A semi-classical Thomas-Fermi model to tune the metallicity of electrodes in classical simulations

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18/11/2020

Thomas-Fermi in classical MD

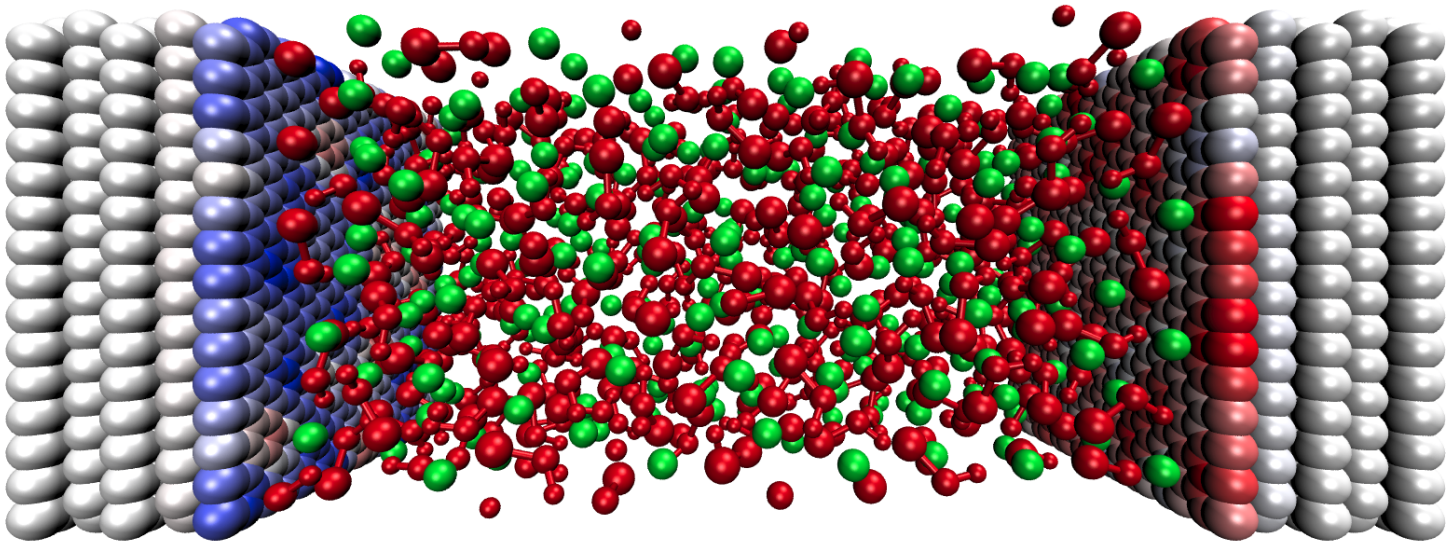
1. Molecular simulations of metallic interfaces
   - Constant potential simulations
   - Applications
   - Highlight on charge fluctuations with BO sampling

2. How to model non-ideal metals?
   - The Thomas-Fermi model
   - Effect of metallicity on electrolyte properties
   - How to study the influence of metallicity on confined phase transitions?

Molecular simulations of metallic interfaces

- Capacitors used for electric energy storage

  BMI-PF_6 ionic liquid with graphite electrodes



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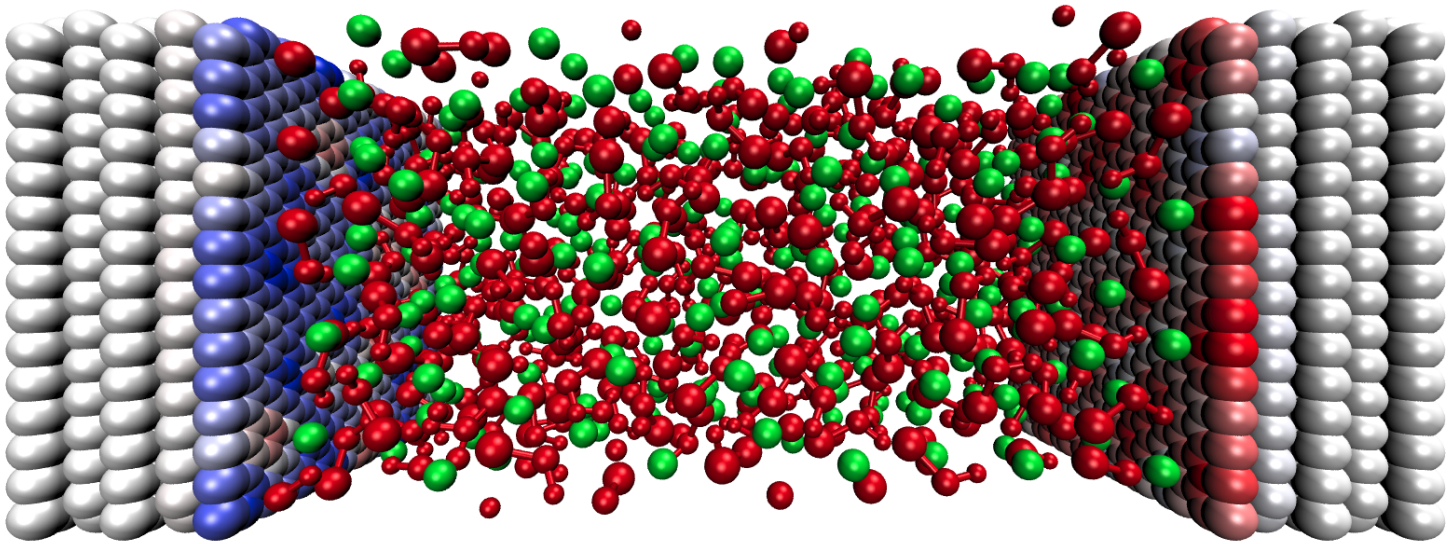

Challenges for molecular simulation

- Finite temperature → sampling configurations with MD

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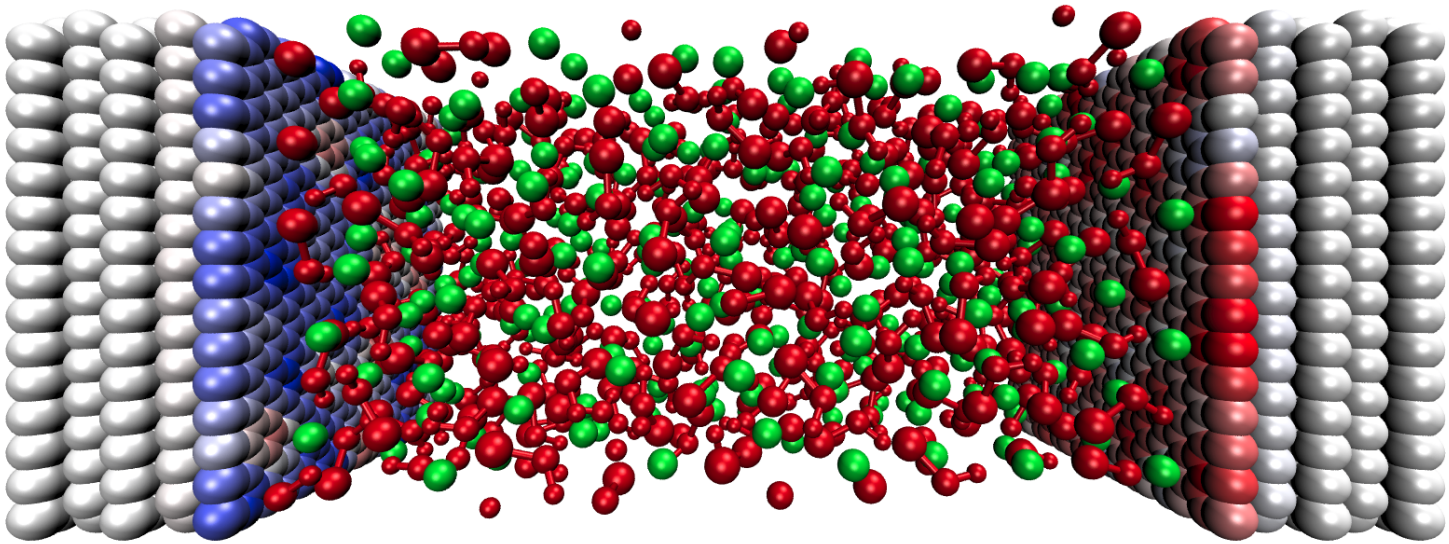

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- Large systems & long times → using classical force fields

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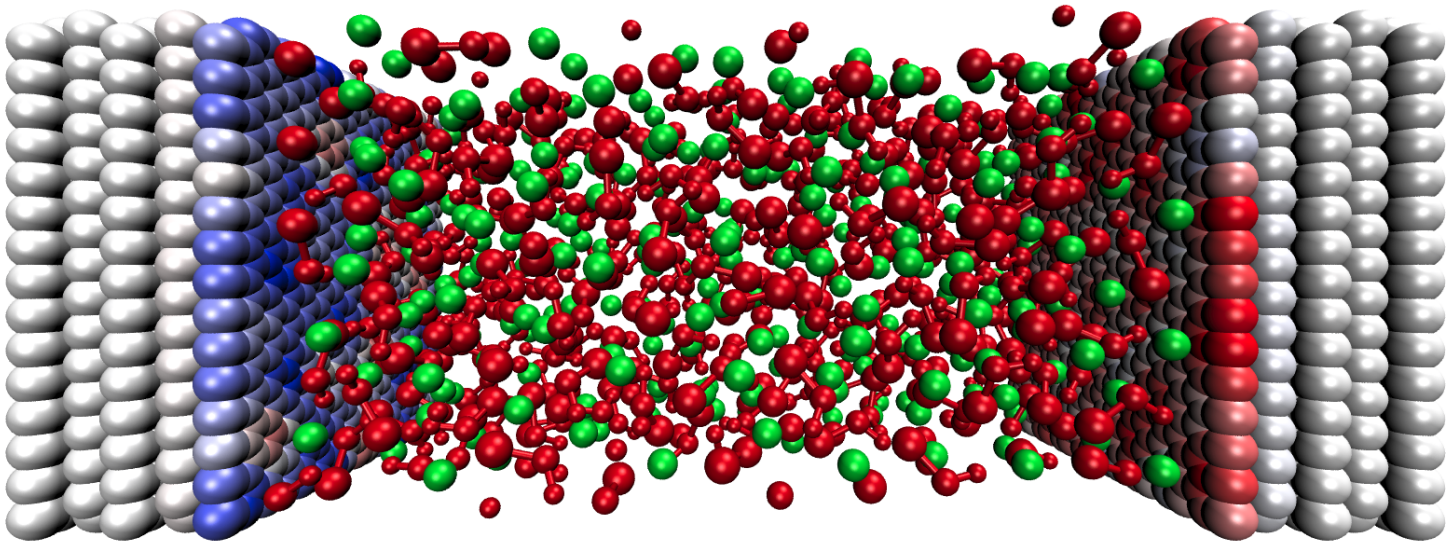

Challenges for molecular simulation

- Finite temperature → sampling configurations with MD
- Large systems & long times → using classical force fields
- Metallic interfaces → accounting for electronic polarization

Molecular simulations of metallic interfaces

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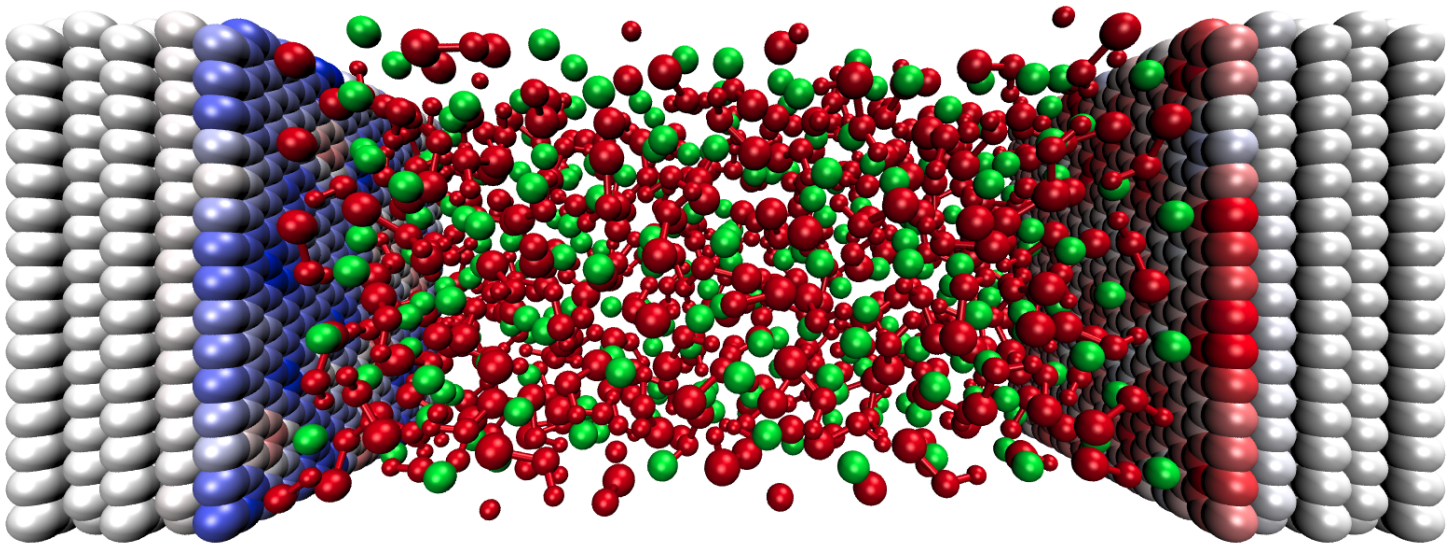


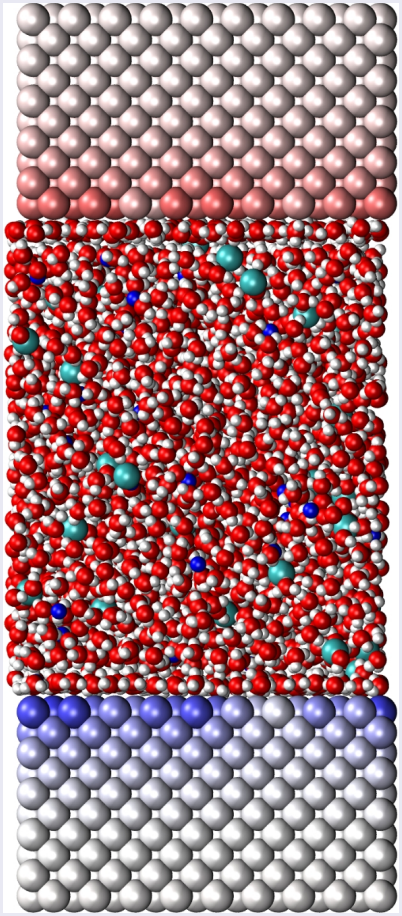
Statistical Physics encounters Quantum Chemistry

(focusing on the electrolyte side)

Molecular simulations of metallic interfaces

- How to account for electronic polarization?

Constant potential simulations



Molecular simulations of metallic interfaces

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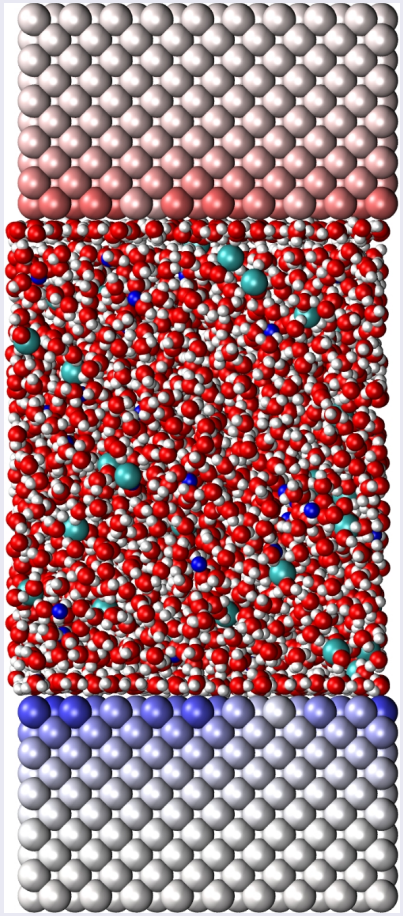

- fluctuating Gaussian charges $\mathbf{q} = \{q_i\}$

Molecular simulations of metallic interfaces

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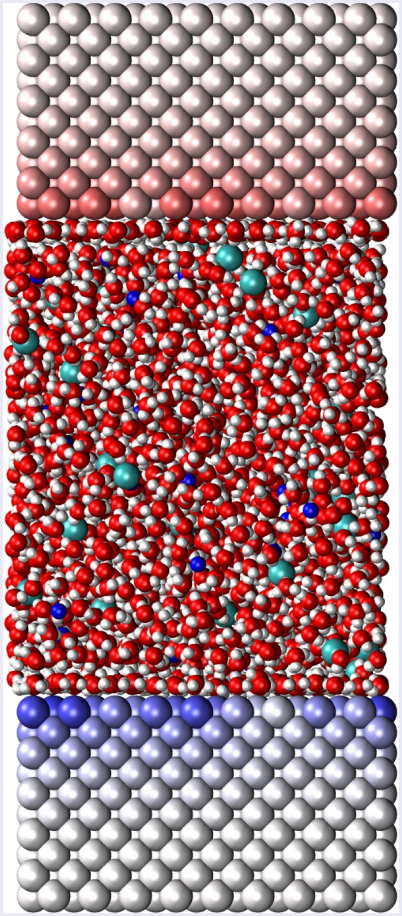


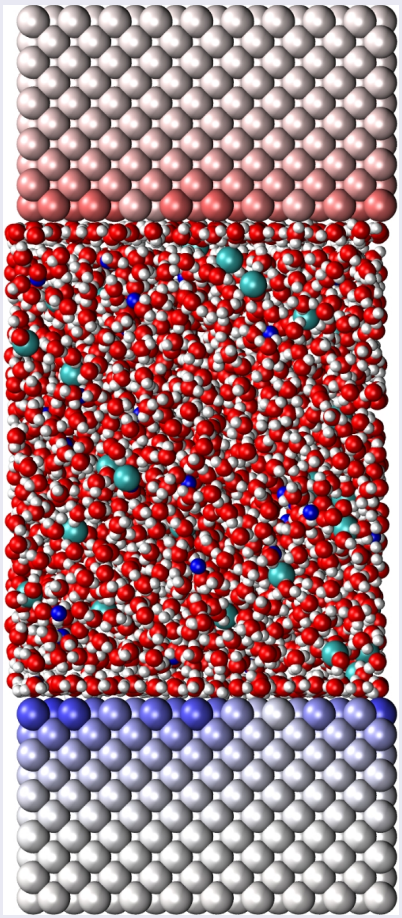
- fluctuating Gaussian charges $\mathbf{q} = \{q_i\}$
- under a constant potential constraint

$$\frac{\partial U}{\partial \mathbf{q}} = \Psi$$

Molecular simulations of metallic interfaces

- How to account for electronic polarization?

Constant potential simulations



- fluctuating Gaussian charges $\mathbf{q} = \{q_i\}$
- under a constant potential constraint

$$\frac{\partial U}{\partial \mathbf{q}} = \Psi$$

- solved using minimization algorithms

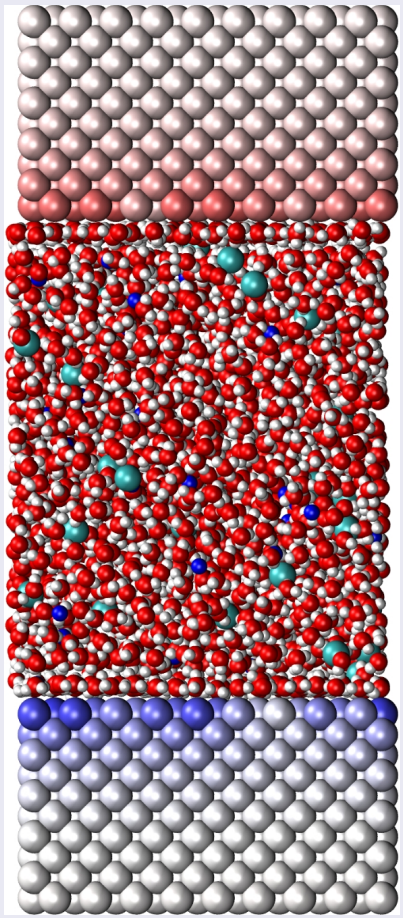
$$\left.\frac{\partial (U - q\Psi)}{\partial \mathbf{q}}\right|_{\mathbf{q}^*} = 0$$

Ψ electric potential vector $\{\Psi_L \ldots, \Psi_R \ldots\}$

Molecular simulations of metallic interfaces

- How to account for electronic polarization?

Constant potential simulations



- fluctuating Gaussian charges $\mathbf{q} = \{q_i\}$
- under a constant potential constraint

$$\frac{\partial U}{\partial \mathbf{q}} = \Psi$$

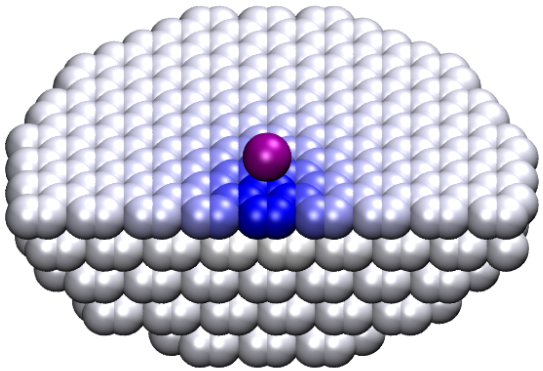
- solved using a matrix inversion

$$\mathbf{q}^* = \mathbf{A_0}^{-1}(\mathbf{B}(\mathbf{r}^N) + \Psi)$$

A_0 electrode - electrode interactions matrix
B electrode - electrolyte interactions vector
Ψ electric potential vector $\{\Psi_L \ldots, \Psi_R \ldots\}$

Constant potential simulations

- Induced charges on the surface in response to the external medium



(a) Li^+ ion

Constant potential simulations

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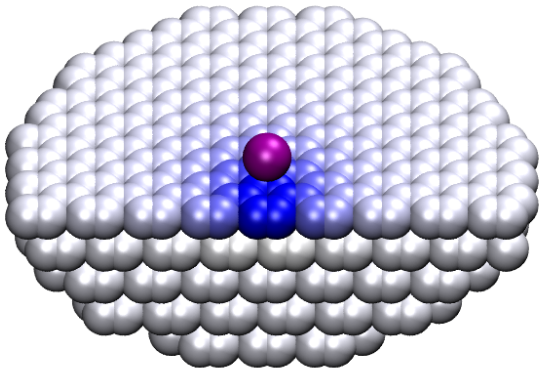

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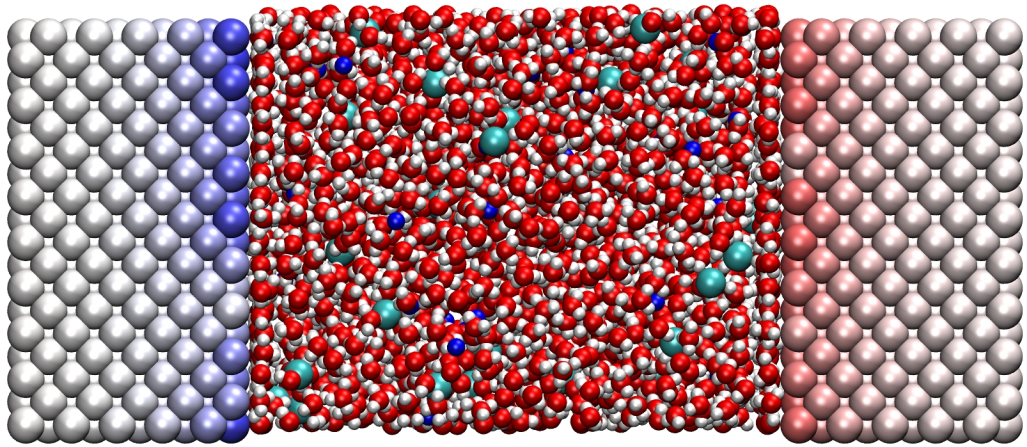
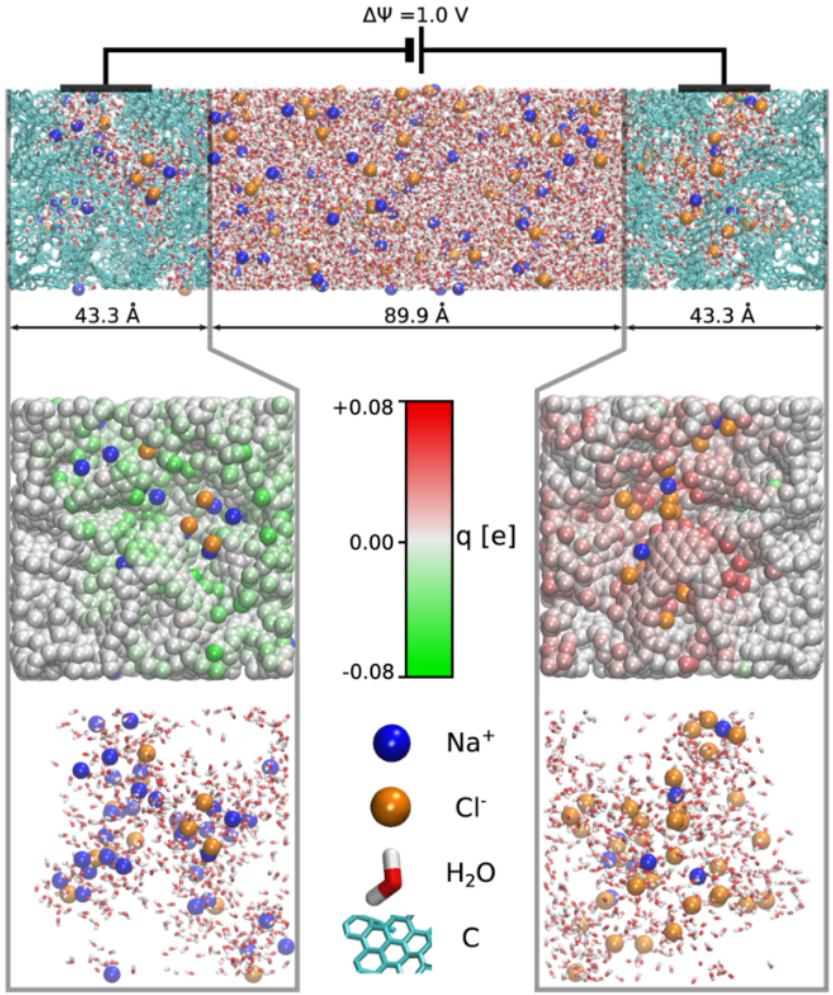


(b) Aqueous NaCl electrolyte

Constant potential simulations

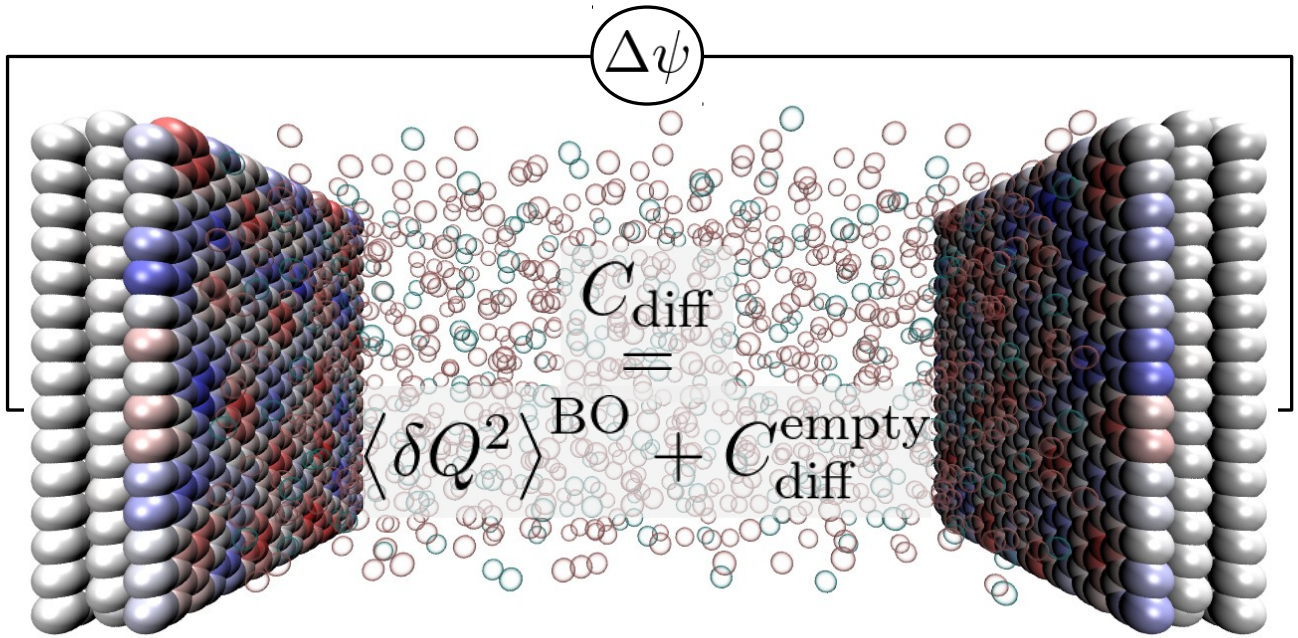
Application: capacitors for blue energy & desalination[1]



[1] Simoncelli et al., *Physical Review X*, 2018.

Highlight on charge fluctuations with BO sampling

- Differential capacitance $C_{\text{diff}} = \frac{\partial Q}{\partial \Delta\Psi} = \beta \langle \delta Q^2 \rangle$
  related to the fluctuations of the total charge on electrodes
- Born-Oppenheimer sampling suppresses some fluctuations
- ⚠need for a correction to the capacitance[2] ($\sim 5\%$)



[2] Scalfi et al., *Phys. Chem. Chem. Phys.* 2020a.

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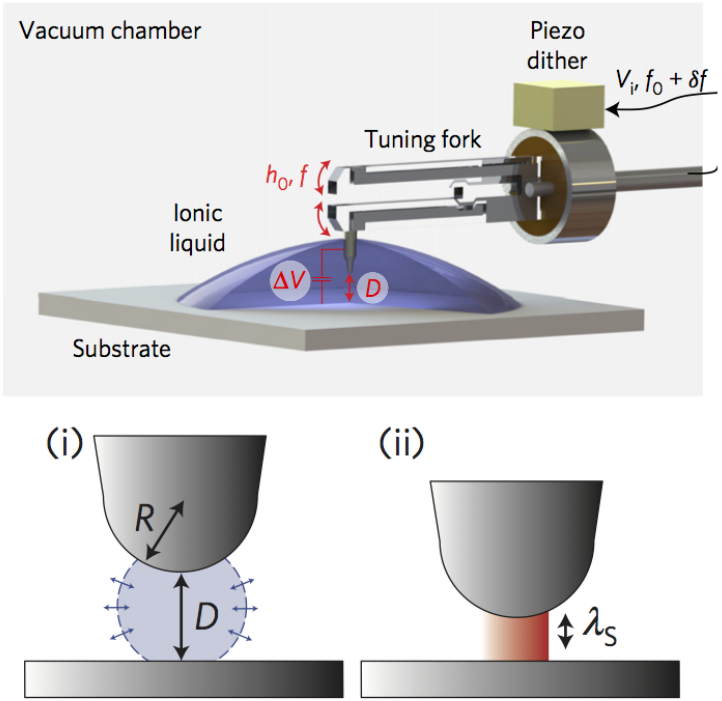
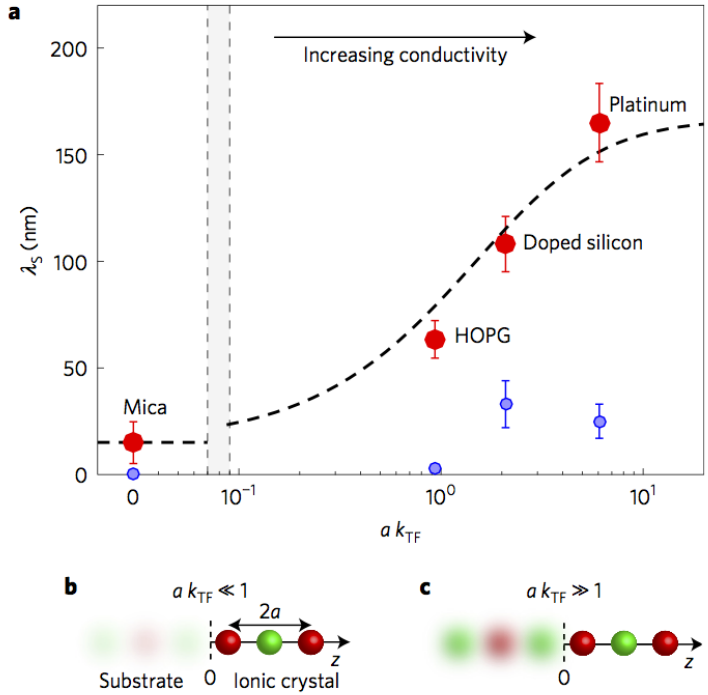
Experimental measurements

- Confined ionic liquid freezing (L. Bocquet, ENS)[3]





Effect of metallicity on electrolyte properties

[3] Comtet et al., *Nature Materials*, 2017.

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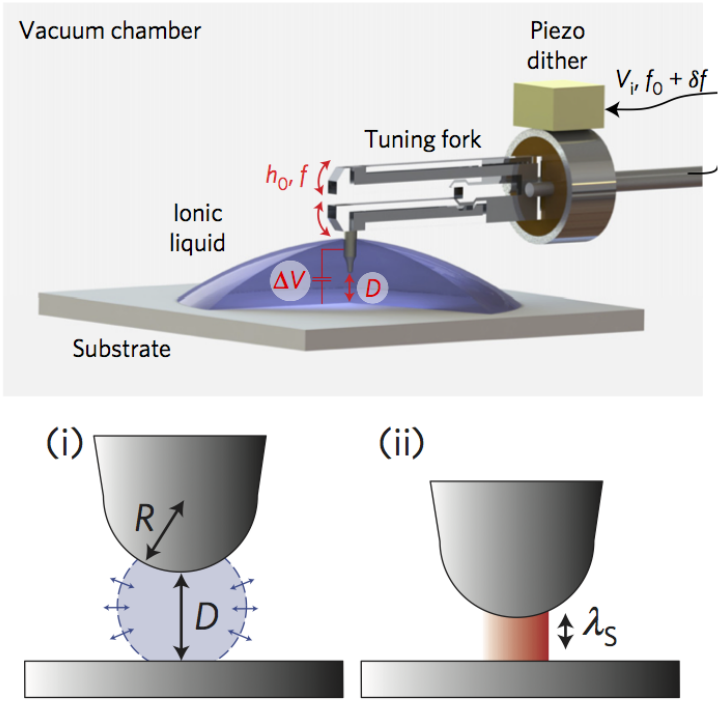
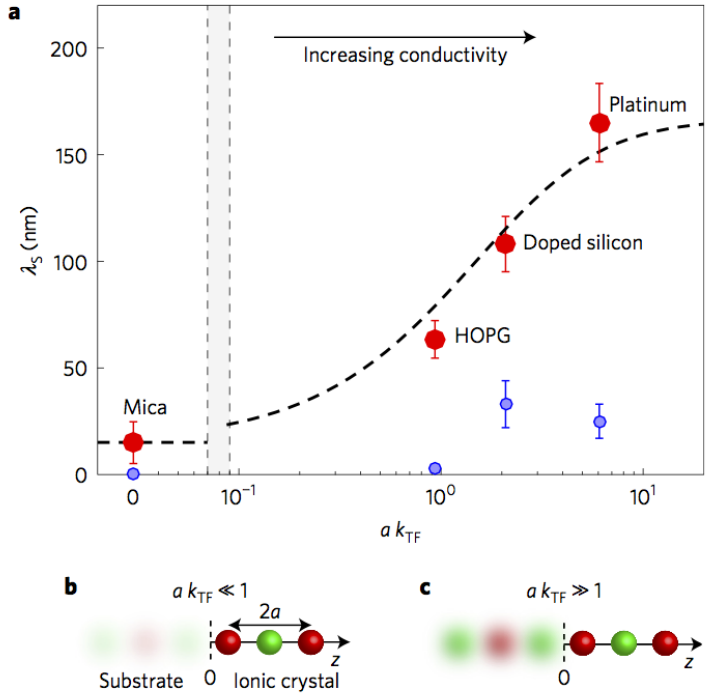




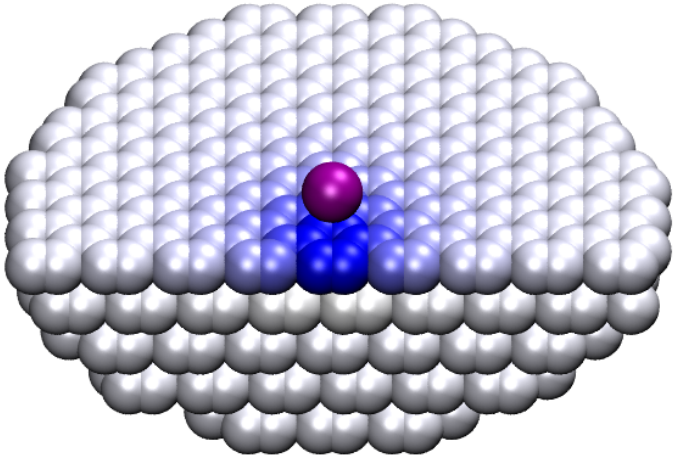
Effect of metallicity on electrolyte properties

→ analytical model based on the Thomas-Fermi model

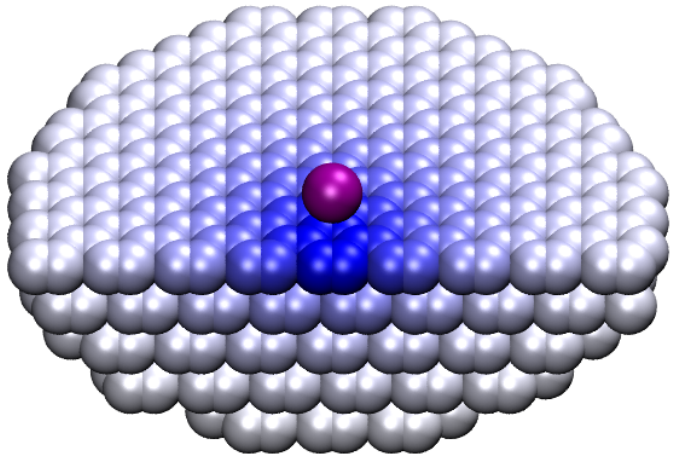
[3] Comtet et al., *Nature Materials*, 2017.

How to model non-ideal metals? Thomas-Fermi model

- Fluctuating charges on the surface respond to an ion



(a) Perfect metal
$l_{TF} = 0.0$ Å.



(b) Thomas-Fermi metal
$l_{TF} = 7.5$ Å.

How to model non-ideal metals? Thomas-Fermi model

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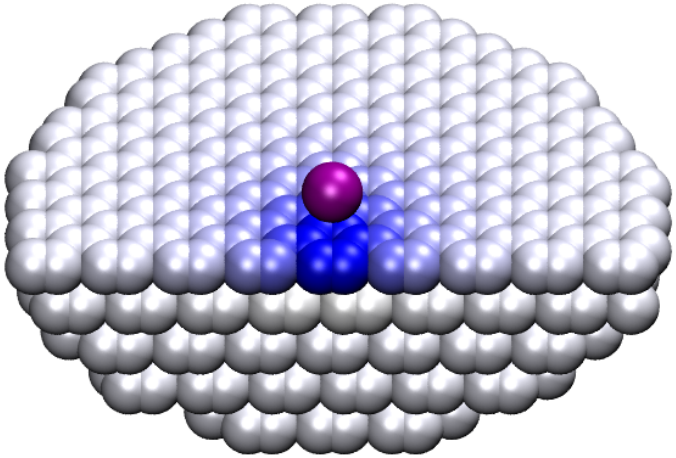

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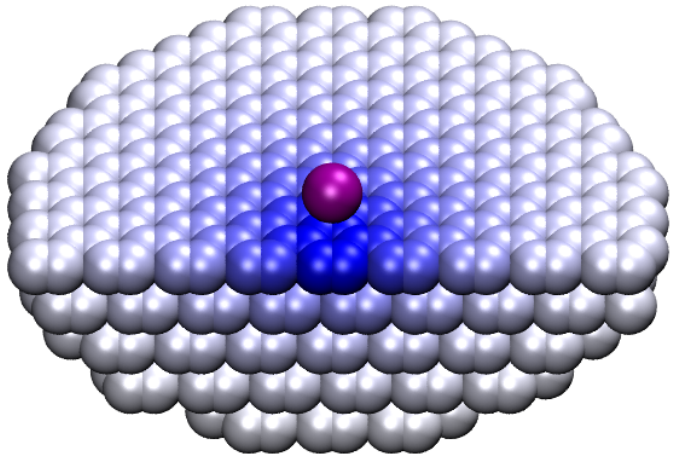

(b) Thomas-Fermi metal
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Characteristic screening length within the material
Thomas-Fermi length

The Thomas-Fermi model

A simple description of the electronic structure

- Electronic DFT within Local Density Approximation
- Kinetic energy of the uniform electron gas

$$U_{TF}[n(\mathbf{r})] = \int \frac{3}{10}\frac{\hbar^2}{m_e}(3\pi^2)^{2/3} n(\mathbf{r})^{5/3} \mathrm{d}\mathbf{r}$$

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- Approximate $n(\mathbf{r})$ within Voronoi cells: $n_i = d\left[Z + \frac{q_i}{-e}\right]$
- Assuming $|q_i| \ll Ze$, we expand energy in powers of q_i

$$U_{TF} = \frac{3}{5} M_s Z E_F - \frac{E_F}{e}\sum_{i=1}^{M_s} q_i + \frac{l_{TF}^2 d}{2\epsilon_0}\sum_{i=1}^{M_s} q_i^2$$

The Thomas-Fermi model

Thomas-Fermi screening length

- $E_F = \hbar^2 k_F^2 / 2m_e$ Fermi level of an electron gas with density Zd
- k_F Fermi wavevector with $k_F^3 / 3\pi^2 = Zd$
- $l_{TF} = \sqrt{\frac{\epsilon_0 \hbar^2 \pi^2}{(m_e e^2 k_F)}}$ Thomas-Fermi screening length of the material

Combining with the classical energy and enforcing electroneutrality[4]

$$U_{tot} = U + \frac{3}{5} MZE_F + \frac{l_{TF}^2 d}{2\epsilon_0} \sum_{i=1}^{M} q_i^2$$

[4] Scalfi et al., *J. Chem. Phys.* 2020b.

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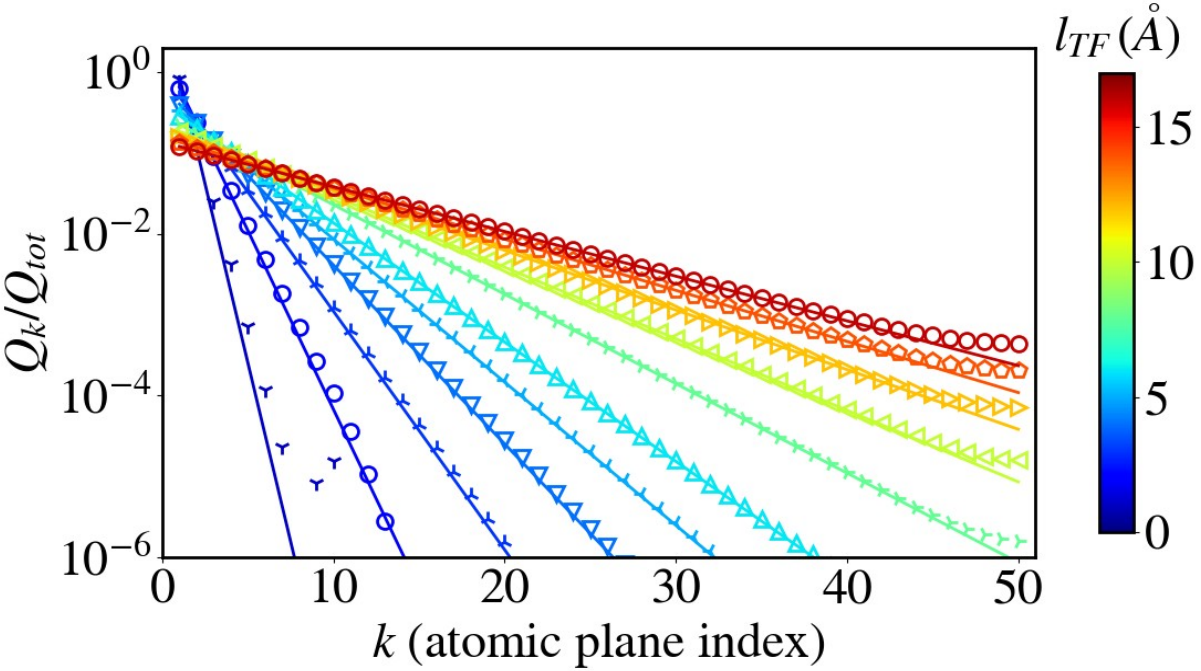
In practice

- Quadratic energy in $\mathbf{q}$ results in additional diagonal elements in $\mathbf{A}$
- $\sim$ no extra cost & faster convergence of conjuguate gradient

[4] Scalfi et al., *J. Chem. Phys.* 2020b.

Screening in an empty capacitor at $\Delta\Psi = 1V$

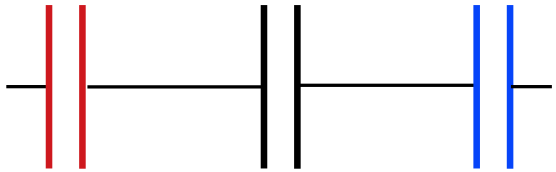
- Exponentially decaying charge distribution within the metal



Screening in an empty capacitor at $\Delta\Psi = 1V$

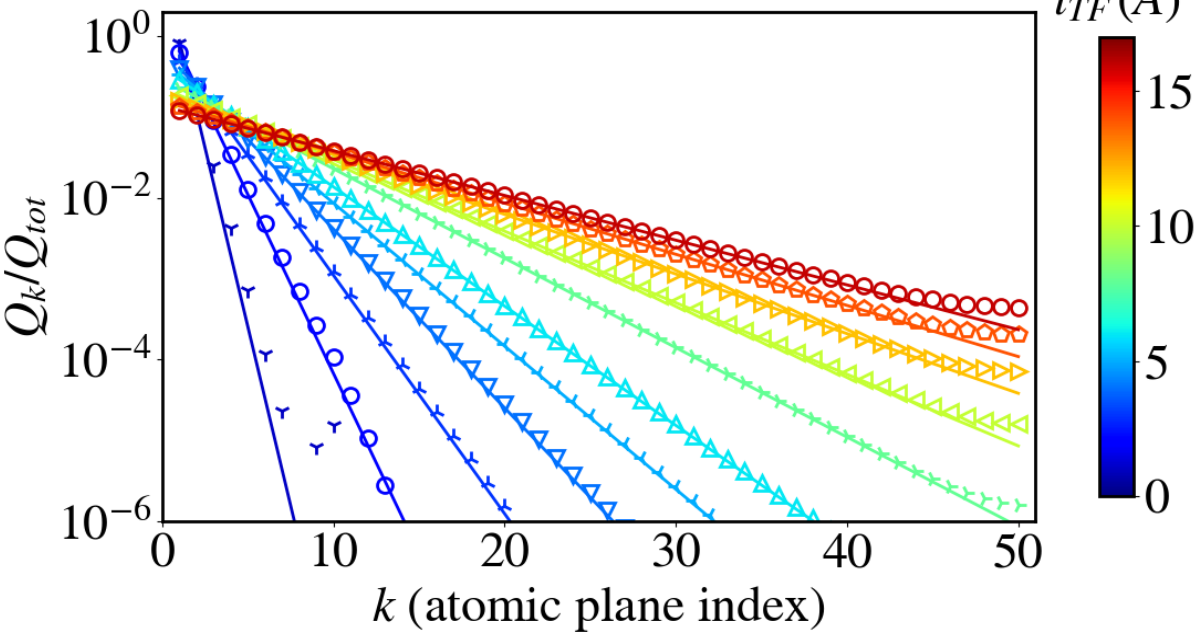
- Capacitance of a parallel-plate empty capacitor $C_{\text{ideal}} = \epsilon_0 / L$

$\longleftrightarrow$



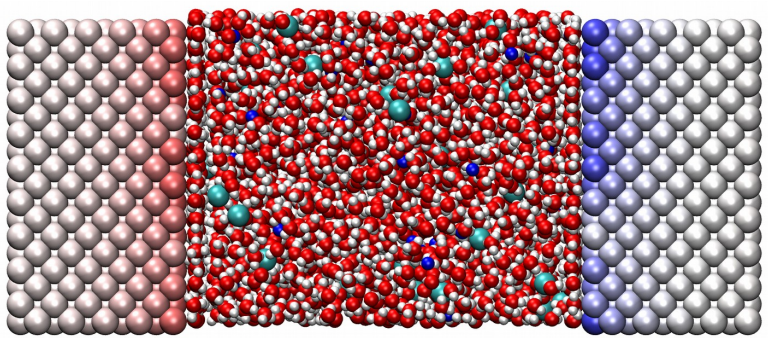
$$\frac{1}{C} \approx \frac{1}{C_{\text{TF}}} + \frac{1}{C_{\text{vac}}} + \frac{1}{C_{\text{TF}}}$$

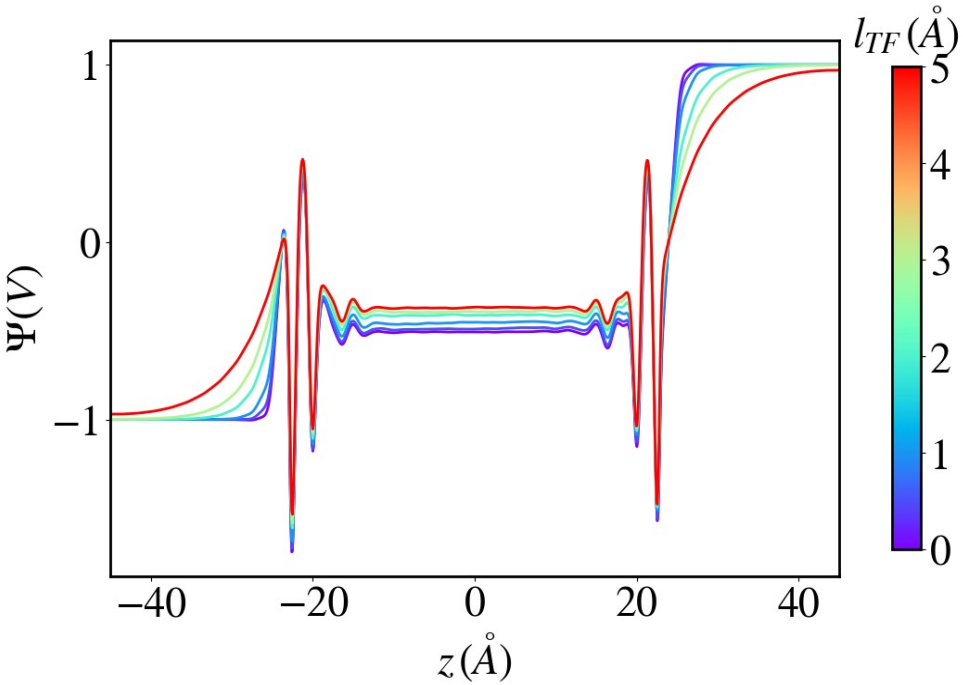
$$\approx \frac{l_{\text{TF}}}{\epsilon_0} + \frac{L_{\text{vac}}}{\epsilon_0} + \frac{l_{\text{TF}}}{\epsilon_0}$$



Screening in electrochemical cells at $\Delta\Psi = 2V$

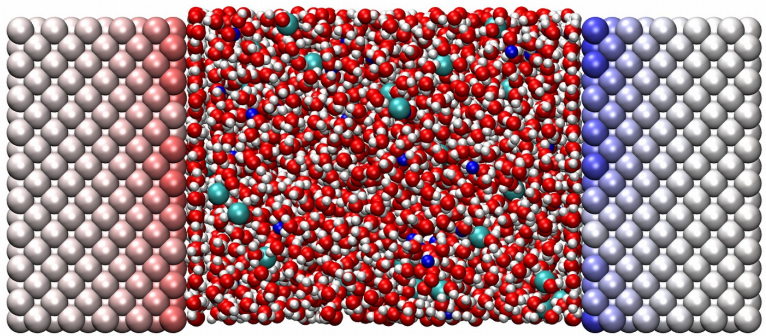
- Electric potential in gold electrochemical cells



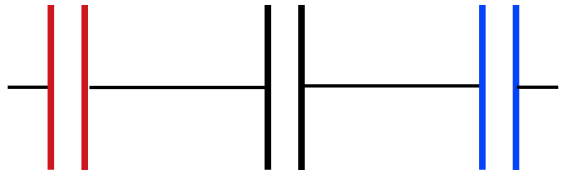


Screening in electrochemical cells at $\Delta\Psi = 2V$

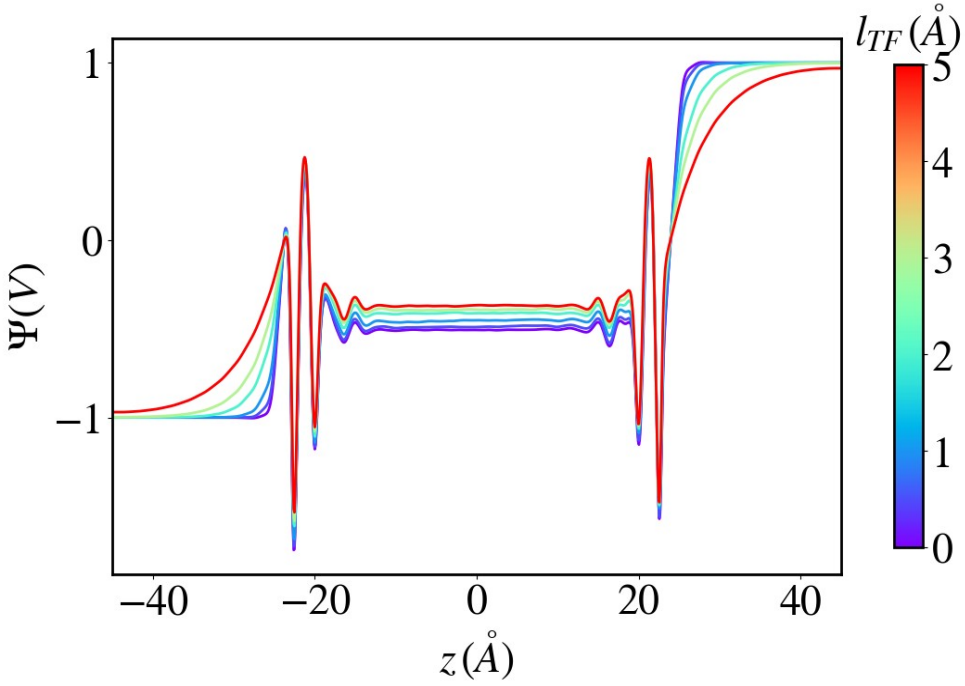
- Capacitance of gold electrochemical cells $C = Q_{tot}/\Delta\Psi$

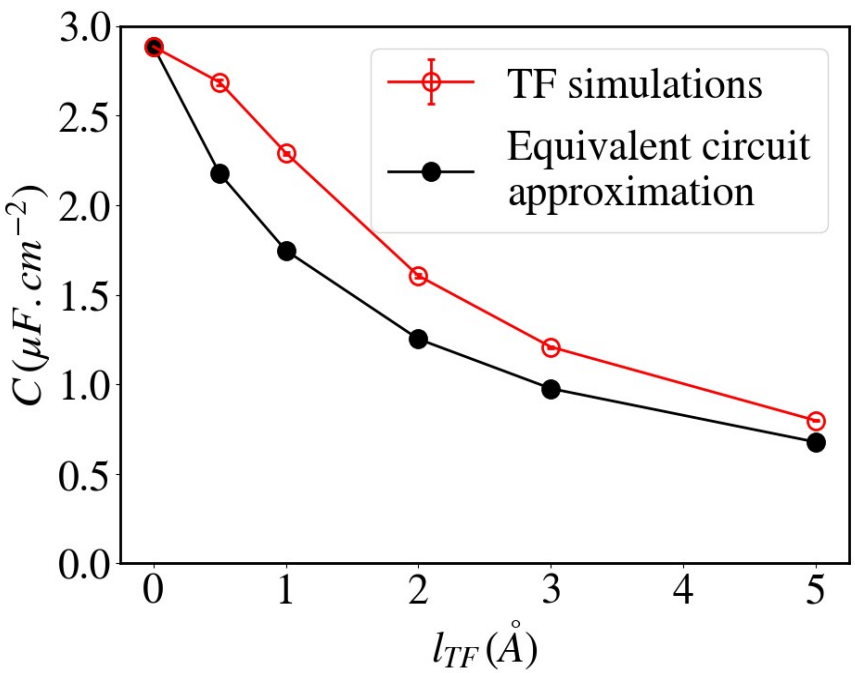


$\leftrightarrow$



$$\frac{1}{C_{EC}} = \frac{1}{C_{\mathrm{TF}}} + \frac{1}{C_{\mathrm{metal}}} + \frac{1}{C_{\mathrm{TF}}}$$





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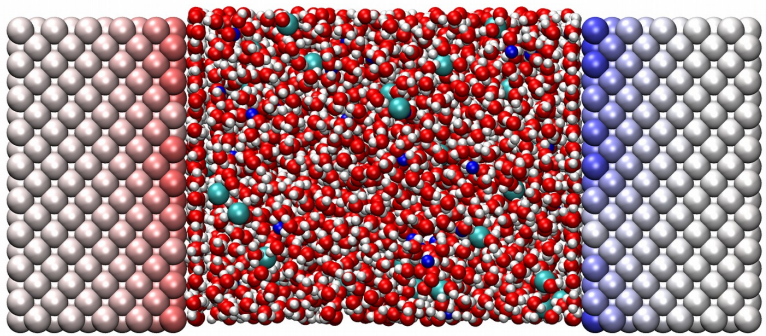

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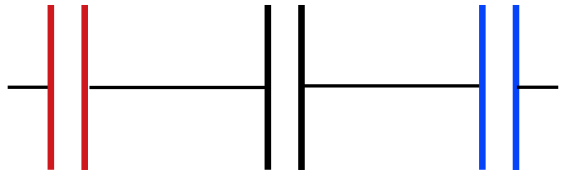
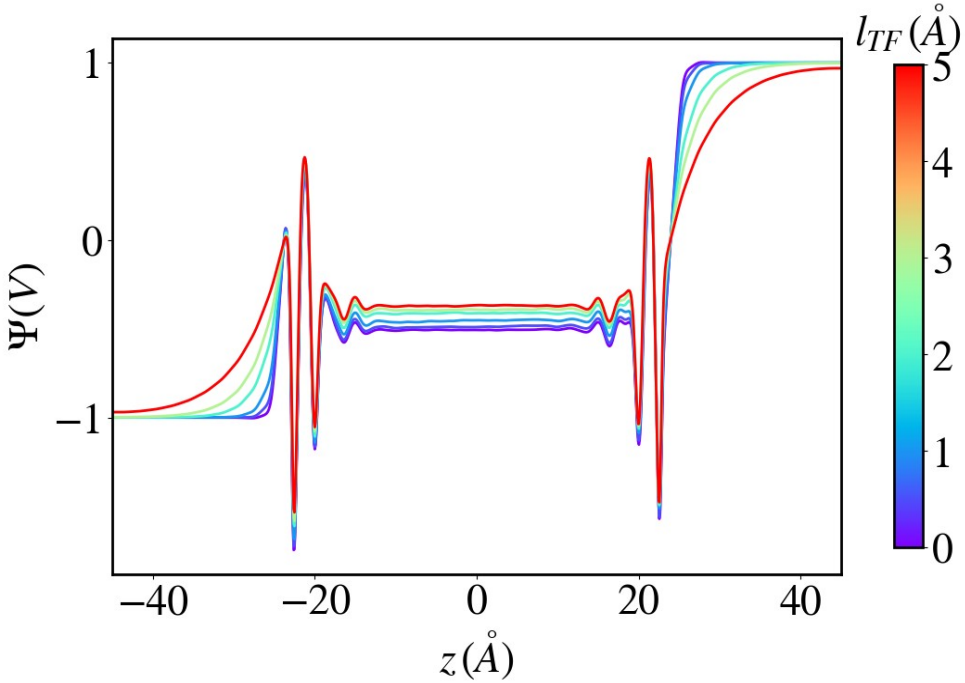
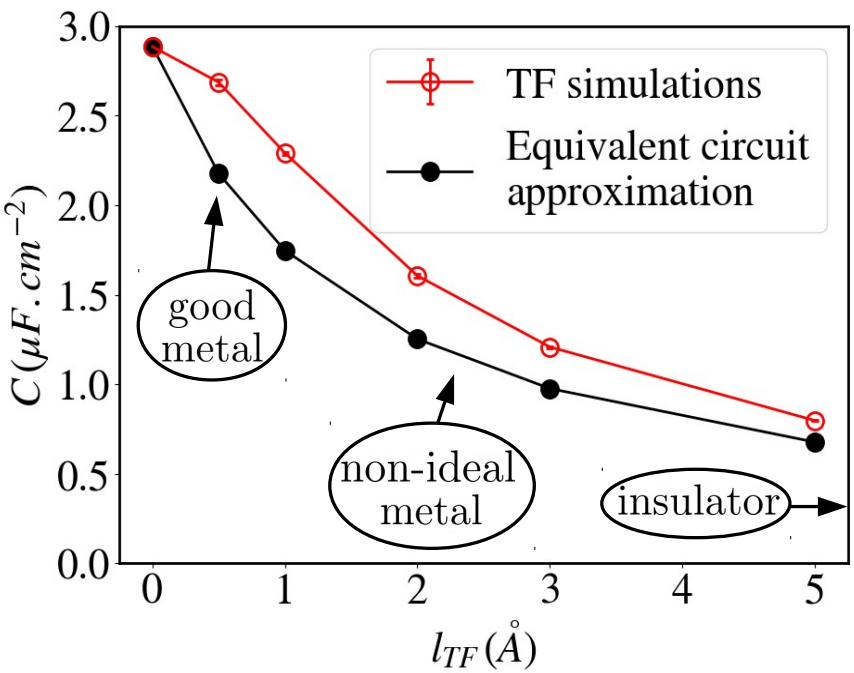


$$\frac{1}{C_{EC}} = \frac{1}{C_{\mathrm{TF}}} + \frac{1}{C_{\mathrm{metal}}} + \frac{1}{C_{\mathrm{TF}}}$$





How to study the influence of metallicity on confined phase transitions?

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Compute the surface tension

- **surface tension** γ_W as a free energy per surface area

$$\gamma_W(l_{TF}) = \frac{F(l_{TF})}{2\mathscr{A}}$$

- **free energy difference** associated with a **change in metallicity** using thermodynamic integration $\Delta F(l_{TF})$

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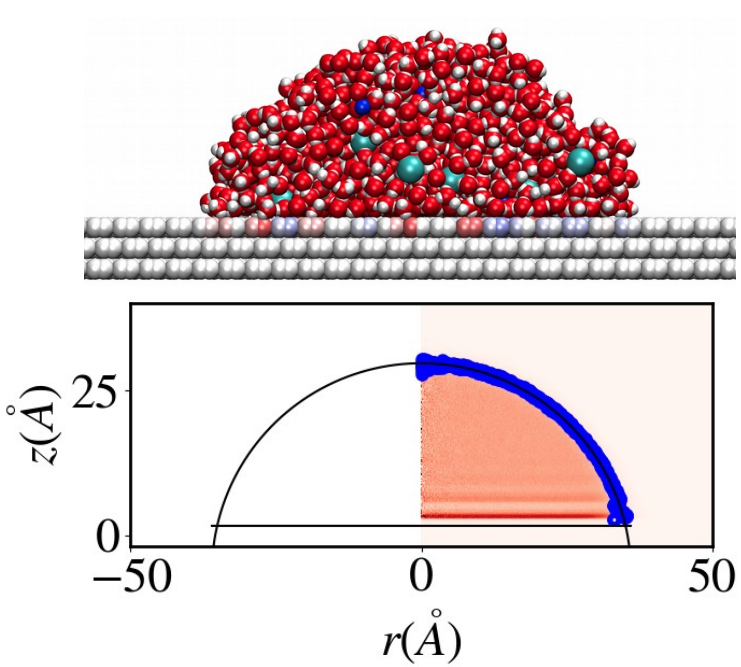
$$\gamma_W(l_{TF}) = \frac{F(l_{TF})}{2\mathscr{A}}$$

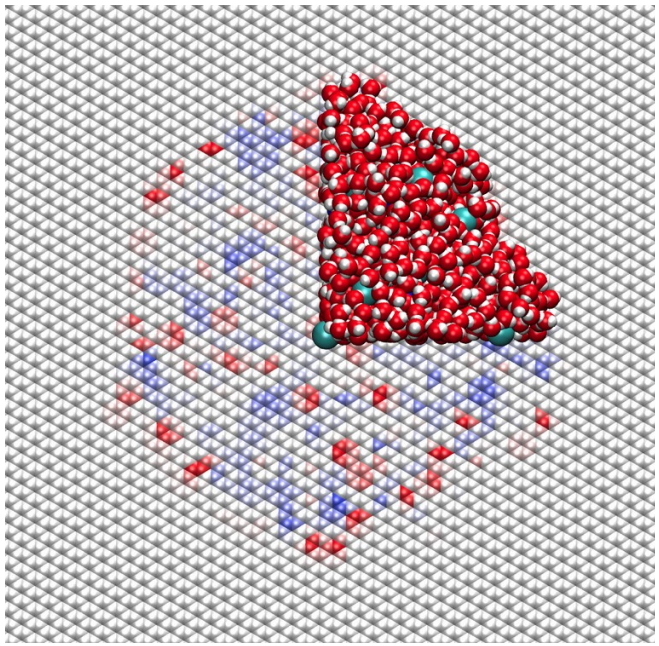
- **free energy difference** associated with a **change in metallicity** using thermodynamic integration $\Delta F(l_{TF})$
- comparison with **contact angle** measurements using the Young equation

$$cos(\theta) = \frac{\gamma_{WV} - \gamma_{WL}}{\gamma_{LV}}$$

Change in contact angle

- Drop simulations of contact angles





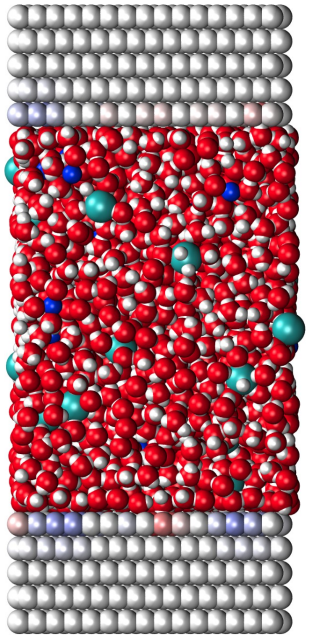
$\rightarrow \Delta\theta(\text{metal-insulator}) \approx 4^\circ$

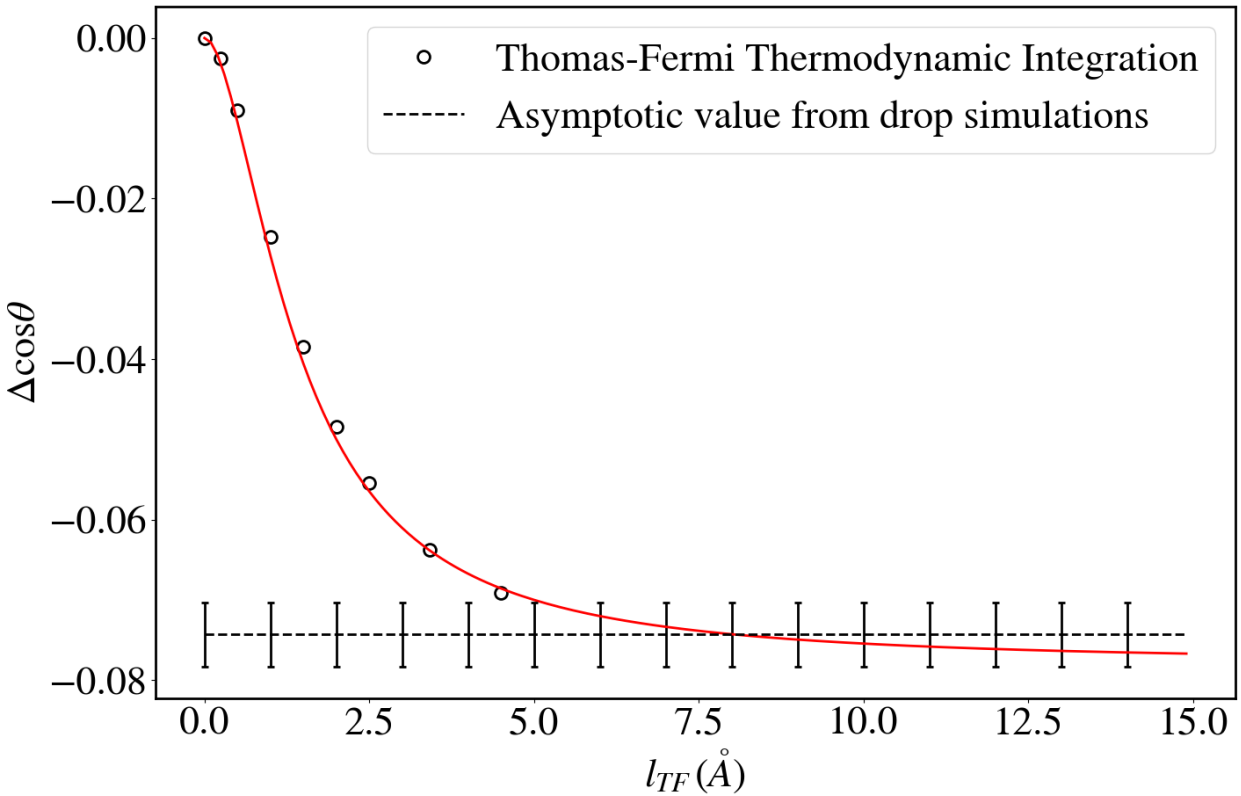
$\rightarrow \Delta F/\mathscr{A} \approx 8\text{mN/m}$ compared to $\gamma_{LV} \approx 60\text{mN/m}$

The more metallic, the more hydrophillic

Change in contact angle

Comparison with thermodynamic integration results at $\Delta\Psi = 0V$





Conclusions and perspectives

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- Improvement of constant potential simulations
  using a **Thomas-Fermi semiclassical model**
- Good agreement with analytical results for empty capacitors
- **Significant impact** on electrolyte and interfacial properties
  - capacitance
  - structure
  - dynamics
  - surface tension...

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Perspectives

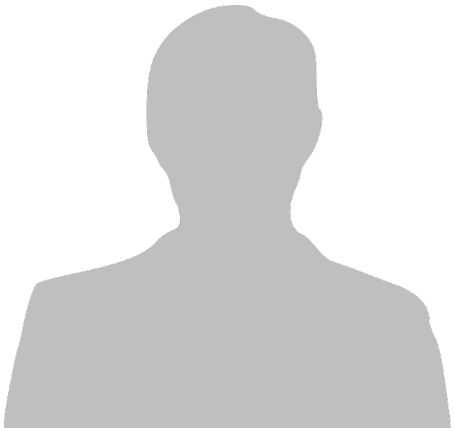
- Better predictions of capacitances
- Application to solid-liquid transition for ionic liquids

JOSS
The Journal of Open Source Software

MetalWalls: A classical molecular dynamics software dedicated to the simulation of electrochemical systems

Abel Marin-Laflèche[1], Matthieu Haefele[1], Laura Scalfi[2], Alessandro Coretti[3, 4], Thomas Dufils[2], Guillaume Jeanmairet[2], Stewart K. Reed[5], Alessandra Serva[2], Roxanne Berthin[2], Camille Bacon[2], Sara Bonella[4], Benjamin Rotenberg[2], Paul A. Madden[6], and Mathieu Salanne[1, 2]

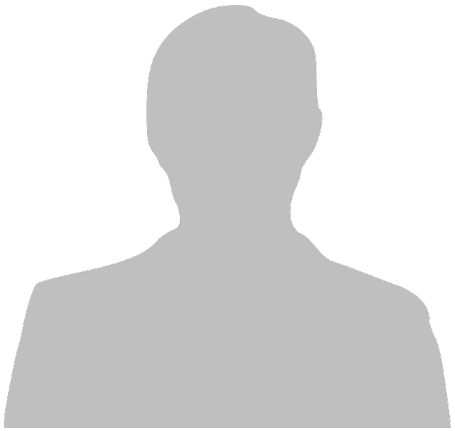
https://gitlab.com/ampere2/metalwalls



Thomas Dufils

Benjamin Rotenberg

Mathieu Salanne

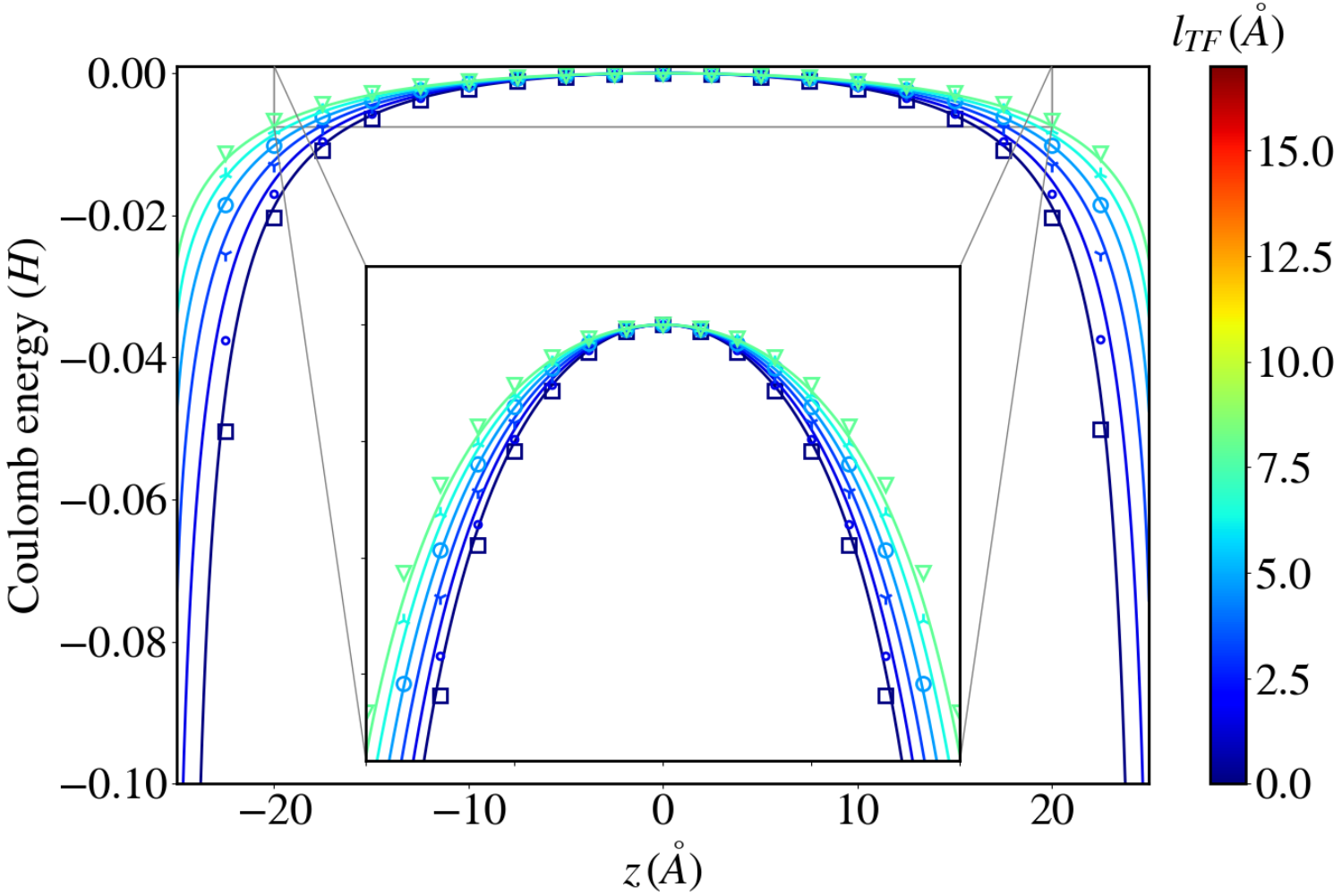


Thomas Dufils Benjamin Rotenberg Mathieu Salanne

Thank you for your attention

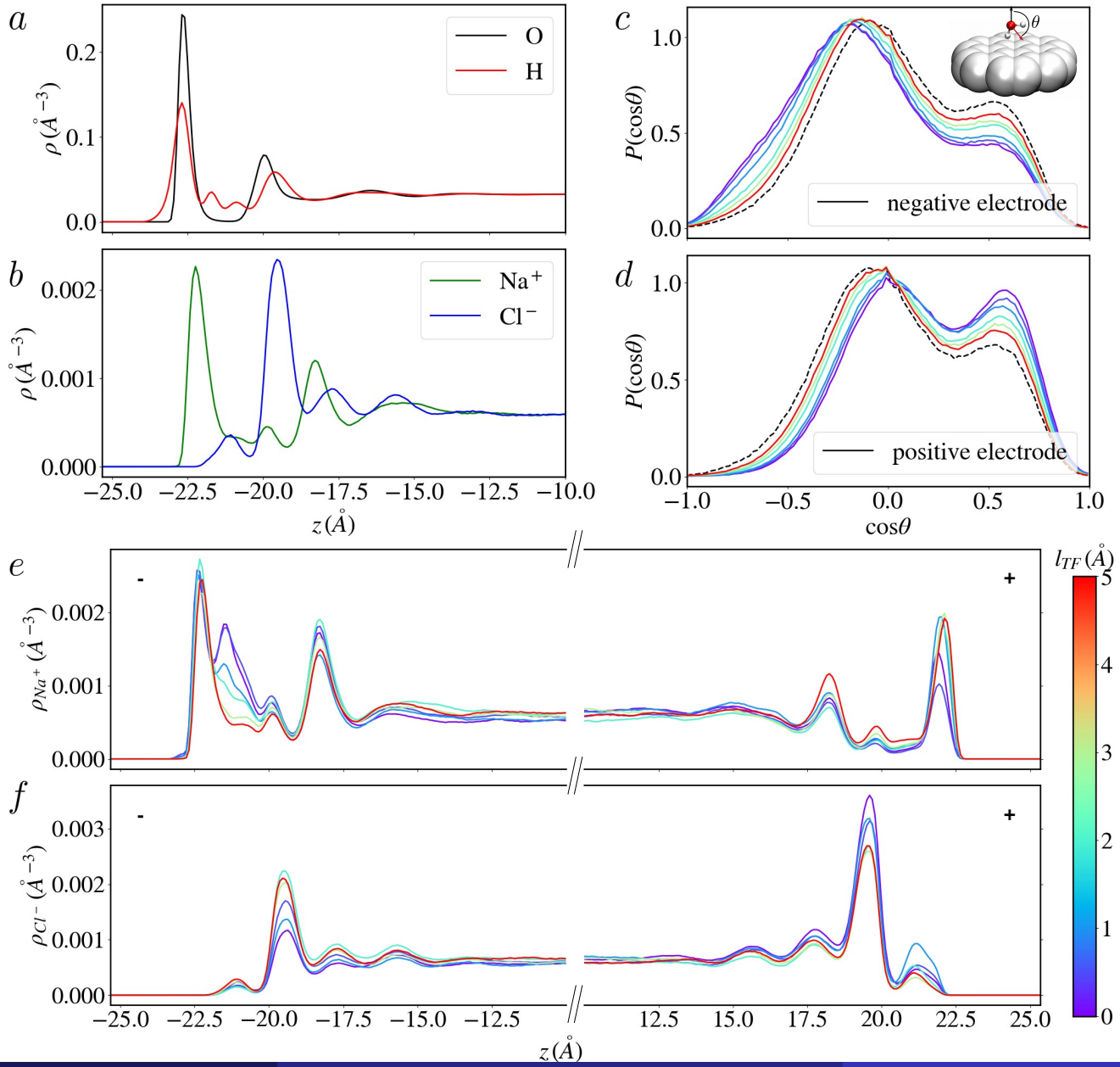
Screening in an empty capacitor

- Energy of a single charge between two parallel plates[5]



[5] Kaiser et al., *Faraday Discussions*, 2017.

Screening in electrochemical cells: structure



Screening in electrochemical cells: dynamics

- Autocorrelation function of the total charge