Semiclassical approach to Mesoscopic EDLs

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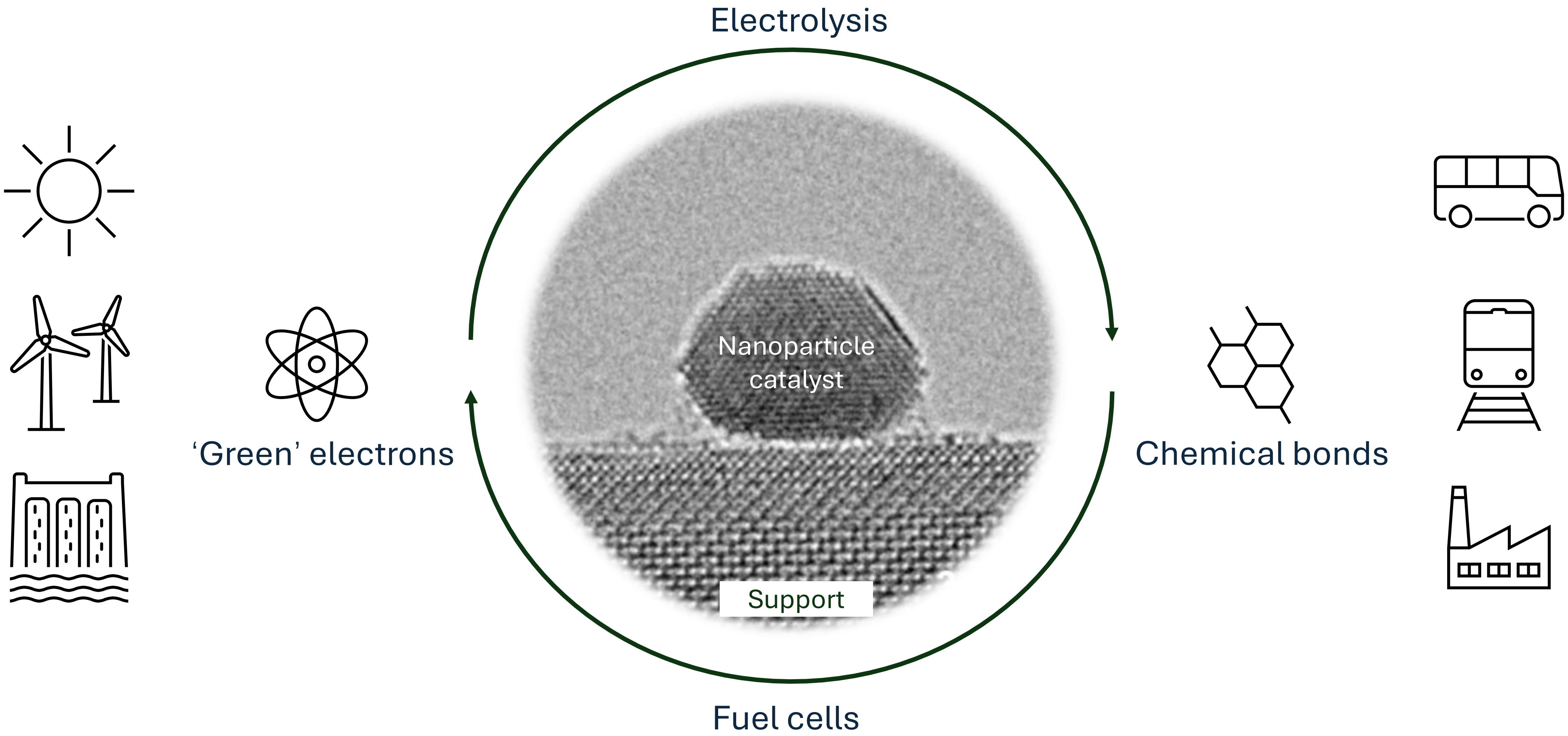
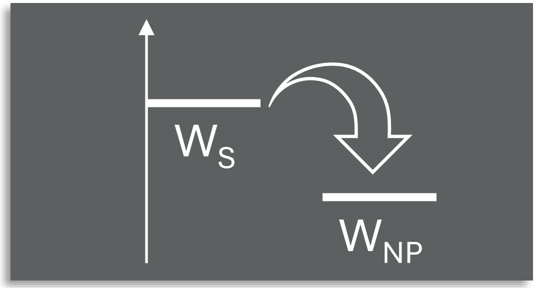
Motivation for a semiclassical approach

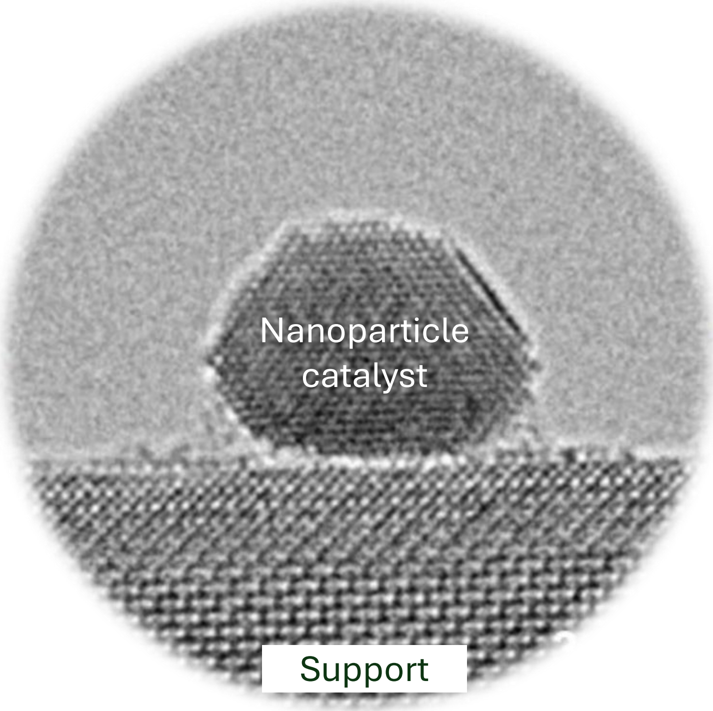
(1) Supported nanoparticle catalysts

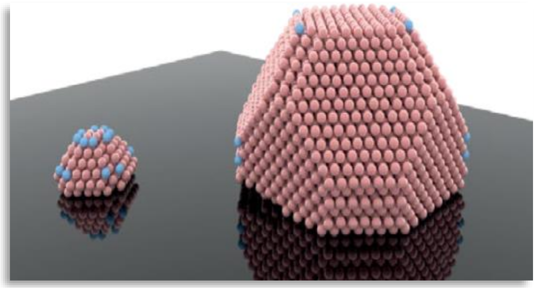


Status quo: electronic metal-support interactions



Electronic equilibrium



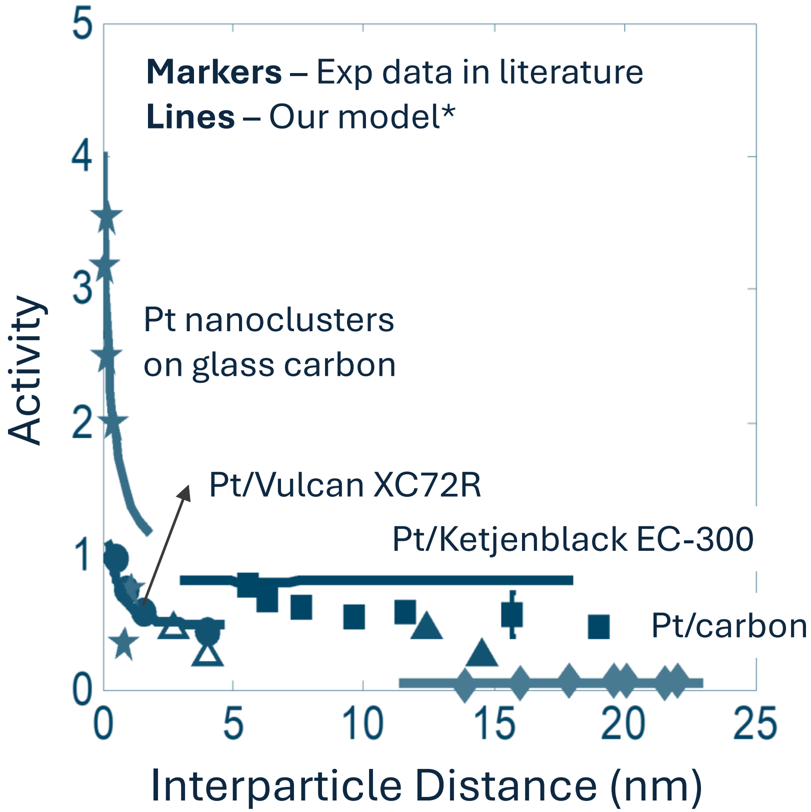


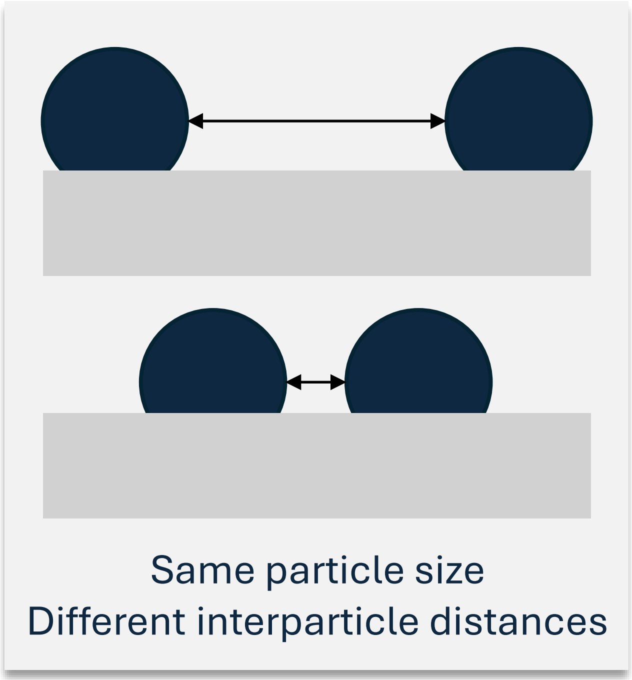
Geometric effects

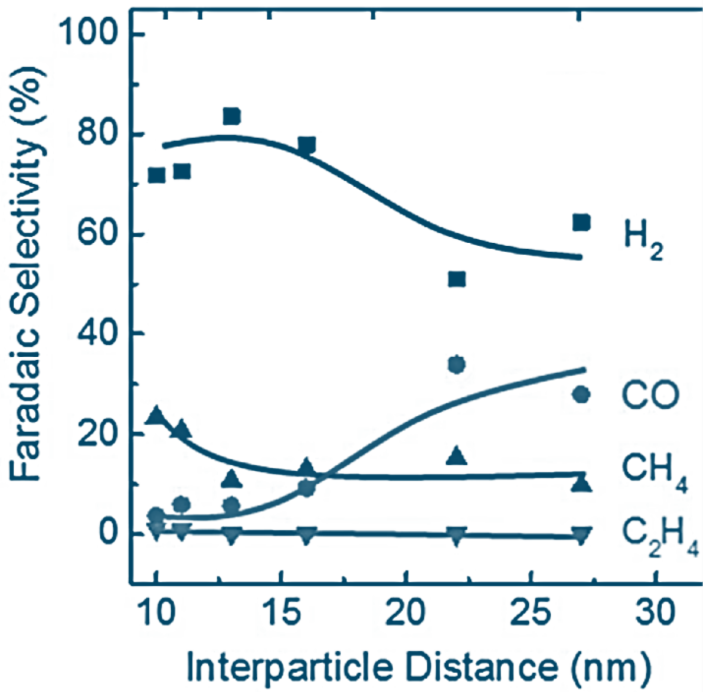
Interfacial perimeter, chemical composition change, spillover, confinement,...

Schwab *et al.*, *Angew. Chem.* **1959**
de Jong *et al.*, *Nat. Catal.*, **2019**
Aso *et al.*, *Science*, **2022**
Vogt, Weckhuysen. *Nat. Rev. Chem.* **2022**

Particle proximity effects indicate new factors on the mesoscale

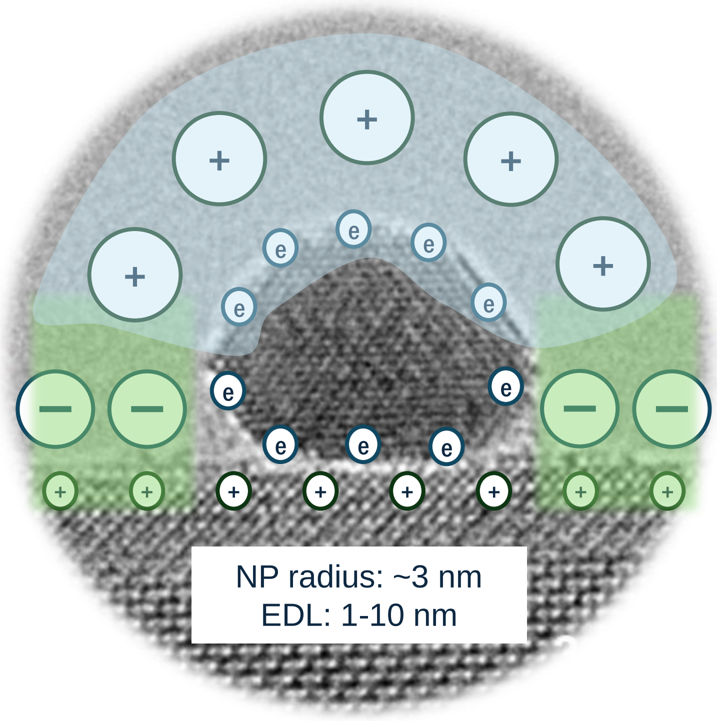






Cuenya et al., *ACS Catal.* **2016**
Inaba et al., *ACS Catal.* **2021**
*Huang, Zhang, Eikerling, *J. Phys. Chem. C* **2017**

Hypothesis: Overlapping EDLs are the new factors



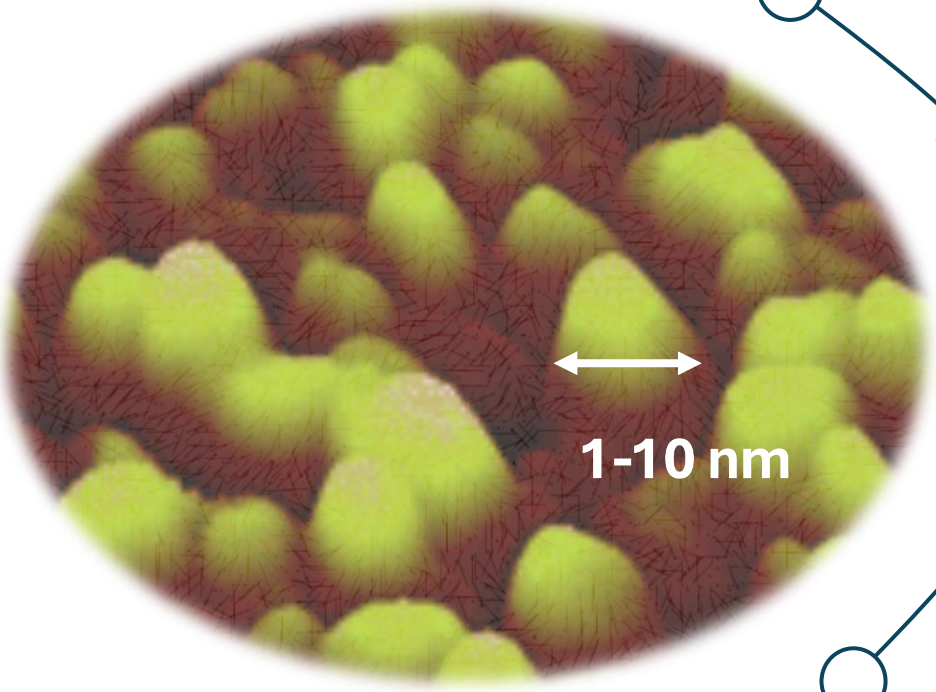
What they look like?

How they impact reactions?

Implications for catalyst design?

Motivation for a semiclassical approach

(2) Mesoscopic EDLs with nanoscale roughness



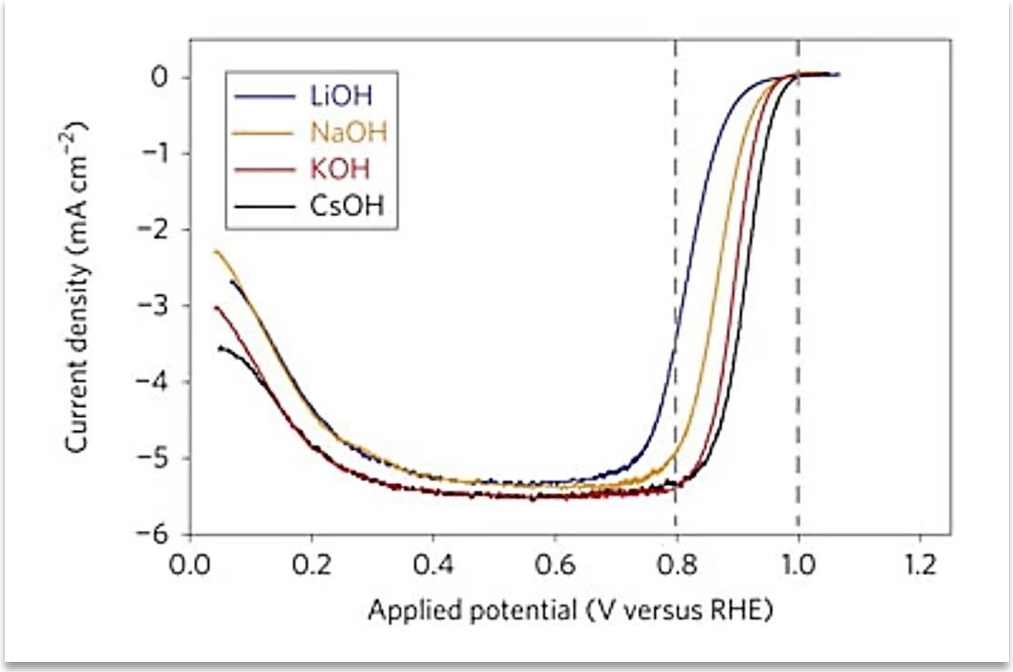
- Activity & selectivity[1,2]
- Local reaction conditions
- Surface charge density and capacitance
- Work function and potential of zero charge
- Electronic properties

How & why nanoscale roughness affects EDL properties?

1) Yoon, Y., Hall, A. S., & Surendranath, Y. *Angew. Chem.* (2016).
2) Nguyen, K. L. C., Bruce, J. P., Yoon, A., Navarro, J. J., Scholten, F., Landwehr, F., ... & Cuenya, B. R. *ACS Energy Lett.* (2024).

Motivation for a semiclassical approach

(3) Electrolyte effects



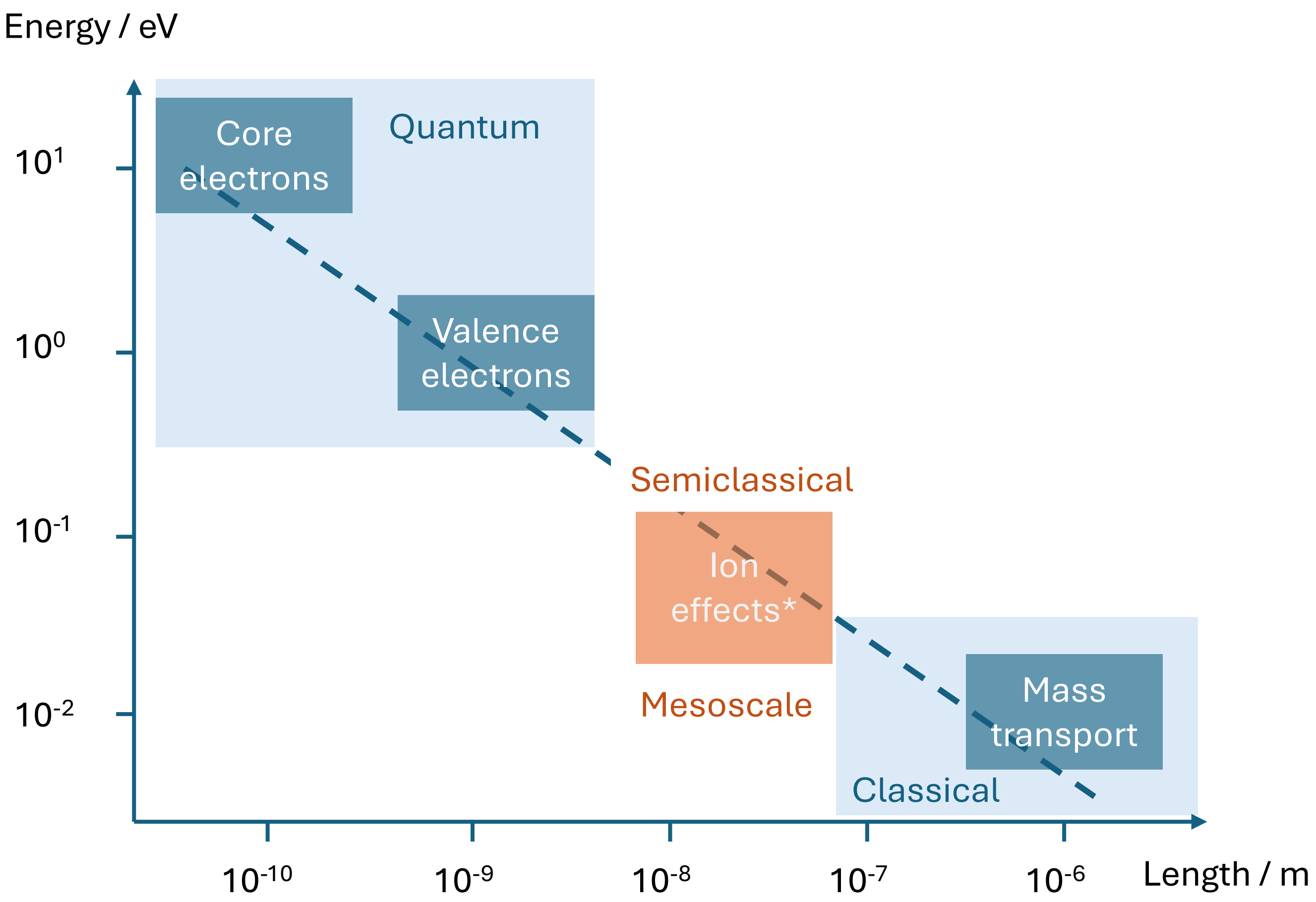
INFLUENCE OF CATION ADSORPTION ON THE KINETICS OF ELECTRODE PROCESSES

BY A. N. FRUMKIN *
Institute of Electrochemistry of the Academy of Sciences of the U.S.S.R., Moscow, Leninsky Prospekt, 31.

Received 17*th July*, 1958

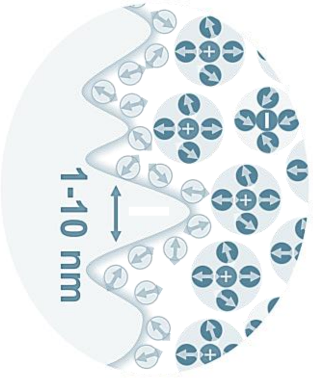
Strmcnik, Dusan, et al. "The role of non-covalent interactions in electrocatalytic fuel-cell reactions on platinum.“ *Nature chemistry* 1.6 (2009): 466-472.

Relevant energy and length scales for ion effects?

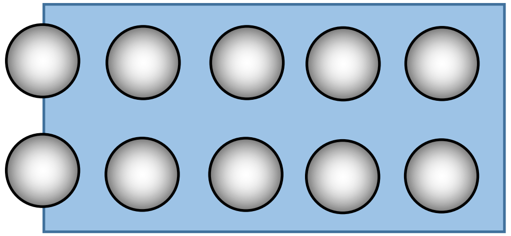


* Activity difference among ions: 1~100. $j \propto \exp\left(-\frac{\Delta G_{\mathrm{a}}}{k_{\mathrm{B}}T}\right) \rightarrow |\Delta\Delta G_{\mathrm{a}}|$: 0.01~0.15 eV

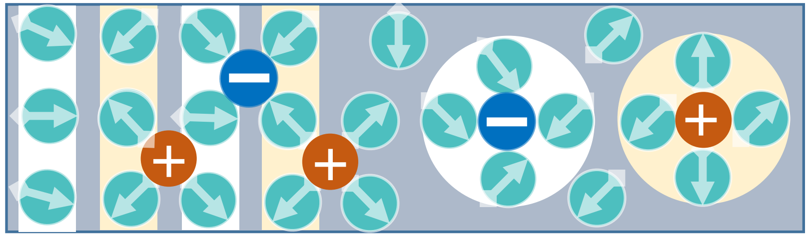
Density-potential functional theory: a semiclassical framework



Electronic conductor



Ionic conductor



Orbital-free
+ Computationally efficient for mesoscopic structures
- w/o covalent effects

$$g = f_{\mathbb{Q}}[n_e] + f_{\mathbb{C}}[\phi, P, \{n_i\}] + f_{\otimes}[n_e, P, \{n_i\}] - \sum_i n_i \tilde{\mu}_i$$

Inhomogen. electron gas $f_{\mathbb{Q}}[n_e, \nabla^n n_e]$	Inhomogen. coulombic fluid $f_{\mathbb{C}}[\phi, \nabla^n \phi, P, \nabla^n P, \{n_i\}]$	Short-range Interaction $f_{\otimes}[\{n_i\}]$
Orbital-free DFT ***Electronic effects***	Statistical field theory ***Electrolyte effects***	Pair-wise relationships ***Phase separation***

Implicit solvent
Field variables
Correlation effects

Grand canonical
Consistency
Direct connection with experiments

1) Huang, J., Chen, S. and Eikerling, M., *JCTC* (2021);
2) Huang, J., *JCTC* (2023);
3) M.K. Zhang, Y. Chen, M. Eikerling, J. Huang, *Phys Rev Appl (In revision)*.

An orbital-free approach

$$T_s[\rho] = \sum_{i=1}^{N} \int d\mathbf{r}\, \varphi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \varphi_i(\mathbf{r}),$$

Kohn-Sham DFT

Exact kinetic energy

An eigenvalue problem to find orbitals

$$E[\rho] = \boxed{T_s[\rho]} + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho],$$

Orbital-free DFT

$$T_s[\rho] = \int d\mathbf{r} \left(c_1 \rho^{5/3} + c_2 \frac{(\nabla\rho)^2}{\rho}\right)$$

Approximate kinetic energy

A partial differential equation problem to find electron density

A few comments on orbital-free DFT

- **Dated back to Thomas and Fermi in 1920s, broad applications[1)]**
  - Metal surface (1960s): Kohn, Lang, Smith,…
  - Metal-solution interfaces (1980s): Badiali, Schmickler, Kornyshev, …
  - Theory of stability of matter (1980s): Lieb (Dirac Medal, 2022), …
  - **Computation of material properties (2000s)**: Carter, Trickey, …
  - Hydrodynamic theory for quantum plasmonics (2010s): Manfredi, Ciracì, Dela Sala, …
- **Machine-learned orbital-free DFT is promising to catch up with Kohn-Sham DFT in terms of accuracy.[2)]**

Advantages for the EDL problem

A unified continuum field description of electrode and electrolyte solution under constant potential

1) Mi, W., Luo, K., Trickey, S.B. and Pavanello, M., **Orbital-free density functional theory: An attractive electronic structure method for large-scale first-principles simulations**. *Chem. Rev.* (2023)
2) Burke K., et al., *J. Chem. Phys.* (2013); Shao B., et al., *Nat. Comput. Sci.* (2024)

Density-Potential Functional Theory: Formalism

Orbital-free DFT of metal electrons

$$F_{\mathbb{Q}} = \underbrace{T_{\text{in}}[n_{\text{e}}, \nabla n_{\text{e}}, \dots]}_{\textit{Kinetic}} + \underbrace{U_{\text{XC}}[n_{\text{e}}, \nabla n_{\text{e}}, \dots]}_{\textit{Exchange-correlation}}$$

The electrostatic potential energy of electrons and cationic cores is included in $F_{\mathbb{C}}$

Kinetic energy functional:
Thomas-Fermi-von Weizsäcker

$$T_{\text{ni}}[n_{\text{e}}, \nabla n_{\text{e}}] = \int_{\text{r}} \text{e}_{\text{au}} \text{a}_0^{-3} t_{\text{TF}} (1 + \theta_{\text{T}} s^2)$$

$$t_{\text{TF}} = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} (n_{\text{e}} a_0^3)^{\frac{5}{3}}$$

$$e_{\text{au}} = \frac{e_0^2}{4\pi\epsilon_0 a_0}$$

$$s = \frac{1}{2} (3\pi^2)^{-\frac{1}{3}} |\nabla n_{\text{e}}| (n_{\text{e}})^{-\frac{4}{3}}$$

Exchange correlation functional:
Perdew-Burke-Ernzerhof

$$U_{\text{XC}} = \int_r \left[u_{\text{X}}^0 (1 + \theta_{\text{X}} s^2) + u_{\text{C}}^0 + (n_{\text{e}} a_0^3) \theta_{\text{C}} t^2\right]$$

$$u_{\text{X}}^0 = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} (n_{\text{e}} a_0^3)^{\frac{4}{3}}$$

$$t = \frac{1}{4} \left(\frac{3}{\pi}\right)^{-\frac{1}{6}} a_0^4 |\nabla n_{\text{e}}| (n_{\text{e}} a_0^3)^{-\frac{7}{6}}$$

$$u_{\text{C}}^0 = -2a_1 (1 + a_2 r_{\text{s}}) (n_{\text{e}} a_0^3) \ln(1/\xi + 1)$$

$$\xi = 2a_1 (a_3 r_{\text{s}}^{1/2} + a_4 r_{\text{s}} + a_5 r_{\text{s}}^{3/2} + a_6 r_{\text{s}}^2)$$

$$r_{\text{s}} = (4\pi n_{\text{e}} a_0^3/3)^{-\frac{1}{3}}$$

The only free parameter is θ_{T}

Density-Potential Functional Theory: Formalism

Statistical field theory of classical particles - microscopic fields and interactions

Charge density field of cations	Charge density field of anions	Polarization field	Charge density field
$\hat{\rho}_{\mathrm{c}} = e_0 \sum_{N_{\mathrm{c}}} \delta(r - r_{\mathrm{c}})$	$\hat{\rho}_{\mathrm{a}} = -e_0 \sum_{N_{\mathrm{a}}} \delta(r - r_{\mathrm{a}})$	$\widehat{\boldsymbol{P}}(r) = p \sum_{N_{\mathrm{s}}} \boldsymbol{n}\delta(r - r_{\mathrm{s}})$	$\hat{\rho}(r) = \hat{\rho}_{\mathrm{c}}(r) + \hat{\rho}_{\mathrm{a}}(r) + \nabla \cdot \widehat{\boldsymbol{P}}(r) + \rho^{\mathrm{ex}}(r)$

$r_{\mathrm{a}}, r_{\mathrm{c}}, r_{\mathrm{s}}$: positions of anions, cations, and solvent molecules; $N_{\mathrm{a}}, N_{\mathrm{c}}, N_{\mathrm{s}}$: number of anions, cations, and solvent molecules; p: dipole moment of solvent molecule; ρ^{ex}: external charge distribution (electrons, metal cationic cores)

$$\widehat{H}\left[\hat{\rho}_{\mathrm{c}}, \hat{\rho}_{\mathrm{c}}, \hat{\rho}, \widehat{\boldsymbol{P}}\right] = \widehat{H}_{\mathrm{es}}[\hat{\rho}] + \widehat{H}_{\mathrm{corr}}\left[\widehat{\boldsymbol{P}}\right] + \widehat{H}_{\mathrm{sr}}\left[\hat{\rho}_{\mathrm{c}}, \hat{\rho}_{\mathrm{a}}, \widehat{\boldsymbol{P}}\right]$$

$$\widehat{H}_{\mathrm{es}}[\hat{\rho}] = \frac{1}{2} \int_{r,r'} \hat{\rho}(r) \frac{1}{4\pi\epsilon_\infty |r-r'|} \hat{\rho}(r')$$

Electrostatic interaction energy

$$\widehat{H}_{\mathrm{corr}}\left[\widehat{\boldsymbol{P}}\right] = \frac{1}{2\epsilon_0} \int_r \left(K_{\mathrm{s}} \widehat{\boldsymbol{P}}^2 + K_\alpha \left(\nabla \cdot \widehat{\boldsymbol{P}}\right)^2 + K_\beta \left(\nabla^2 \widehat{\boldsymbol{P}}\right)^2\right)$$

Short-range correlation energy between solvent molecules[1]

$$\widehat{H}_{\mathrm{sr}}\left[\hat{\rho}_{\mathrm{c}}, \hat{\rho}_{\mathrm{a}}, \widehat{\boldsymbol{P}}\right] = \alpha_{\mathrm{c}} \int_r \hat{\rho}_{\mathrm{c}} \nabla \cdot \widehat{\boldsymbol{P}} + \alpha_{\mathrm{a}} \int_r \hat{\rho}_{\mathrm{a}} \nabla \cdot \widehat{\boldsymbol{P}}$$

Hydration effects of ions

1) R. Blossey and R. Podgornik, *Phys Rev Res* (2022); *J. Phys. Math. Theo.* (2023)
2) M.K. Zhang, Y. Chen, M. Eikerling, J. Huang, *Phys Rev Appl (In revision).*

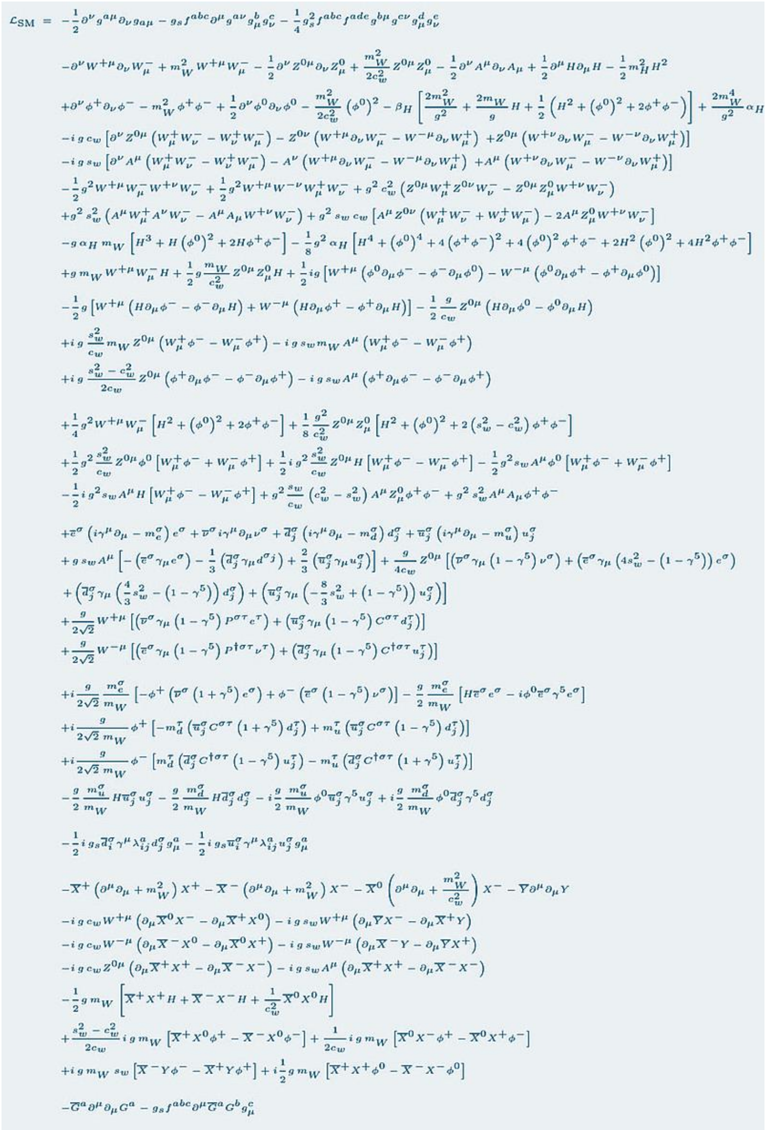
Density-Potential Functional Theory: Formalism

Grand potential functional

$$\Omega = \int_r g, \text{ with, } g =$$

Electrons	$e_{\mathrm{au}} a_0^{-3} t_{\mathrm{TF}}\left(1 + \theta_{\mathrm{T}} s^2\right) + e_{\mathrm{au}} a_0^{-3} u_{\mathrm{X}}^0\left(1 + \theta_{\mathrm{X}} s^2\right) + e_{\mathrm{au}} a_0^{-3}\left(u_{\mathrm{C}}^0 + \left(n_{\mathrm{e}} a_0^3\right)\theta_{\mathrm{C}} t^2\right)$
Classical Electrolyte species	$+\frac{1}{2}\rho(r)G(r,r')\rho(r') + \frac{1}{2\epsilon_0}\left(K_s \boldsymbol{P}^2 + K_\alpha(\nabla\cdot\boldsymbol{P})^2 + K_\beta\left(\nabla^2\boldsymbol{P}\right)^2\right) - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{P} - \phi\rho + \phi\rho^{\mathrm{ex}} + n_{\mathrm{c}} e_0(\phi + \alpha_{\mathrm{c}}\nabla\cdot\boldsymbol{P}) - n_{\mathrm{a}} e_0(\phi + \alpha_{\mathrm{a}}\nabla\cdot\boldsymbol{P}) - \frac{n_{\mathrm{s}}}{\beta}\log\frac{\sinh(\beta p\lvert\boldsymbol{\mathcal{E}} - \nabla\phi\rvert)}{\beta p\lvert\boldsymbol{\mathcal{E}} - \nabla\phi\rvert}$
Entropy	$+\sum_{i=\mathrm{a,c,s}}\frac{1}{\beta}\left(n_i\log\left(n_i\Lambda_i^3\right) - n_i\right) + \Phi_{\mathrm{ex}}$
M-S interactions	$+\sum_{i=\mathrm{a,c,s}} n_i w_i$
GC condition	$-\left(n_{\mathrm{e}}\tilde{\mu}_{\mathrm{e}} + \sum_{i=\mathrm{a,c,s}} n_i\tilde{\mu}_i\right)$

Standard Model Lagrangian



Density-Potential Functional Theory: Formalism

Controlling equations of three fields

Euler-Lagrange equation $\frac{\delta\Omega}{\delta X}=0 \;\; (X=\rho,\phi,\boldsymbol{\mathcal{E}},\boldsymbol{P},n_\mathrm{e},n_\mathrm{c},n_\mathrm{a},n_\mathrm{s})$

$X=n_\mathrm{e}$	$\overline{\nabla}\overline{\nabla}\bar{n}_\mathrm{e}=\frac{20}{3}\bar{n}_\mathrm{e}\frac{\omega}{(\theta_\mathrm{T}\omega-\theta_\mathrm{XC})}\left(\frac{\partial t_\mathrm{TF}}{\partial\bar{n}_\mathrm{e}}+\frac{\partial u_\mathrm{X}^0}{\partial\bar{n}_\mathrm{e}}+\frac{\partial u_\mathrm{C}^0}{\partial\bar{n}_\mathrm{e}}-\frac{(\tilde{\mu}_\mathrm{e}+e_0\phi)}{e_\mathrm{au}}\right)+\frac{\left(\theta_\mathrm{T}\omega-\frac{4}{3}\theta_\mathrm{XC}\right)}{2\bar{n}_\mathrm{e}(\theta_\mathrm{T}\omega-\theta_\mathrm{XC})}\left(\overline{\nabla}\bar{n}_\mathrm{e}\right)^2$	Electron density
$X=\rho$	$\phi=\int_{r'}G(r,r')\rho(r')=\int_{r'}\frac{\rho(r')}{4\pi\epsilon_\infty\lvert r-r'\rvert}$	Definition of electric potential
$X=\boldsymbol{\mathcal{E}}$	$\boldsymbol{P}=-\frac{pn_s\mathcal{L}(\beta p\lvert\boldsymbol{\mathcal{E}}-\nabla\phi\rvert)}{\lvert\boldsymbol{\mathcal{E}}-\nabla\phi\rvert}(\boldsymbol{\mathcal{E}}-\nabla\phi)$	Modified Langevin polarization equation
$X=\phi$	$\nabla\cdot(\epsilon_\infty\nabla\phi+\boldsymbol{P})=-(n_c-n_a)e_0-(n_{cc}-n_\mathrm{e})e_0$	Modified Poisson-Boltzmann equation
$X=\boldsymbol{P}$	$\epsilon_0^{-1}\left(K_\mathrm{s}\boldsymbol{P}-K_\alpha\nabla^2\boldsymbol{P}+K_\beta\nabla^4\boldsymbol{P}\right)-\alpha_\mathrm{c}e_0\nabla n_\mathrm{c}+\alpha_\mathrm{a}e_0\nabla n_\mathrm{a}=\boldsymbol{\mathcal{E}}$	Controlling equation of polarization field

Density-Potential Functional Theory: Formalism

Densities of classical particles

Euler-Lagrange equation

$$\frac{\delta\Omega}{\delta X} = 0 \quad (X = \rho, \phi, \boldsymbol{\mathcal{E}}, \boldsymbol{P}, n_\mathrm{e}, n_\mathrm{c}, n_\mathrm{a}, n_\mathrm{s})$$

$X = n_\mathrm{c}, n_\mathrm{a}, n_\mathrm{s}$

Electrochemcial potential of electrolyte component

$$\tilde{\mu}_\mathrm{c} = \frac{1}{\beta}\log\frac{n_\mathrm{c}\Lambda_\mathrm{c}^3}{1-\sum_i n_i\gamma_i\Lambda_\mathrm{B}^3} + e_0(\phi + \boxed{\alpha_\mathrm{c}\nabla\cdot\boldsymbol{P}}) + w_\mathrm{c}$$

$$\tilde{\mu}_\mathrm{a} = \frac{1}{\beta}\log\frac{n_\mathrm{a}\Lambda_\mathrm{a}^3}{1-\sum_i n_i\gamma_i\Lambda_\mathrm{B}^3} - e_0(\phi + \boxed{\alpha_\mathrm{a}\nabla\cdot\boldsymbol{P}}) + w_\mathrm{a}$$

$$\tilde{\mu}_\mathrm{s} = \frac{1}{\beta}\log\frac{n_\mathrm{s}\Lambda_\mathrm{s}^3}{1-\sum_i n_i\gamma_i\Lambda_\mathrm{B}^3} - \frac{1}{\beta}\log\frac{\sinh(\beta p|\boldsymbol{\mathcal{E}}-\nabla\phi|)}{\beta p|\boldsymbol{\mathcal{E}}-\nabla\phi|} + w_\mathrm{s}$$

Solvation effects

Spatial distribution of electrolyte component i

$$n_i = n_\mathrm{max}\frac{\chi_i\Theta_i}{\chi_\mathrm{v} + \sum_i \gamma_i\chi_i\Theta_i}$$

$\chi_i = n_i^\mathrm{b}/n_\mathrm{max}$, $\chi_\mathrm{v} = n_\mathrm{v}^\mathrm{b}/n_\mathrm{max}$, n_v^b the number density of vacancies in bulk

with the thermodynamic factors

$$\Theta_\mathrm{c} = \exp(-\beta e_0(\phi + \alpha_\mathrm{c}\nabla\cdot\boldsymbol{P}) - \beta w_\mathrm{c}),\ \Theta_\mathrm{a} = \exp(\beta e_0(\phi + \alpha_\mathrm{a}\nabla\cdot\boldsymbol{P}) - \beta w_\mathrm{a})$$

$$\Theta_\mathrm{s} = \frac{\sinh(\beta p|\boldsymbol{\mathcal{E}}-\nabla\phi|)}{\beta p|\boldsymbol{\mathcal{E}}-\nabla\phi|}\exp(-\beta w_\mathrm{s})$$

Density-Potential Functional Theory: Formalism

Relation to other formalisms

Full DPFT

$$\bar{\nabla}\bar{\nabla}\bar{n}_{\mathrm{e}}-\frac{\left(\theta_{\mathrm{T}}\omega-\frac{4}{3}\theta_{\mathrm{XC}}\right)}{2\bar{n}_{\mathrm{e}}(\theta_{\mathrm{T}}\omega-\theta_{\mathrm{XC}})}\left(\bar{\nabla}\bar{n}_{\mathrm{e}}\right)^2=\frac{20}{3}\bar{n}_{\mathrm{e}}\frac{\omega}{(\theta_{\mathrm{T}}\omega-\theta_{\mathrm{XC}})}\left(\frac{\partial t_{\mathrm{TF}}}{\partial\bar{n}_{\mathrm{e}}}+\frac{\partial u_{\mathrm{X}}^0}{\partial\bar{n}_{\mathrm{e}}}+\frac{\partial u_{\mathrm{C}}^0}{\partial\bar{n}_{\mathrm{e}}}-\frac{(\tilde{\mu}_{\mathrm{e}}+e_0\phi)}{e_{\mathrm{au}}}\right)$$

$$\nabla\cdot(\epsilon_\infty\nabla\phi+\boldsymbol{P})=-(n_c-n_a)e_0-(n_{cc}-n_{\mathrm{e}})e_0$$

$$\epsilon_0^{-1}\left(K_s\boldsymbol{P}-K_\alpha\nabla^2\boldsymbol{P}+K_\beta\nabla^4\boldsymbol{P}\right)-\alpha_c e_0\nabla n_c+\alpha_a e_0\nabla n_a=\boldsymbol{\mathcal{E}}$$

$$\boldsymbol{P}=-\frac{p n_s\mathcal{L}(\beta p|\boldsymbol{\mathcal{E}}-\nabla\phi|)}{|\boldsymbol{\mathcal{E}}-\nabla\phi|}(\boldsymbol{\mathcal{E}}-\nabla\phi)$$

Neglect short-range correlations, *i.e.*, $K_s, K_\alpha, K_\beta, \alpha_a, \alpha_c=0$

$$\boldsymbol{\mathcal{E}}=0, \boldsymbol{P}=\frac{p n_s\mathcal{L}(\beta p|\nabla\phi|)}{|\nabla\phi|}\nabla\phi$$

Simplified DPFT

$$\bar{\nabla}\bar{\nabla}\bar{n}_{\mathrm{e}}-\frac{\left(\theta_{\mathrm{T}}\omega-\frac{4}{3}\theta_{\mathrm{XC}}\right)}{2\bar{n}_{\mathrm{e}}(\theta_{\mathrm{T}}\omega-\theta_{\mathrm{XC}})}\left(\bar{\nabla}\bar{n}_{\mathrm{e}}\right)^2=\frac{20}{3}\bar{n}_{\mathrm{e}}\frac{\omega}{(\theta_{\mathrm{T}}\omega-\theta_{\mathrm{XC}})}\left(\frac{\partial t_{\mathrm{TF}}}{\partial\bar{n}_{\mathrm{e}}}+\frac{\partial u_{\mathrm{X}}^0}{\partial\bar{n}_{\mathrm{e}}}+\frac{\partial u_{\mathrm{C}}^0}{\partial\bar{n}_{\mathrm{e}}}-\frac{(\tilde{\mu}_{\mathrm{e}}+e_0\phi)}{e_{\mathrm{au}}}\right)$$

$$\nabla\cdot\left(\left(\epsilon_\infty+\frac{p n_s\mathcal{L}(\beta p|\nabla\phi|)}{|\nabla\phi|}\right)\nabla\phi\right)=-(n_c-n_a)e_0-(n_{cc}-n_{\mathrm{e}})e_0$$

Neglect the electrolyte components → **Orbital-Free DFT**

Neglect metal electronic effects → **Modified Poisson-Boltzmann Theory**

1) M.K. Zhang, Y. Chen, M. Eikerling, J. Huang, *Phys Rev Appl (In revision)*.

Numerical implementation to a 1D problem

(1) Controlling equations

Dimensionless quantities

$$\bar{n}_i = {a_0}^3 n_i, \bar{x} = \frac{x}{a_0}, \bar{\phi} = \frac{e_0\phi}{k_B T}, \bar{p} = \frac{p}{e_0 a_0}, \bar{\epsilon}_\infty = \frac{\epsilon_\infty}{\epsilon_0}, \bar{P} = \frac{\kappa a_0^2 P}{e_0}, \bar{\mathcal{E}} = \frac{e_0 a_0 \mathcal{E}}{k_B T}, \bar{K}_\alpha = \frac{K_\alpha}{a_0^2}, \bar{K}_\beta = \frac{K_\beta}{a_0^4}, \bar{\alpha}_i = \frac{\epsilon_0 \alpha_i}{a_0^2}, \bar{\beta}_i = \beta_i a_0$$

Dimensionless differential equations

$$\bar{\nabla}\bar{\nabla}\bar{n}_{\mathrm{e}} = \frac{20}{3}\bar{n}_{\mathrm{e}}\frac{\omega}{(\theta_{\mathrm{T}}\omega - \theta_{\mathrm{XC}})}\left(\frac{\partial t_{\mathrm{TF}}}{\partial \bar{n}_{\mathrm{e}}} + \frac{\partial u_{\mathrm{X}}^0}{\partial \bar{n}_{\mathrm{e}}} + \frac{\partial u_{\mathrm{C}}^0}{\partial \bar{n}_{\mathrm{e}}} - \frac{(\tilde{\mu}_{\mathrm{e}} + e_0\phi)}{e_{\mathrm{au}}}\right) + \frac{\left(\theta_{\mathrm{T}}\omega - \frac{4}{3}\theta_{\mathrm{XC}}\right)}{2\bar{n}_{\mathrm{e}}(\theta_{\mathrm{T}}\omega - \theta_{\mathrm{XC}})}\left(\bar{\nabla}\bar{n}_{\mathrm{e}}\right)^2$$

$$\bar{\nabla}\left(\bar{\epsilon}_\infty \bar{\nabla}\bar{\phi} + \bar{P}\right) = -\kappa(\bar{n}_{\mathrm{cc}} - \bar{n}_{\mathrm{e}} + \bar{n}_{\mathrm{c}} - \bar{n}_{\mathrm{a}})$$

$$K_{\mathrm{s}}\bar{P} - \bar{K}_\alpha \bar{Q} + \bar{K}_\beta \bar{\nabla}^2 \bar{Q} - \kappa\bar{\alpha}_{\mathrm{c}}\bar{\nabla}\bar{n}_{\mathrm{c}} + \kappa\bar{\alpha}_{\mathrm{a}}\bar{\nabla}\bar{n}_{\mathrm{a}} = \bar{\mathcal{E}}$$

$\bar{\nabla}^2\bar{P} = \bar{Q}$ introduced to reduce the order of ODE

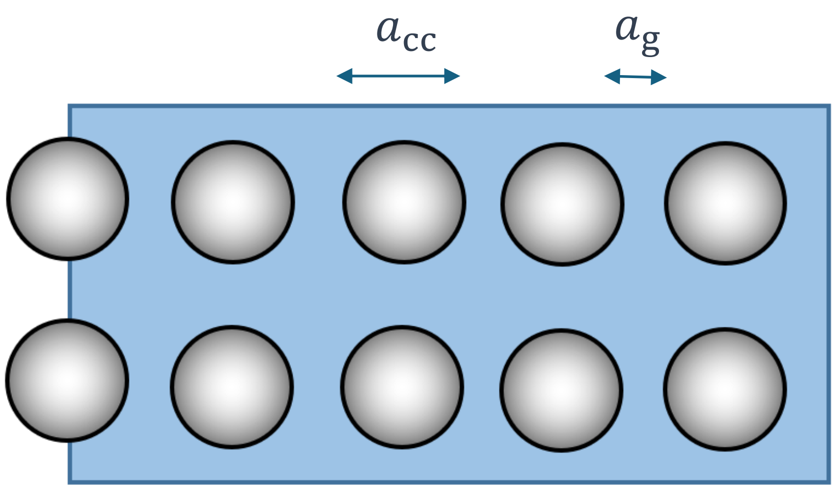
$$\bar{P} = -\frac{\kappa\bar{p}\bar{n}_{\mathrm{s}}\mathcal{L}\left(\bar{p}\left|\bar{\mathcal{E}} - \bar{\nabla}\bar{\phi}\right|\right)}{\left|\bar{\mathcal{E}} - \bar{\nabla}\bar{\phi}\right|}\left(\bar{\mathcal{E}} - \bar{\nabla}\bar{\phi}\right)$$

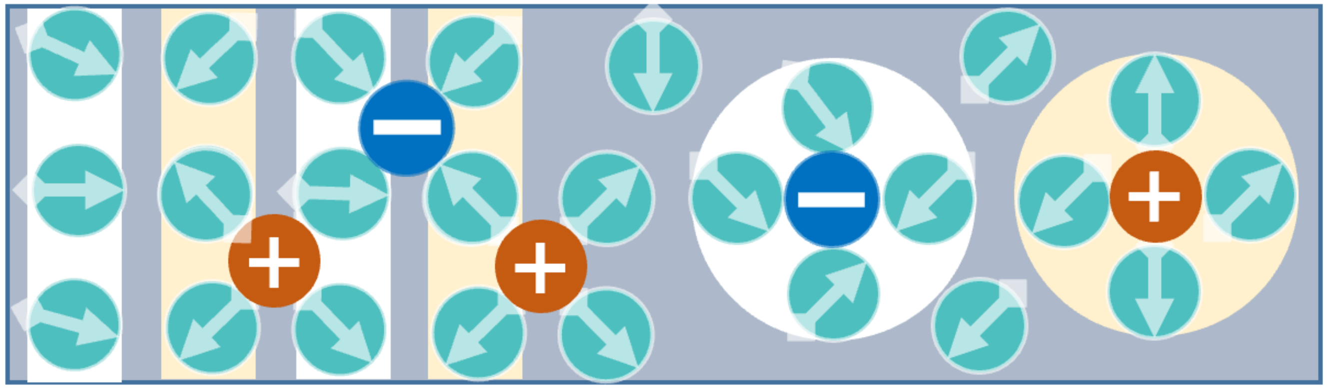
Implemented in COMSOL Multiphysics using the Mathematical Equation Interface, details provided in the SI

M.K. Zhang, Y. Chen, M. Eikerling, J. Huang, *In preparation.*

Numerical implementation to a 1D problem

(2) Boundary conditions





Left BCs in the metal bulk

$\nabla n_e = 0, \nabla\phi = 0, \boldsymbol{P} = 0, \nabla^2\boldsymbol{P} = 0$

Right BCs in the solution bulk

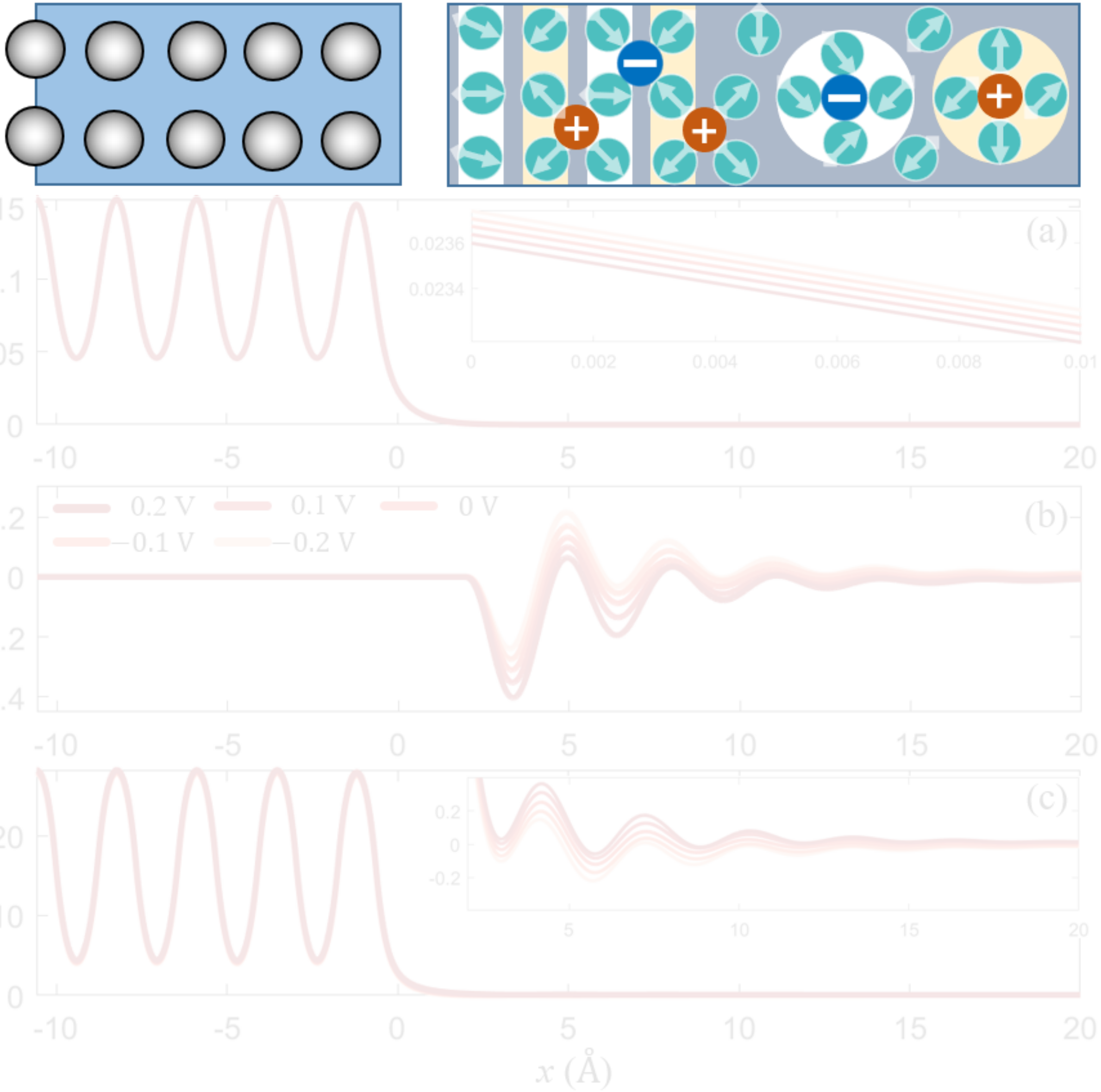
$n_e = 0, \phi = 0, \boldsymbol{P} = 0, \nabla^2\boldsymbol{P} = 0$

Description of metal cationic cores

- Jellium: $\frac{\bar{n}_{cc}}{\bar{n}_{cc}^0} = \theta(\bar{x}_M - \bar{x})$, θ is a Heaviside function
- Atomic structure: $\frac{\bar{n}_{cc}(x)}{\bar{n}_{cc}^0} = \theta(x) - \theta\left(x - \frac{a_{cc}}{2}\right) + \theta\left(x - \frac{a_{cc}}{2} - t\right) - \theta\left(x - \frac{3a_{cc}}{2} - t\right) + \theta\left(x - \frac{3a_{cc}}{2} - 2t\right) - \theta\left(x - \frac{5a_{cc}}{2} - t\right) + \theta\left(x - \frac{5a_{cc}}{2} - 3t\right) - \theta\left(x - \frac{7a_{cc}}{2} - 3t\right) + \theta\left(x - \frac{7a_{cc}}{2} - 4t\right) - \theta\left(x - \frac{9a_{cc}}{2} - 4t\right)$

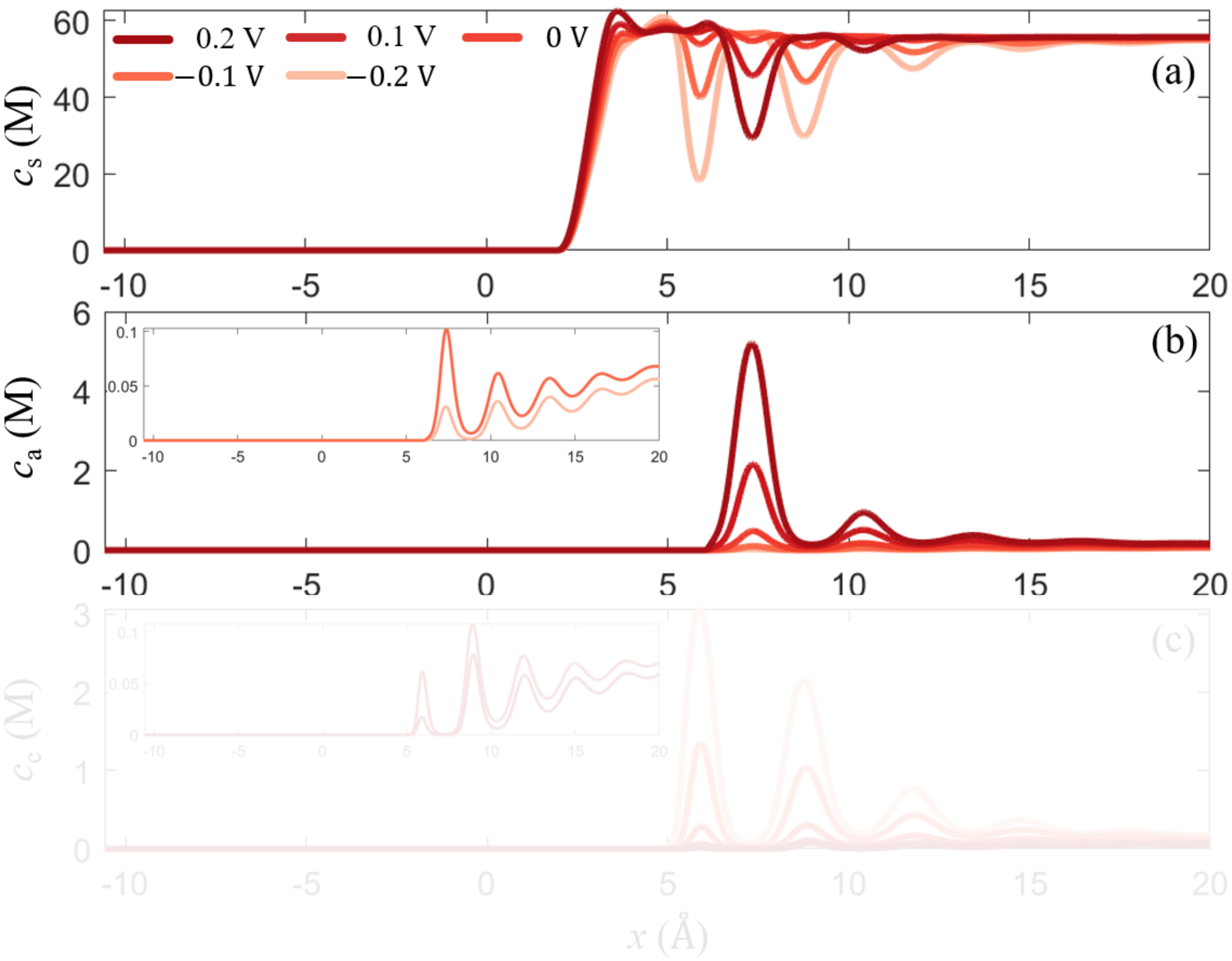
EDL of Ag(110)-0.1 M KPF_6 aqueous interface

Oscillation in model results at five electrode potentials referenced to the PZC



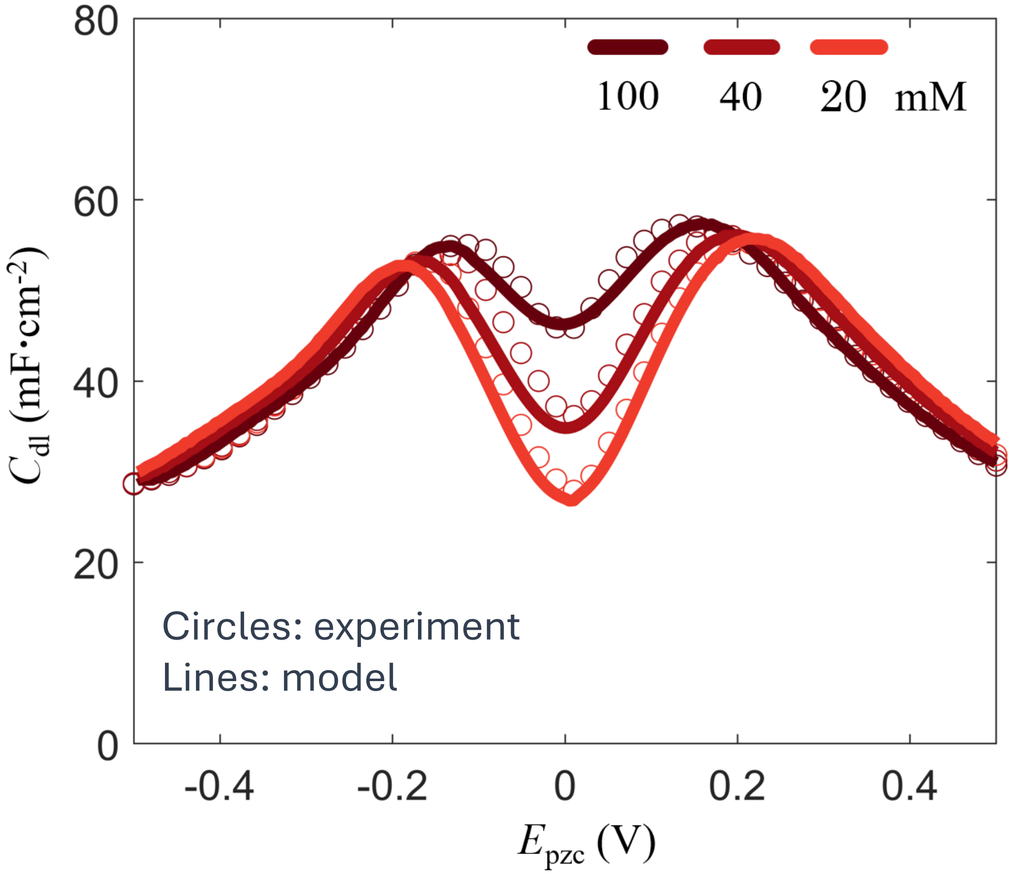
EDL of Ag(110)-0.1 M KPF_6 aqueous interface

Layering in model results at five electrode potentials referenced to the PZC



EDL of Ag(110)-0.1 M KPF_6 aqueous interface

Benchmark with experimental C_{dl} data – concentration dependence



Fitted parameters

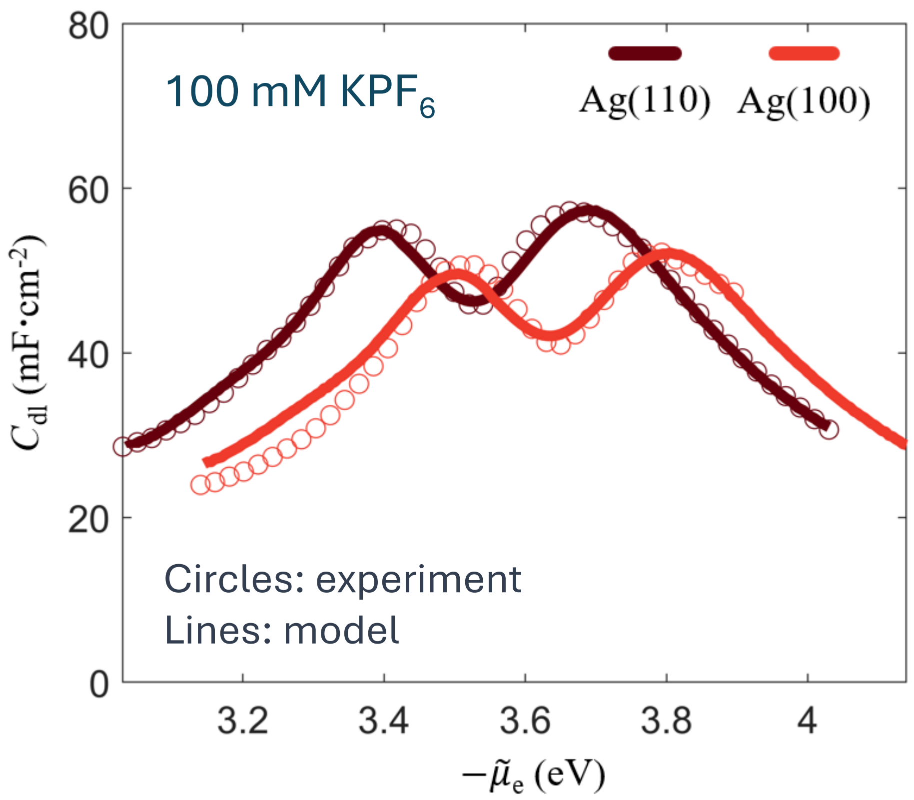
- **OF-DFT parameter**: $\theta_{\mathrm{T}} = 1.663$
- **Electrolyte solution parameters**: $\bar{K}_\alpha = -0.35, \bar{K}_\beta = 0.145, \bar{\alpha}_{\mathrm{c}} = -0.05, \bar{\alpha}_{\mathrm{a}} = -0.081$
- **Effective equilibrium distance* and coefficients in the Morse potential)**: $d_{\mathrm{s}}^{\mathrm{M}} = 6.6\ a_0, d_{\mathrm{c}}^{\mathrm{M}} = 13.3\ a_0, d_{\mathrm{a}}^{\mathrm{M}} = 11.6\ a_0, \bar{\beta}_{\mathrm{s}} = 0.95, \bar{\beta}_{\mathrm{c}} = 0.19, \bar{\beta}_{\mathrm{a}} = 4.5$

* M-S interactions are described by the repulsive part of Morse potential: $w_i = D_i \exp\left(-2\beta_i(d - d_i)\right) = \beta^{-1} \exp\left(-2\beta_i\left(d - d_i^{\mathrm{M}}\right)\right)$ with effective equilibrium distance $d_i^{\mathrm{M}} = d_i + \frac{\ln(\beta D_i)}{2\beta_i}$.

G. Valette, *J. Electroanal. Chem. Interfacial Electrochem.* (1981, 1982)

EDL of Ag(hkl)-0.1 M KPF_6 aqueous interface

Benchmark with experimental C_{dl} data – Facet dependence

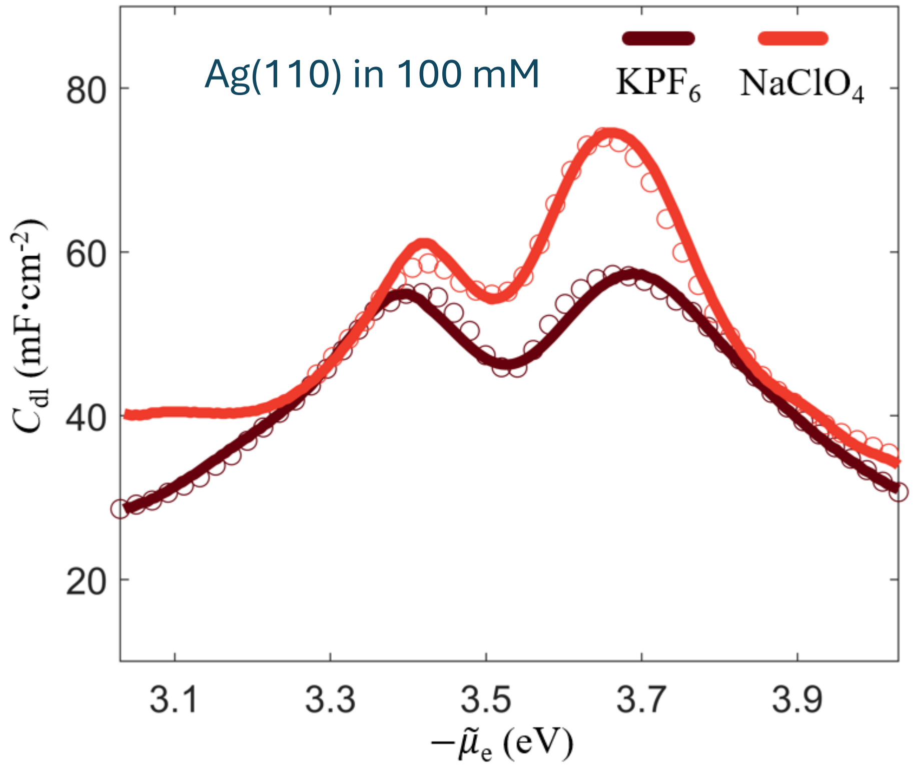


θ_T is 1.663 for Ag(110), 1.777 for Ag(100)

G. Valette, *J. Electroanal. Chem. Interfacial Electrochem.* (1981, 1982)

EDL of Ag(hkl)-0.1 M KPF_6 aqueous interface

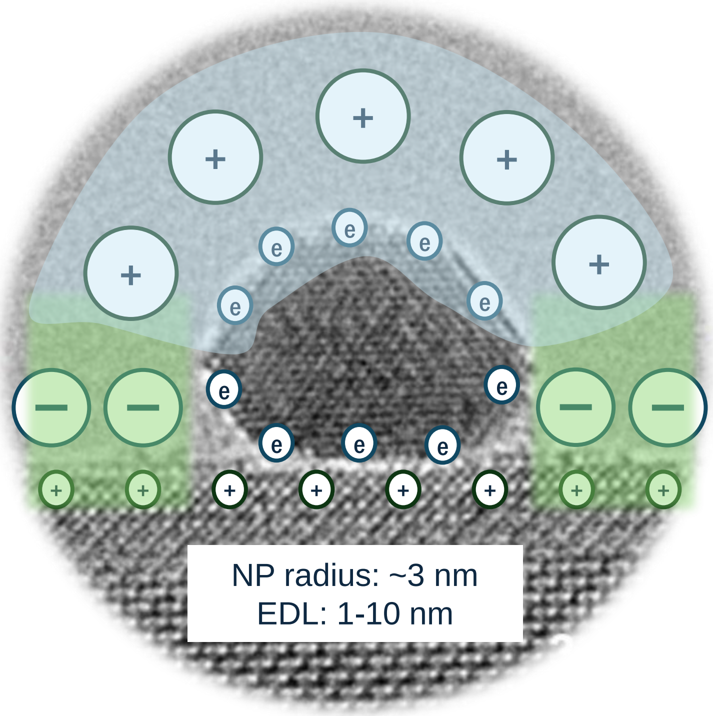
Benchmark with experimental C_{dl} data – Electrolyte dependence



Ion parameters	$r_i/\text{Å}$	$\bar{\alpha}_i$	d_i^{M}/a_0	$\bar{\beta}_i$
Solvated K^+	3.60	-0.050	13.3	0.19
Solvated Na^+	3.25	-0.022	13.3	0.15
Bare PF_6^-	2.70	-0.081	11.6	4.50
Bare ClO_4^-	2.75	-0.040	09.4	1.00

G. Valette, *J. Electroanal. Chem. Interfacial Electrochem.* (1981, 1982)

Hypothesis: Overlapping EDLs are the new factors



DPFT

What they look like?

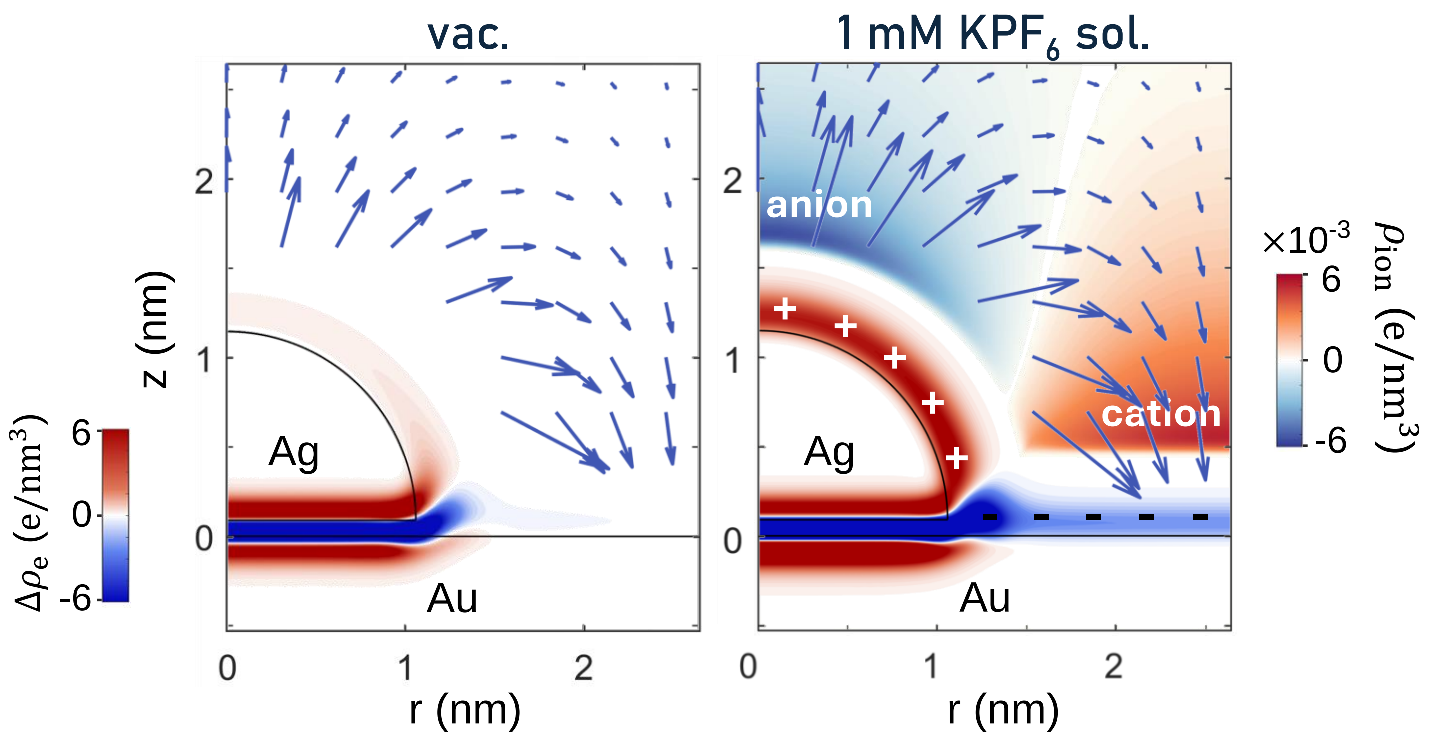
How they impact reactions?

Implications for catalyst design?

Electronic equilibration and outer surface charging

1 nm radius Ag NP on Au support,
(a) in vacuum and (b) in solution.

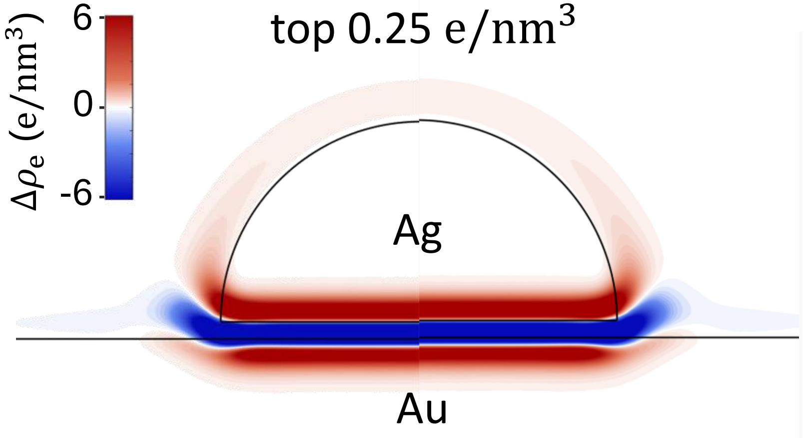
Net electronic charge density: $\rho_{\mathrm{e}} = e_0(n_{\mathrm{cc}} - n_{\mathrm{e}})$
Electronic charge density <u>difference</u>: $\Delta\rho_{\mathrm{e}} = \rho_{\mathrm{e}}^{\mathrm{sc}} - \rho_{\mathrm{e}}^{\mathrm{c}} - \rho_{\mathrm{e}}^{\mathrm{s}}$
Net ionic charge density: $\rho_{\mathrm{ion}} = e_0(n_{\mathrm{c}} - n_{\mathrm{a}})$



- Outer surface charging is more pronounced in solution environment than in vacuum.
- Outer surface charging causes ionic charge separation in solution phase.

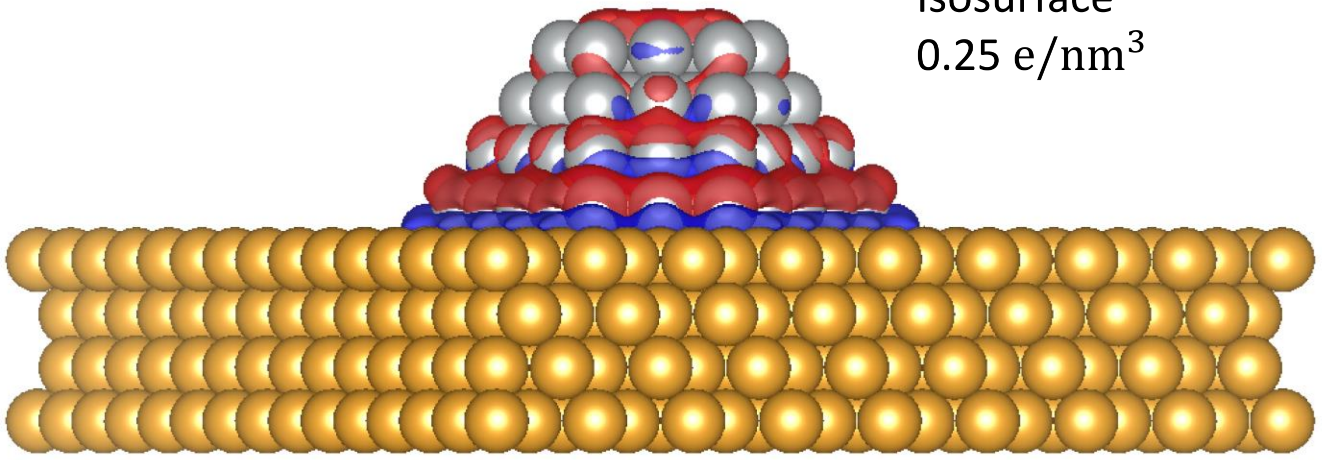
Y. Zhang, T. Binninger, J. Huang, M. Eikerling., *Phys Rev Lett, Accepted*

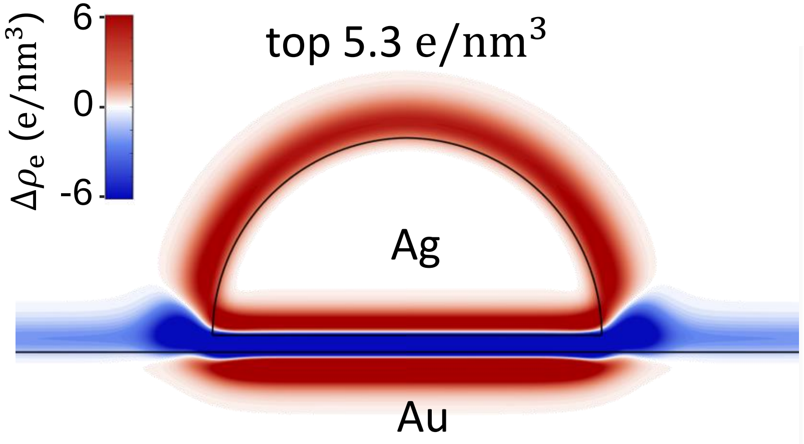
Comparison with DFT results



vac

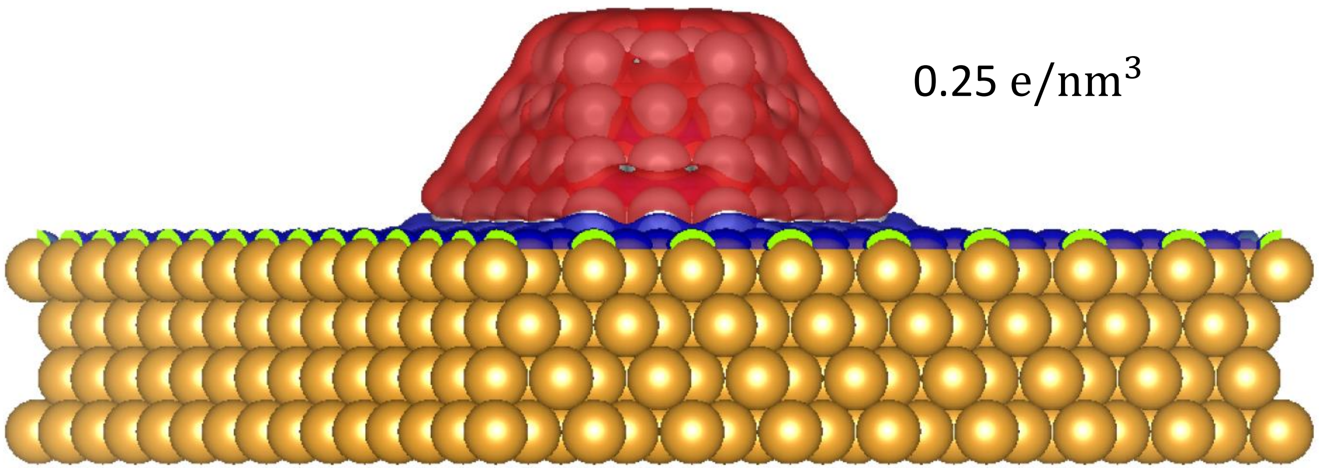
CHGDIFF_cov15%_vac.vasp



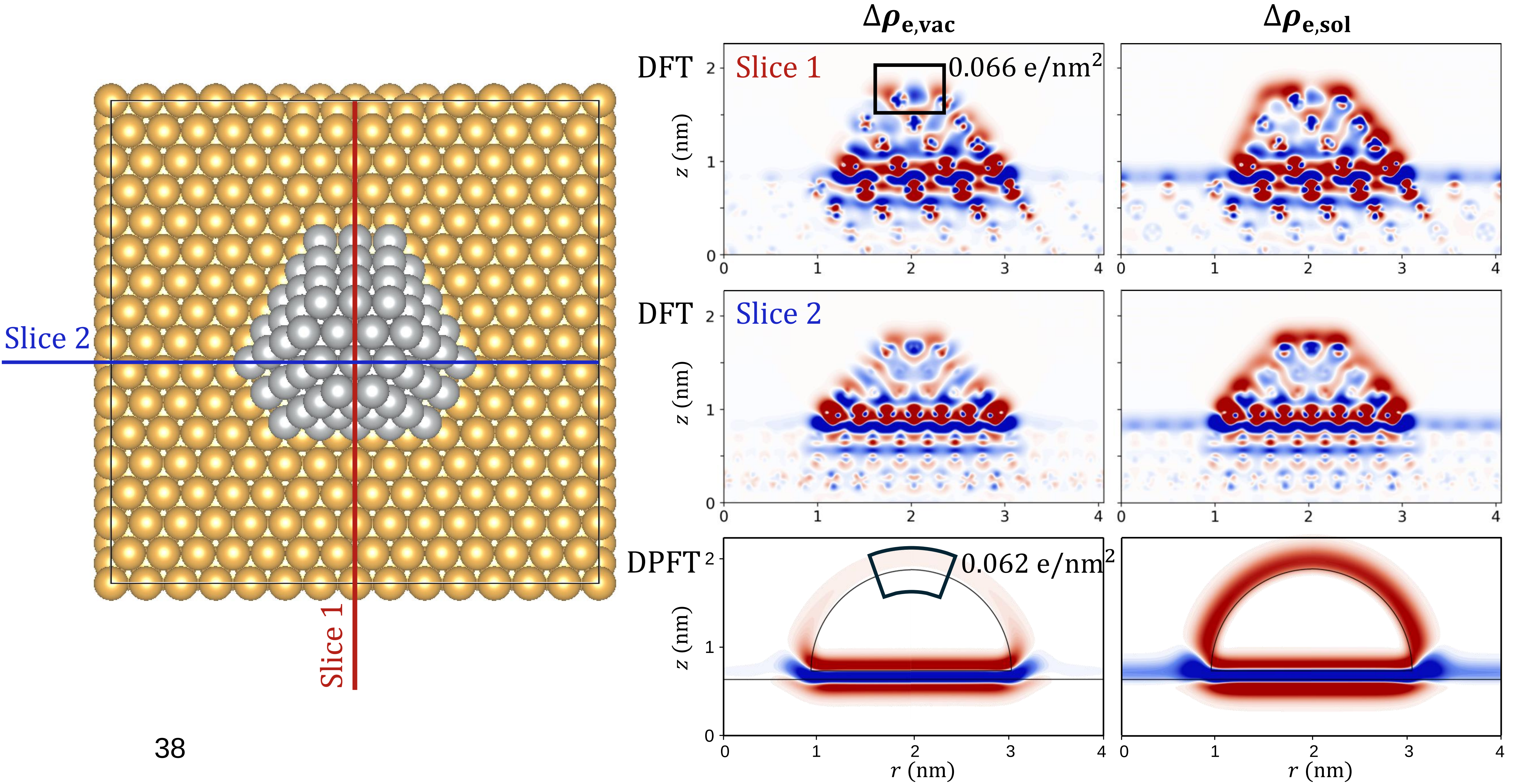


sol

CHGDIFF_cov15%_sol.vasp

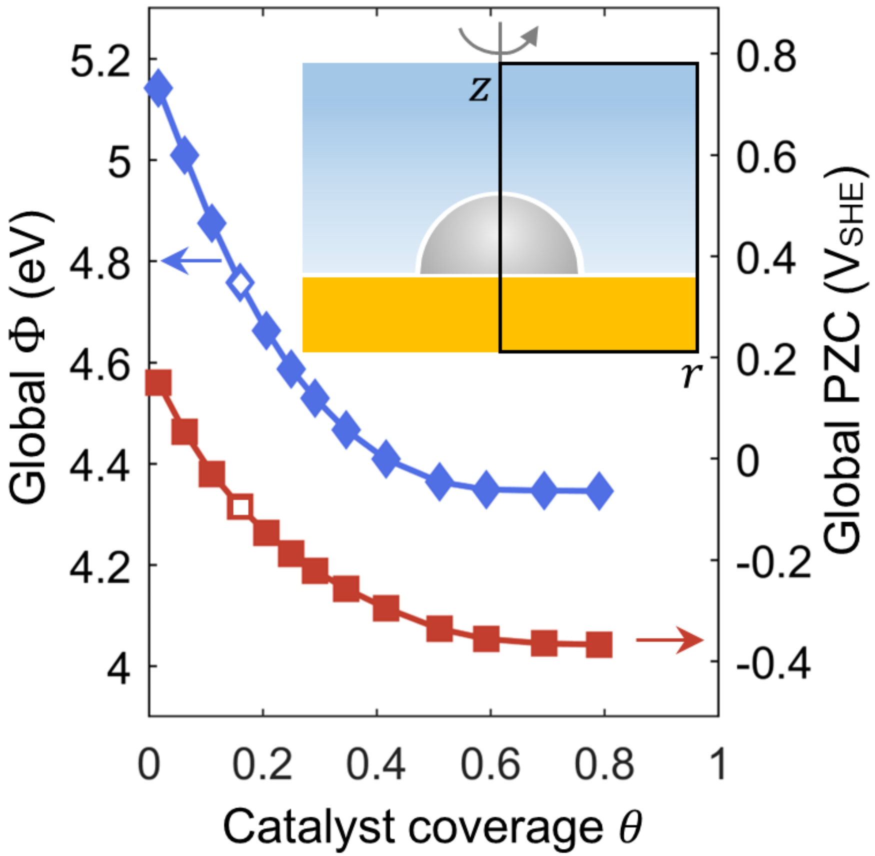


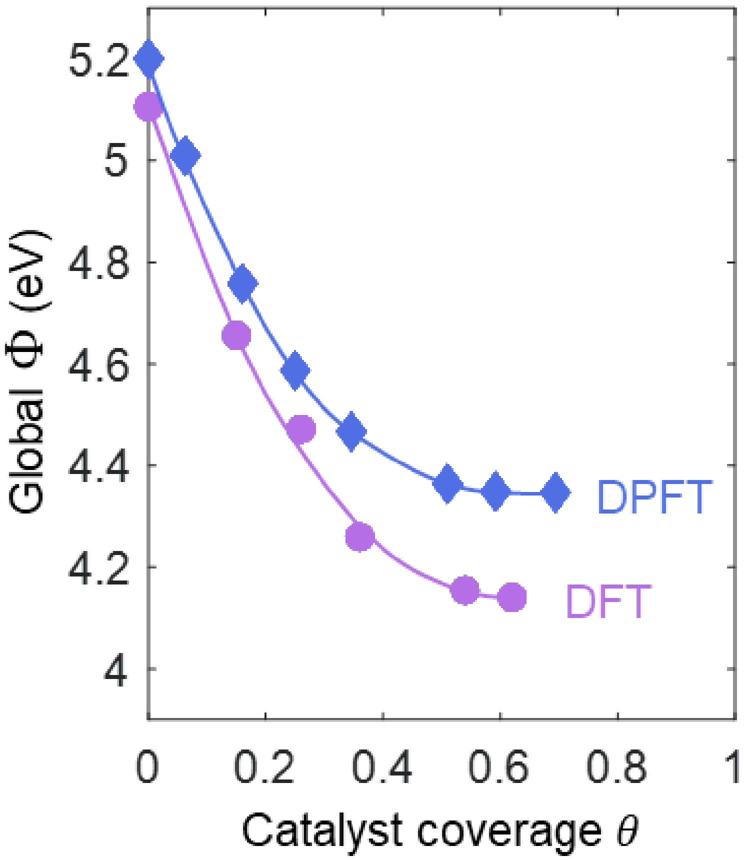
Quantitative agreement between DFT and DPFT

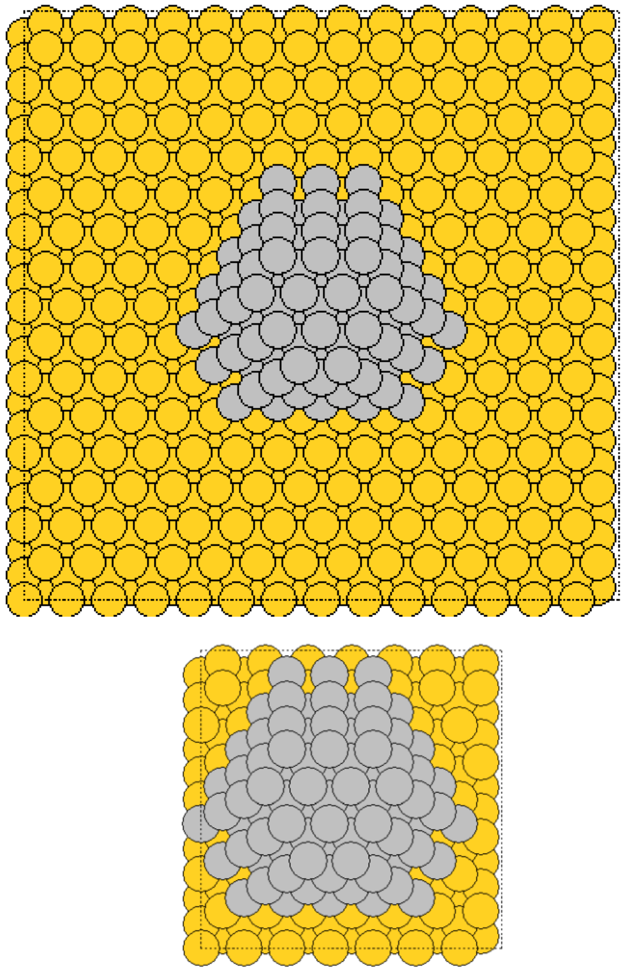


Effect of NP coverage on global Φ and global PZC

DPFT results

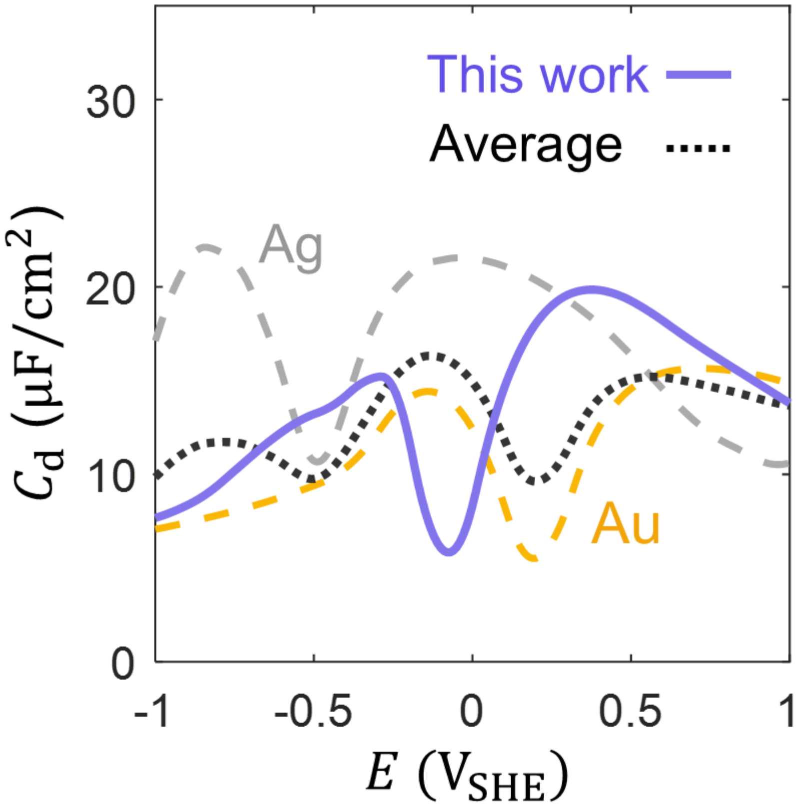


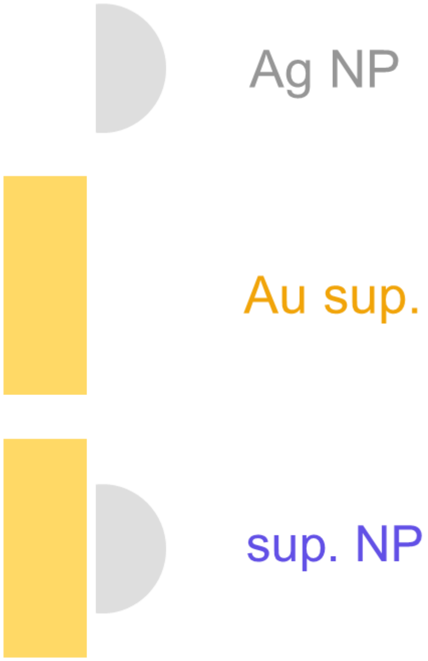




Y. Zhang, T. Binninger, J. Huang, M. Eikerling., *Phys Rev Lett, Accepted*

Differential capacitance: C_d





$$C_{d,ave} = C_{d,Ag}\frac{S_{Ag}}{S_{Ag}+S_{Au}} + C_{d,Au}\frac{S_{Au}}{S_{Ag}+S_{Au}}$$

- Cd of heterogeneous surface resembles that of homogeneous surface: the only one minimum corresponds to the global potential of zero charge.
- Electron redistribution tends to homogenize the capacitive response of the heterogeneous surface.

Ag NP has a radius of 1 nm
Coverage of 16%
1 mM $KClO_4$ solution

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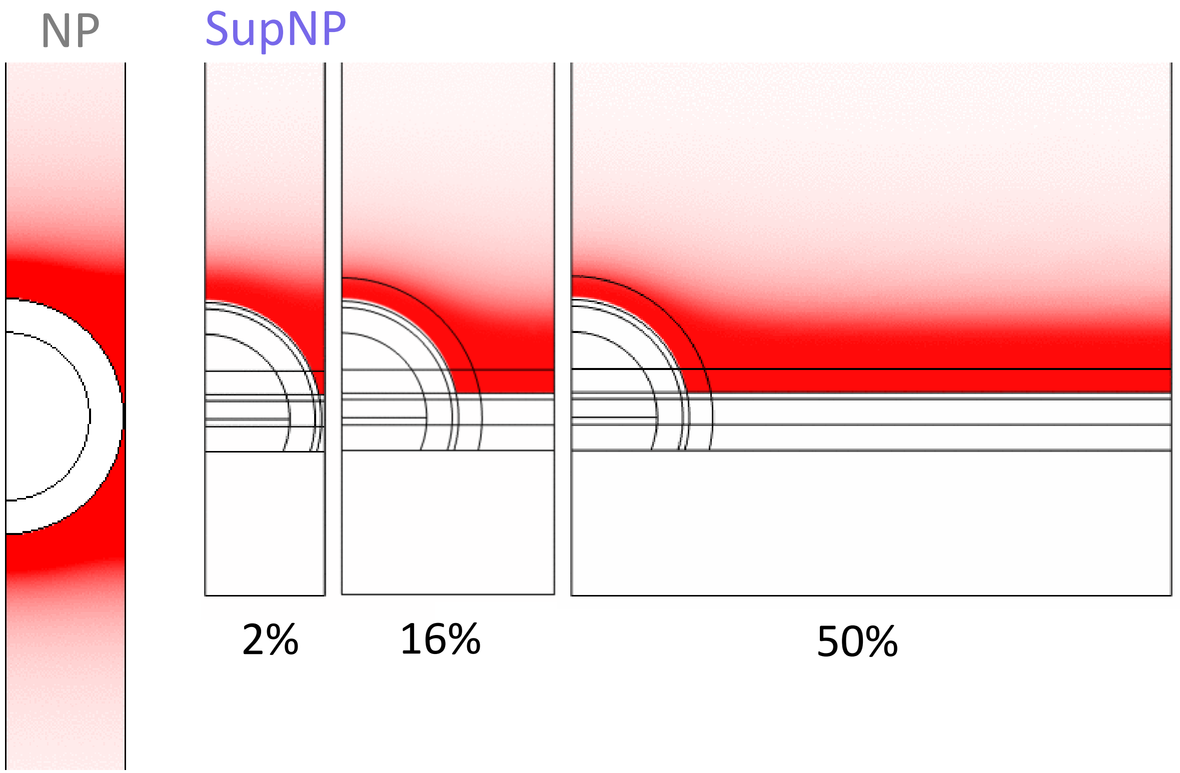
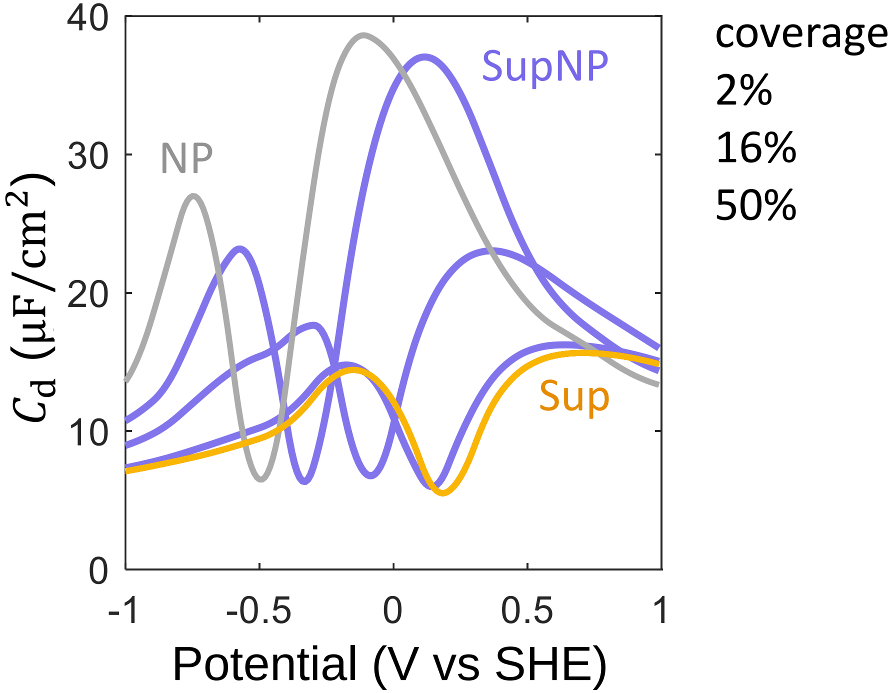
Differential capacitance: C_d

Coverage effect





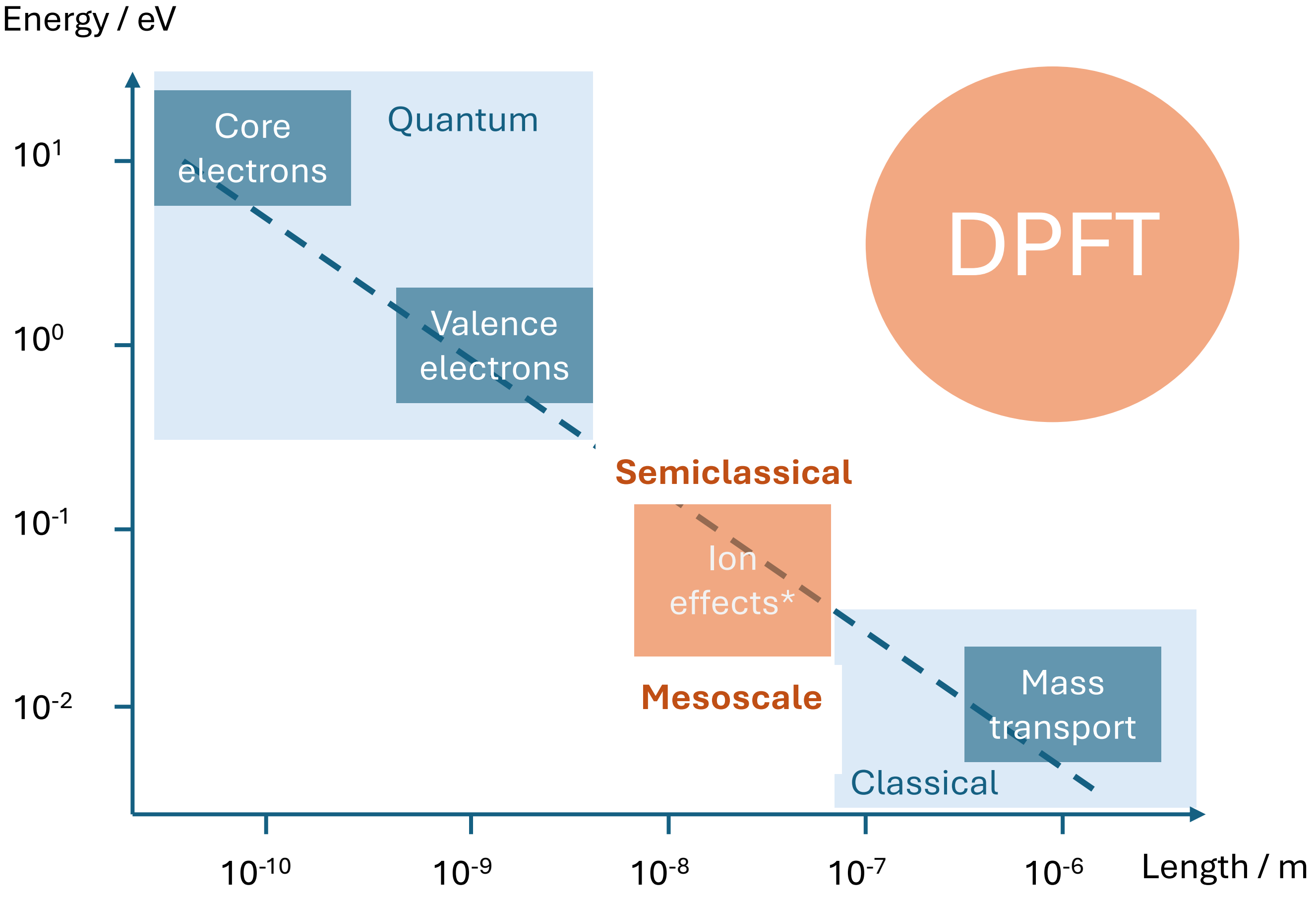
$R_{cat} = 1$ nm

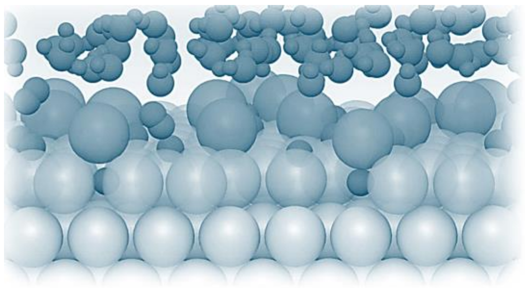
coverage = R_{NP}^2 / R_{sup}^2

At lower and upper coverage limit, C_{dl} of supported NP approaches the bare support and unsupported NP, respectively.

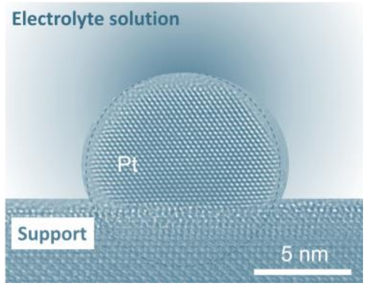
Summary

HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES
Helmholtz Young Investigators Award





Planar surfaces



Supported NPs

Key collaborators: M. Eikerling (Jülich), M. Melander (Jyväskylä), J. Feliu & V. Climent (Alicante), Y. Tong (Duisburg-Essen), Y. Chen (Hefei)