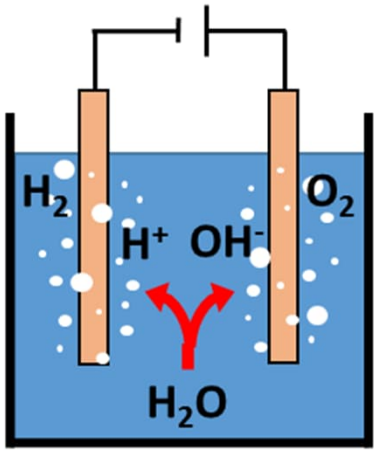
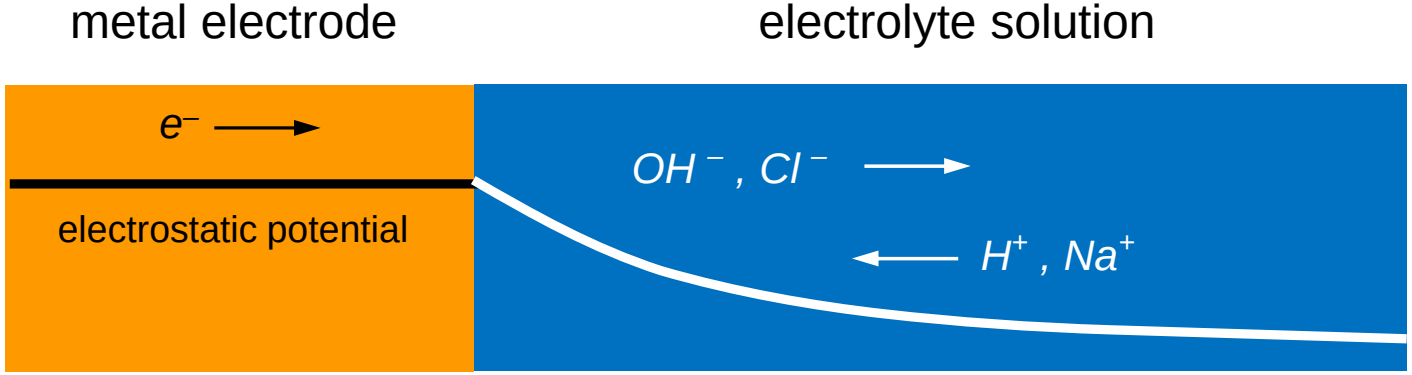
FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

FIRST-PRINCIPLES BASED MODELLING OF ELECTROCATALYSIS BEYOND THE POTENTIAL OF ZERO CHARGE

Karsten Reuter
Fritz-Haber-Institut der Max-Planck-Gesellschaft

Solid-Liquid Interface in Electrocatalysis





Reactive chemistry

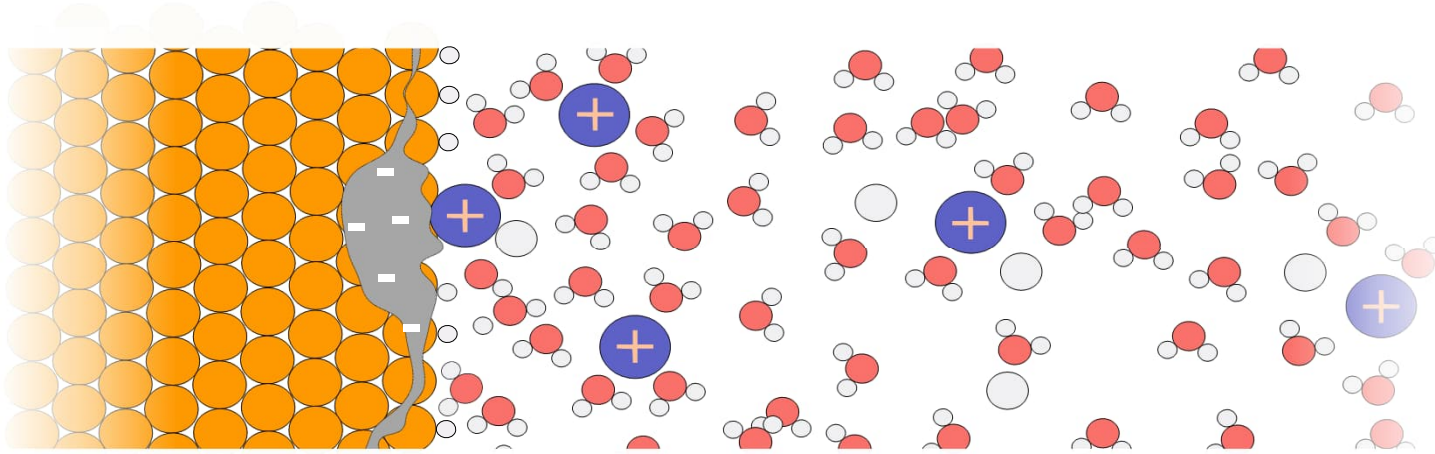
at extended

(*operando* evolving) surface

plus

long-range electrostatics

and solvent dynamics



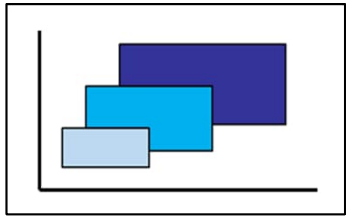
electric surface charge

inner double layer

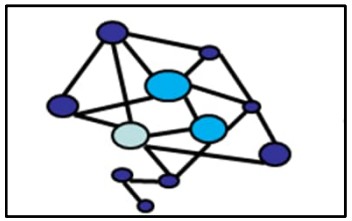
diffuse double layer

Agenda

i) Implicit Solvation Models as Gateway to Capacitive Charging

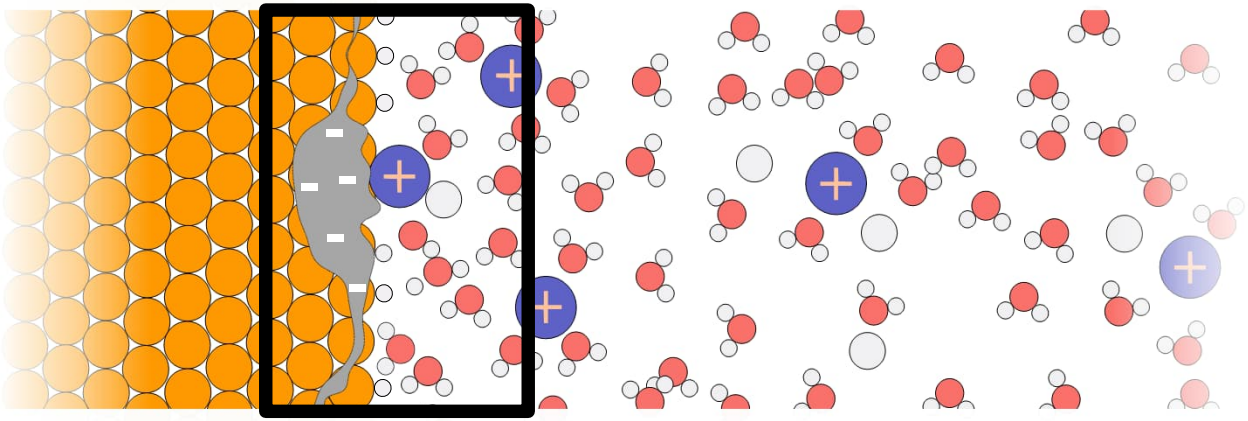


ii) ML Surrogate Models as Gateway to Efficient Explicit Simulations



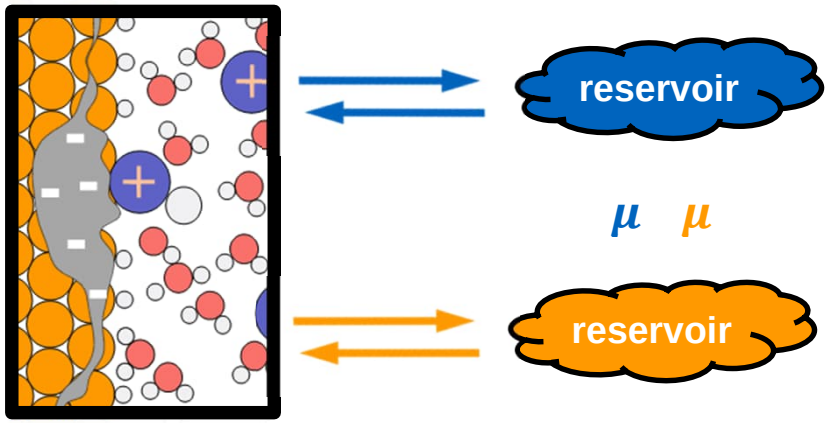
ii) Coupled Microkinetic-Continuum Models as Gateway to Mesoscale Transport

Ab Initio Thermodynamics Approach to Electrocatalysis



DFT supercell
(typically with periodic
boundary conditions)

How to model a finite „q“ in
an overall charge-neutral supercell?

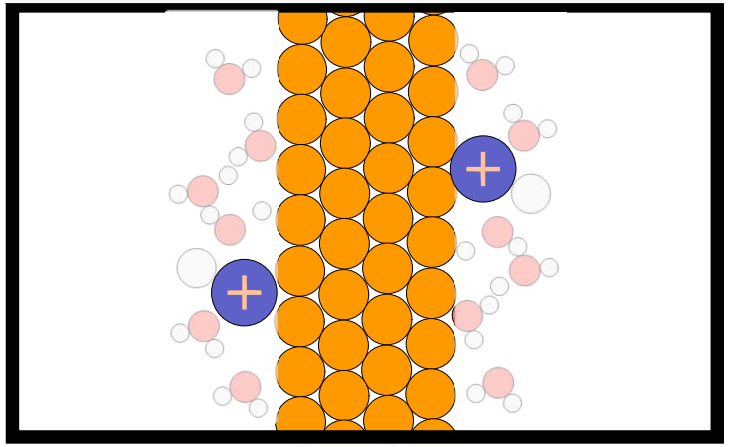


$$\gamma_{\text{surf}} = {}^{1}/_{A}\left\{G_{\text{surf}}\left(\sum_{\text{species}} N_{\text{sp}}\right) - \sum_{\text{species}} N_{\text{sp}}\mu_{\text{sp}}\right\}$$

$$= {}^{1}/_{A}\left\{\begin{array}{l} G_{\text{surf}}\left(\sum_{\text{species}} N_{\text{sp}}, q\right) \\ -\sum_{\substack{\text{neutral}\\ \text{species}}} N_{\text{nsp}}\mu_{\text{nsp}} - \sum_{\text{ions}} N_{\text{i}}\tilde{\mu}_{\text{i}} - N_{\text{el}}\tilde{\mu}_{\text{el}} \end{array}\right\}$$

e.g. K. Reuter, Catal. Lett. 146, 541 (2016); review

Computational Hydrogen Electrode (CHE)



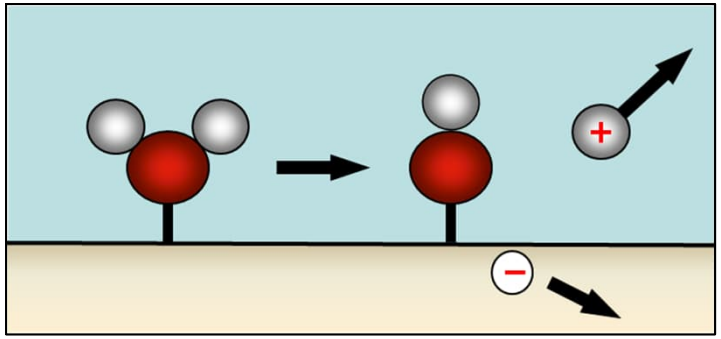
J.K. Nørskov, J. Rossmeisl, *et al.*,
J. Phys. Chem. B 108, 17886 (2004)
>9000 citations
>90% of existing theory electrocatalysis work

$$\gamma_{\text{surf}} = {}^{1}/_{A}\left\{G_{\text{surf}}\left(\sum_{\text{species}} N_{\text{sp}}\right) - \sum_{\text{species}} N_{\text{sp}}\,\mu_{\text{sp}}\right\}$$

$$= {}^{1}/_{A}\left\{\begin{matrix} G_{\text{surf}}\left(\sum_{\text{species}} N_{\text{sp}}, \boldsymbol{q}\right) \\ -\sum_{\substack{\text{neutral}\\ \text{species}}} N_{\text{nsp}}\,\mu_{\text{nsp}} - \sum_{\text{ions}} N_{\text{i}}\tilde{\mu}_{\text{i}} - N_{\text{el}}\tilde{\mu}_{\text{el}} \end{matrix}\right\}$$

$\tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{\text{el}} = 1/2\,\mu_{\text{H}_2}{}^{\text{gas}}(298\text{K}, 1\text{bar}) + U$ with U the applied bias w.r.t. RHE

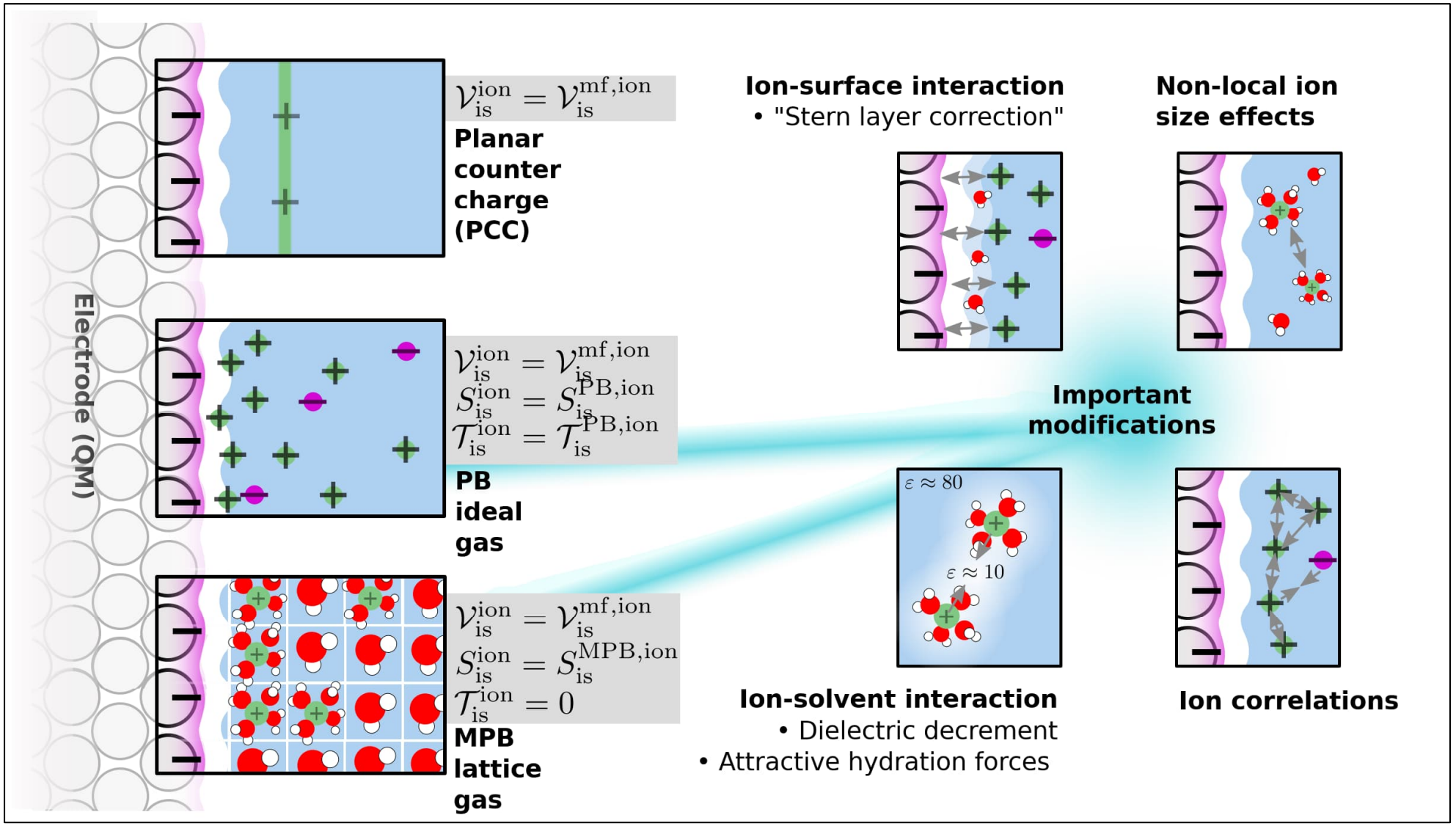
Electron density remains as the one at the PZC



$\boldsymbol{q = 0}$: $\sum_{\text{ions}} N_{\text{i}}\,q_{\text{i}} + N_{\text{el}}\,e = 0$ — no surface polarization / capacitive double layer charging

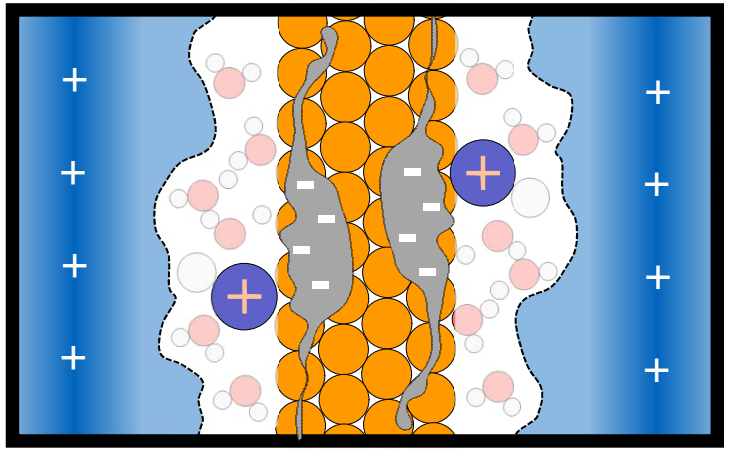
$N_{\text{H}^+} + N_{\text{el}} = 0$ — only PCET in aqueous electrolyte

Implicit Electrolyte: Modeling the Counter Charge



S. Ringe, N.G. Hörmann, H. Oberhofer, and K. Reuter, Chem. Rev. 122, 10777 (2022)

Fully Grand-Canonical (FGC) Simulations



N.G. Hörmann, O. Andreussi, and N. Marzari,
J. Chem. Phys. 150, 041730 (2019)

$$\gamma_{\mathrm{surf}} = {}^{1}/_{A}\left\{G_{\mathrm{surf}}\left(\sum_{\mathrm{species}} N_{\mathrm{sp}}\right) - \sum_{\mathrm{species}} N_{\mathrm{sp}}\mu_{\mathrm{sp}}\right\}$$

$$= {}^{1}/_{A}\left\{\begin{array}{l} G_{\mathrm{surf}}\left(\sum_{\mathrm{species}} N_{\mathrm{sp}}, \boldsymbol{q}\right) \\ -\sum_{\substack{\mathrm{neutral} \\ \mathrm{species}}} N_{\mathrm{nsp}}\mu_{\mathrm{nsp}} - \sum_{\mathrm{ions}} N_{\mathrm{i}}\tilde{\mu}_{\mathrm{i}} - N_{\mathrm{el}}\tilde{\mu}_{\mathrm{el}} \end{array}\right\}$$

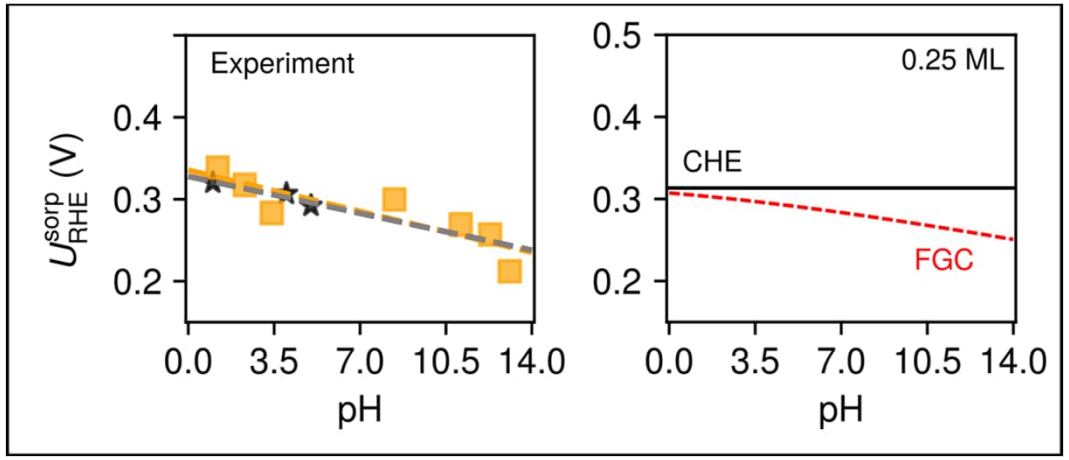
Electrolyte countercharges in implicit solvation model enable $\boldsymbol{q \neq 0}$ calculations at overall charge-neutral supercell ($\tilde{\mu}_{\mathrm{el}}$ referenced to experimental SHE)

Calculations at variable $\boldsymbol{q}$ determine charge-equilibrated G_{surf} that accounts for capacitive charging of the double layer

Nicolas Hörmann

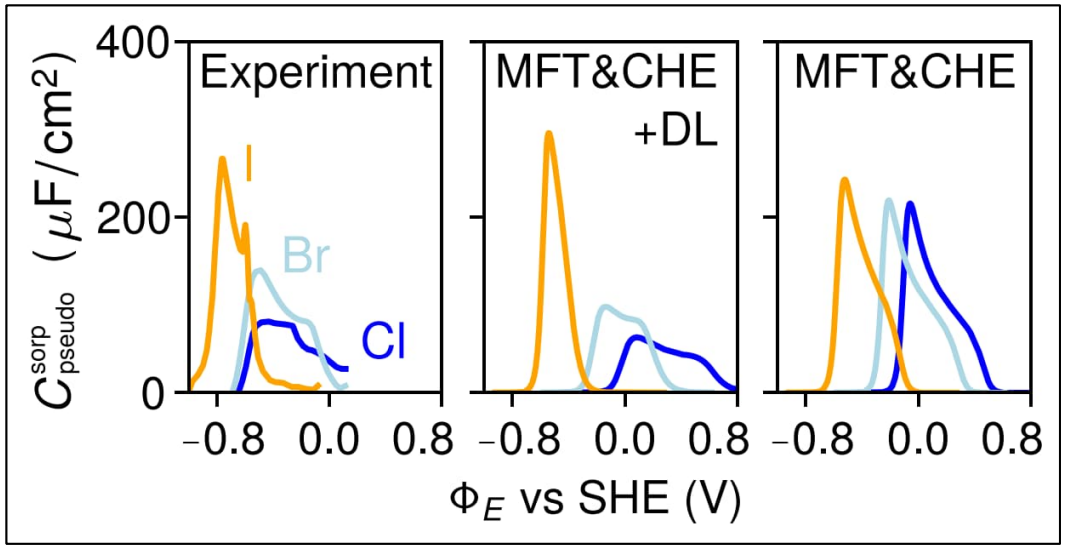
Improved Electrochemistry

Non-Nernstian peak shifts



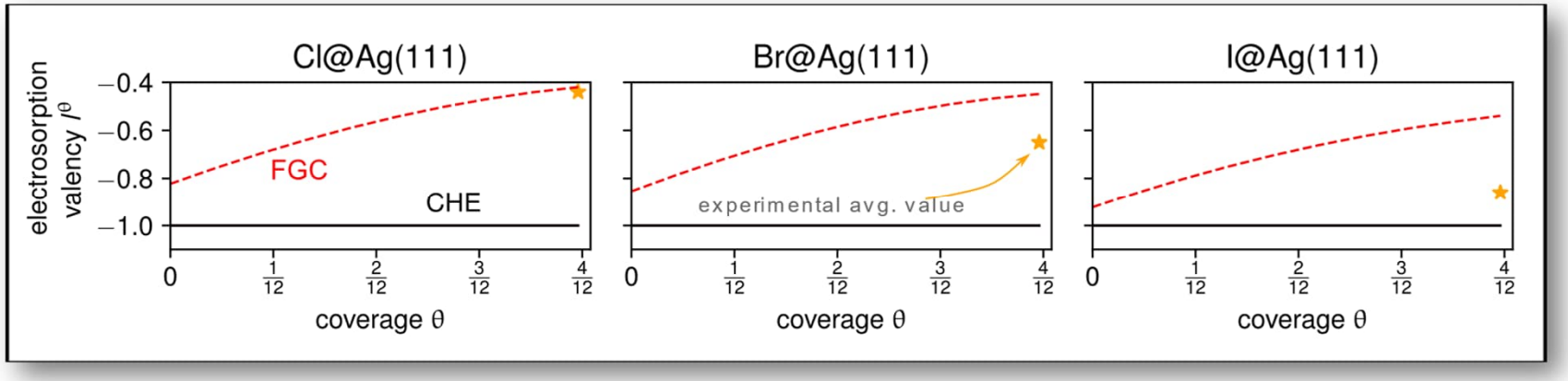
N.G. Hörmann, N. Marzari, and K. Reuter,
npj Comp. Mater. 6, 136 (2020)

Peak shapes



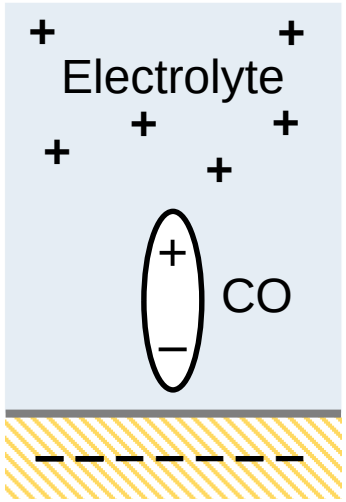
N.G. Hörmann and K. Reuter, J. Phys. CM 33, 264004 (2021)

Non-integer electrosorption valencies

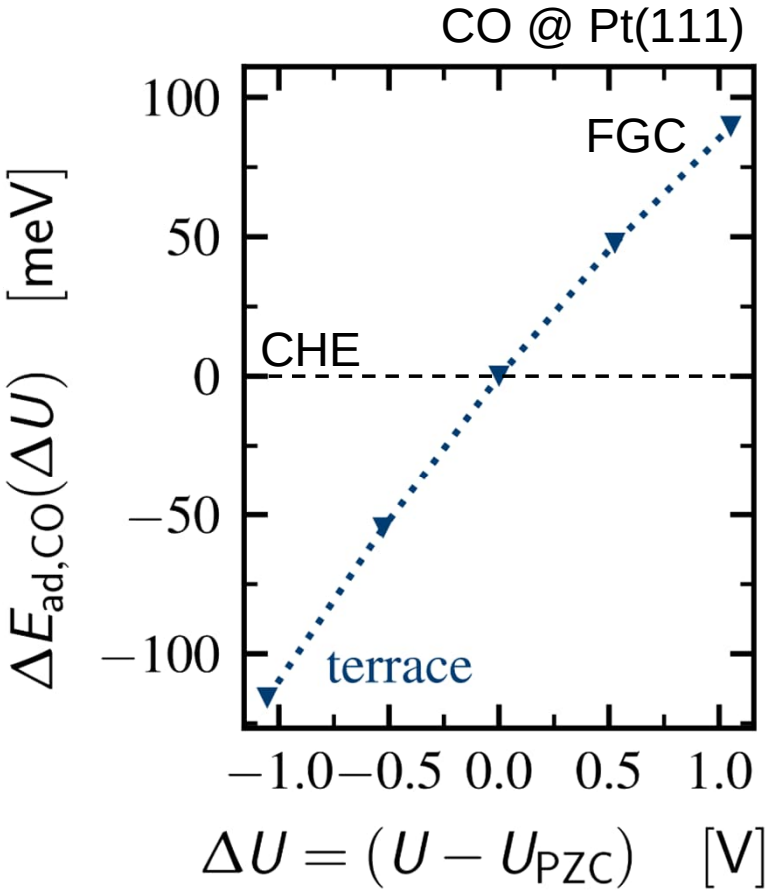


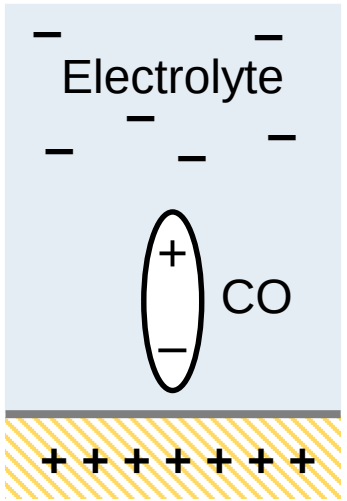
N.G. Hörmann and K. Reuter, J. Chem. Theory Comput. 17, 1782 (2021)

Potential-Dependent Adsorption Energies



$U < U_{PZC}$
weaker binding

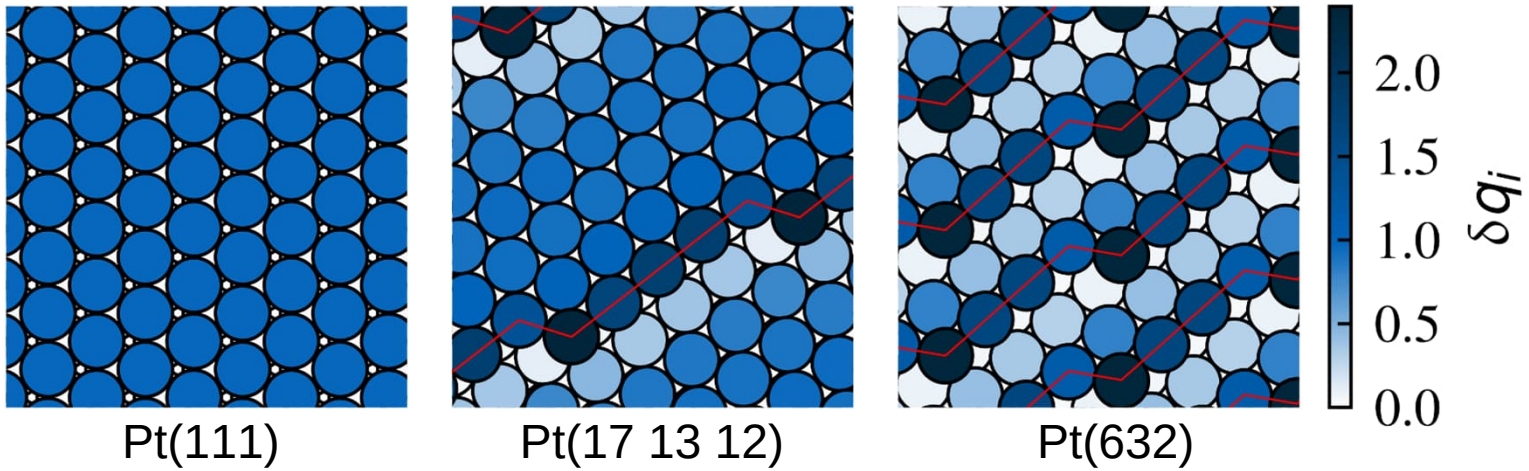


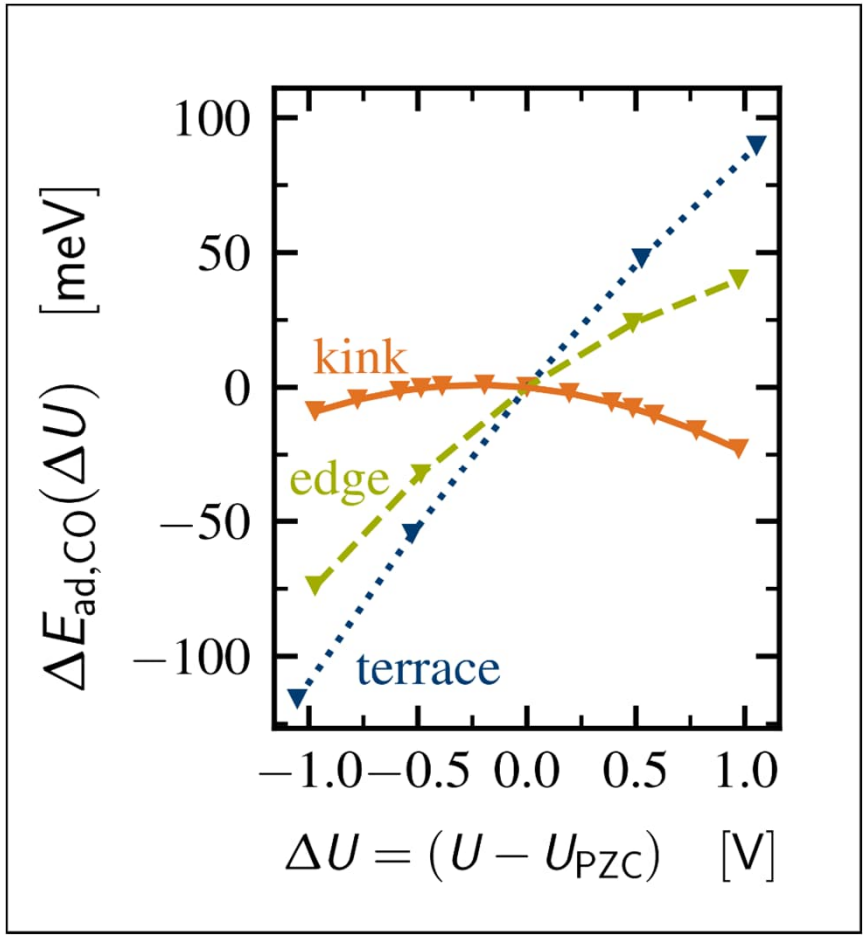


$U > U_{PZC}$
stronger binding

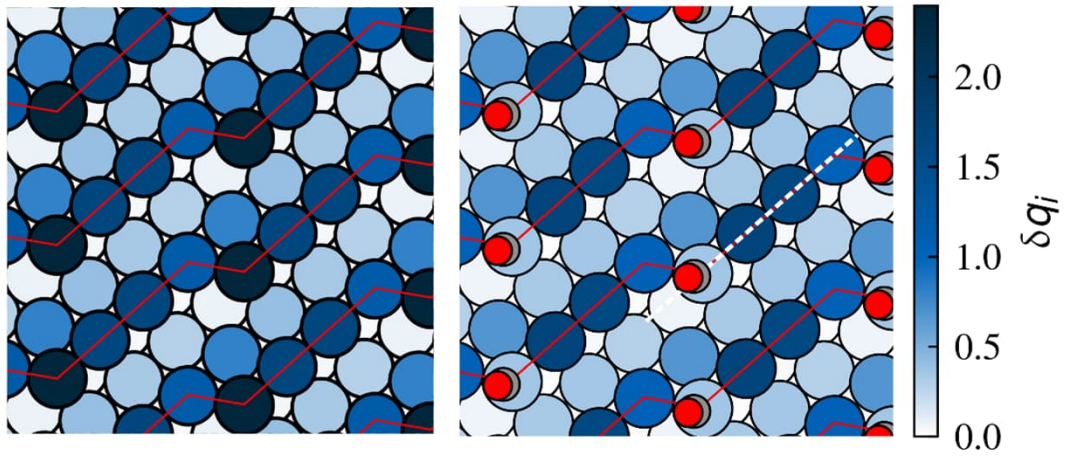
Trend and magnitude consistent with dipole-field interaction picture
(1 V/Å * 0.1 Debye ≈ 20 meV/V)

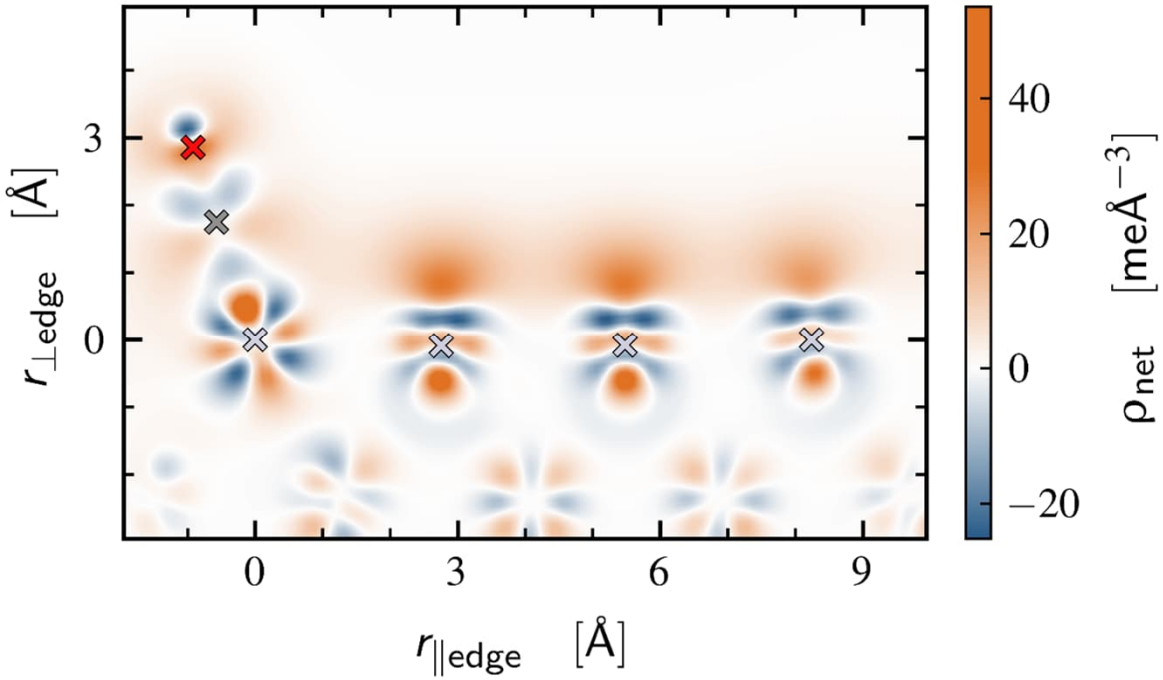
Field Effects at Protruding Sites?





Effective Dipole-Field Picture





$$\mathbf{E}^{\text{eff}}(\Delta U(Q)) = \frac{Q}{\varepsilon_o A_{\text{surf}}}$$ (plate-capacitor type field)

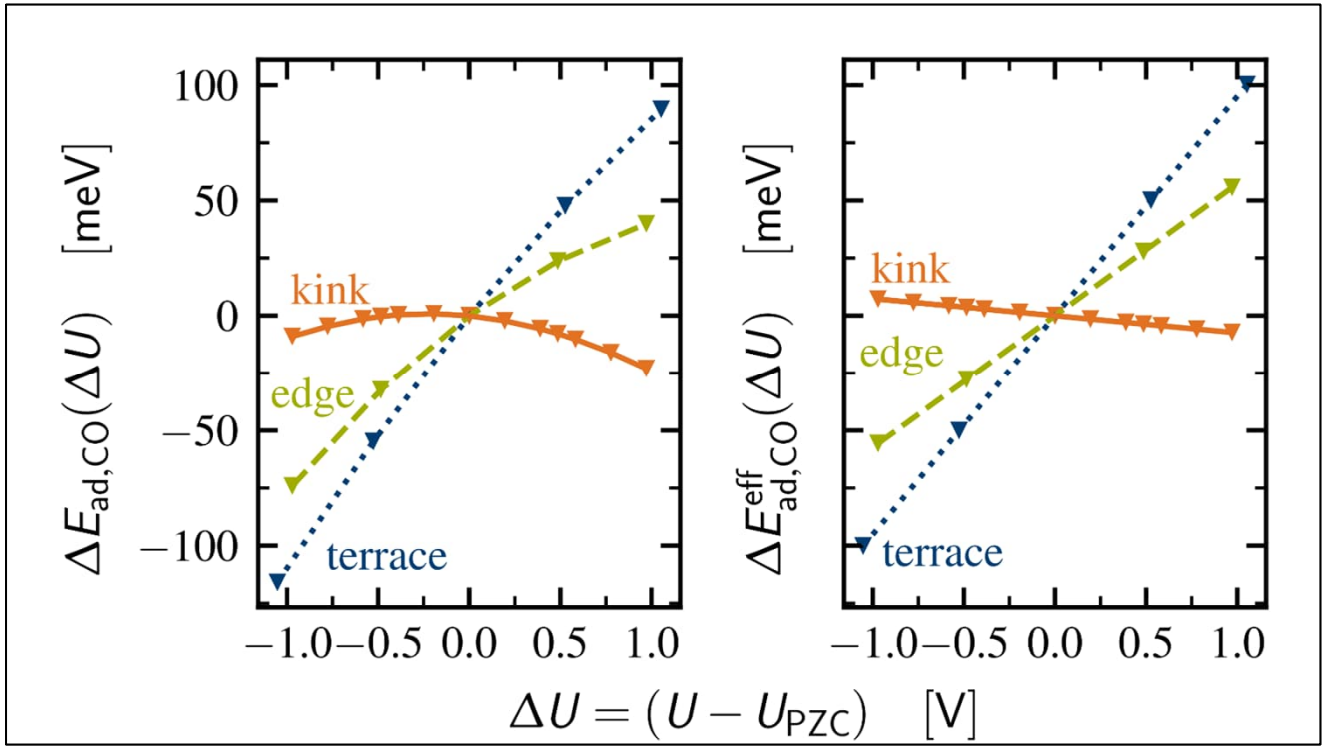
$$\mathbf{d}_\alpha^{\text{surf}} = \varepsilon_o A_{\text{surf}} \Delta\Phi_{\text{PZC},\alpha} / N_\alpha$$ (surface dipole moment)

$$\begin{aligned}\Delta E_{\text{ad},\alpha}^{\text{eff}}(\Delta U(Q)) &= \mathbf{d}_\alpha^{\text{surf}} \cdot \mathbf{E}^{\text{eff}}(\Delta U(Q)) + \ldots \\ &= \Delta\Phi_{\text{PZC},\alpha} Q / N_\alpha + \ldots \quad .\end{aligned}$$

$$\Delta E_{\text{ad},\alpha}(\Delta U(Q)) = l_e \, e \Delta U$$

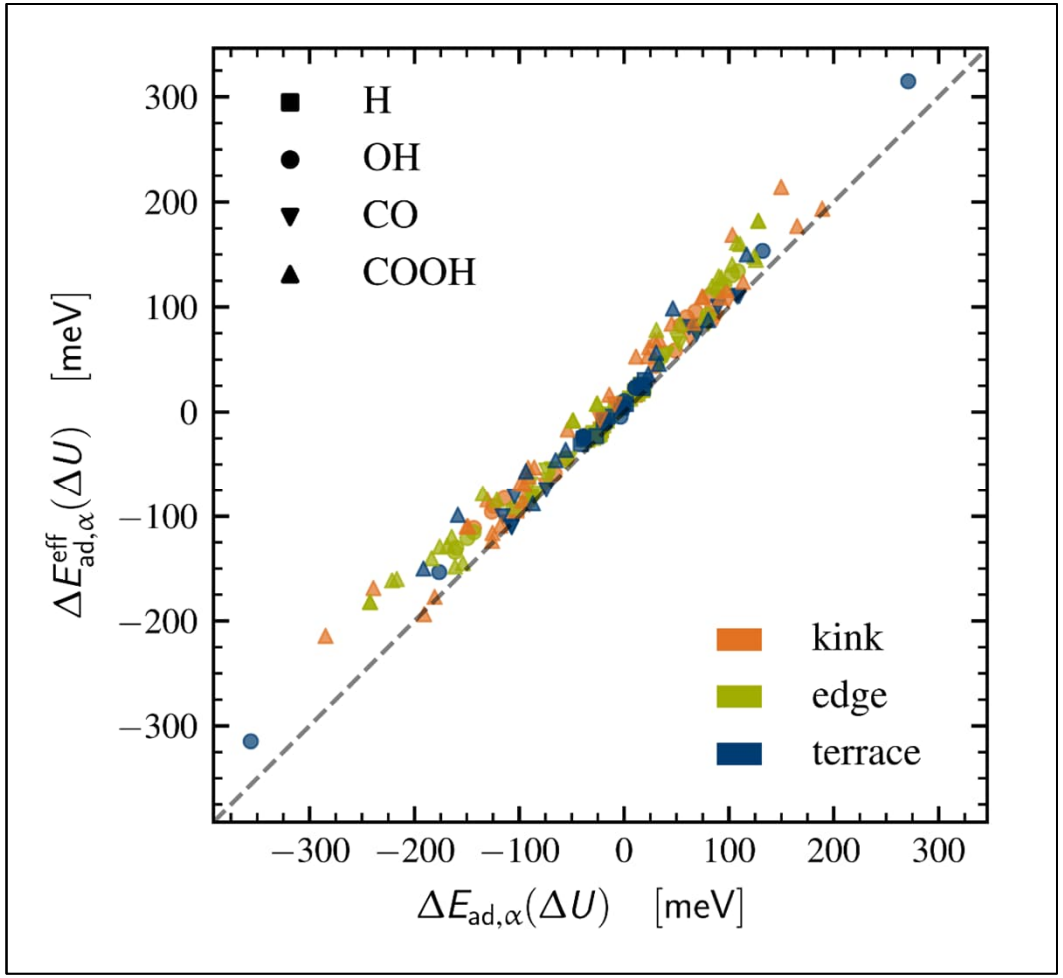
(work required to compensate the adsorbate-induced charge flow at constant potential…)

Surface Energetics Beyond the Potential of Zero Charge



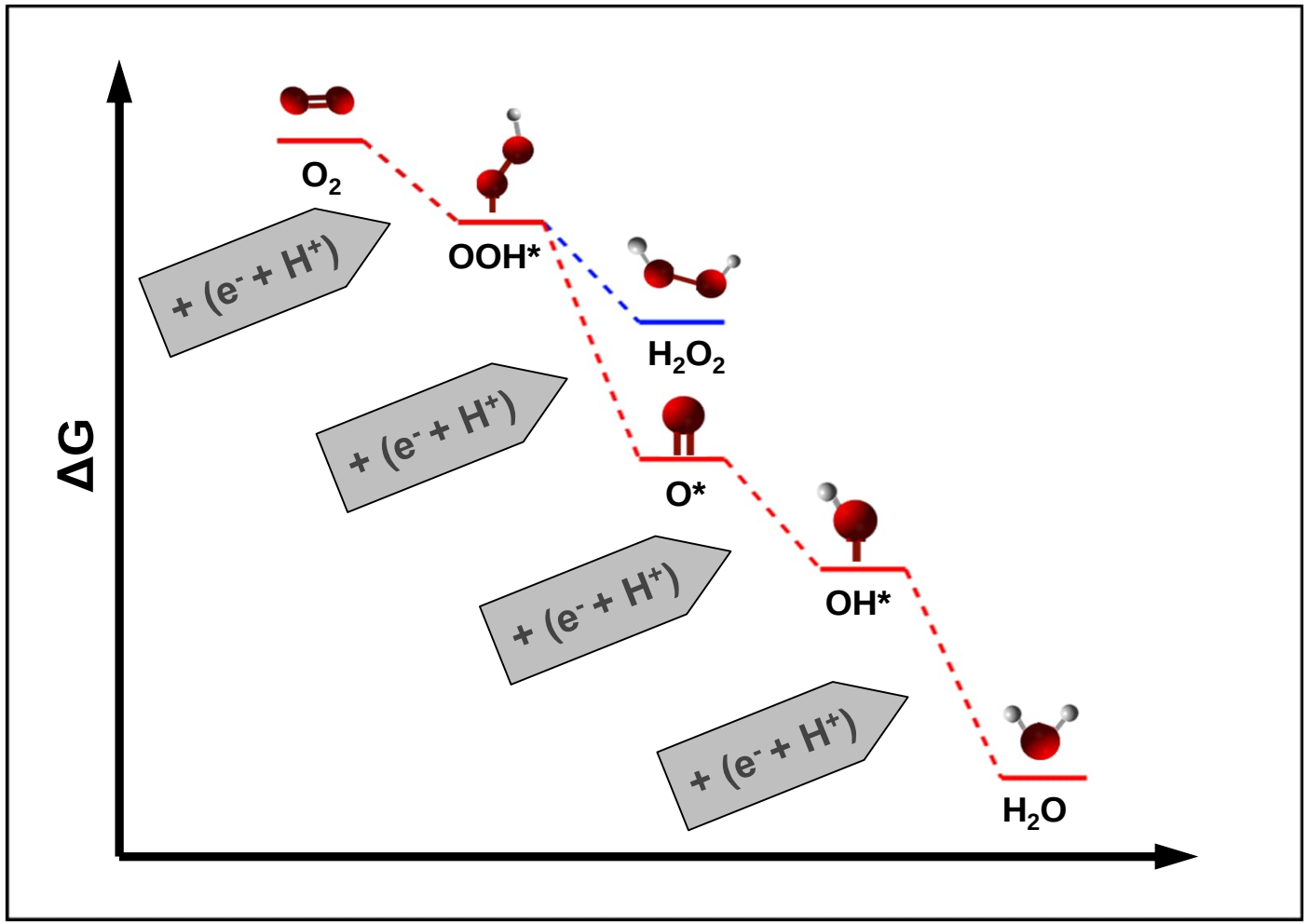
Simeon Beinlich

- Variations neither predictable from molecular dipole moment, nor from mere adsorption site geometry
- Magnitude large enough to critically affect reaction mechanisms



S.D. Beinlich, N.G. Hörmann, and K. Reuter, ACS Catal. 12, 6143 (2022)

Tackling “Chemical Steps”: ORR at Au(111)



A. Kulkarni, S. Siahrostami, A. Patel, and J.K. Nørskov, Chem. Rev. 118, 2302 (2018)

Alexandra Dudzinski

Elias Diesen

- Unclear selectivity:

  $O_2 + 4\,(H^+ + e^-) \rightarrow 2\,H_2O$

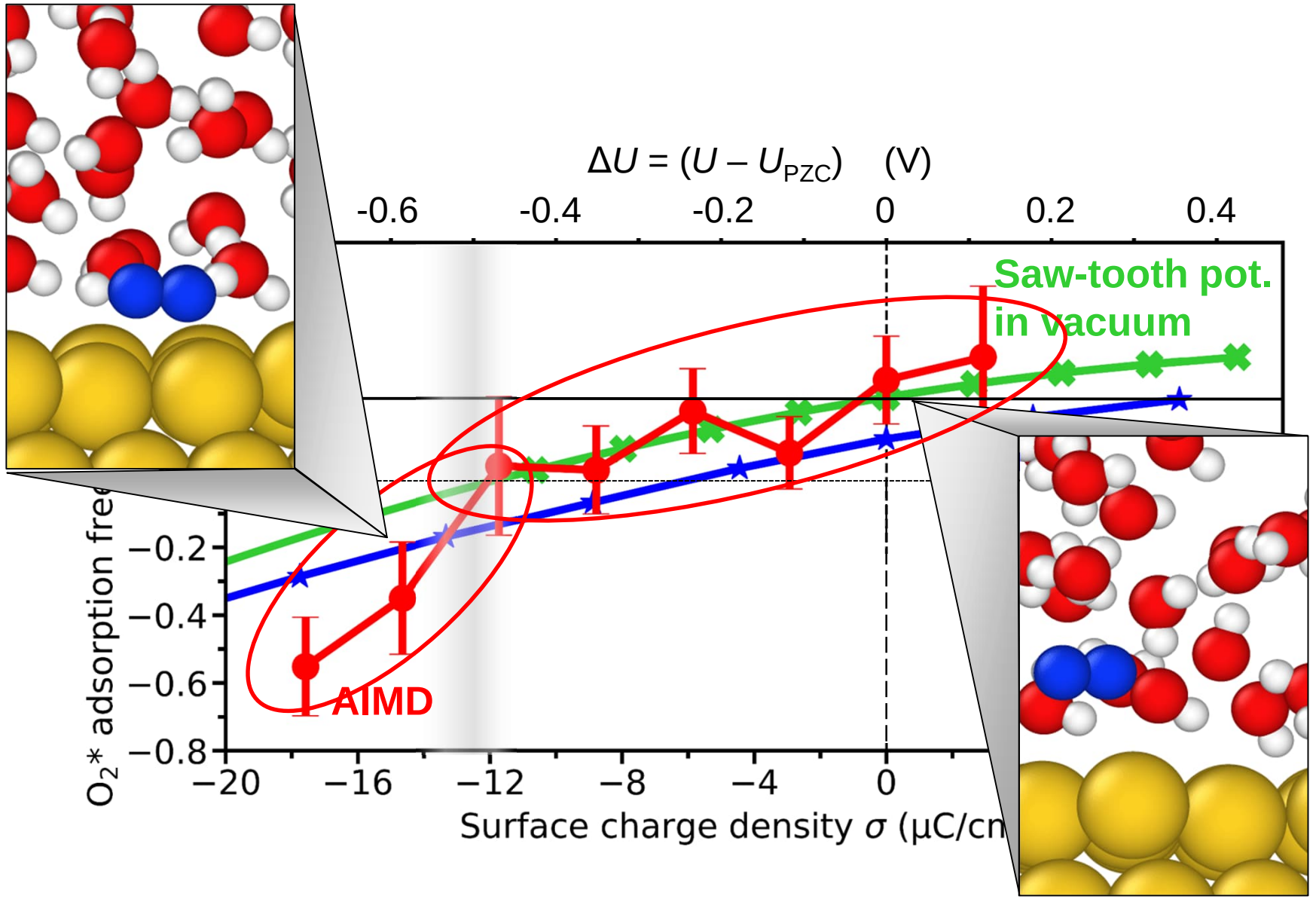
  $O_2 + 2\,(H^+ + e^-) \rightarrow H_2O_2$

- $4e^-$ path for strong binding catalysts, e.g. Pt(111)

- $2e^-$ path for weak binding catalysts, e.g. Au(111)

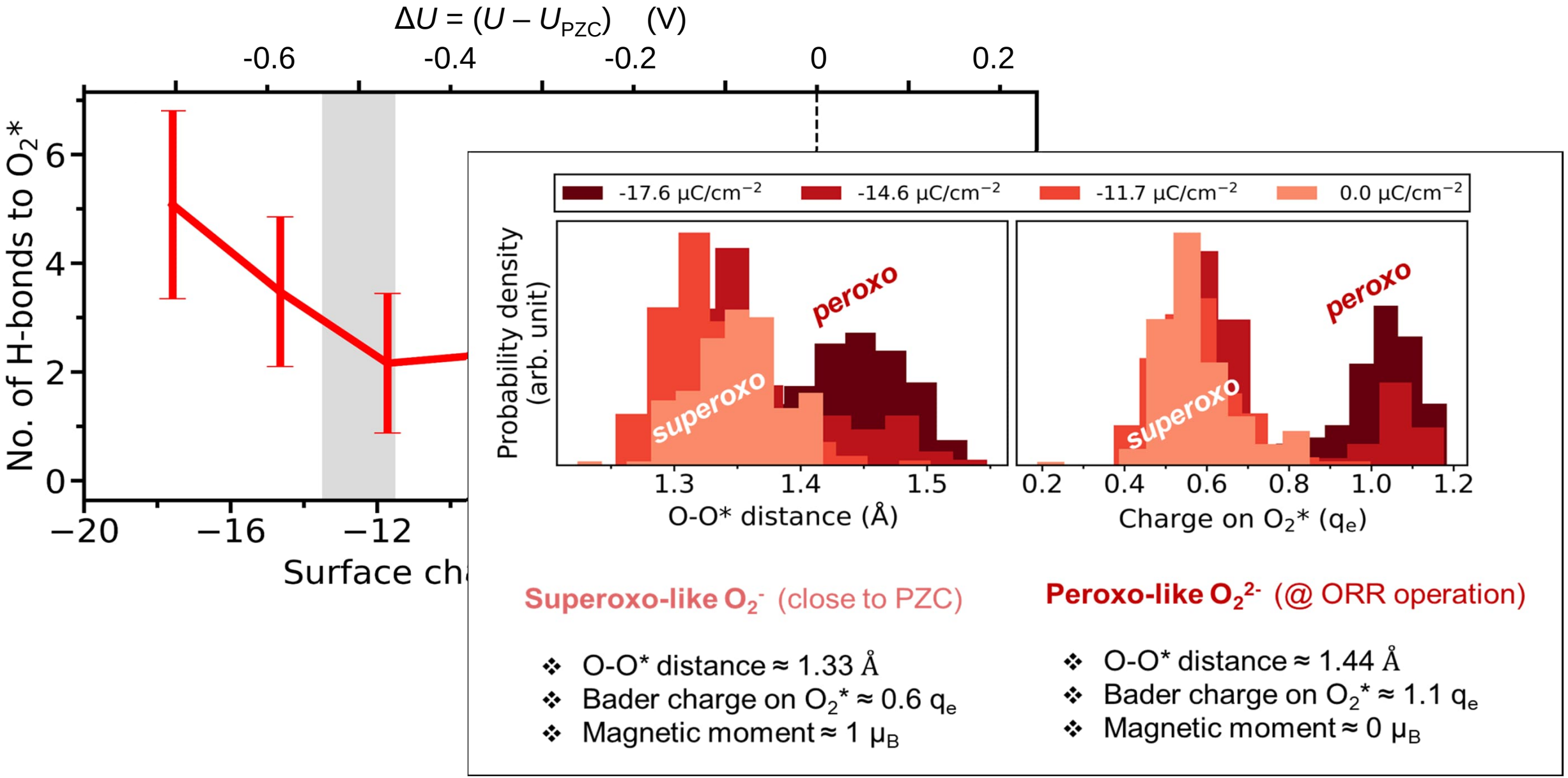
…but how to get the O_2 at the surface in the first place?

Potential-Driven O_2 Adsorption at Au(111)



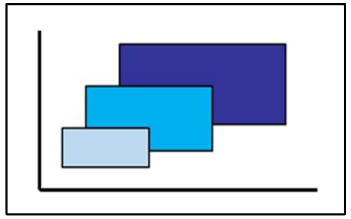
A. Dudzinski, E. Diesen, H.H. Heenen, V.J. Bukas, and K. Reuter, ACS Catal. 13, 12074 (2023)

Role of the H-Bonding Network



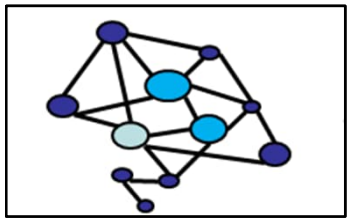
Agenda

i) Implicit Solvation Models as Gateway to Capacitive Charging

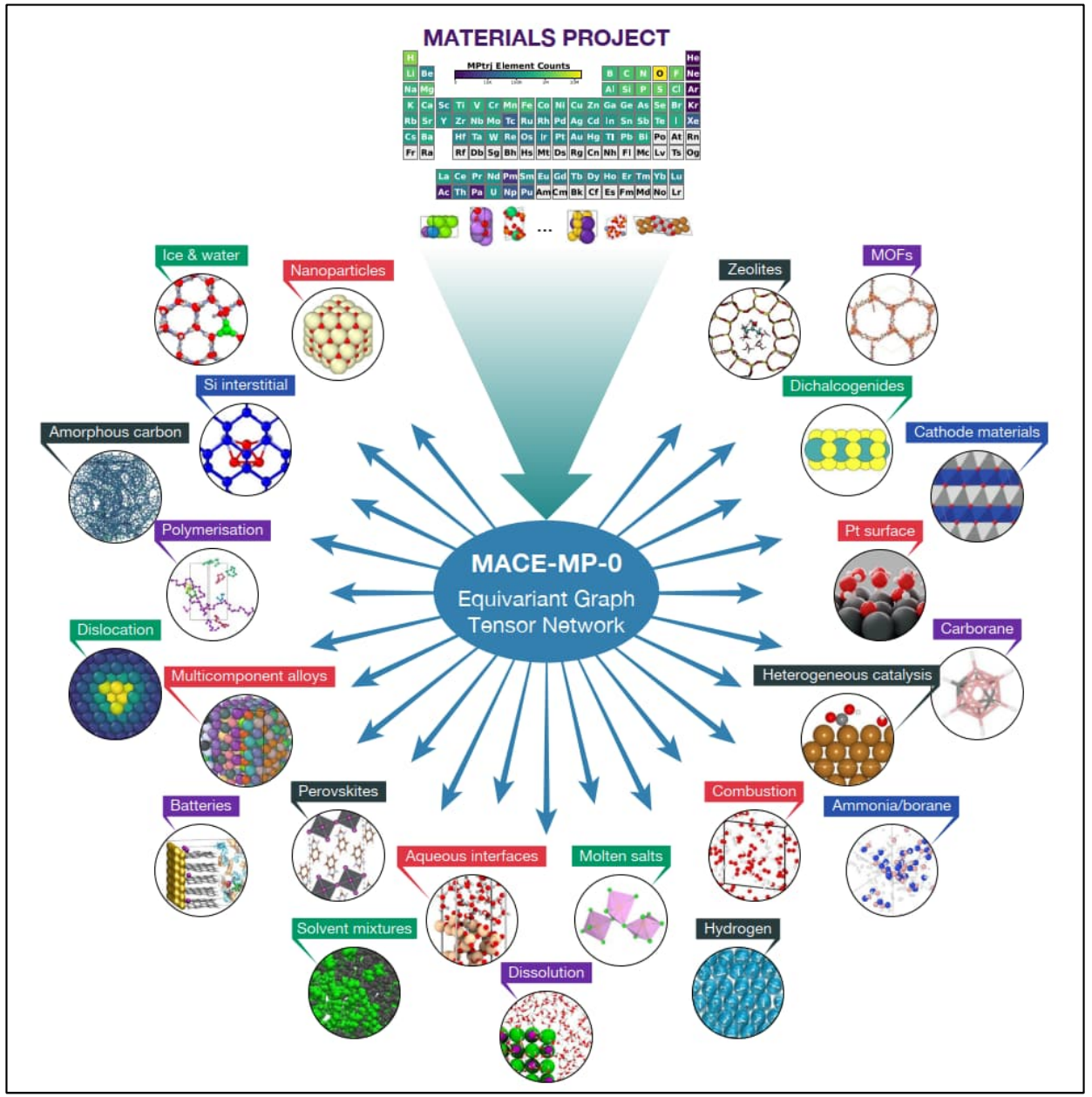


ii) ML Surrogate Models as Gateway to Efficient Explicit Simulations

ii) Coupled Microkinetic-Continuum Models as Gateway to Mesoscale Transport



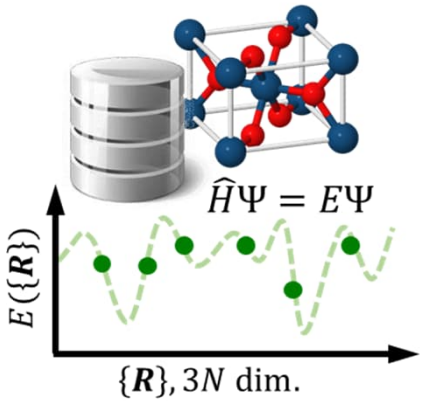
MLIPs Galore…

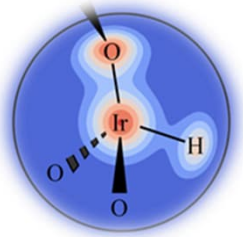


I. Batatia *et al.*,
J. Chem. Phys. (submitted)

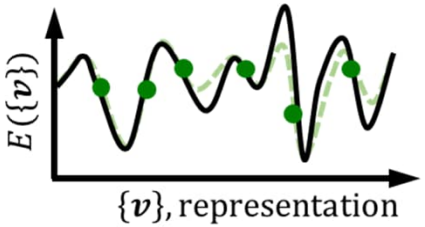
Machine-Learning Interatomic Potentials (MLIPs)

Reference database

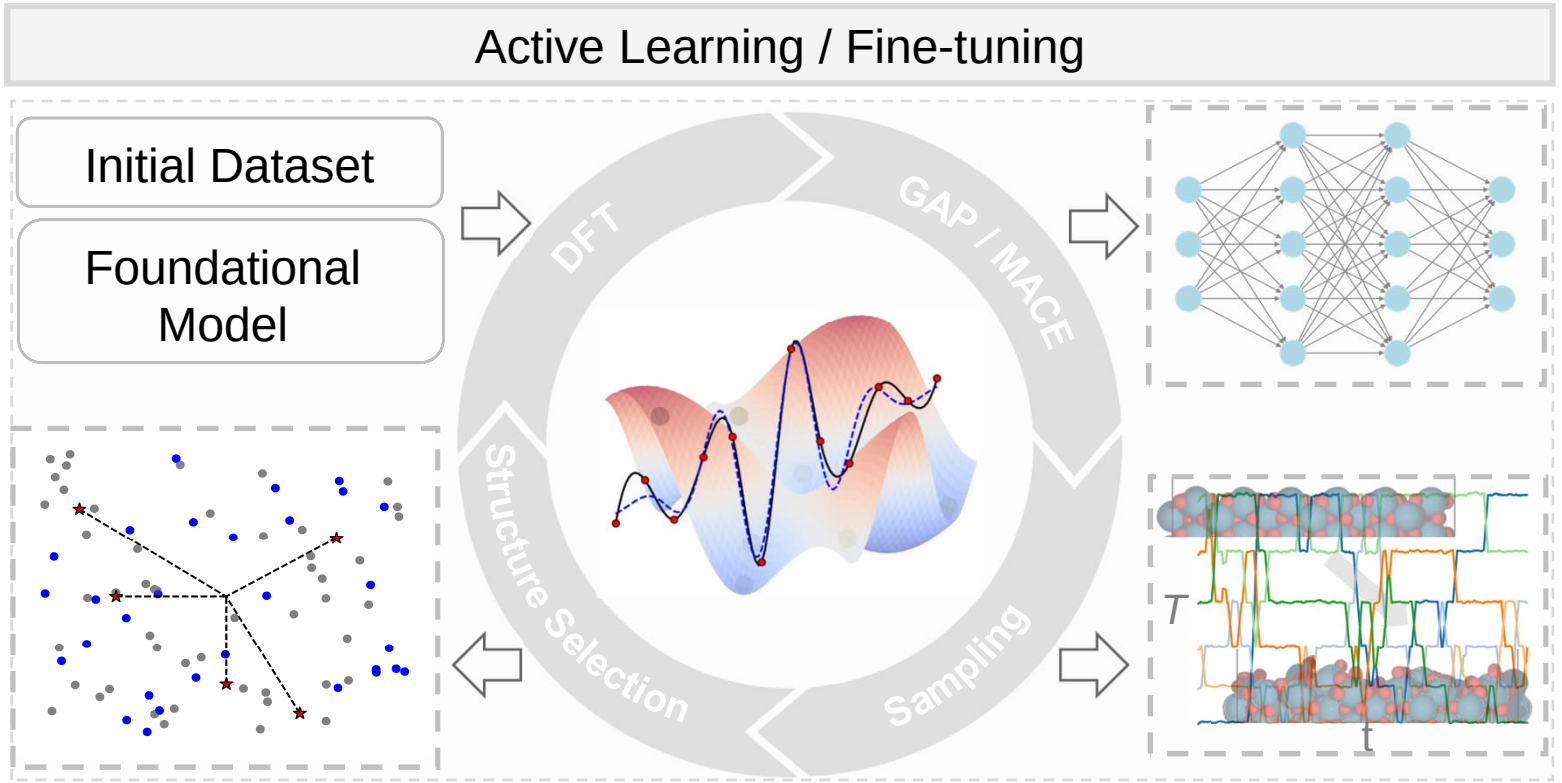




Representation of atomic environments

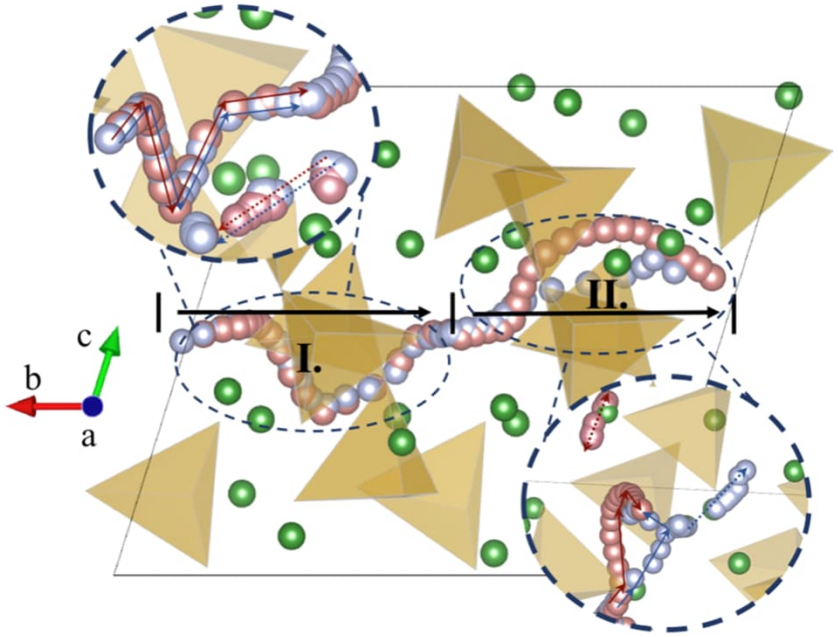


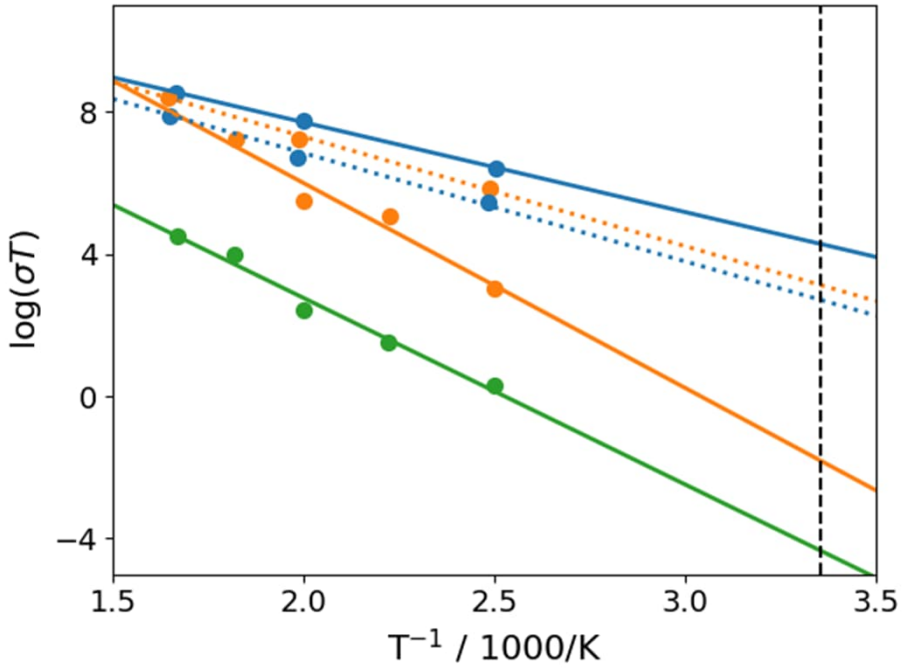
PES learning



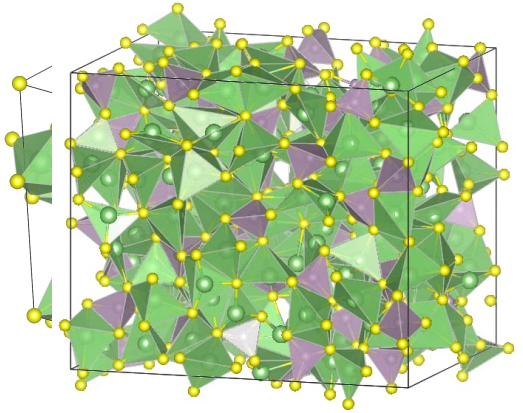
V.L. Deringer, M.A. Caro, and G. Csanyi,
Adv. Mater. 31, 1902765 (2019)
J. Timmermann *et al.*,
J. Chem. Phys. 155, 244107 (2021)

Case in Point: Ion Mobilities in LPS Solid-State Electrolytes

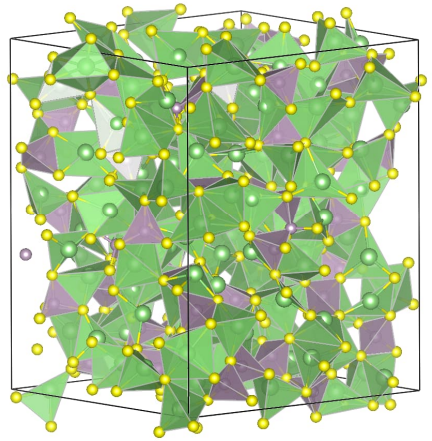




Li_3PS_4 glass



$Li_7P_3S_{11}$ glass

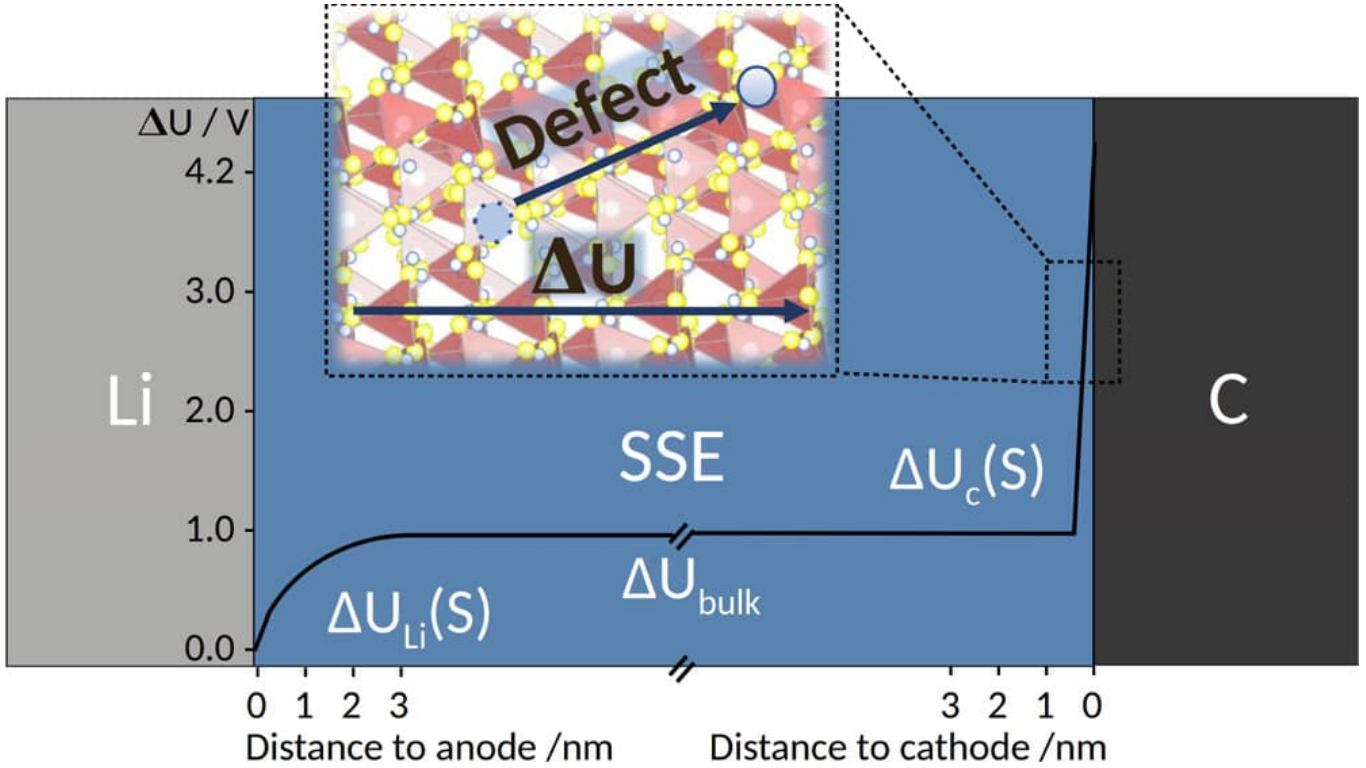


Carsten Staacke

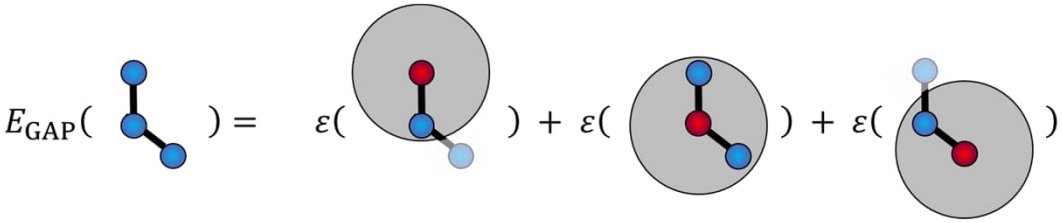
Iteratively trained ML potential
accurately predicts Li mobilities
in crystalline and amorphous Li-thiophosphate phases

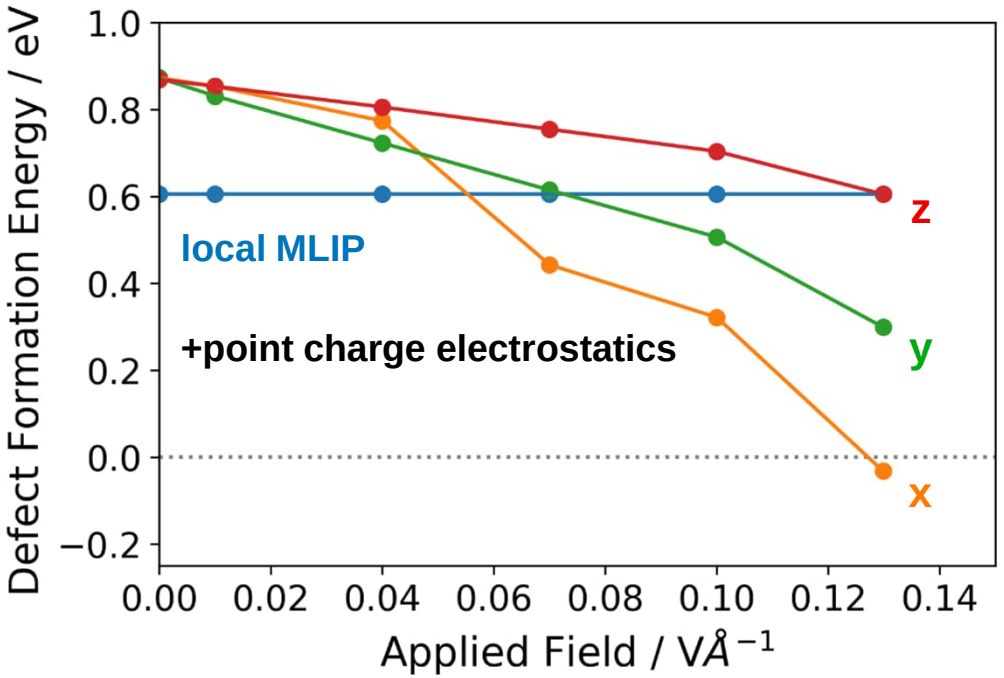
C.G. Staacke *et al.*, Nanomaterials 12, 2950 (2022)

Field-Dependence of $Li_7P_3S_{11}$ Defect Formation Energies



Local ML potentials cannot capture field dependencies





A.C. Luntz, J. Voss, and K. Reuter, J. Phys. Chem. Lett. 6, 4599 (2015)

C.G. Staacke *et al.*, ACS Appl. Energy Mater. 4, 12562 (2021)

Fourth-Generation MLIPs: Coupling to Charge Equilibration (QEq)

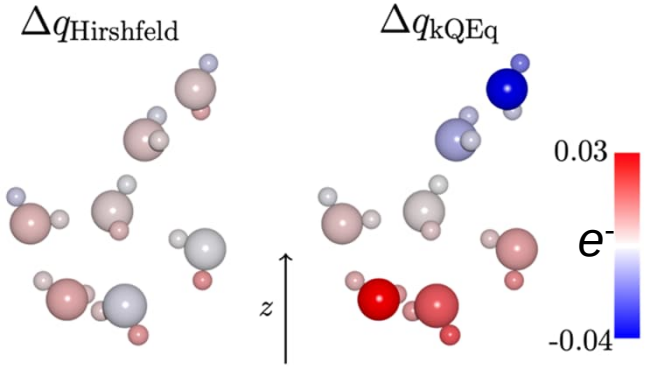
$$E(q) = E_{\mathrm{MLIP}} + E_{\mathrm{QEq}} = E_{\mathrm{MLIP}} + \sum_{i=1}^{N_{\mathrm{atom}}} \left(\chi_i q_i + \tfrac{1}{2} J_i q_i^2 \right) + \sum_{i,j}^{N_{\mathrm{atom}}} \frac{q_i q_j}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

$$\frac{\partial E_{\mathrm{QEq}}}{\partial q_i} = 0 \quad ; \quad \sum_{i}^{N_{\mathrm{atom}}} q_i = q$$

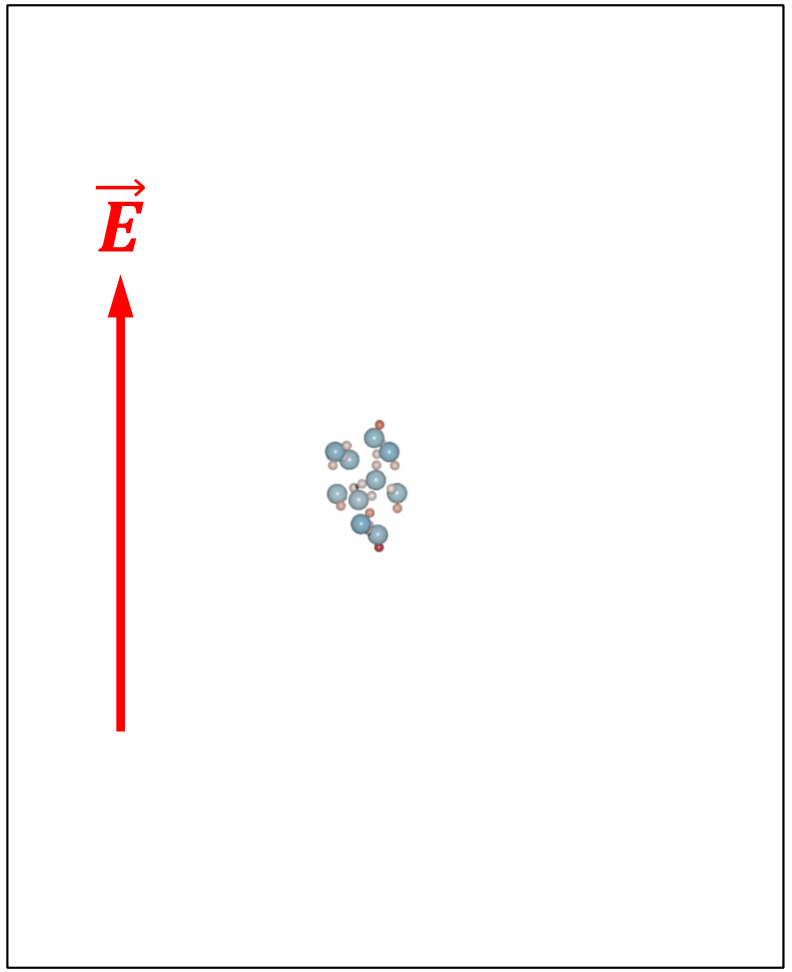
χ_i Electronegativity
J_i Atomic Hardness

A.K. Rappe and W.A. Goddard, J. Phys. Chem. 95, 3358 (1991)
T.W. Ko, J.A. Finkler, S. Goedecker, and J. Behler, Acc. Chem. Res. 54, 808 (2021)

Martin Vondrák



Short-range MLIP + QEq fundamentally inadequate
to capture polarization and charge transfer
in non-metallic systems under external fields



M. Vondrak, K. Reuter, and J.T. Margraf,
npj Comp. Mater 11, 288 (2025)

Machine-Learning Electrified Solid-Liquid Interfaces: RAZOR

$$E(q) = E_0 + \left.\frac{\partial E}{\partial q}\right|_0 q + \frac{1}{2}\left.\frac{\partial^2 E}{\partial q^2}\right|_0 q^2 + \ldots = E_0 + \phi_0\, q + \frac{1}{2}\frac{1}{C_{\mathrm{el},0}} q^2 + \ldots$$

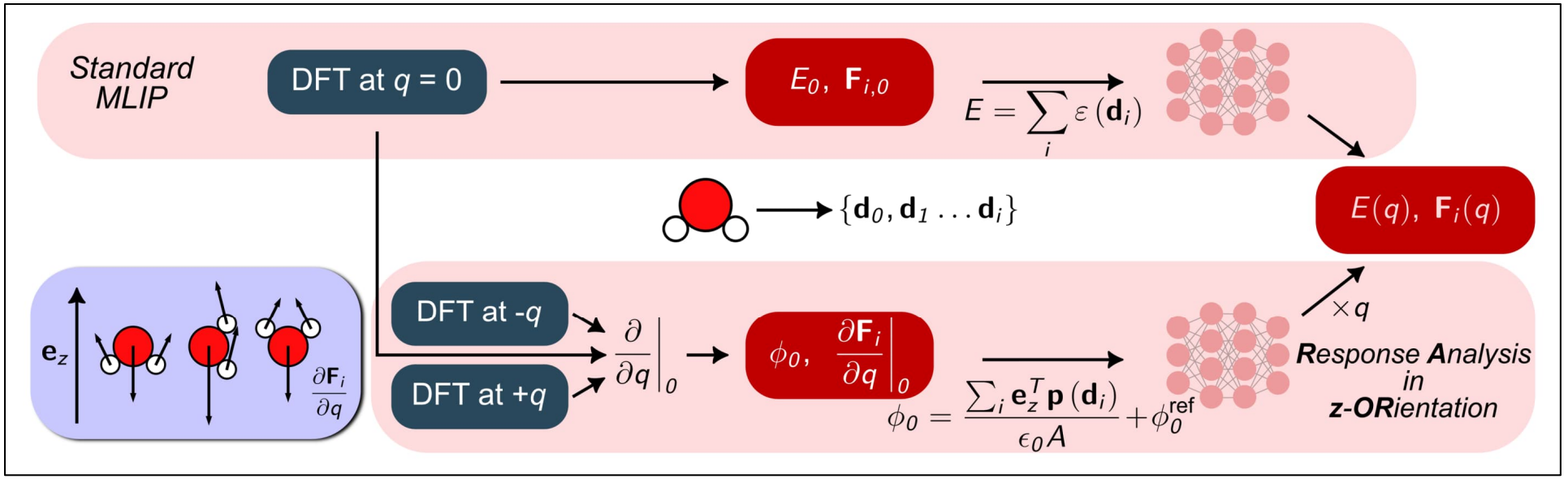
$$E_0 = \sum_{i=1}^{N_{\mathrm{atom}}} \varepsilon_0(d_i)$$

$$\Delta\phi_0 = \frac{1}{\epsilon_0 A} P_z = \frac{1}{\epsilon_0 A} \sum_{i=1}^{N_{\mathrm{atom}}} p_z(d_i)$$

≈ configuration-independent, (implicit solvent model)

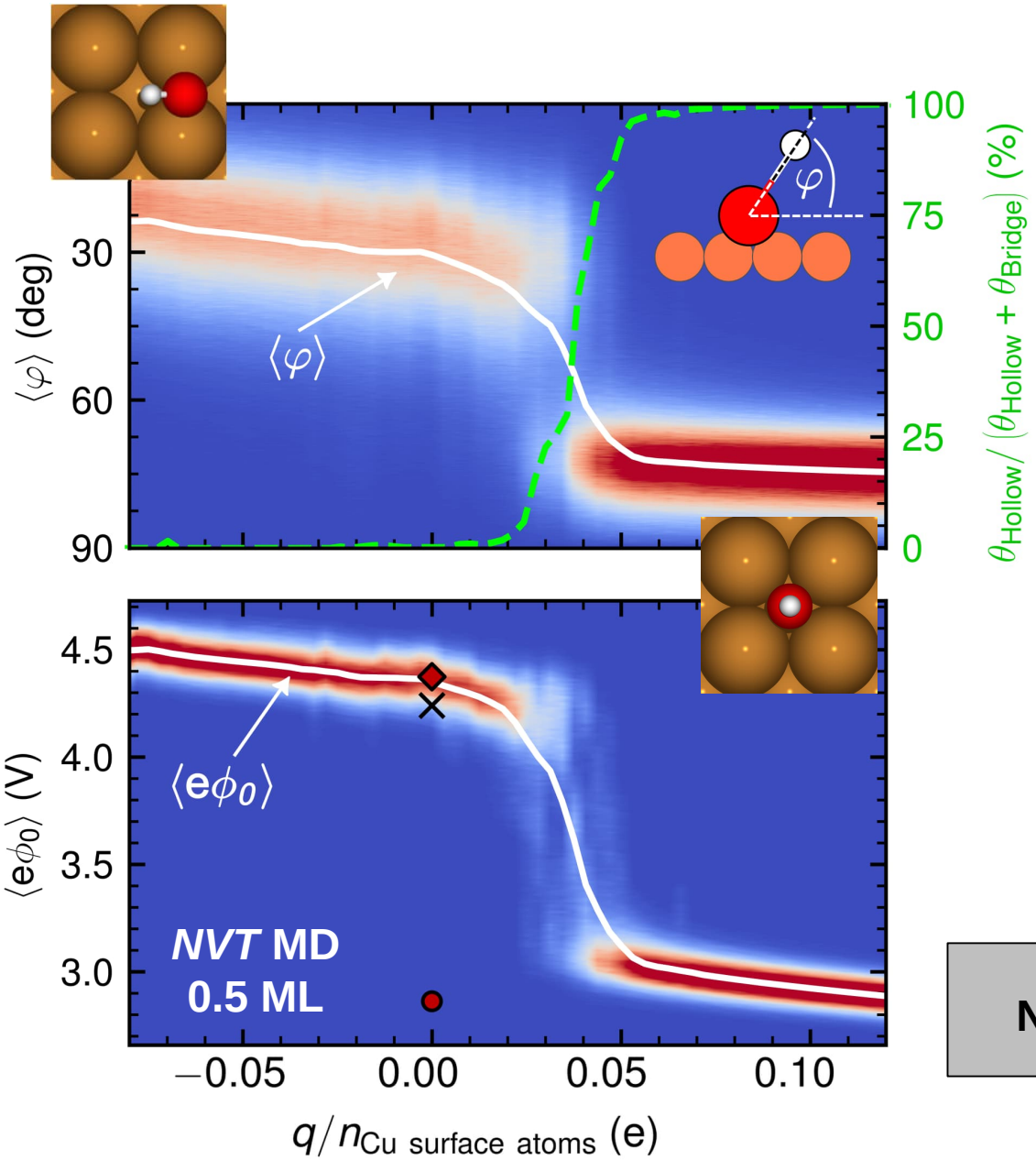
$$\boldsymbol{F}_{0,i} = -\frac{\partial E_0}{\partial \boldsymbol{r}_i}$$

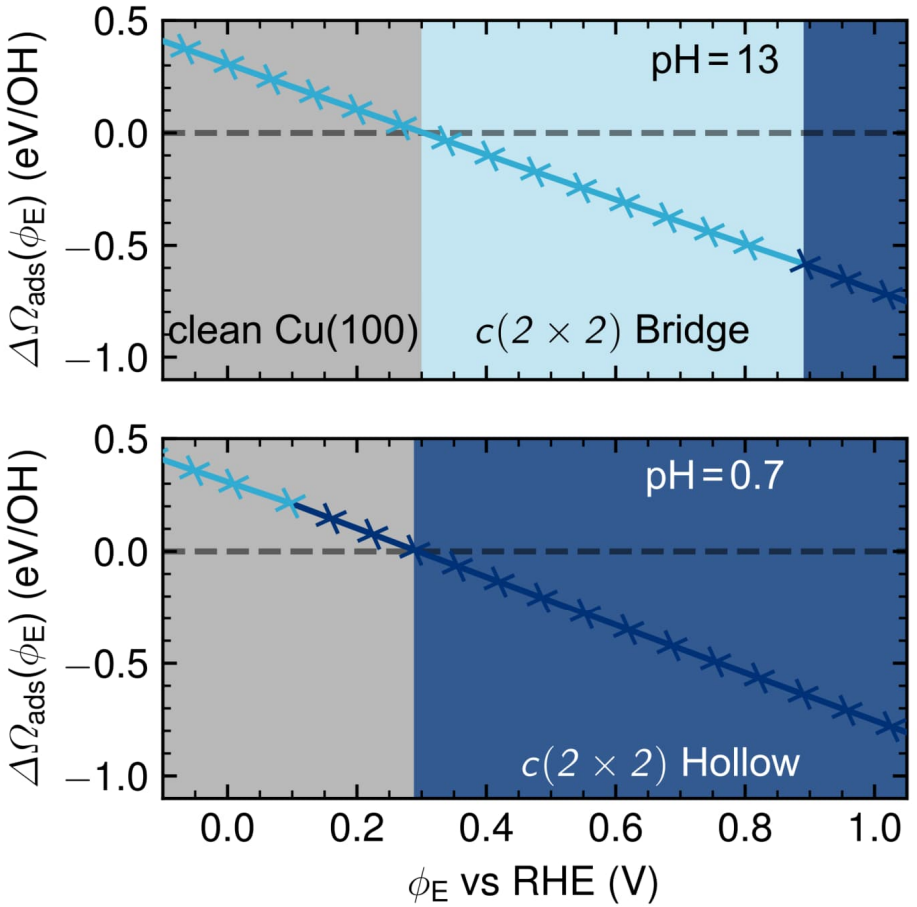
$$\boldsymbol{Z}_i^* = -\epsilon_0 A \frac{\partial \phi_0}{\partial \boldsymbol{r}_i} = \epsilon_0\, A \frac{\partial \boldsymbol{F}_{0,i}}{\partial q}$$



N. Bergmann *et al.*, Phys. Rev. Lett. 135, 146201 (2025)

Charge-Dependent Adsorption Site Switch: OH @ Cu(100)





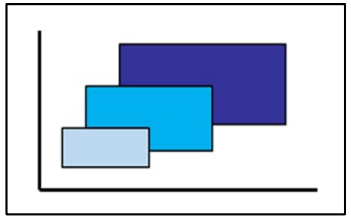
Nicolas Bergmann

Non-Nernstian pH-dependence of on-set adsorption site

N. Bergmann *et al.*, Phys. Rev. Lett. 135, 146201 (2025)

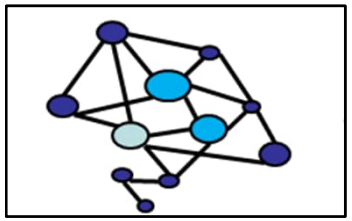
Agenda

i) Implicit Solvation Models as Gateway to Capacitive Charging

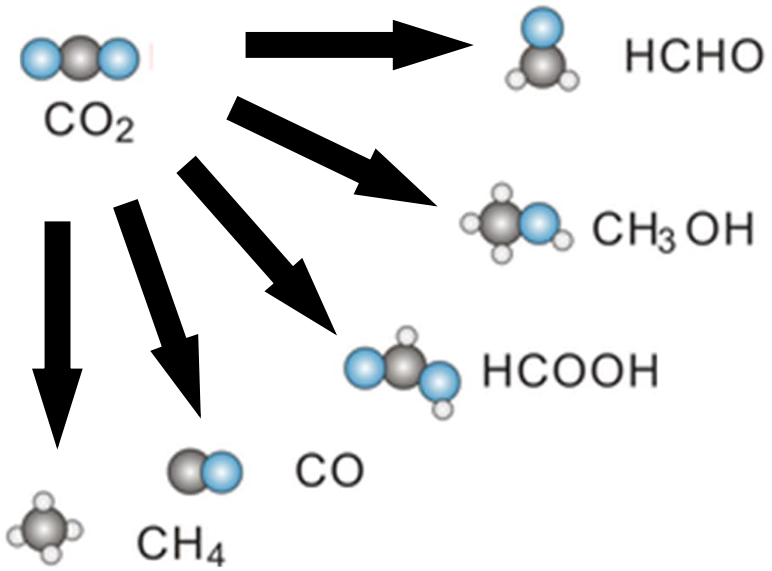


ii) ML Surrogate Models as Gateway to Efficient Explicit Simulations

ii) Coupled Microkinetic-Continuum Models as Gateway to Mesoscale Transport



Product Selectivity in Electrocatalysis



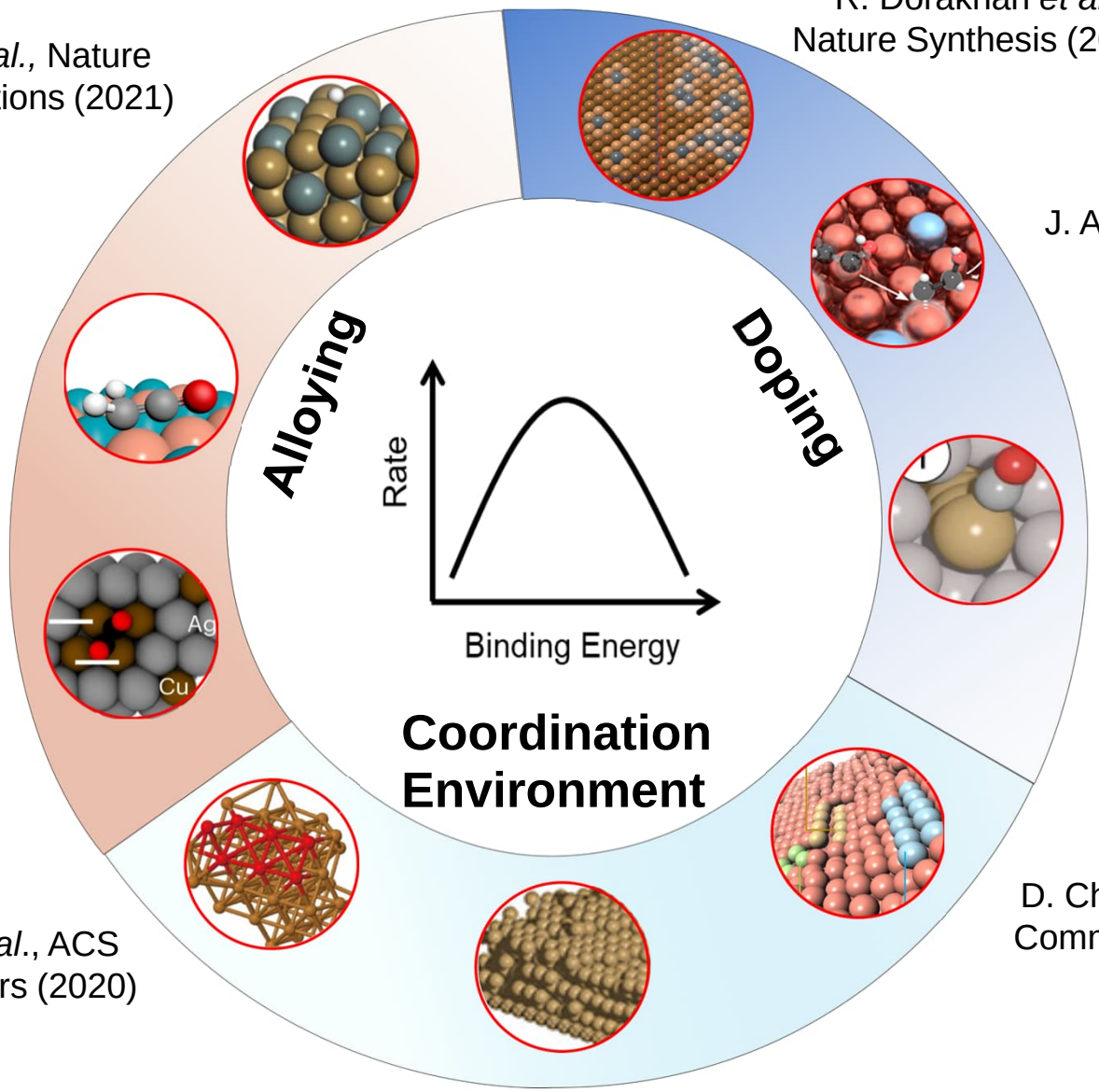
Nanostructured Electrocatalysts

Nanoparticles
- Size, shape
- Interparticle distance, loading
- Support effects
- …

3D interconnected electrodes
- Oxidation/reduction
- Sputter deposition
- Dealloying
- …

Nanostructuring is one key approach to tune selectivity in CO2RR, ORR, NRR, MeOH-OR, EtOH-OR, …

CO2RR @ Cu: Novel Active Sites Galore…



W. Ren *et al.,* Nature Communications (2021)

R. Dorakhan *et al.*, Nature Synthesis (2023)

Y.C. Li *et al.*, J. Am. Chem. Soc. (2019)

Y. Ji *et al.,* Nature Catalysis (2022)

M. Zhong *et al.*, Nature (2020)

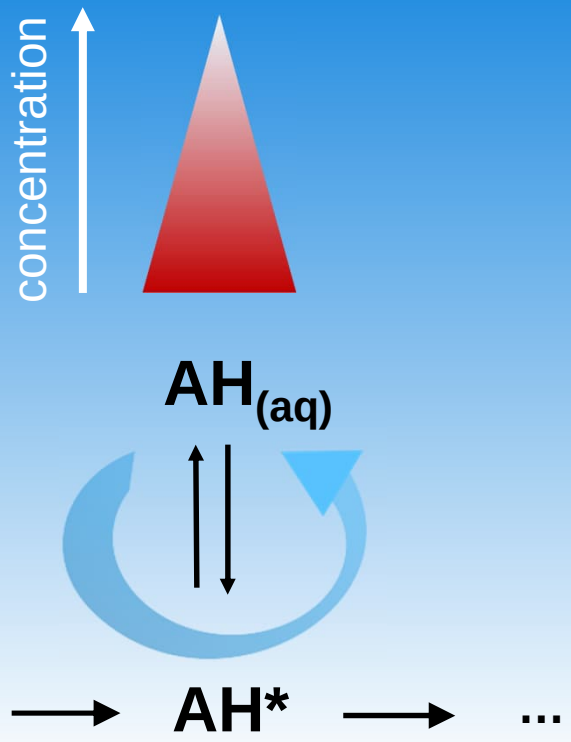
J.-Y. Kim *et al.,* Nature Synthesis (2023)

D. Cheng *et al.*, Nature Communications (2021)

K. Jiang *et al.*, ACS Energy Letters (2020)

J. Gauthier *et al.*, ACS Energy Letters (2021)

Mesoscopic Mass Transport of Intermediates



Diffusion

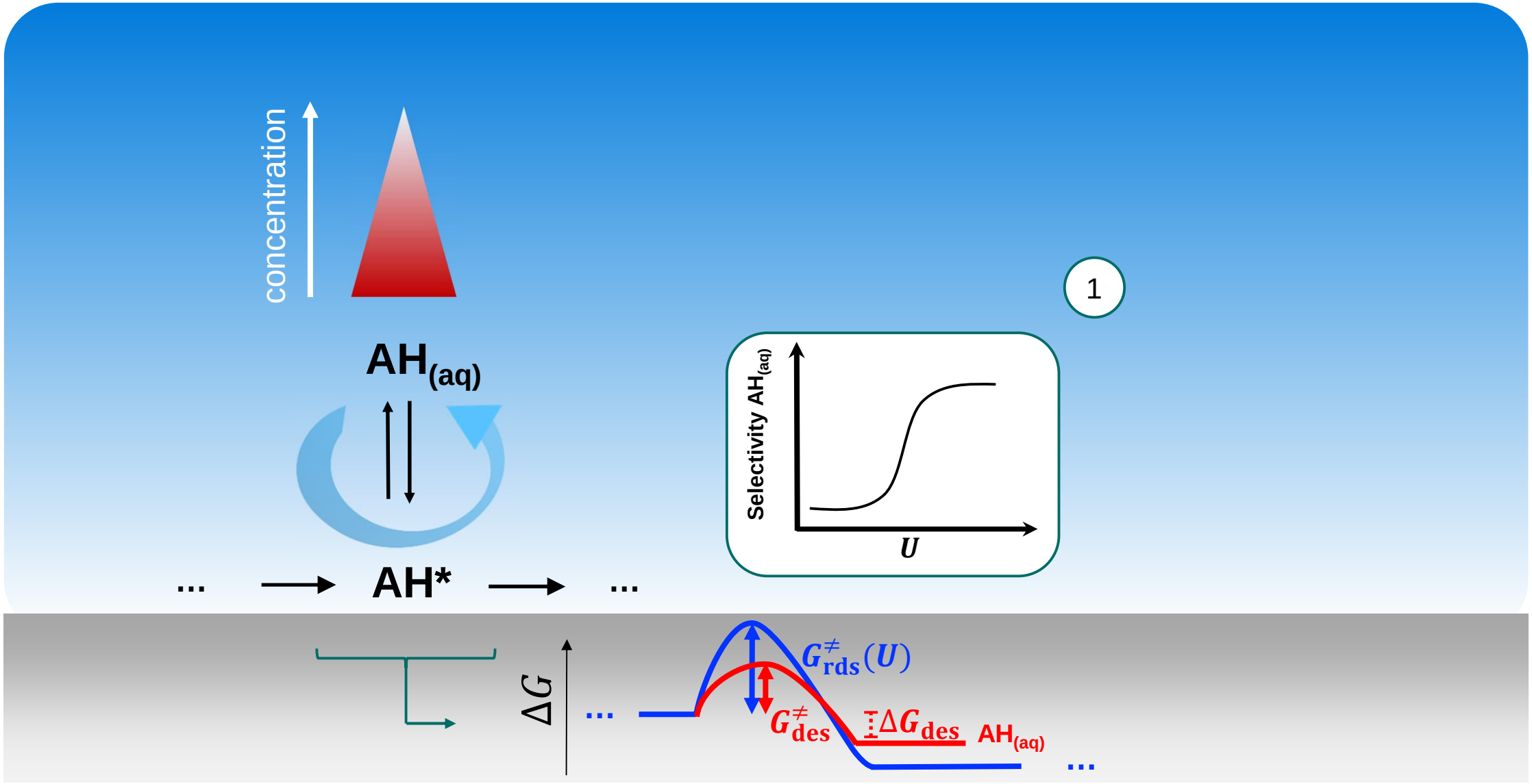
vs.

Surface Chemistry

”Desorption – Diffusion – Re-adsorption”

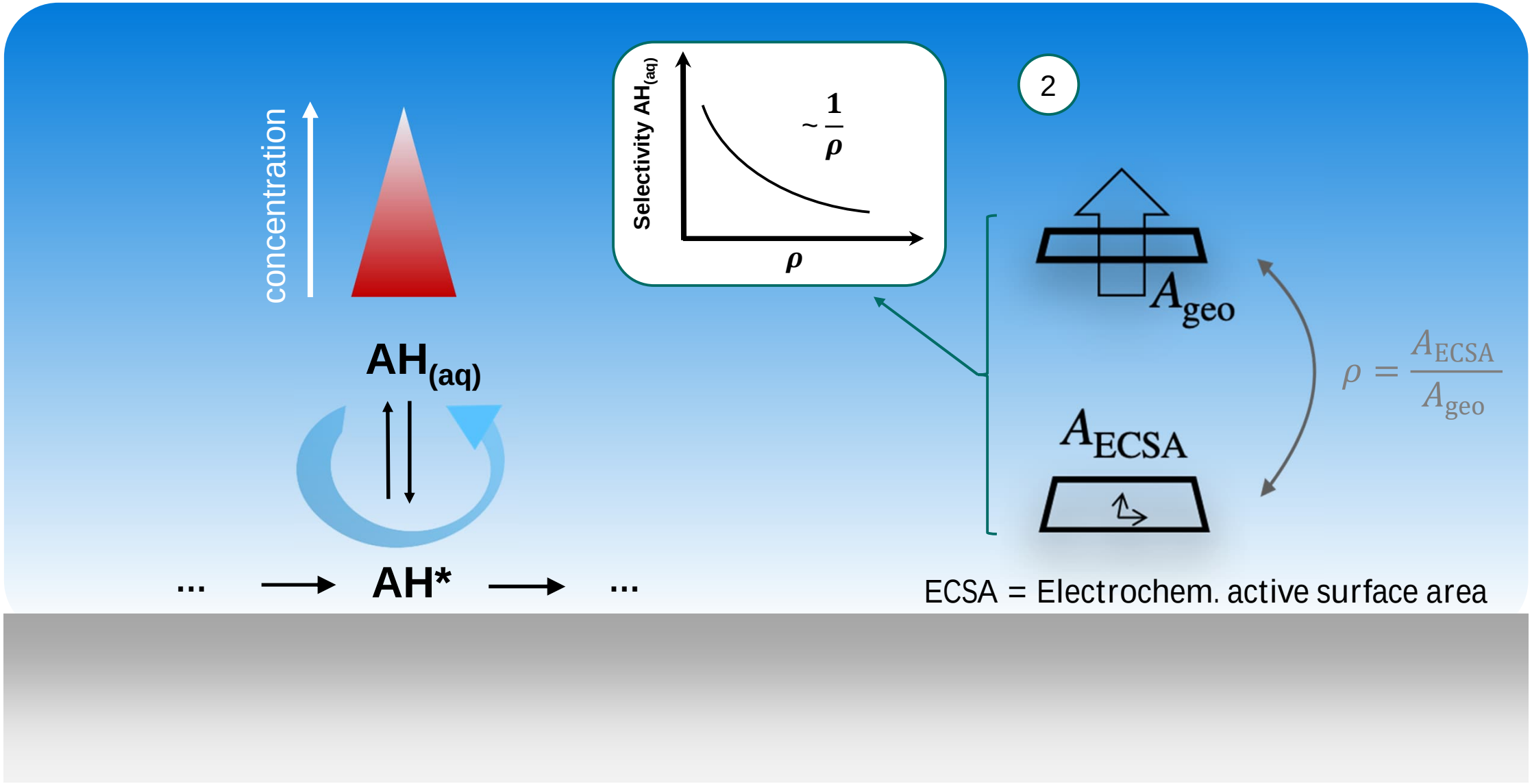
Y. Seidel, R.J. Behm *et al.,* Faraday Discuss. 140, 1676 (2009)

Characteristic Selectivity Trends

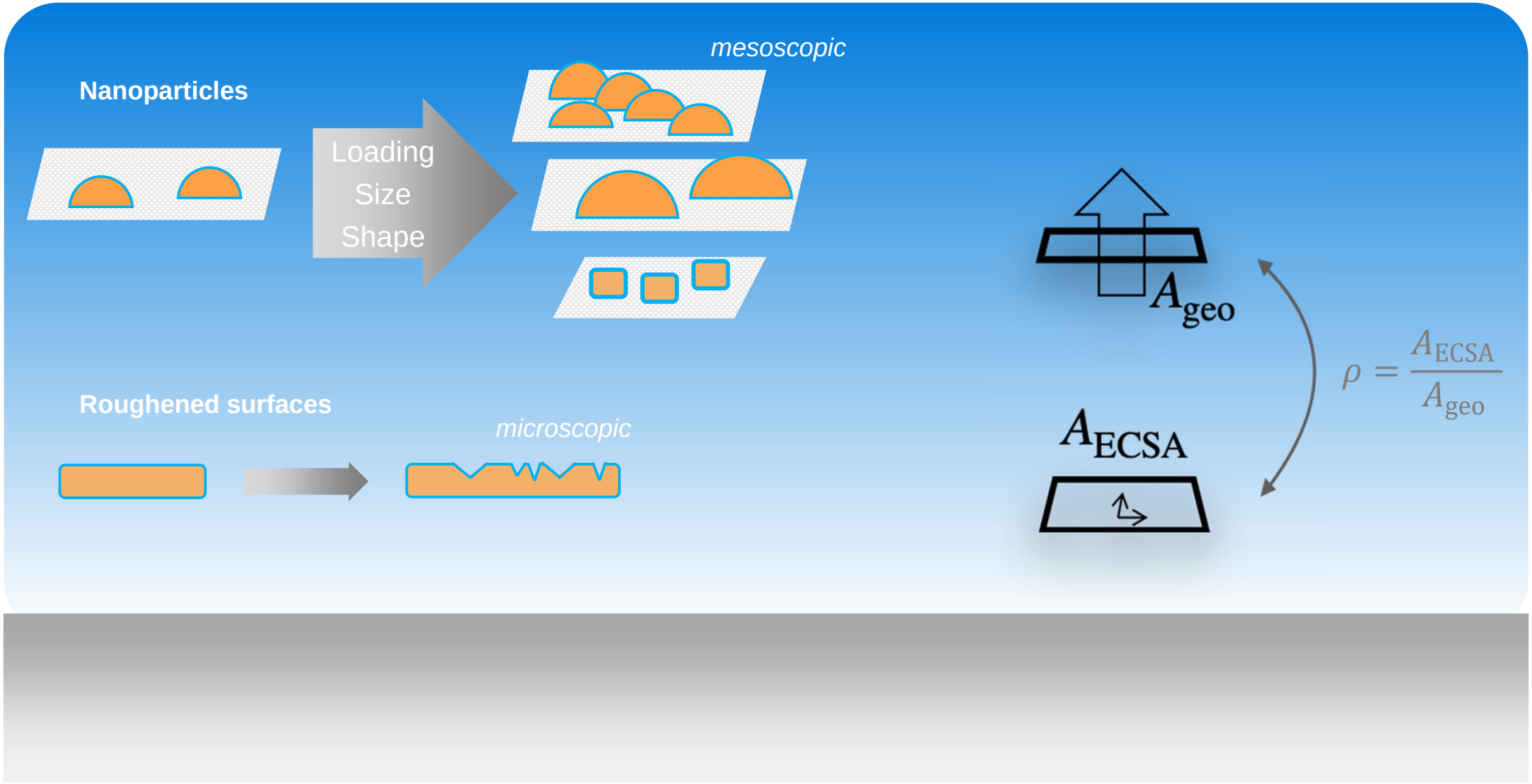


N. Govindarajan, H.H. Heenen, K. Chan *et al.,* Chem. Sci. 13, 14 (2022)

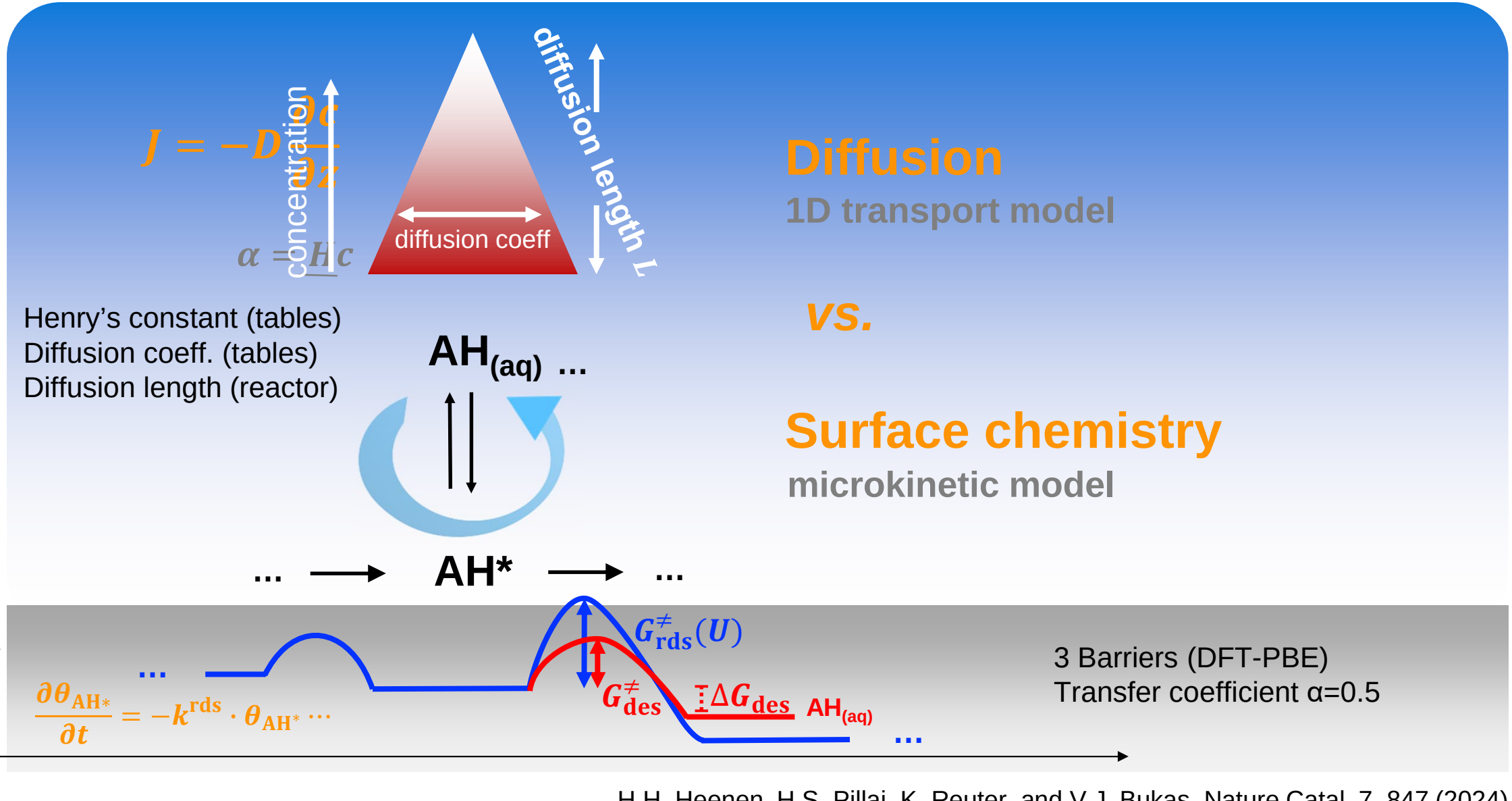
Characteristic Selectivity Trends



Influence of Catalyst Morphology



A Simple Kinetic Model

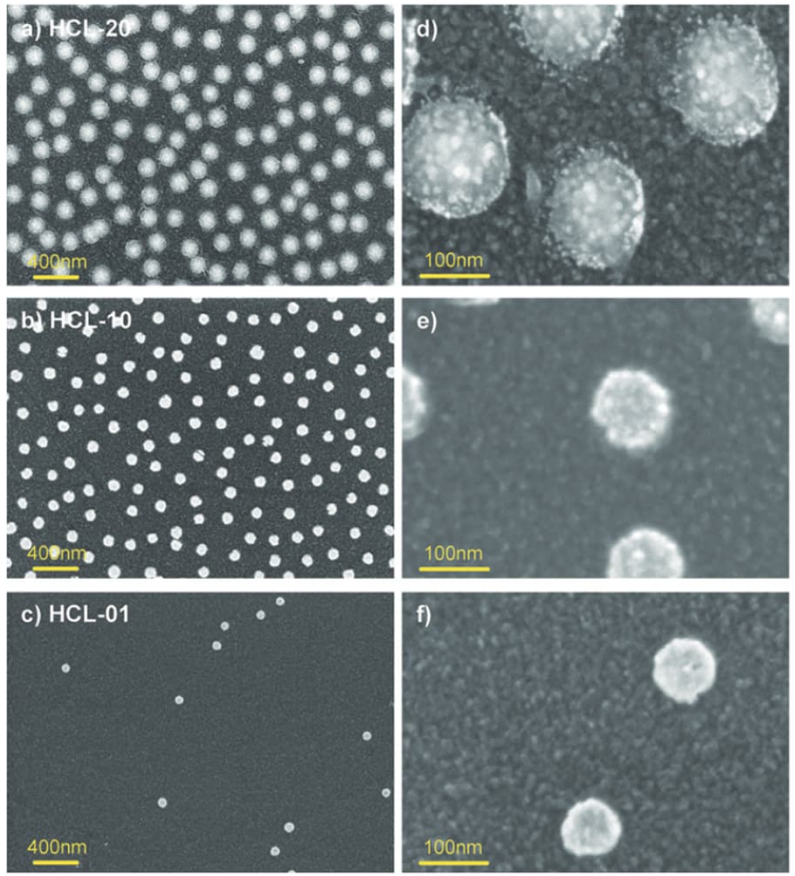


H.H. Heenen, H.S. Pillai, K. Reuter, and V.J. Bukas, Nature Catal. 7, 847 (2024)

Seminal Experiments: ORR on Pt Model Electrodes

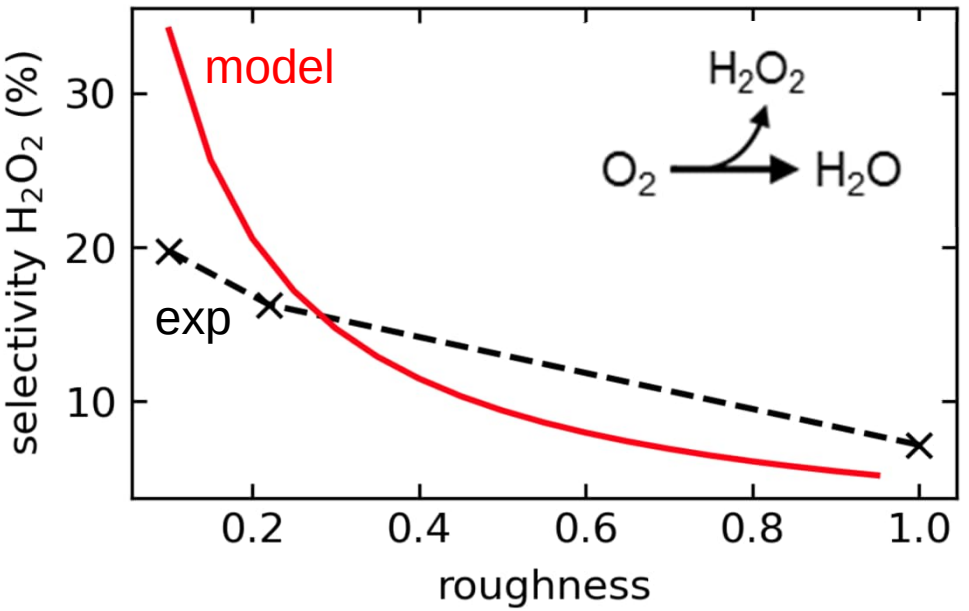
Hole-mask colloidal lithography employed to yield structurally well-defined arrays of Pt nanodiscs (~100 nm) of varying loading (= roughness)

higher roughness



Y.E. Seidel, A. Schneider, Z. Jusys, B. Wickman, B. Kasemo, and R.J. Behm, Faraday Discuss. 140, 167 (2009)

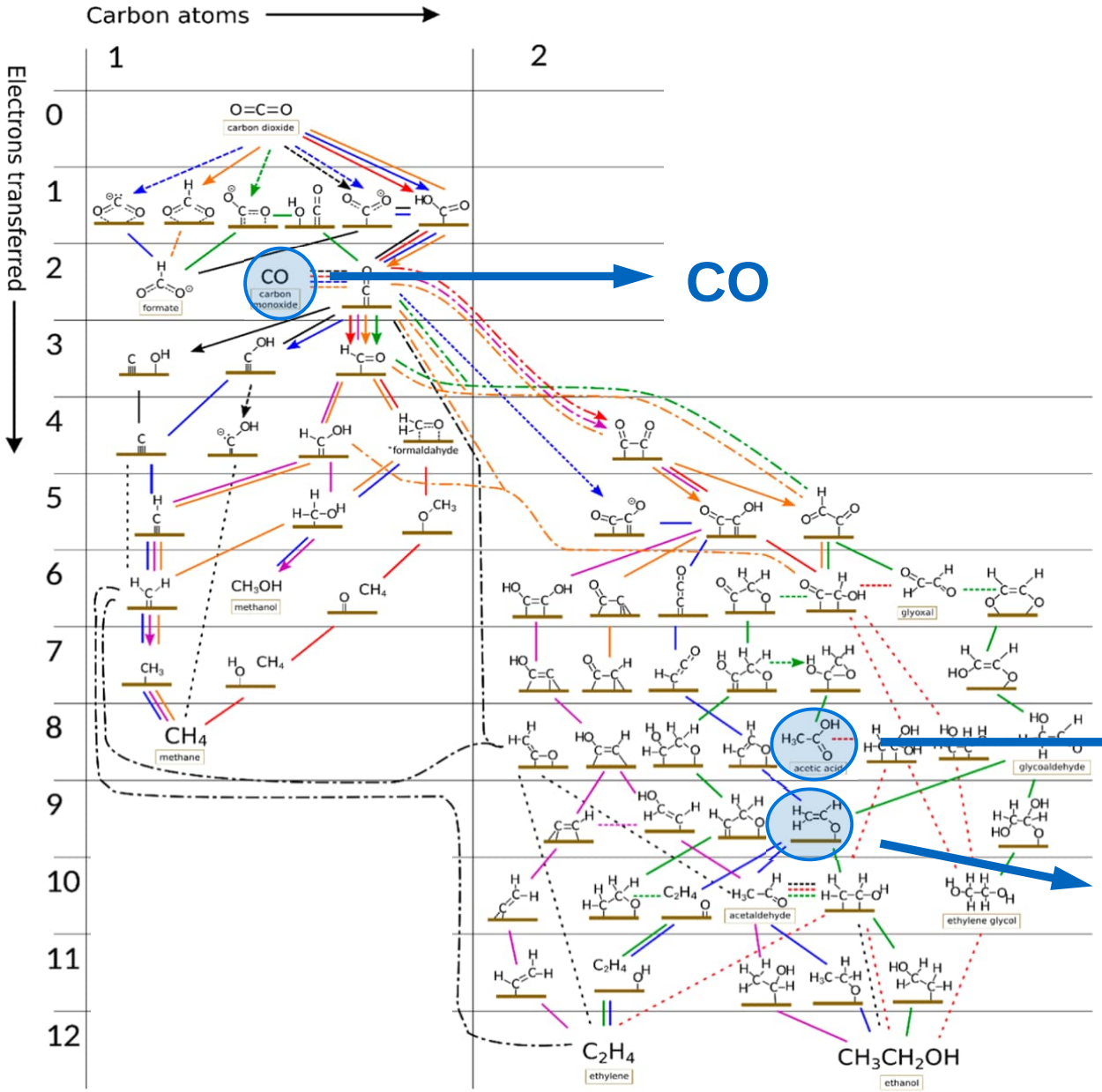
more re-adsorption



- **Model fits like a charm, but…**
  ultra-low loadings, model reactor, proof-of-concept.

- **Does it also work more generally?**

Mesoscopic Mass Transport in CO2RR @ Cu



CO

Acetate (Ac)

Acetaldehyde (MeCHO)

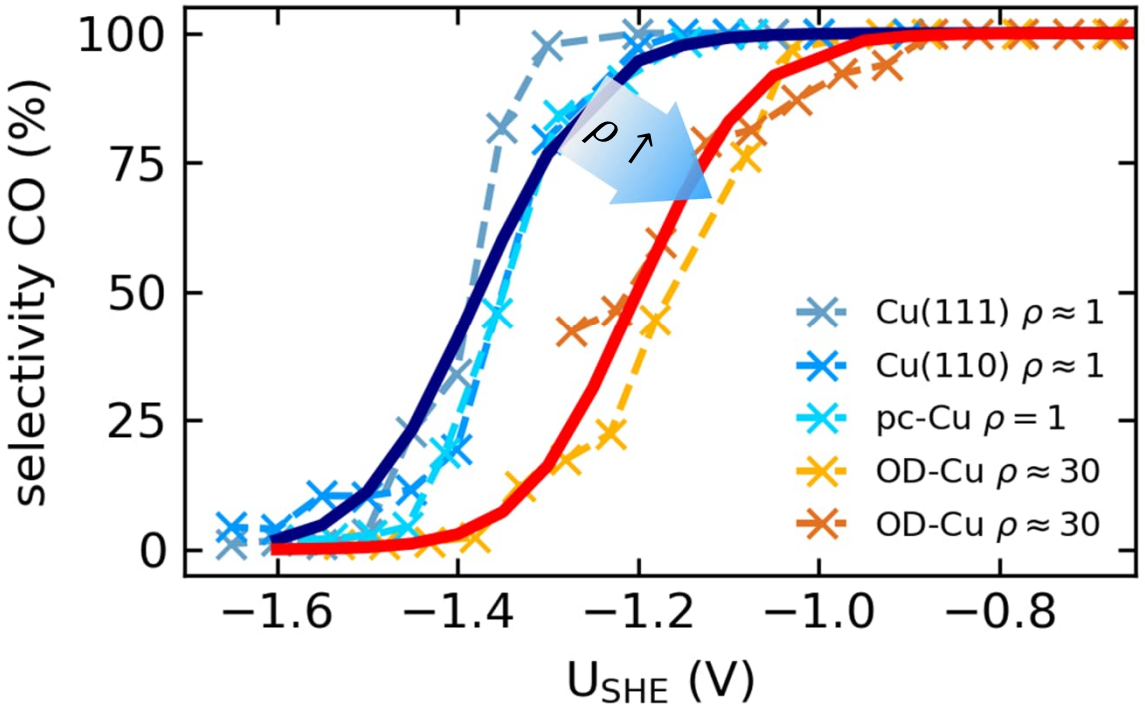
- ***vs. potential (U)?***
- ***vs. roughness (ρ)?***

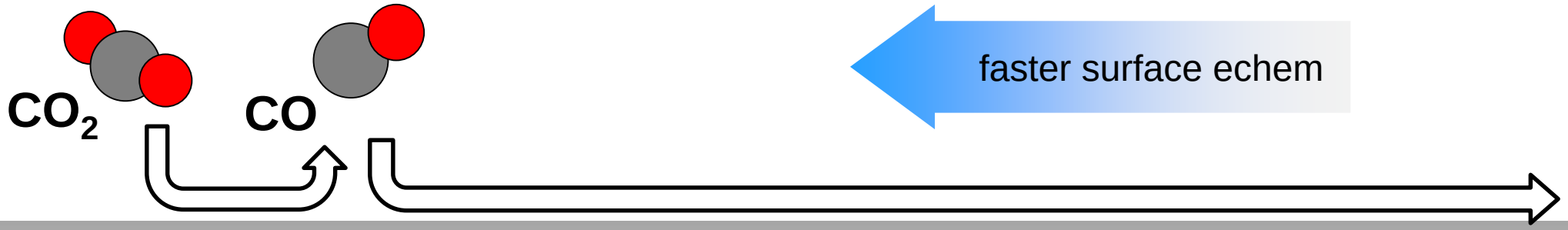
S. Nitopi, I. Chorkendorff *et al.,* Chem. Rev. 119, 7610 (2019)

Mesoscopic Mass Transport in CO2RR @ Cu

Lower selectivity to ‘early’ product:

- More reducing potentials (faster surface echem)
- Higher roughness (more re-adsorption)



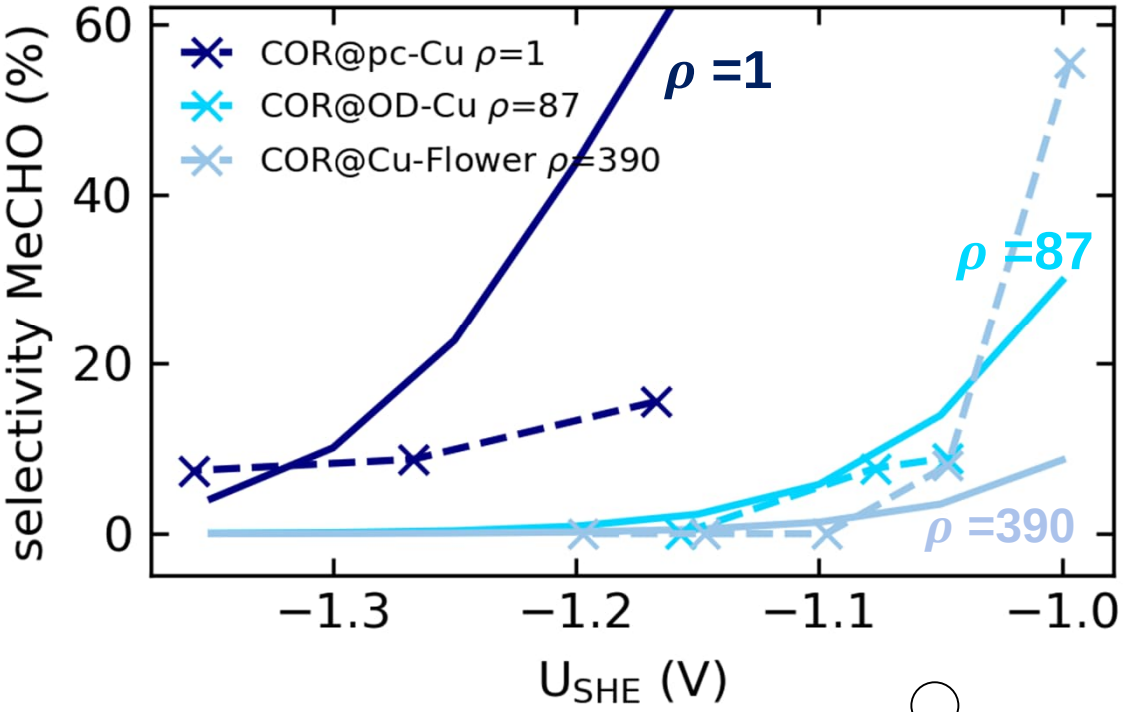


faster surface echem

K.P. Kuhl, T.F. Jaramillo *et al.*, Energy Environ. Sci. 5, 7050 (2012)
Y. Huang, B.S. Yeo *et al.*, ACS Catal. 7, 1749 (2017)
C.W. Li, M.W. Kanan, J. Am. Chem Soc. 134, 7231 (2012)

Mesoscopic Mass Transport in CO2RR @ Cu

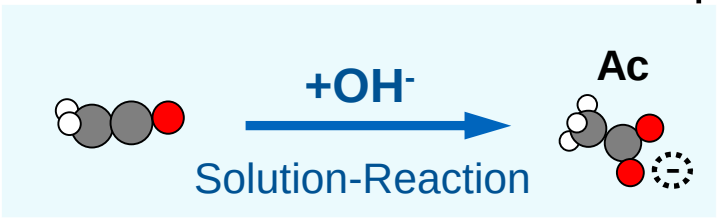
Same same for acetaldehyde…



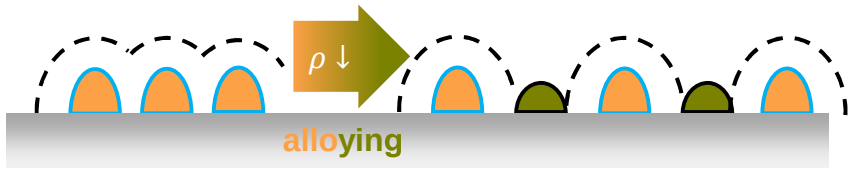
E. Bertheussen, I. Chorkendorff *et al.*, Angew. Chem. Int. Ed. 128, 1472 (2016)
E. Bertheussen, I.E. Stephens *et al.*, ACS Energy Lett. 3, 634 (2018)
L. Wang, T.F. Jaramillo *et al.*, Nature Catal. 2, 702 (2019)

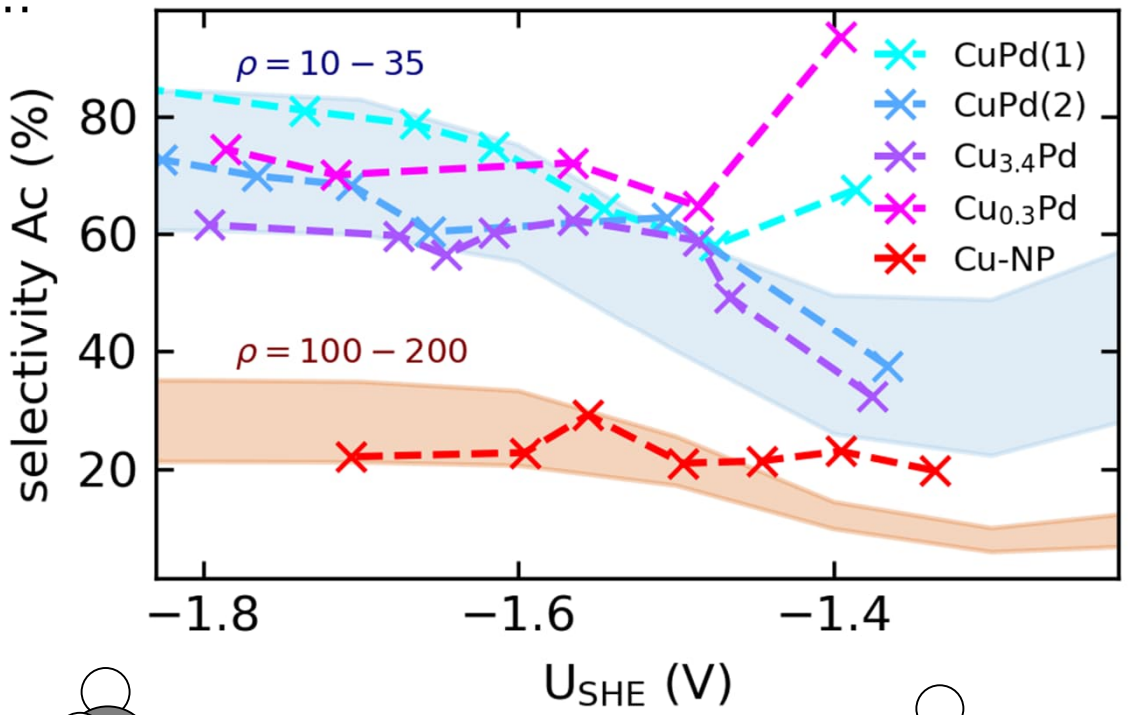
Mesoscopic Mass Transport in CO2RR @ Cu

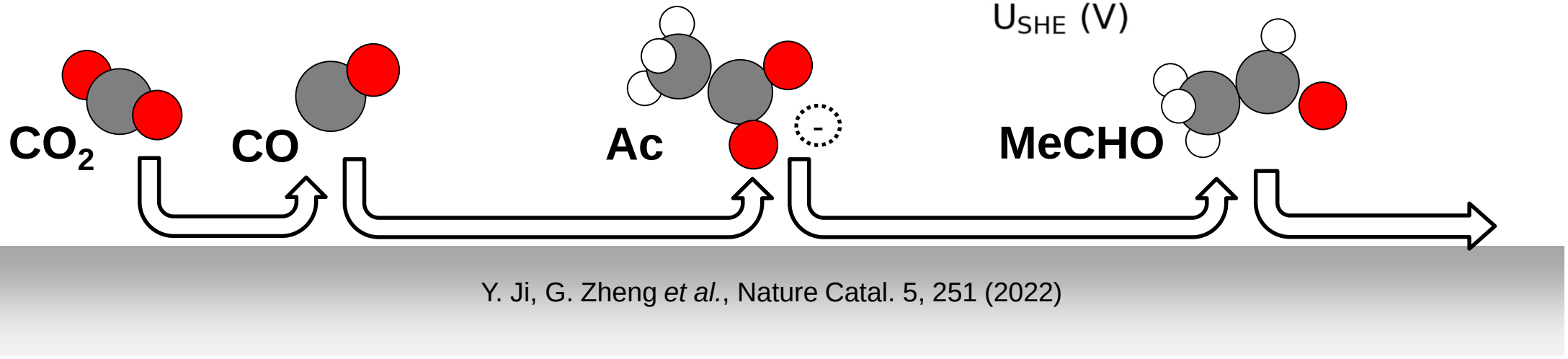
Acetate: Curves have more complex shape…



H.H. Heenen, K. Chan *et al.*,
Energy Environ. Sci. 15, 3978 (2022)

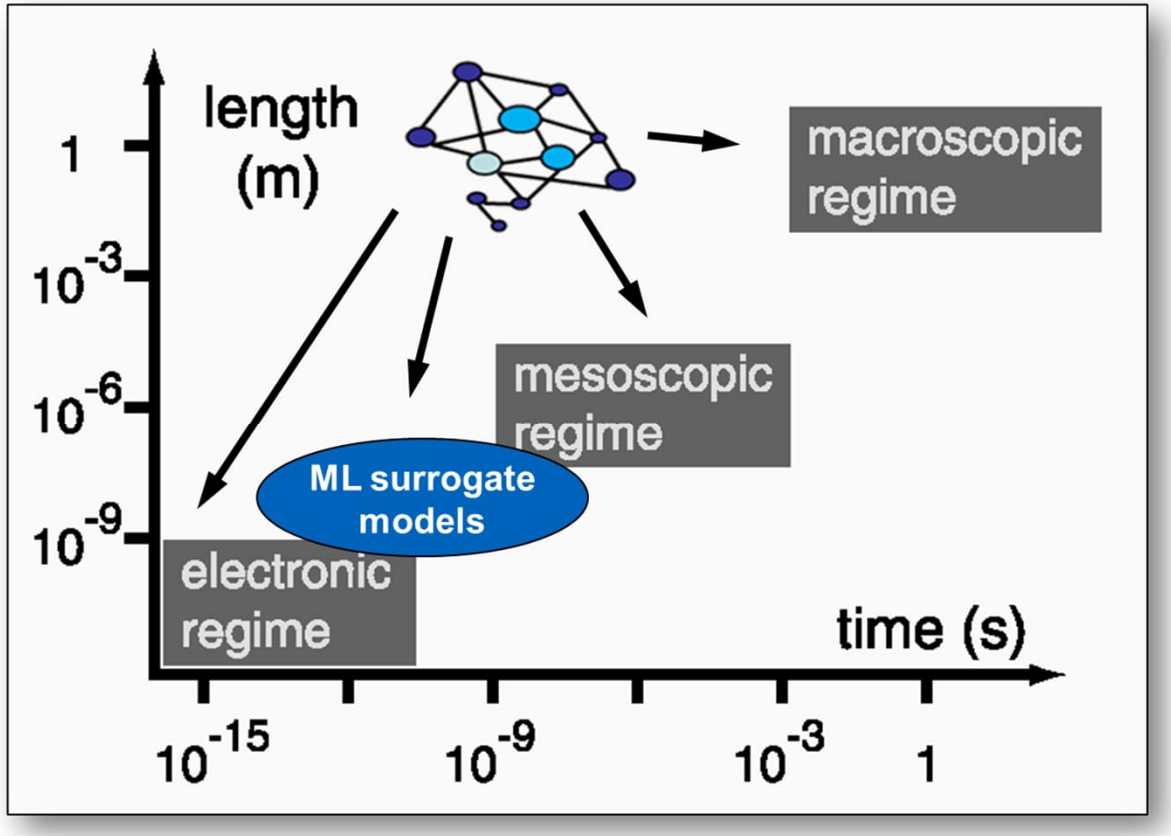






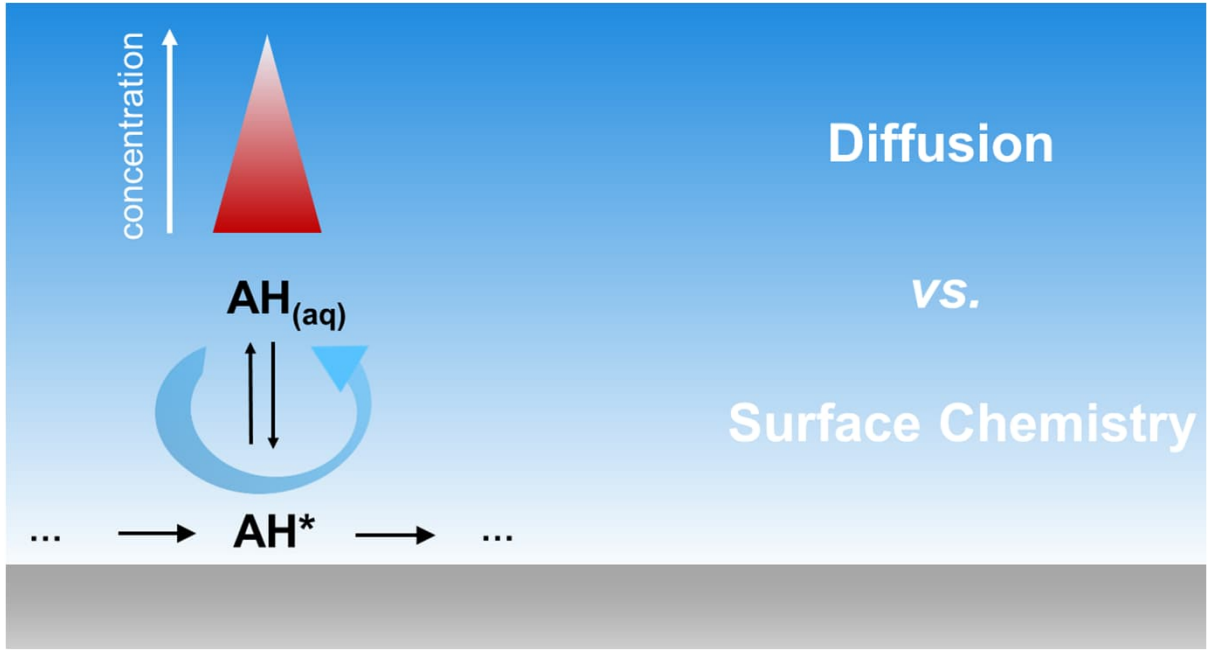
Y. Ji, G. Zheng *et al.*, Nature Catal. 5, 251 (2022)

Tackling Electrified Interfaces with Machine Learning & Multiscale Theory



J.T. Margraf, H. Jung, C. Scheurer, and K. Reuter, Nature Catal. 6, 112 (2023)

S. Ringe, N.G. Hörmann, H. Oberhofer, and K. Reuter, Chem. Rev. 122, 10777 (2022)



THANK YOU!

Nicolas Hörmann

Vanessa Bukas

Johannes Margraf

Christoph Scheurer

DFG e-conversion Bundesministerium für Bildung und Forschung BasCat UniCat BASF JointLab CatLab CATALYSIS LABORATORY HORIZON 2020 ellis