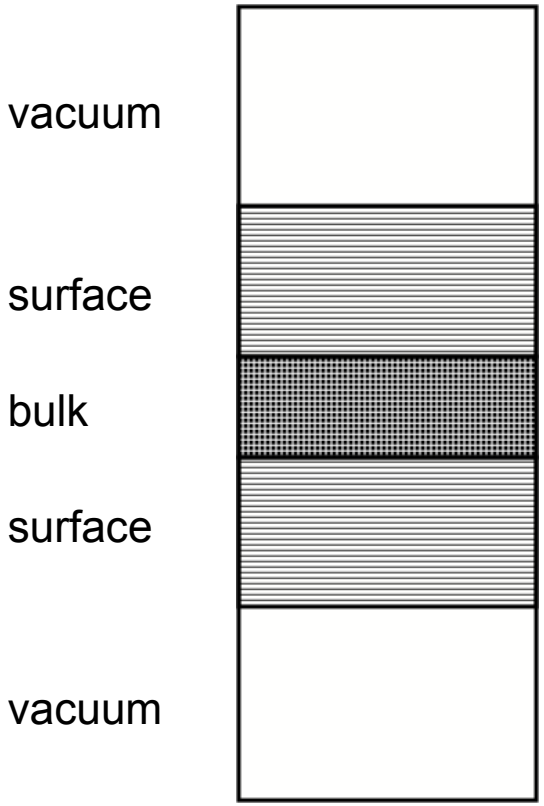
A: unit cell area

E_C: cohesive energy

E_{tot}: total energy of the system

N_x: number of atoms x

Calculation scheme:



Surface calculation

Results for different Cu surfaces

(hkl)	Unit cell	Nr. of layers	Nr. of fixed layers	Nr. of atoms	Surface area / Å^2	E_{tot} / kcal mol^{-1}	γ / J m^{-2}	$\Delta\gamma$ / J m^{-2}
111	1x1	11	3	11	5.99	-876.55	0.97	0.00
100	1x1	11	3	11	6.92	-871.57	1.09	0.12
110	1x1	11	3	11	9.79	-861.22	1.14	0.17
111	1x1	4	2	4	5.99	-308.17	0.96	0.00
100	1x1	4	2	4	6.92	-303.19	1.09	0.12
110	1x1	4	2	4	9.79	-292.86	1.13	0.17

Vacuum: 15 Å

Surface calculation

Comparison to other available values

(hkl)	γ / J m^{-2}	$\Delta\gamma$ / J m^{-2}
111	0.97	0.00
100	1.09	0.12
110	1.14	0.17

(hkl)	γ / J m^{-2}	$\Delta\gamma$ / J m^{-2}	γ / J m^{-2}
111	1.95[a]*	0.00	1.790; 1.825[a]**
100	2.17[a]*	0.22	
110	2.24[a]*	0.29	

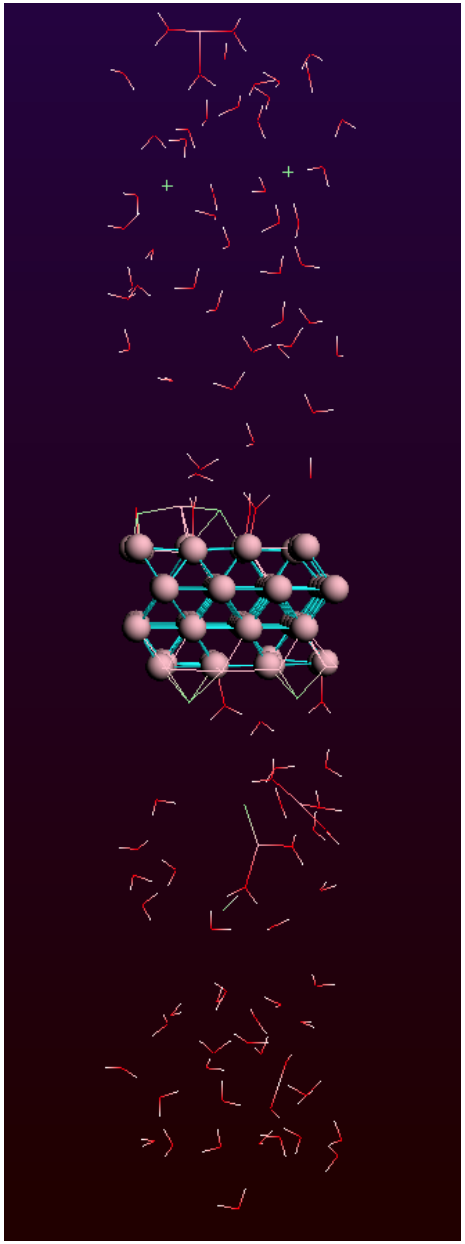
* Caculated by the FCD method, **experimental value

[a] L. Vitos, A. Ruban, H. Skriver, and J. Kollár, *Surface Science* **411, 186 (1998)**.

Interface calculation

Reactive simulation

1. Build four layer Cu(100) slab, 4x4x1 supercell
2. Add vacuum
3. Fill vacuum with liquid water (ρ~1g/cm^3)
   e.g. z=56.304Å, add 150 waters
4. Include 4 Cu^{2+} and 8 Cl^-
5. Run MD
   - Use cu-cl.ff forcefield
   - NVT dynamics
   - T=298.15K
   - Method: VV+Berendsen
   - Damping=10fs
   - Non-reactive iterations=0
   - Reactive iterations=40000
   - Simulation time: each 0.3ns
   - Δt=0.25fs
6. Map molecular fraction



Interface calculation

Analysis of the reaction products