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22 – 24 September 2021, Portorož

Model study of penetration of ions from solution into organic self-assembled-monolayer on metal substrate

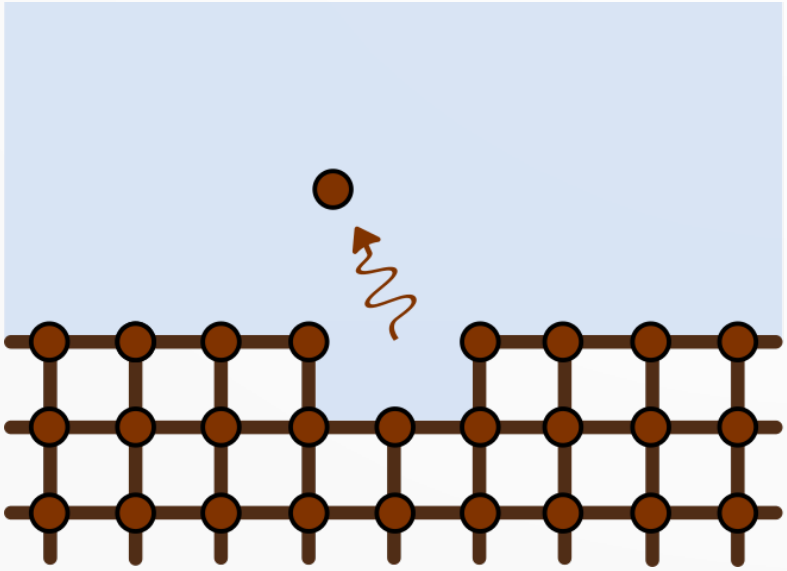
Anton Kokalj
Department of Physical and Organic Chemistry

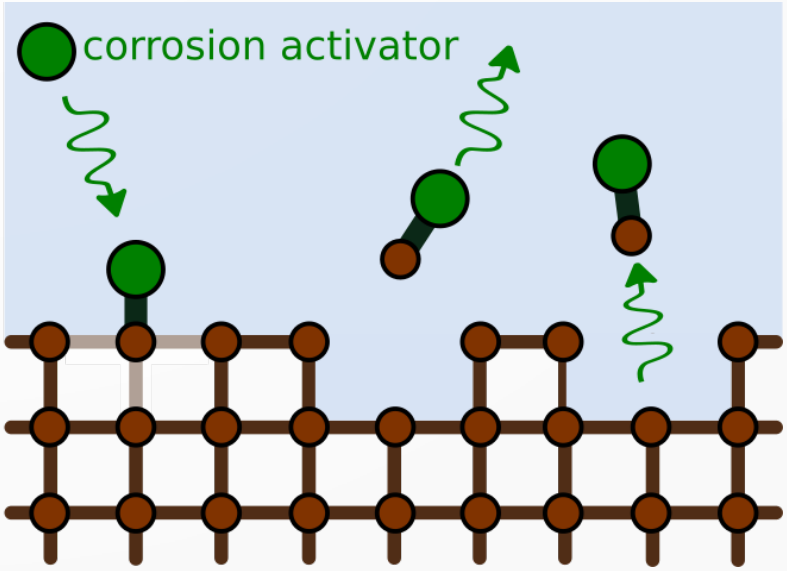
in cooperation with: D. Costa
Chemie ParisTech

Jožef Stefan Institute, Ljubljana, Slovenia

Introducing the context

Corrosion of metals: $M \rightarrow M^{z+} + ze^{-}$

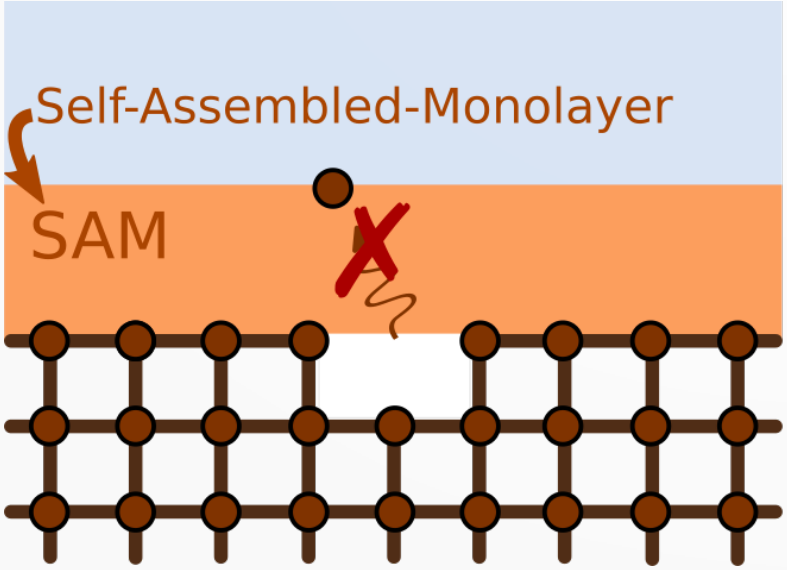


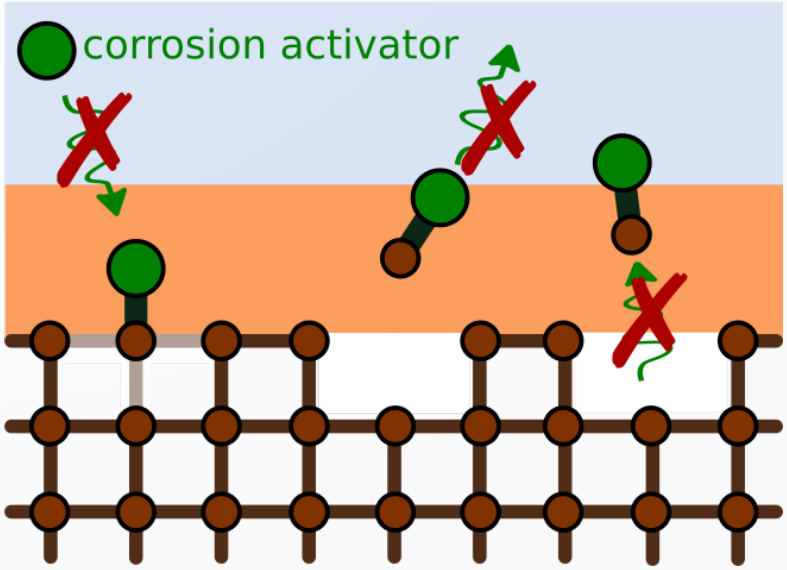


Introducing the context

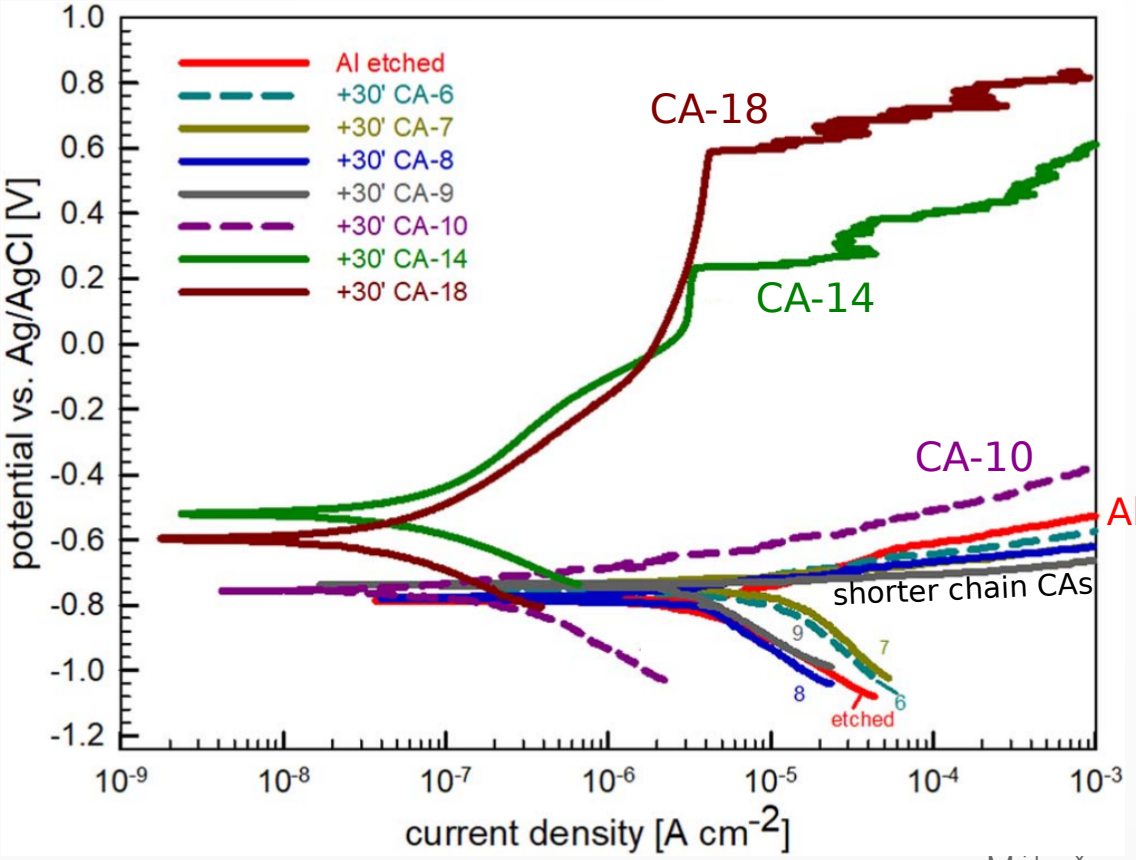
Corrosion of metals: $M \rightarrow M^{z+} + ze^{-}$

corrosion can be reduced with surfactant inhibitors that form a self-assembled-monolayer (SAM) on the surface of a metal





Carboxylic acids (CA) as inhibitors of Al



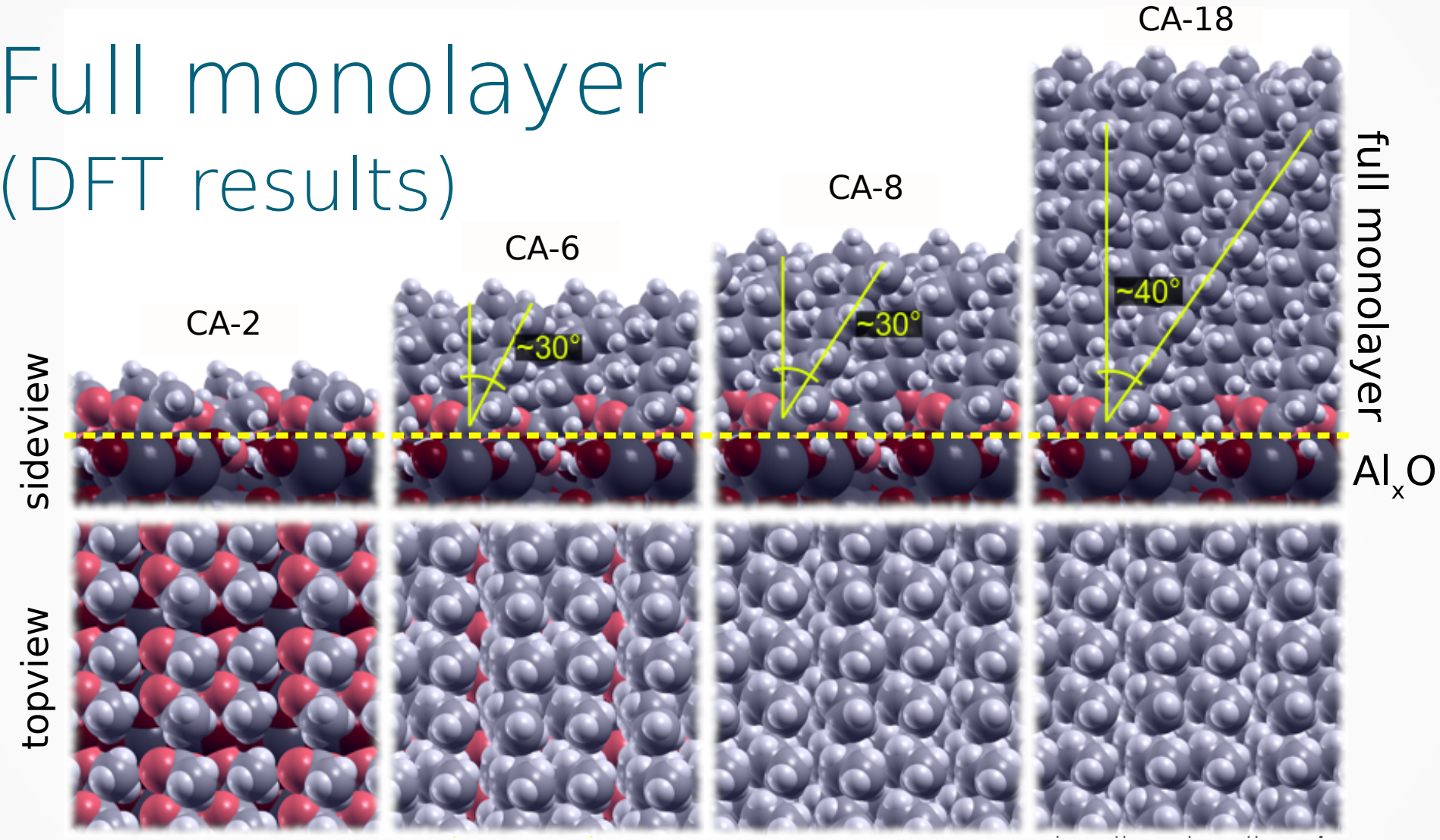
CA-n = $C_nH_{2n}O_2$
(CA-8 = octanoic acid)

only long-chain CAs are efficient inhibitors

WHY?

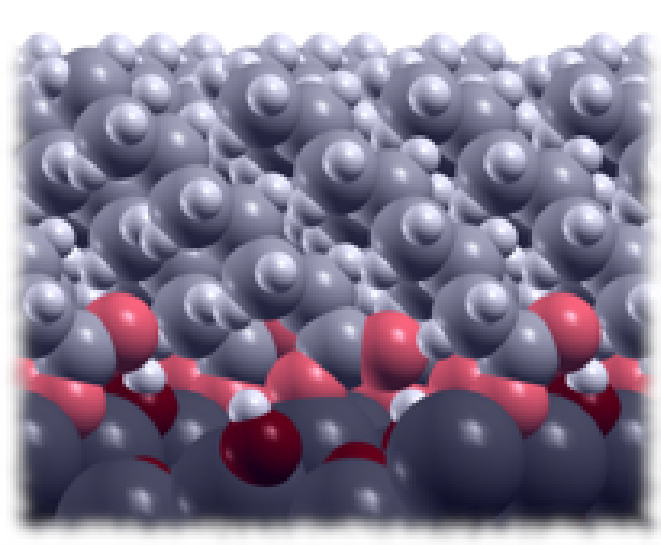
Milošev et al., J. Electrochem. Soc. **166**, C3131

Full monolayer
(DFT results)

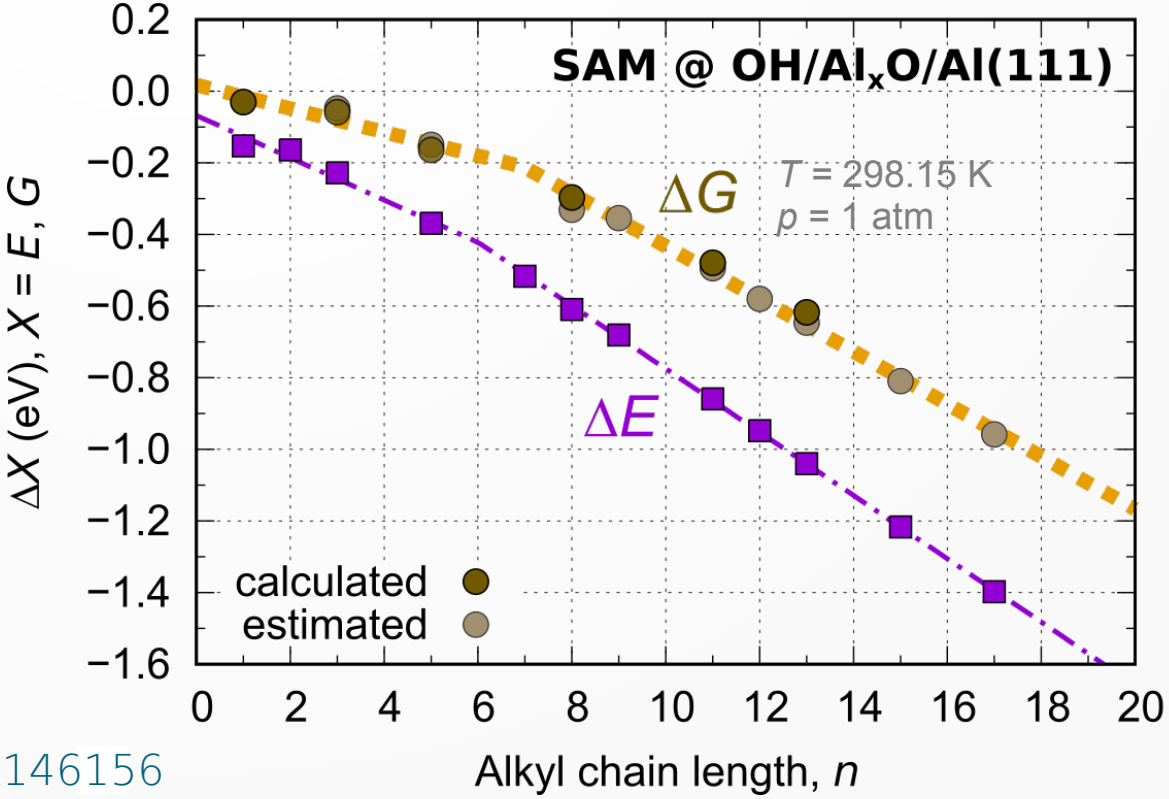


Adsorption energy at full monolayer

1 eV ≈ 100 kJ/mol
≈ 25 kcal/mol

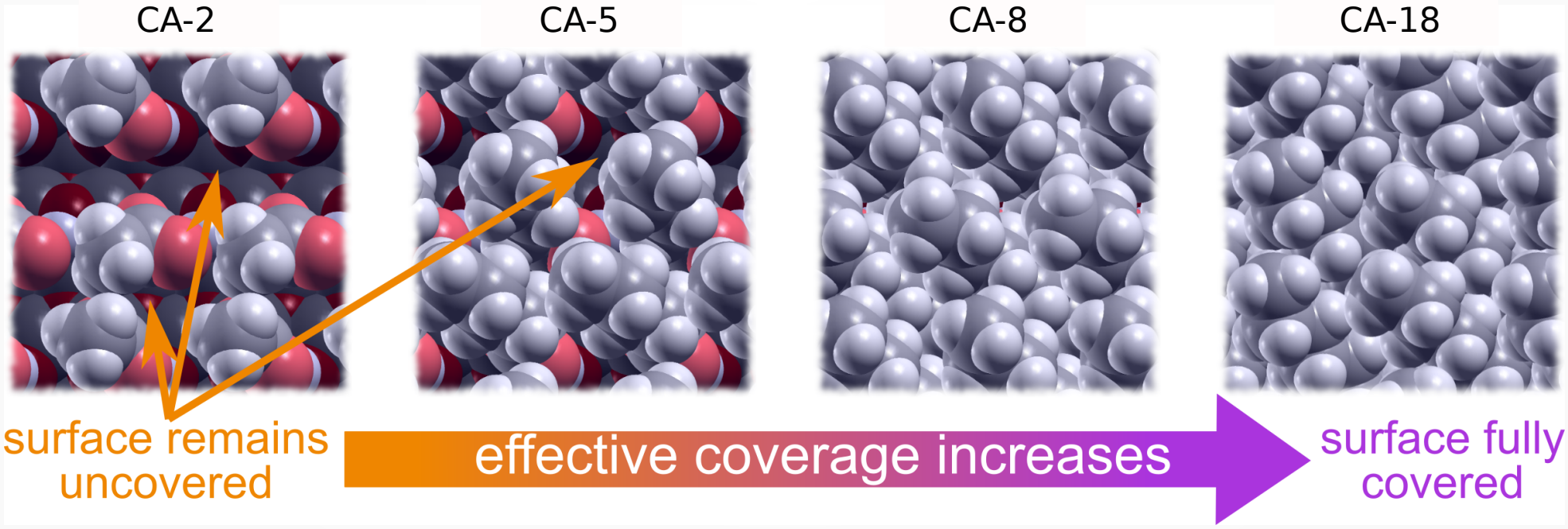


ΔE and ΔG vs. alkyl chain length



Poberžnik et al., Appl. Surf. Sci. **525**, 146156

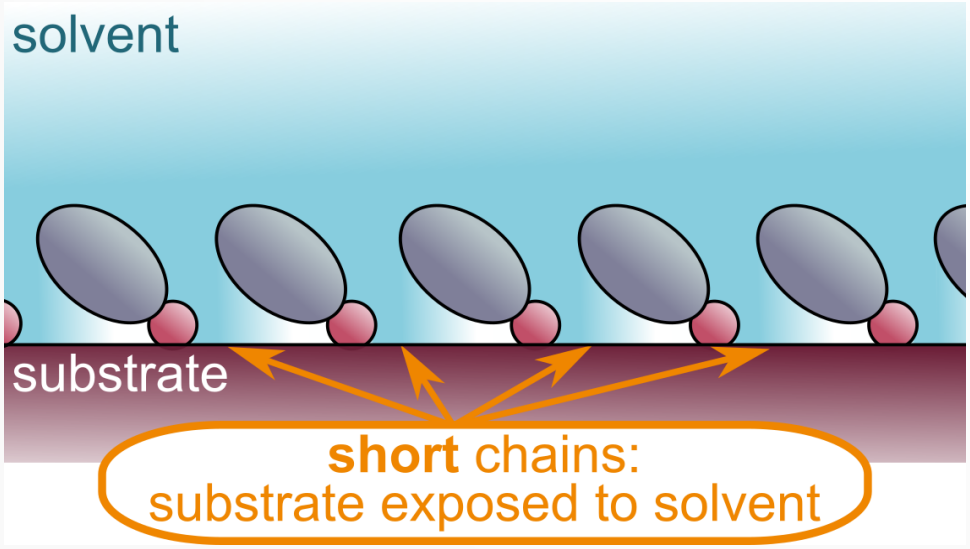
Effective coverage

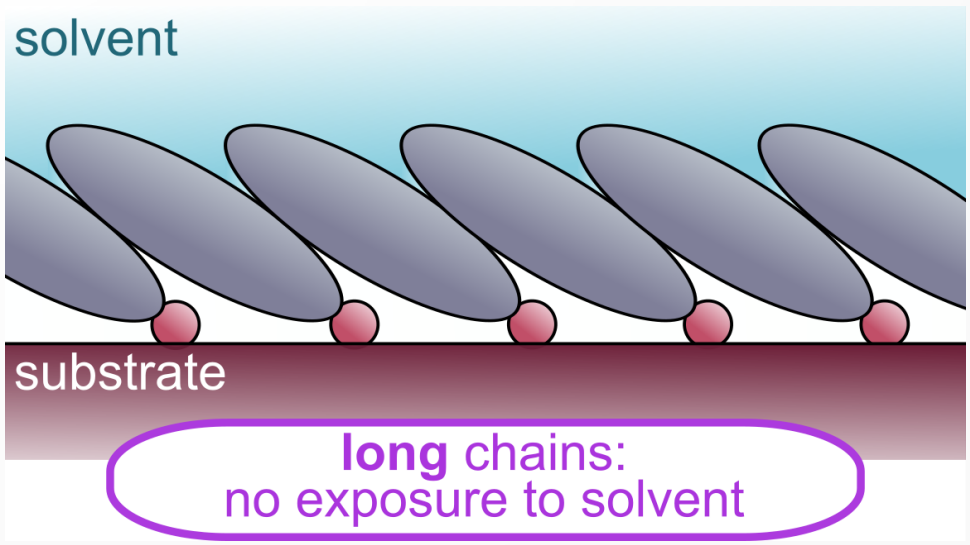


longer alkyl chain = smaller gaps = greater effective coverage

Milošev et al., J. Electrochem. Soc. **166**, C3131

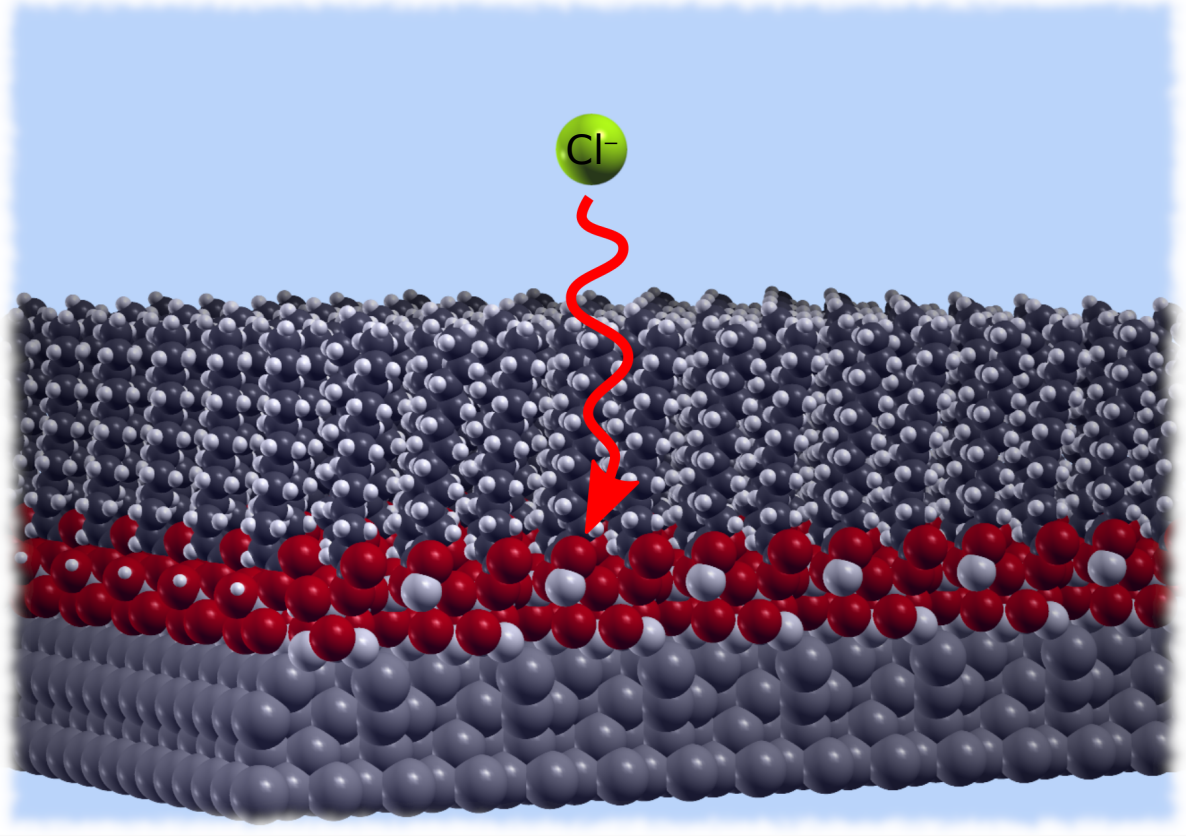
Effective coverage





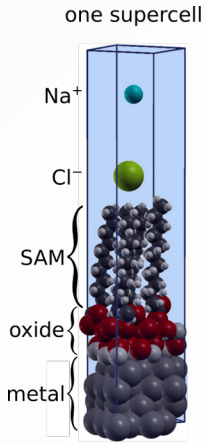
Milošev et al., J. Electrochem. Soc. **166**, C3131

Penetration of Cl^- through SAM



Kokalj & Costa, J. Electrochem. Soc. **168**, 071508

Beware of PBC (periodic boundary conditions) !



PBC & divergent Coulomb interactions:

add Na^+ to make supercell neutral

SAM = self assembled monolayer

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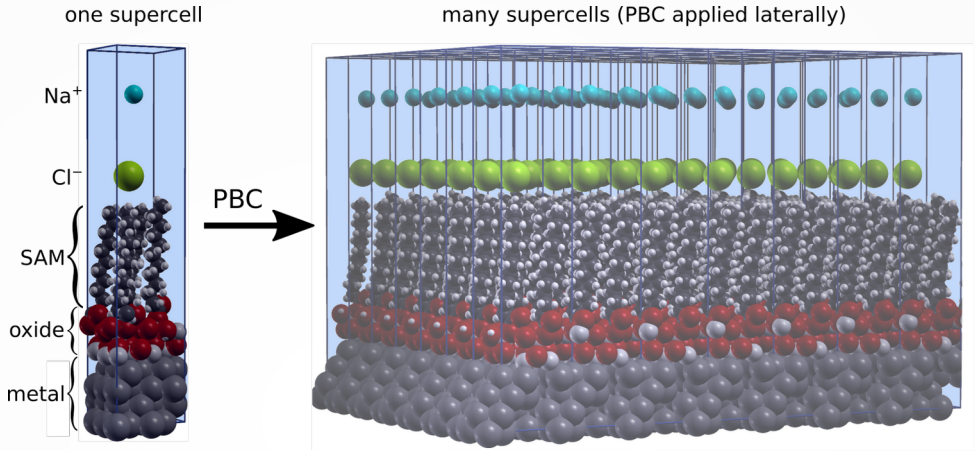

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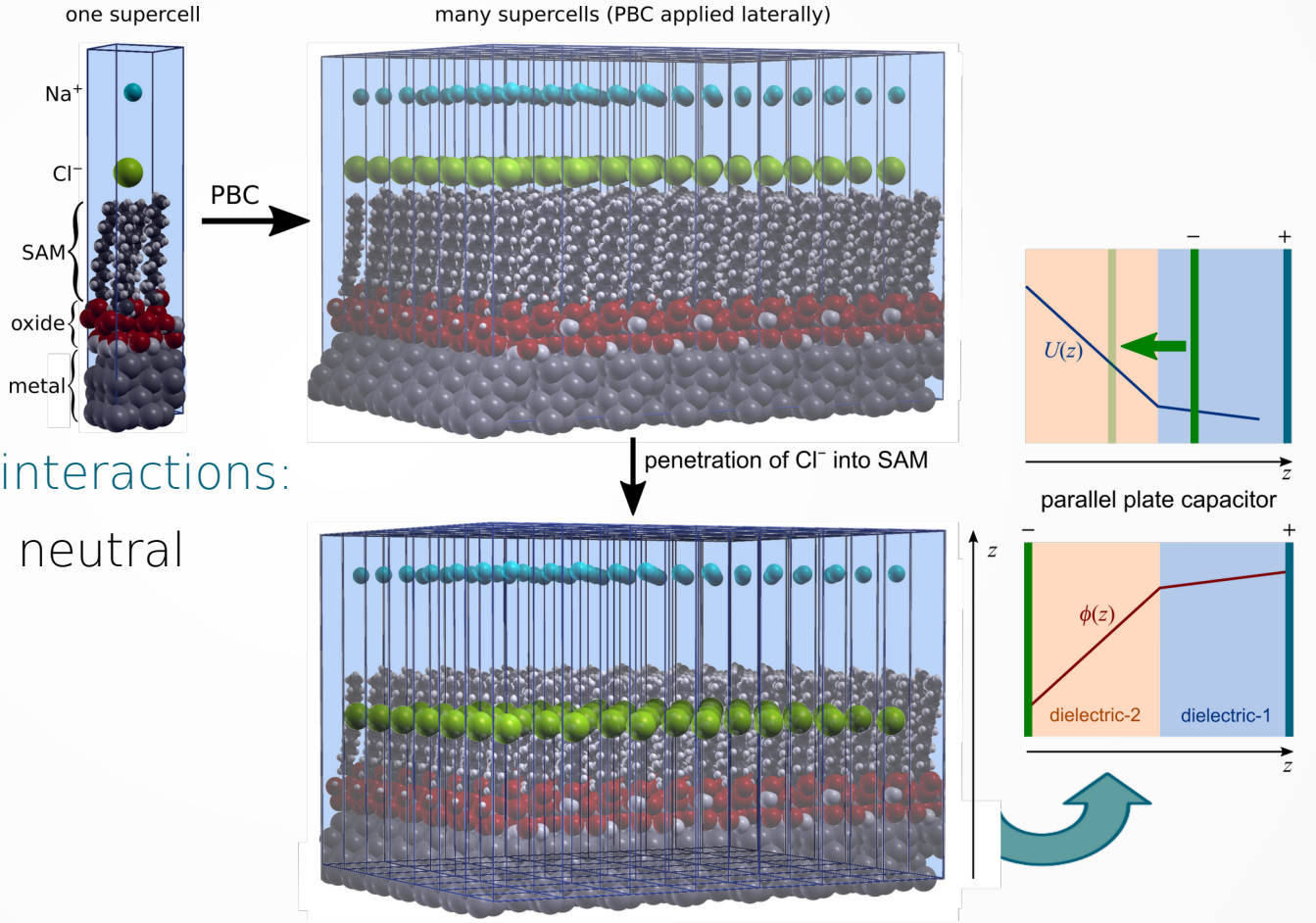
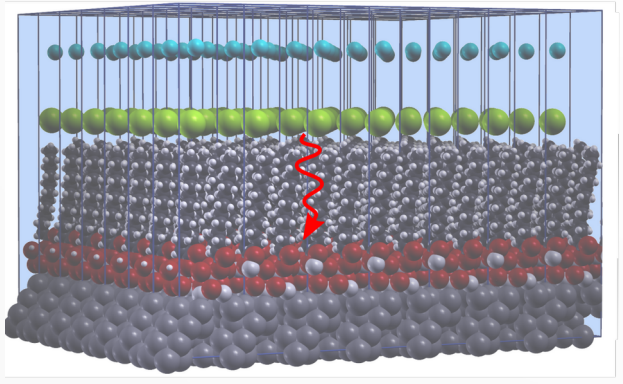


PBC & divergent Coulomb interactions:

add Na^+ to make supercell neutral

Beware of PBC

many supercells (PBC applied laterally)



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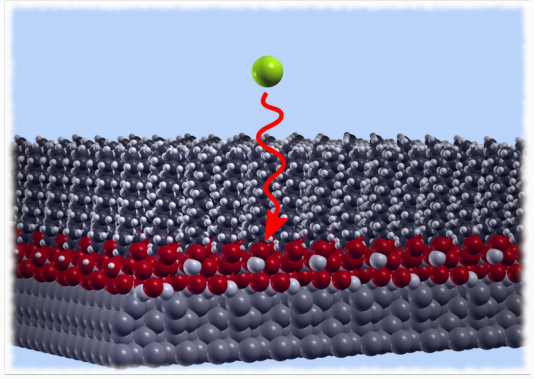
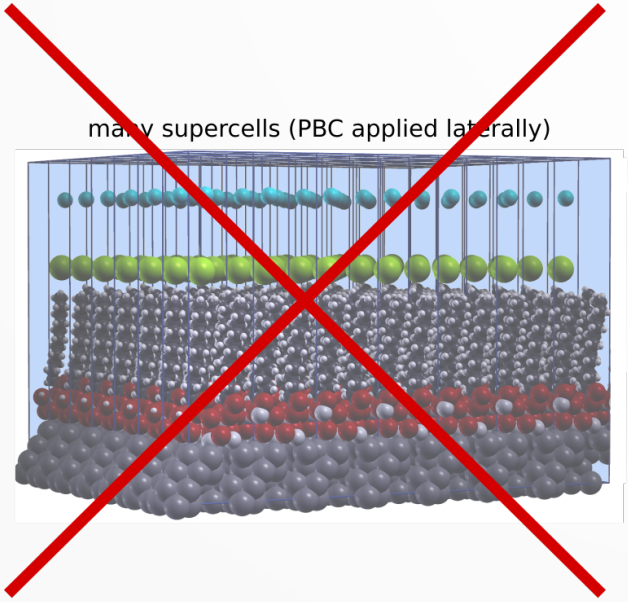
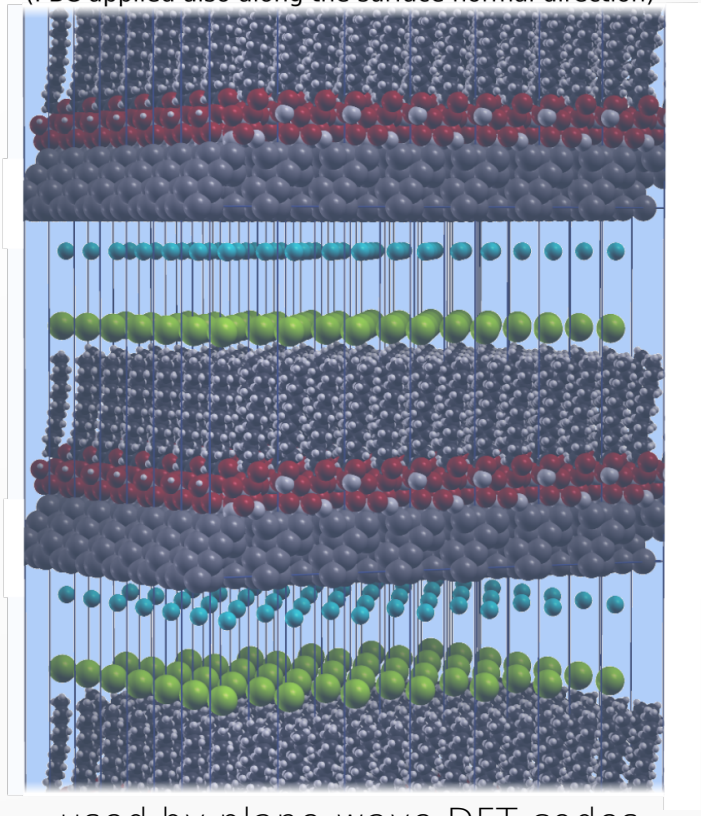


3D PBC: beware of artifacts

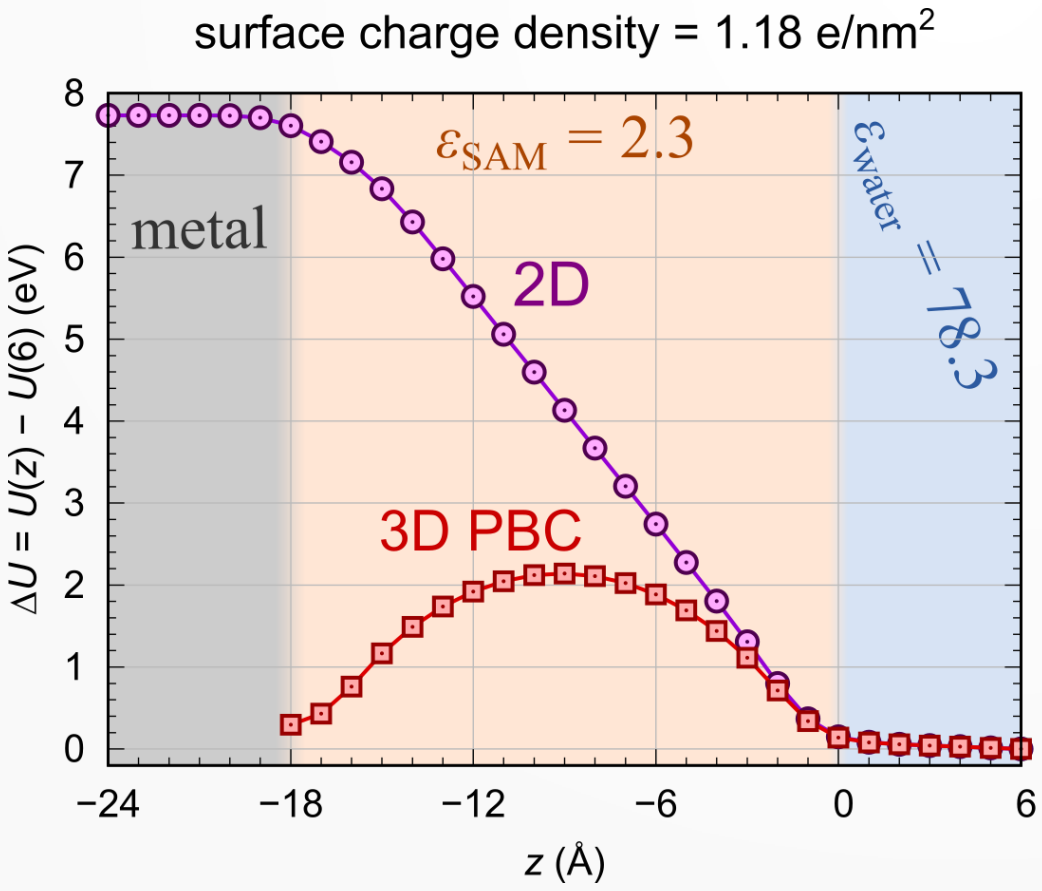


multi-slab model
(PBC applied also along the surface normal direction)

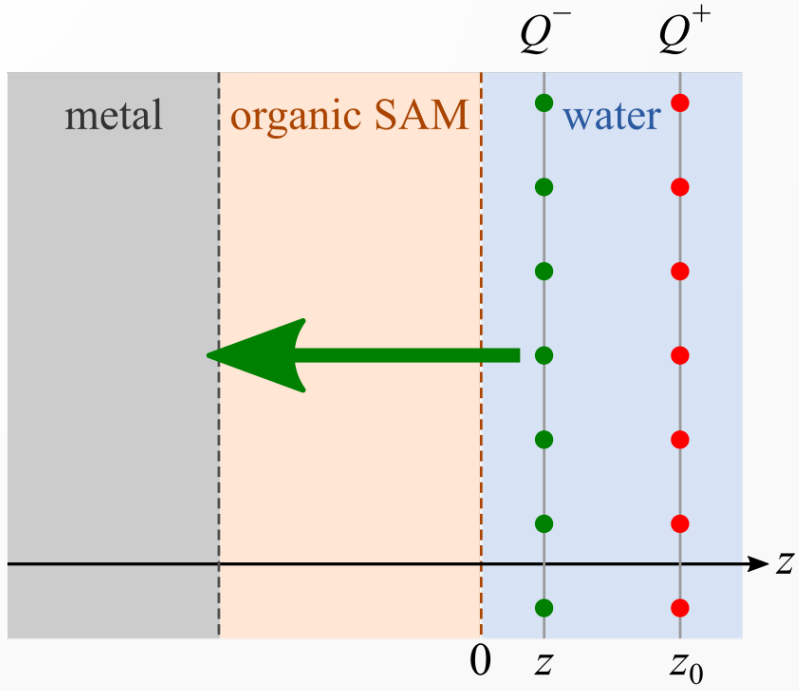


used by plane-wave DFT codes

3D PBC: beware of artifacts



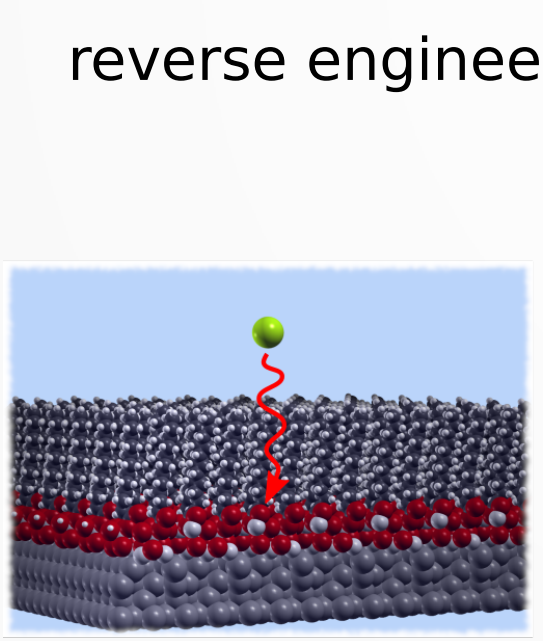
inter-ion electrostatic energy

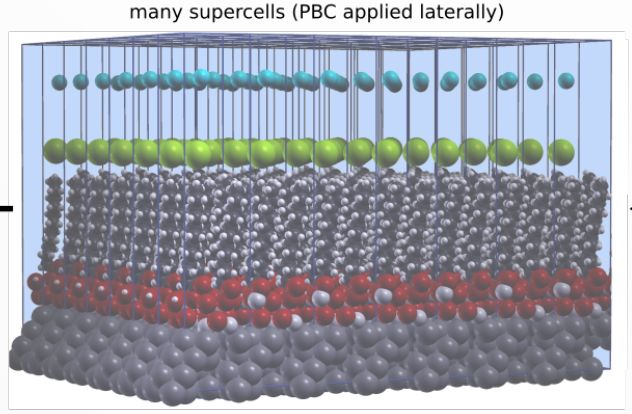


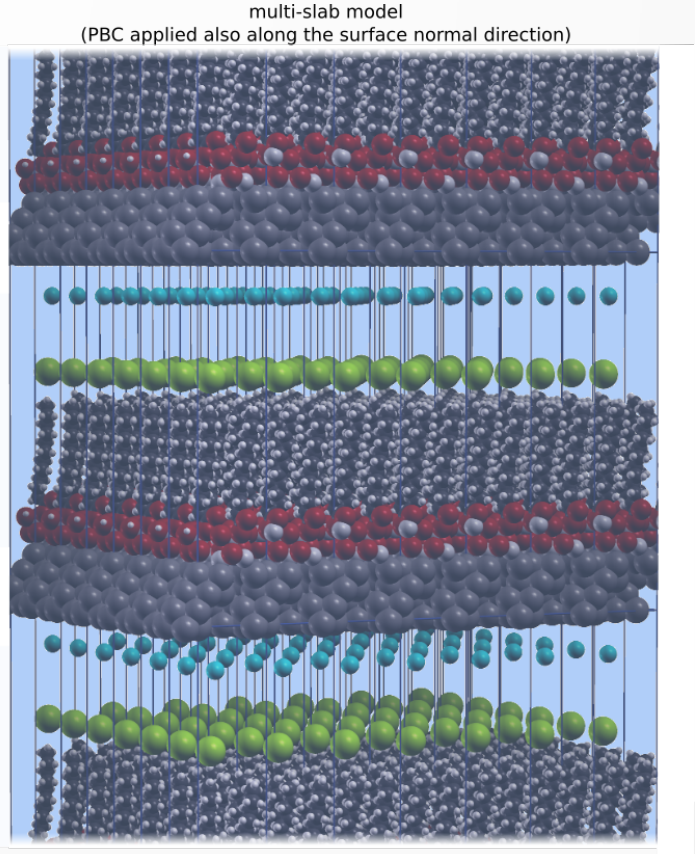
SAM = self assembled monolayer

3D PBC: beware of artifacts

reverse engineer to get rid of PBC artifacts

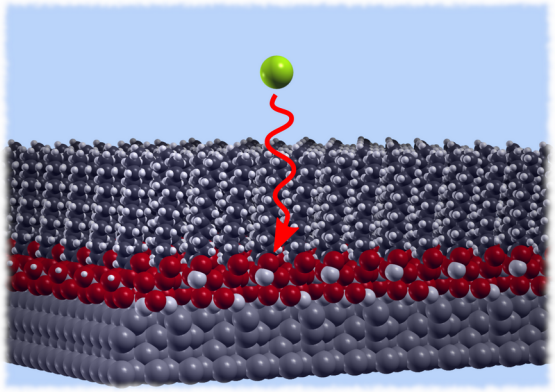


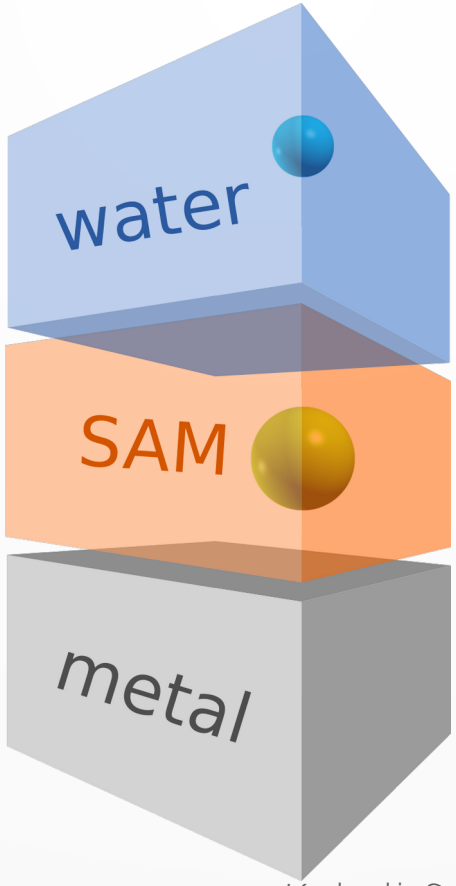




Kokalj & Costa, J. Electrochem. Soc. **168**, 071508

Penetration of Cl^- through SAM





Simplified model calculations:

- metal/SAM/water described by implicit continuum slabs
- ions treated explicitly (ionic solvation considered)
- elastic penalty for Cl^- penetration into SAM neglected

SAM = self assembled monolayer

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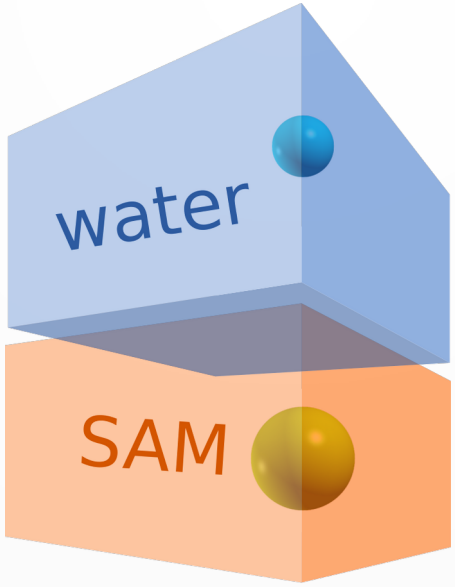
Simpler system: SAM/water



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QUANTUMESPRESSO

www.quantum-espresso.org

Environ plugin of Quantum ESPRESSO (QE)

www.quantum-environ.org

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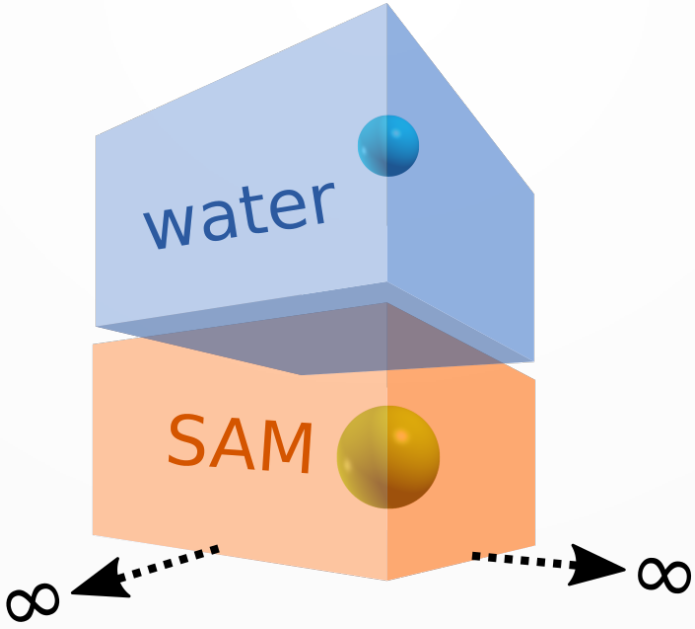

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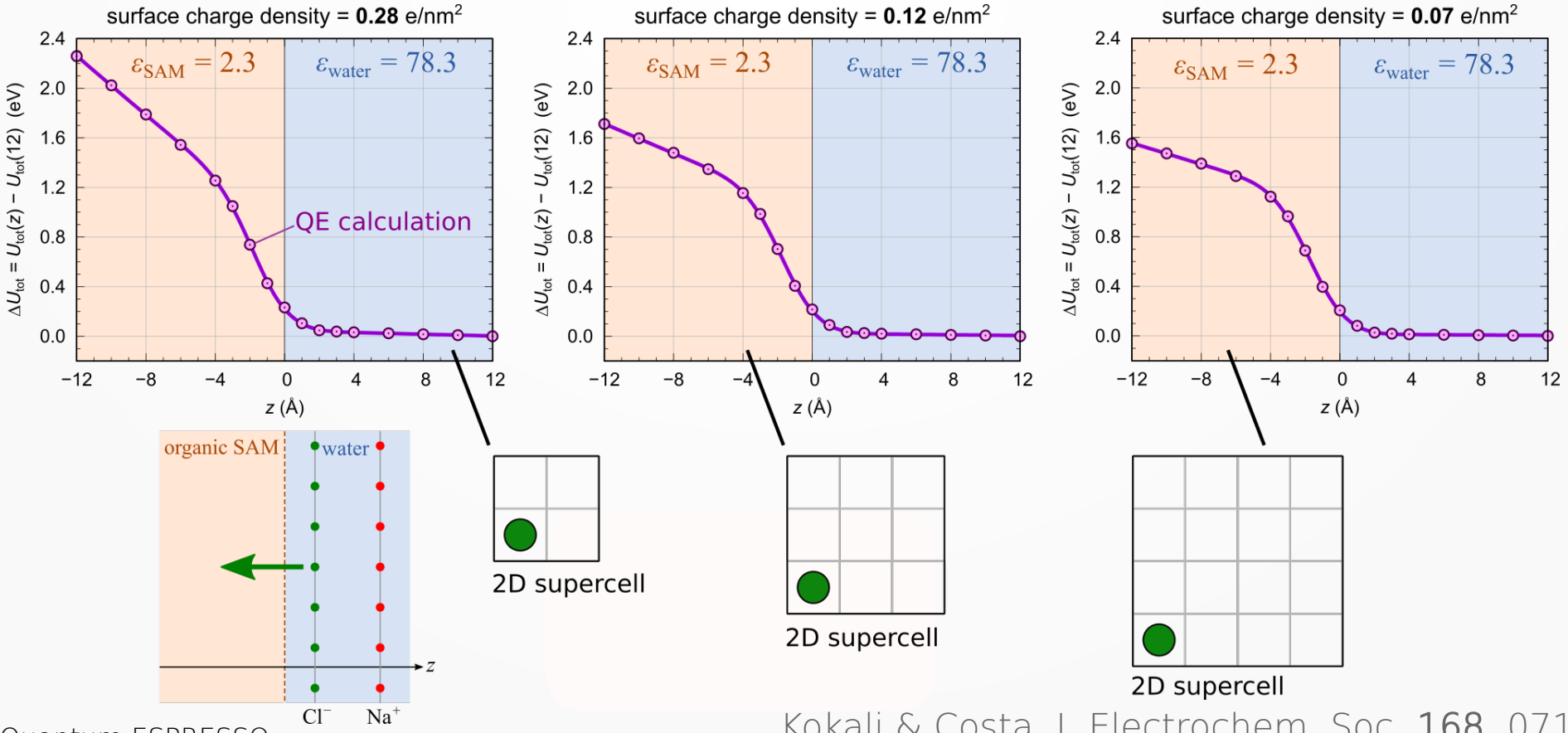

QE = Quantum ESPRESSO

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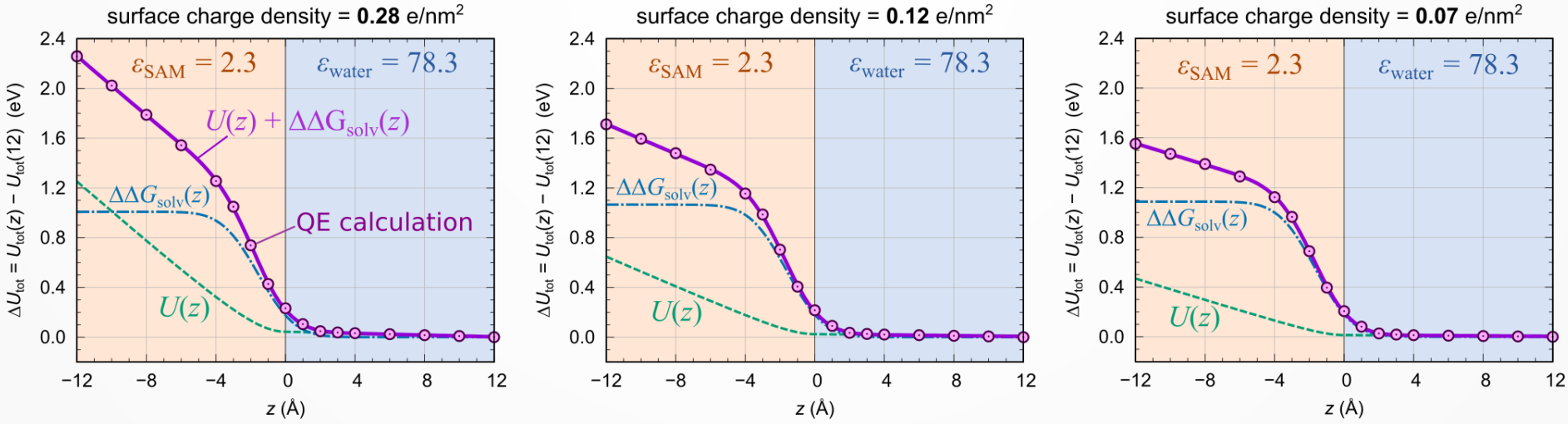
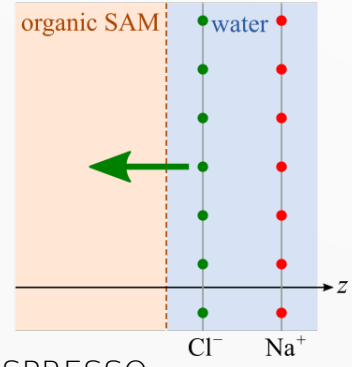
Simpler system: SAM/water





$U(z)$ = electrostatic interactions between ions

$\Delta\Delta G_{solv}(z)$ = difference between ionic solvation (ΔG_{solv}) in SAM and water

QE = Quantum ESPRESSO

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How to understand $\Delta\Delta G_{\mathrm{solv}}$

- Born solvation model:

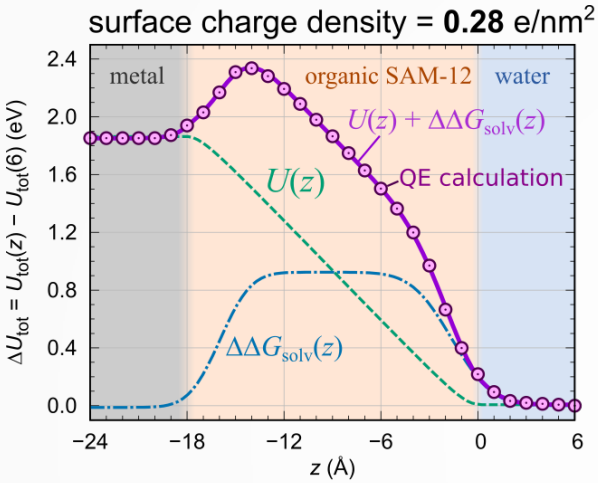
$$\Delta G_{\mathrm{solv}}^{\mathrm{Born}} = -\frac{q_{\mathrm{ion}}^2}{2r_{\mathrm{ion}}}\left(1-\frac{1}{\varepsilon}\right) \quad \text{[in Hartree atomic units]}$$

- SAM vs. water difference:

$$\Delta\Delta G_{\mathrm{solv}}^{\mathrm{Born}} = \Delta G_{\mathrm{solv}}^{\mathrm{Born}}(\mathrm{SAM}) - \Delta G_{\mathrm{solv}}^{\mathrm{Born}}(\mathrm{water}) = \frac{q_{\mathrm{ion}}^2}{2r_{\mathrm{ion}}}\left(\frac{1}{\varepsilon_{\mathrm{SAM}}}-\frac{1}{\varepsilon_{\mathrm{water}}}\right)$$

SAM = self assembled monolayer

Full system: metal/SAM/water



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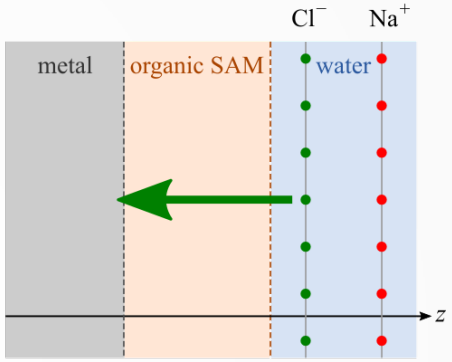

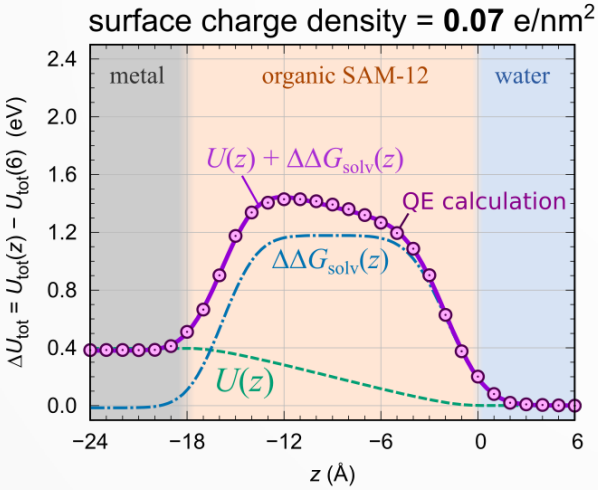

SAM-12 = SAM composed of CA-12
(CA = carboxylic acid)

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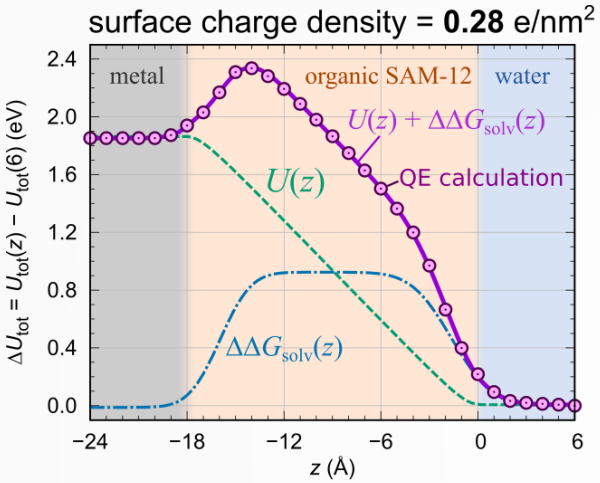
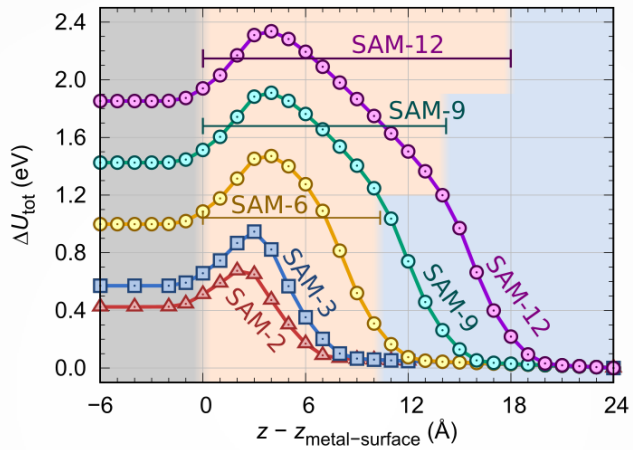
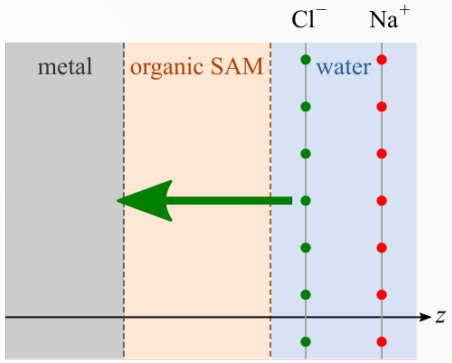
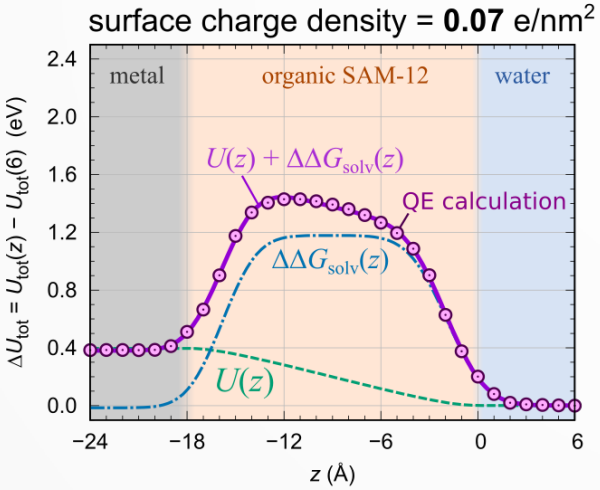
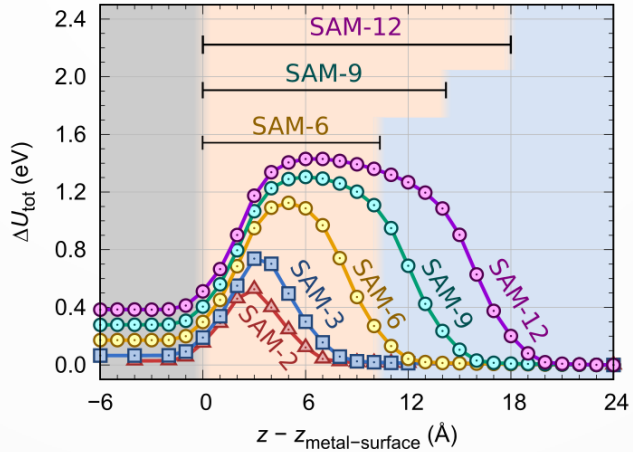
Full system: metal/SAM/water









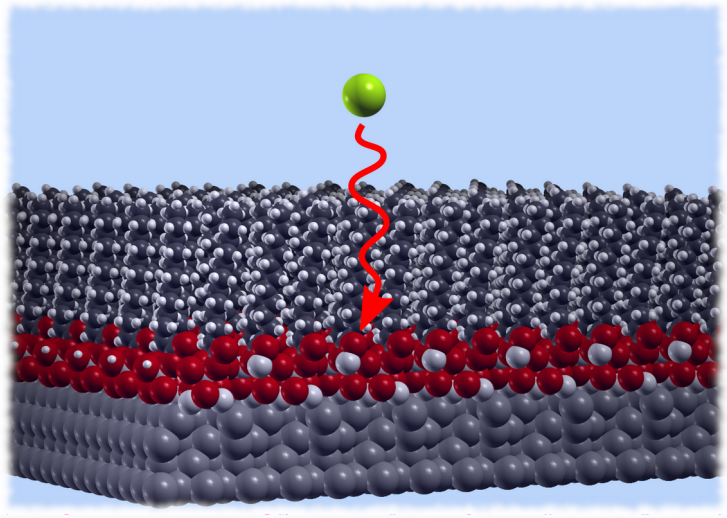


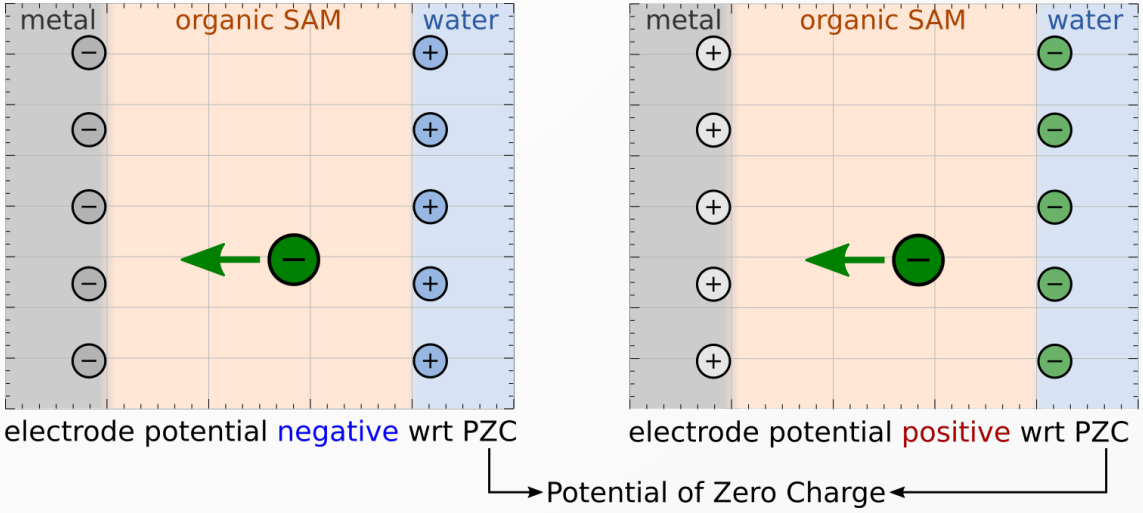
SAM-*x* = SAM composed of CA-*x*
(CA = carboxylic acid)

SAM needs some thickness for solvation barrier to fully develop !

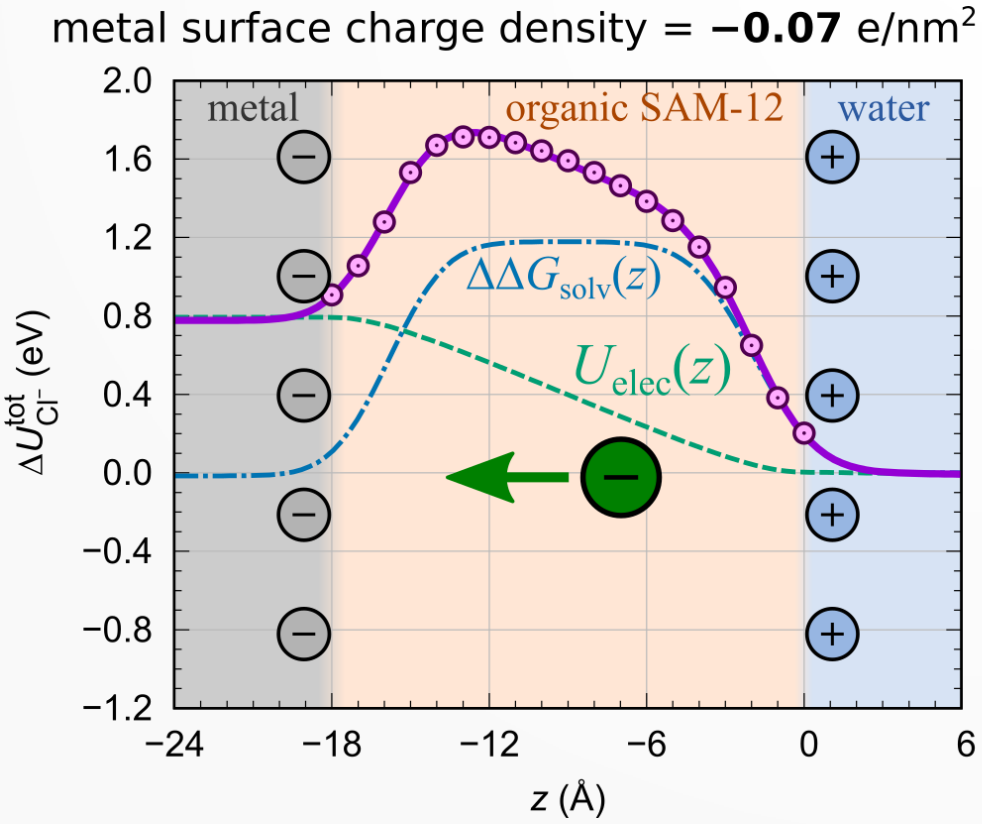
Penetration of a single Cl^-

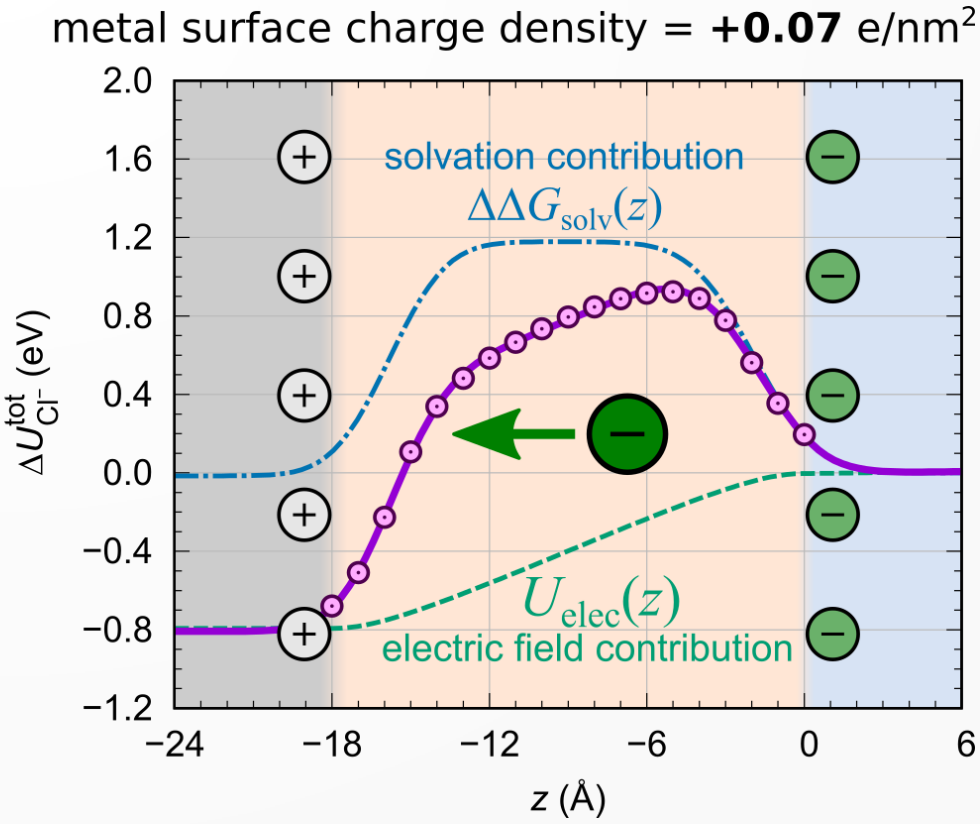
... as a function of electrode potential
(simple Helmholtz double-layer picture)





Penetration of a single Cl^-





Kokalj & Costa, J. Electrochem. Soc. **168**, 071508

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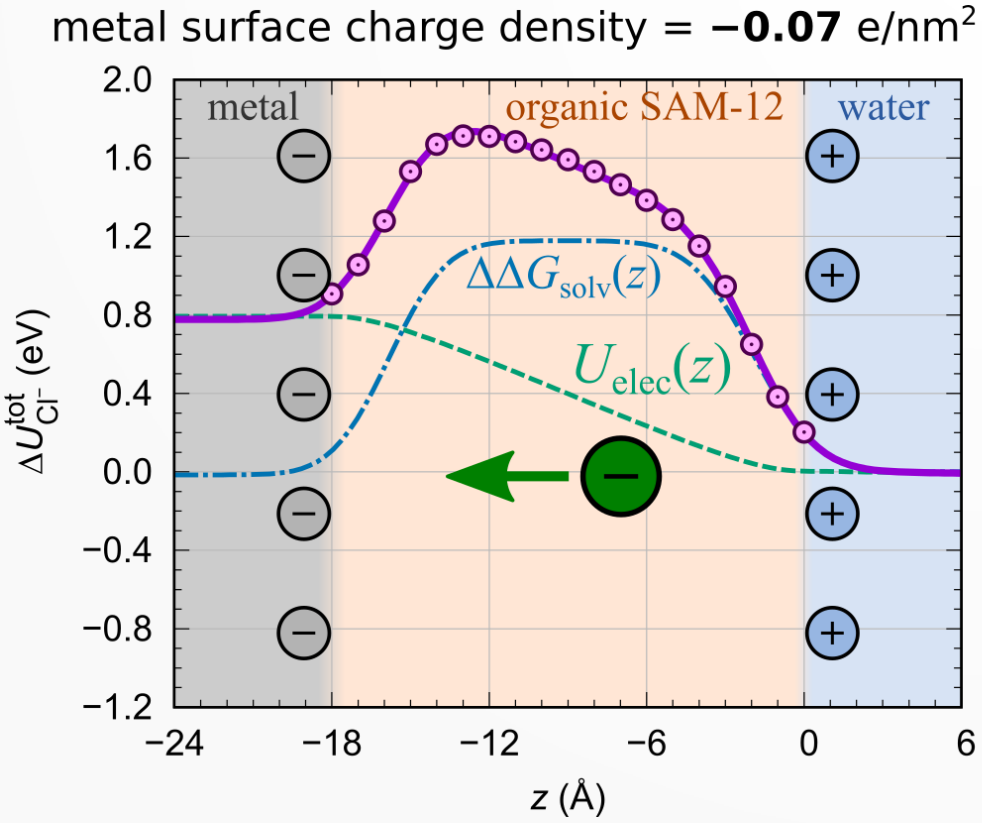

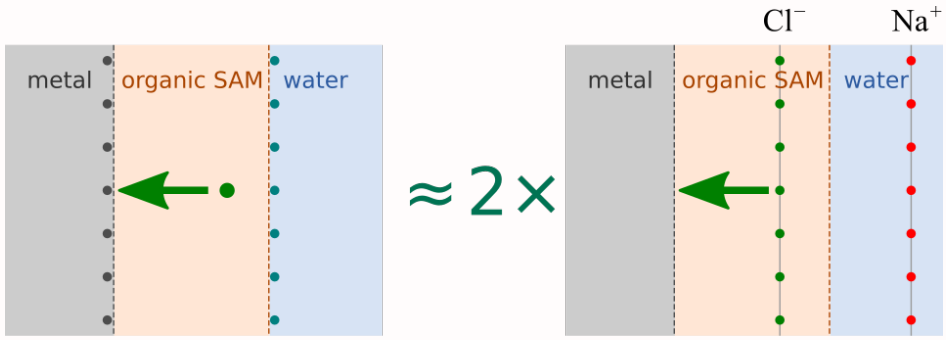

$$U_{\mathrm{elec}}(z) = 2U(z)$$

elec ≡ electric field contribution

Note also: electrode potential is associated with $U_{\mathrm{elec}}(z)$

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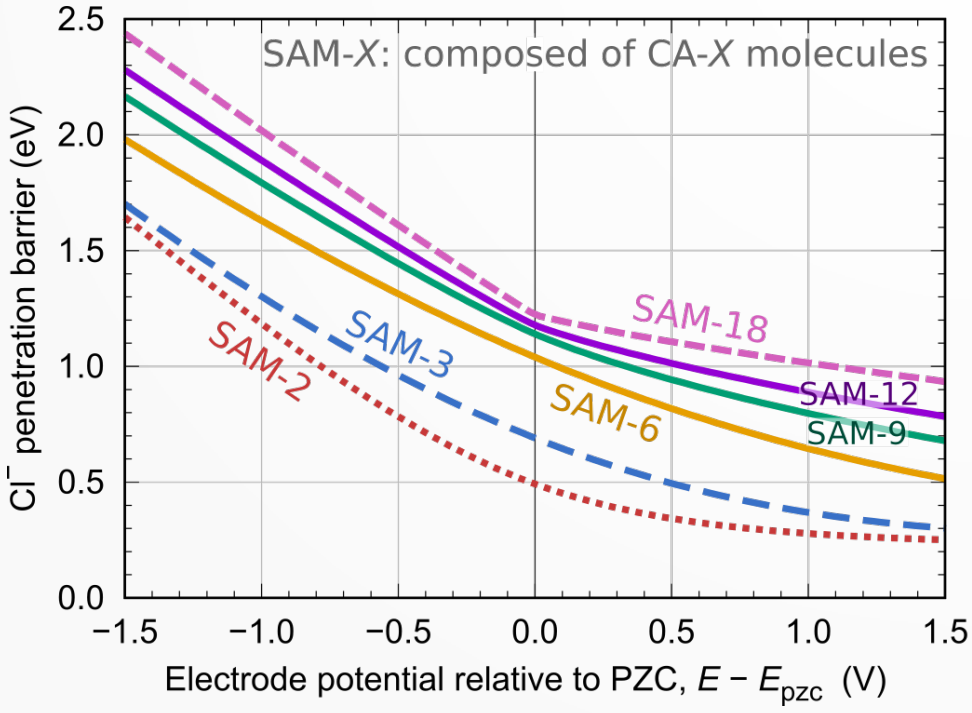
Cl^- penetration vs. electrode potential



Simplifying assumptions:

- CA molecules fully cover the surface irrespective of the alkyl chain length
  (in reality only long-chain CAs form a complete SAM)
- surface is fully covered by SAM at all electrode potentials
- elastic penalty for Cl^- penetration is neglected
- ...

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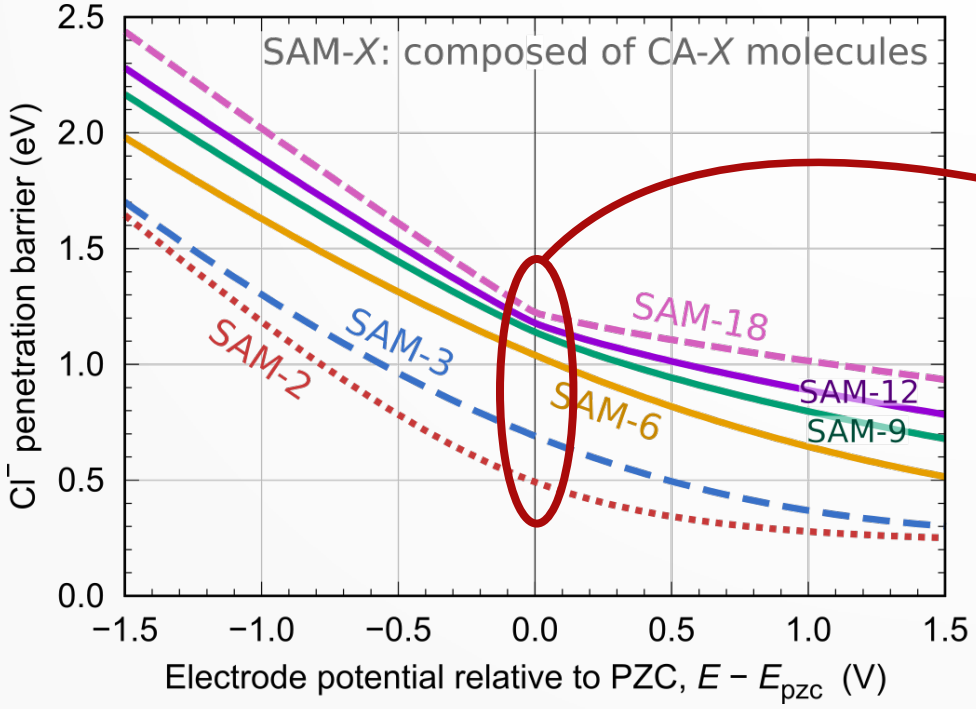
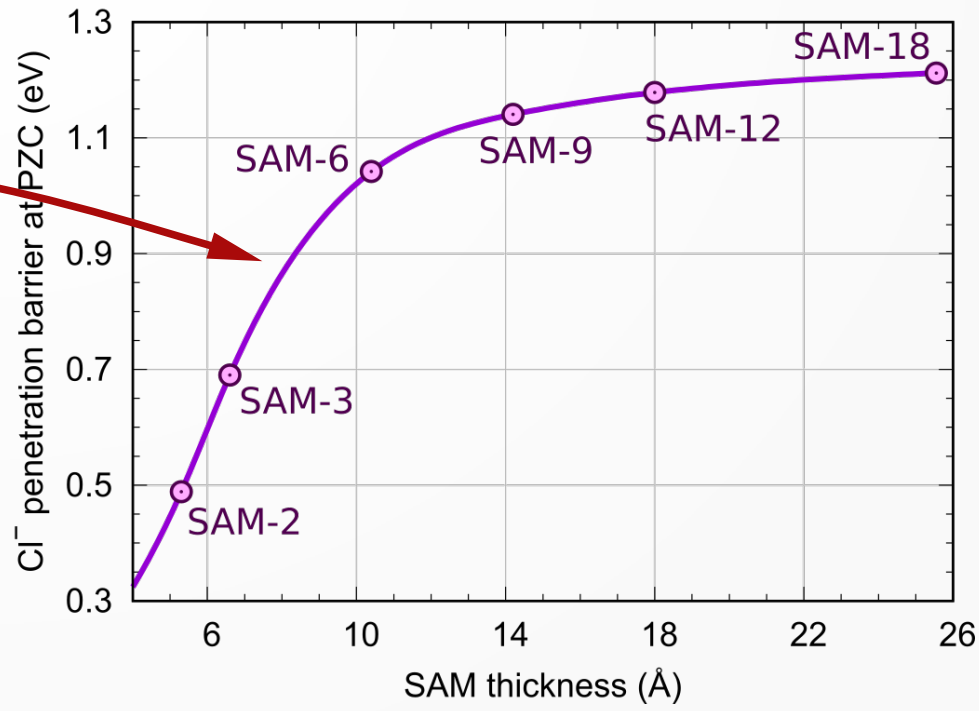
Cl^- penetration vs. electrode potential





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Conclusions

- The mechanism by which SAM hinders the penetration of Cl^- ions into SAM understood with aid of a simple model
- Contributions to penetration barrier:
  - inferior solvation of ions in SAM ($\Delta\Delta G_{solv}$)
  - contribution due to electric field in the Helmholtz double-layer (U_{elec})
  - elastic penalty (currently neglected)
- SAM needs to be thicker than about 10 Å for barrier to fully develop
- Developed model is based on electrostatic arguments and is thus generally applicable (can treat the penetration of any ions, including the dissolution of metals)

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DFT group:

Matic Poberžnik
Matjaž Dlouhy
Lea Gašparič
Matic Lozišek
Dunja Gustinčić
Nataša Kovačević
Sebastijan Peljhan

Electrochemistry group:

Ingrid Milošev
Peter Rodič
Barbara Kapun
Dolores Zimerl
Dževad Kozlica
...

IJS

Dept. Physical & Organic Chemistry,
Jožef Stefan Institute, Slovenia

Slovenian Research Agency

REPUBLIC OF SLOVENIA
MINISTRY OF EDUCATION, SCIENCE AND SPORT

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Thank you for your attention

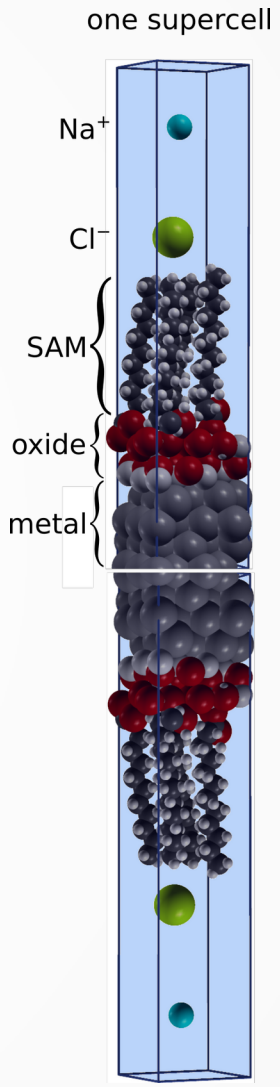
Chimie Paris ParisTech | PSL

Agence Nationale de la Recherche ANR

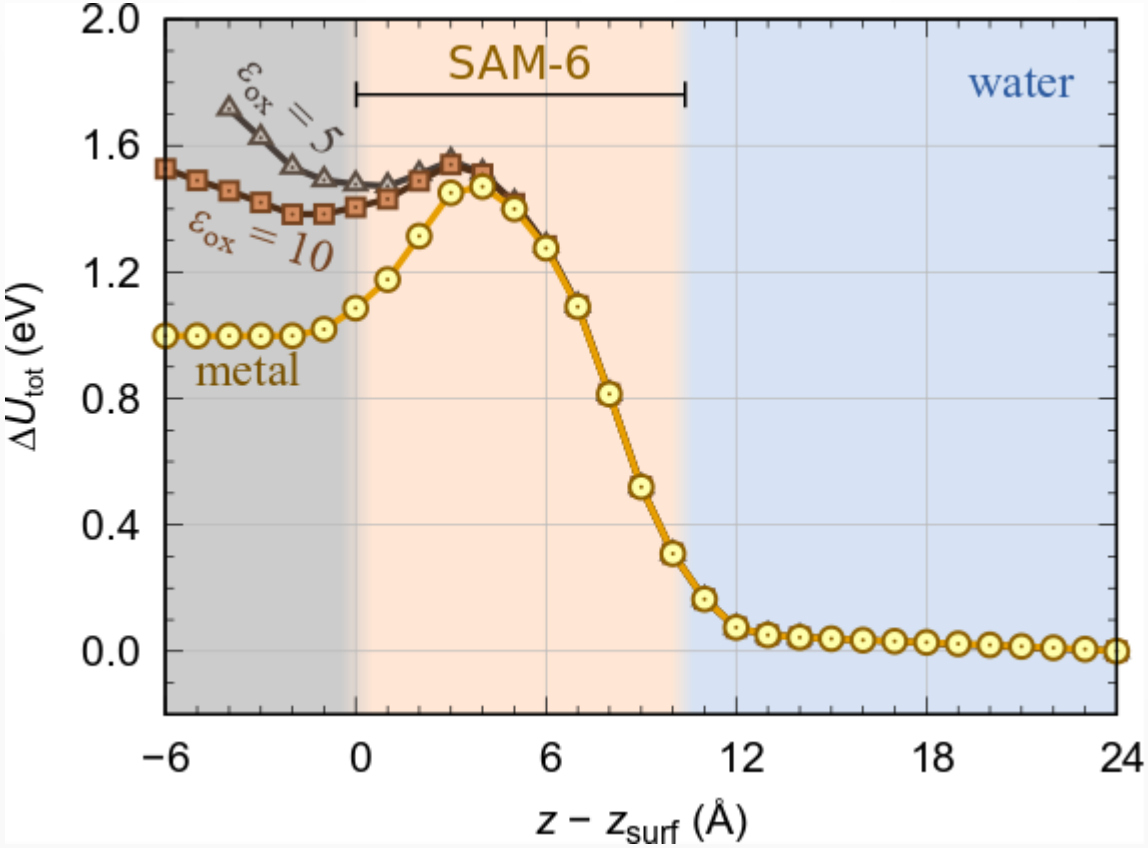
D. Costa
P. Marcus
F. Chiter

How to get rid of 3D PBC artifacts

simple but computationally inefficient method is to use symmetric setup



Oxide/SAM/water



Oxide/SAM/water