Getting the Basics Right: Capacitance, Entropy and Stress of Electrified Solid/Liquid Interfaces

854. WE-Heraeus-Seminar

03 - 06 May 2026

at the Physikzentrum Bad Honnef, Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 854. WE-Heraeus-Seminar:

Technological breakthroughs in the energy transition hinge on finding earth-abundant materials that can convert between electricity and chemical bond energy at a faster rate for a prolonged lifetime. This mission can only be accomplished with a fundamental understanding of the solid/liquid interfaces, also known as the electrical double layer (EDL), at which most important conversion processes occur. However, we are struggling with precise measurement and high-fidelity modeling of basic thermodynamic quantities, notably the capacitance, entropy and surface stress, of EDL. It is thus imperative to bring together scientists with a wide range of expertise in experiments (single-crystal preparation and characterization, electrochemical impedance, microcalorimetry, etc) and theory (continuum theory, molecular dynamics simulation, density functional theory, machine learning potentials) to discuss these specific topics in a level of depth greater than that in regular scientific meetings and conferences.

The main topics to be discussed include,

(1) Development of a general thermodynamic framework for the EDL at solid/liquid interfaces, with surface stress properly treated and its experimental validation.

(2) Major sources of errors in existing electrochemical, mechanical, and thermal measurements of capacitance, entropy and surface stress of the EDL.

(3) Origins of ultrahigh capacitance values and ultralow Parsons-Zobel slopes reported on the EDL at several transition metals.

(4) Modelling and computation of above thermodynamic quantities of the EDL.

(5) Key factors of the formation entropy of the EDL and the relationship between the formation entropy of the EDL and the electrocatalytic activity.

Introduction

Scientific Organizers:

Junior Prof. Dr. Jun Huang	Forschungszentrum Jülich GmbH Institute of Energy Technology (IET-3) Jülich, Germany
Prof. Dr. Aliaksandr Bandarenka	Technical University of Munich Department of Physics Garching, Germany
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Introduction

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Registration:

Marion Reisinger (WE Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (16:00 h – 20:00 h) and Monday morning

Program

Program

Sunday, 03 May 2026

16:00 - 20:00	Registration	
18:00 – 19:30	*BUFFET SUPPER and informal get-together*	
19:30 – 20:00	Jun Huang, Aliaksandr Bandarenka, Kathleen Schwarz	**Welcoming Note & Video Presentation: "About the Wilhelm and Else Heraeus Foundation"**
20:00 - 20:45	Jörg Weißmüller	**Electrocapillary Coupling – Surface Phenomena and Implications for Materials Behavior**

Program

Monday, 04 May 2026

07:30 - 08:45	*BREAKFAST*	
08:45 – 09:30	Galina Tsirlina	**Thermodynamics of the perfectly polarizable electrodes: complicating and less known issues**
09:30 - 10:00	Michael Eikerling	**Cracking the interface problem: going deep and wide with (almost classical) analytical theory**
10:00 – 10:30	Marcel Risch	**Measurement of Enthalpy and Entropy of the Cobaltite-Water Interface**
10:30 – 10:35	Conference Picture	
10:35 - 11:00	*COFFEE BREAK*	
11:00 - 11:30	Victor Climent	**Thermodynamic Characterization of Electrochemical Interphases on Noble Metal Single-Crystal Electrodes Using Temperature-Dependent and Laser-Induced Techniques**
11:30 - 11:50	Nicci Fröhlich	**The electric double layer structure of bare and ad-atom modified stepped platinum electrodes**
11:50 - 12:10	Jinwen Liu	**Multiscale Modeling of Surface Heterogeneity and Adsorbates effects on Electrochemical Interfaces**
12:10 – 12:30	Sudarshan Vijay	**Quantifying Electrical Double Layer Thermodynamics via 2D Periodic DFT and Machine Learning Interatomic Potentials**
12:30 – 14:00	*LUNCH*	

Program

Monday, 04 May 2026

14:00 - 14:30	Jun Cheng	**AI acceleration of AIMD simulation of electrochemical interfaces**
14:30 - 15:00	Olaf Magnussen	**X-ray scattering studies of the molecular structure of the aqueous electrolyte near platinum electrodes**
15:00 – 15:30	Marko Melander	**Thermodynamics of water-metal interface formation from DFT-MD Simulations**
15:30 – 16:00	*COFFEE BREAK*	
16:00 – 16:30	Manuel Landstorfer	**Thermodynamic modelling of the electrode–electrolyte interface — Double-layer capacitance, solvation number, and validation**
16:30 – 17:00	Tao Wang	**EDL Structure at Potentials Significantly Deviated from the PZC**
17:00 – 18:30	POSTER FLASH	
18:30 – 20:00	*DINNER*	
From 20:00	POSTER SESSION	

Program

Tuesday, 05 May 2026

07:30 - 08:45	*BREAKFAST*	
08:45 - 09:30	Tamas Pajkossy	**How to measure the double layer capacitance of electrocatalytic interfaces?**
09:30 – 10:00	Yitao Long	**Confinement controlled electrochemistry**
10:00 – 10:30	Jahan Dawlaty	**Dissecting the Electrochemical Response of the Double Layer into Spectroscopically Resolvable Molecular Dynamics**
10:30 - 11:00	*COFFEE BREAK*	
11:00 – 11:30	Vanessa J. Bukas	**Entropy-enthalpy compensation in electrocatalytic rates**
11:30 – 11:50	Fabiola Dominguez Flores	**Electrosorption Valency and Capacitance of Weakly Adsorbed Cations in the Compact Double Layer**
11:50 – 12:10	Alfred Larsson	**Anomalous charging of platinum seen by X-ray spectroscopy**
12:10 – 12:30	Albert Engstfeld	**A Step Towards FAIR Electrochemical Data: A Database of Cyclic Voltammograms for Metal Single-Crystals**
12:30 – 14:00	*LUNCH*	

Program

Tuesday, 05 May 2026

14:00 – 14:30	Guang Feng	**Interfacial Structure, Ion Transport, and Heat Generation in Electrified Solid/Liquid Interfaces**
14:30 – 15:00	Marco Schoenig	**Measuring the entropy of interface formation at Au(111)**
15:00 – 15:30	Nicolas G. Hörmann	**Charging, Chemisorption, and Water Structure at applied potential conditions: Insights from Atomistic Simulations**
15:30 – 16:00	*COFFEE BREAK*	
16:00 - 16:30	Chris-Kriton Skylaris	**Large-scale atomistic simulations of battery materials and interfaces**
16:30 – 17:00	Peter Dunne	**Magnetic Field Effects in the Electrochemical Double Layer**
17:00 – 18:00	Moderator: Aliaksandr Bandarenka	**PANEL DISCUSSION:** **Today's education and supervision in electrochemistry** **Panelists: Galina Tsirlina, Olaf Magnussen, Jörg Weißmüller, Jun Cheng**
18:30	*HERAEUS DINNER & Poster Award Ceremony* *(social event with cold & warm buffet with complimentary drinks)*	

Program

Wednesday, 06 May 2026

07:30 - 08:45	*BREAKFAST*	
08:45 - 09:30	David Raciti	**Probing the Electrified Solid–Liquid Interface with Surface Stress, Spectroscopy, and Mass Spectrometry**
09:30 – 10:00	Jan Rossmeisl	**Electrocatalysis on alloys**
10:00 – 10:30	Matthew Gebbie	**Exploring how ionic correlations impact electric double layer formation and electrocatalytic activity**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:30	Katharina Doblhoff-Dier	**Potential of zero (free) charge: Why we should care**
11:30 – 11:50	Xiao Yu Li	**The Breath of Solid-Liquid Interface during Electrocatalysis**
11:50 – 12:10	Alexander von Rueden	**Electrochemical free energy barriers from first principles**
12:10 – 12:30	Xinwei Zhu	**Understanding Cation effects in Alkaline Hydrogen Evolution Reaction: An Electrostatic Perspective**
12:30 – 12:35	Scientific Organizers	**Closing Remarks**
12:35 - 14:00	*LUNCH*	

End of the seminar and departure

Posters

Poster Session, Monday 04 May 2026, 20:00 CEST

Katrin Bickel	**Solvent effects on the reaction entropy of an outer sphere electron transfer process**
Tim Bolter	**Dynamics of Au electrode surfaces probed by electro catalytic reactions**
Marine Bossert	**Capillary rise of electrolyte-alkane mixtures between gold plates: wetting transition or electrocapillary effect?**
Steffen Braun	**Comparing microcalorimetric and temperature-variation approaches for determining the reaction entropy of electrochemical reactions**
Yuchen Cai	**Confinement effect of cation on proton transport**
Alper Tunga Celebi	**A thermodynamic origin of ion-specific adsorption at charged interfaces**
Hao Chen	**Single-molecule detection of small molecules enabled by charge regulation at the solid–liquid interface of silicon nitride solid-state nanopores.**
Junxiang Chen	**DPχ: A Constant-Potential Machine-Learning Potential for Large-Scale Electrocatalysis**
Lucas de Kam	**Poisson-Boltzmann theory in practice**
Qiuhan Deng	**Electronic and Ionic Charge Redistribution in Electric Double Layers under Curvature and Steric Constraints**
Laurin Derr	**Entropy Profiling of Hard Carbon/Na Metal Batteries with Stepwise Temperature Changes: Deciphering the Cell Voltage Response**
Hannah Dickinson	**Impact of Electrolyte pH on the Morphology of Silver Electrodeposition Studied Using in-situ Transmission Electron Microscopy**

Poster Session, Monday 04 May 2026, 20:00 CEST

Martin Durner	**Scanning Impedance Microscopy under Potential Control to Probe Local Electrochemical Properties**
Jordy Eggebeen	**Using electrochemical impedance spectroscopy to deconvolute (pseudo) capacitance from metal oxide interfaces**
Mikhail Elkhimov	**Influence of the electronics and cell resistances on electrochemical noise measurements**
Victoria Gamez	**Anion-Water and Hydroxyl Adsorption at the Pt(111) Interface: Influence of pH and Electrolyte Composition**
Antonia Gerstenberg	**The effect of bias and temperature on interfacial water at pristine Pt(111) electrodes: Insights from atomistic MLIP simulations**
Greta Grossman	**Surface Electrochemistry of the Au(111)/acetonitrile Interface: Formation of a Solvent Related Adsorbed Layer and its Implications for the Electrochemical Double Layer**
Siyuan Han	**Machine-Learning-Accelerated First-Principles Simulations Reveal Ion-Correlated Structures at Concentrated Electrochemical Interfaces**
Zetong Jia	**Long-Range Ordered Pt Facets Govern Methane Electro-oxidation via Interfacial Solvent Dynamics**
Rick Kort	**Linking Interfacial Water Structure to AFM Forces under Electrochemical Control**
Justus Leist	**Probing Surface Structure and Vibrational Stark Effects in Ni Anodes with SERS during Alkaline OER**
Chenkun Li	**Constant-Potential Kohn-Sham-Poisson-Boltzmann Theory for Electrified Metal-Solution Interfaces**
Antony Litovoilis	**Cation Effects On Solvated Electron Generation**

Poster Session, Monday 04 May 2026, 20:00 CEST

Julius Lonnes	**Disentangling Temperature Effects in Proton Adsorption Barriers at Electrified Pt(111): Roles of Water Structure, Potential, and Vibrational Free Energies**
Alessandro Mangiameli	**Benchmarking QM/RISM method for the Au–Electrolyte Interface**
Ricardo Alonso Martinez Hincapie	**Double Layer Capacity at Pt(111) Electrode in Near-Neutral Electrolytes**
Daniel Metzger	**Concentration dependent entropy determination for sodium deposition**
Marcus Frahm Nygaard	**Electron Redistribution Between Coadsorbed Species at the Electrochemical Interface**
Emmanouil Pervolarakis	**The Computational Cation Electrode: A Case Study on CO2RR**
Jorik Schaap	**The influence of the Electric-Double layer and Cathodic Bias on the Ultrafast Dynamics of Silver Nanoparticles**
Barbara Sumic	**First Steps Matter Most: Free Energy Barriers of the Volmer Step in Hydrogen Evolution at Pt(111)**
Yu Chen Sun	**Probing Nafion structure at Electrified Pt Interfaces via in-situ Polarization-Modulated Infrared Spectroscopy**
Rose Marie Tom Petersen	**Machine-Learning Assisted Determination of Reaction Paths for Electrocatalytic Reactions**
Harsh Wadhwani	**3D porous model systems for electrocatalysis**
Haowei Wang	**Raman Scattering Measurement of Single Nanoparticle Collision**
Xiwei Wang	**Density-Potential Functional Theoretic (DPFT) Schemes of Modeling Reactive Solid-Liquid Interfaces**

Poster Session, Monday 04 May 2026, 20:00 CEST

Johanna Weidelt	**Towards a DFT-based Workflow to Simulate Competitive Adsorption of Electrolyte Species at a Pt Electrode**
Lulu Zhang	**Correlating electric double layer structure and electrochemical plasmonics of nanoparticles: a theoretical study**
Zengming Zhang	**Potential of Zero Stress of Solid-Liquid Interfaces**
Jia-Xin Zhu	**Reactive electrical double layers under confinement: insights from atomistic to continuum**

Abstracts of Lectures

(in alphabetical order)

Entropy-enthalpy compensation in electrocatalytic rates

A. J.-W. Wong[1], B. Sumić[1], H. H. Heenen[1], N. G. Hörmann[1], K. Reuter[1], E. Diesen[1] and V. J. Bukas[1]

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Measuring the temperature dependence of a reaction rate is a powerful way of probing the underlying kinetics. While Arrhenius type analyses are a widespread standard in thermal catalysis, however, this approach is way less mature in the field of electrochemistry and lacks a solid theoretical foundation. With this contribution, we aim to develop the understanding behind such kinetic measurements.

As with any thermally activated process, an Arrhenius analysis of electrocatalytic rates involves two central parameters: the apparent activation energy (E^{app}) in the exponent determines the temperature dependence, while the entropy-dependent prefactor (A) determines the overall rate. The Arrhenius formalism is very simple, but raises the key question of how these parameters change with the reaction overpotential (η)? Assuming a constant prefactor A recovers the conventional Butler-Volmer kinetics and suggests that the reaction's (apparent) activation entropy does not change with potential. Although this approximation is widely adopted, experimental evidence has long suggested that it is not universal [1]. A changing E^{app} with η can be compensated in the overall reaction rate by a simultaneous change in A, thus defining an entropy-enthalpy correlation which has come to be known in many fields as a compensation effect [2]. The origin of this compensation effect has been heavily debated in the literature and most commonly attributed to the potential-driven reorganization of interfacial water [1,3].

Here, we analyze and explain the compensation effect through the surface reaction kinetics. We develop a very simple model for the hydrogen evolution reaction and find that this is enough to reproduce an entropy-enthalpy correlation in the overall rate, even when there is no potential-dependent entropic term in describing individual elementary steps. Distinct kinetic fingerprints emerge for different groups of metal catalysts that are in remarkable qualitative agreement with recent experiments [3]. We elucidate these characteristic fingerprints in terms of shifting kinetic regimes and generalize our findings to other electrocatalytic reactions and setups.

References

[1] Z. -D. He et al., Angew. Chem. Int. Ed. **57**, 7948 (2018)
[2] T. Bligaard et al., J. Phys. Chem. B **107**, 9325 (2003)
[3] J. M. Gisbert-González et al., J. Am. Chem. Soc. **147**, 5472 (2025)

AI acceleration of AIMD simulation of electrochemical interfaces

Jia-Xin Zhu[1], Xiang-Long Du[1], Qi You[1], Si-Yuan Han[1], Jia-Bo Le[2], Fujie Tang[3,4], Jun Cheng[1,4]

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Ab initio molecular dynamics (AIMD) has been proven to be a powerful tool to study complex chemical systems such as electrochemical interfaces [1]. Insisting on rigorous treatment of electrochemical interfaces both quantum and statistical mechanically, not only has AIMD helped resolve the microscopic structures of electric double layers under bias potential [2], often in collaboration with *in situ* spectroscopic characterization, but also demonstrated that water adsorption on metal electrodes like Pt has significant impact on dielectric properties of the interfaces, leading to negative capacitive response and thus bell-shaped differential capacitances of Helmholtz layers [3].

The high computational cost of AIMD however limits its application to small model systems consisting of hundreds of atoms at timescale of tens of ps. While, the latest development of AI accelerated AIMD (AI^{2}MD) significantly increases the size and timescale, showing great promise for in situ modeling of realistic electrochemical systems. The prerequisite is that the machine learning potential (MLP), often short-sighted in the common implementations, should be able to accurately capture long-range electrostatics, as well as both local and non-local dielectric responses of electrode-electrolyte interfaces. In this talk, I will present our recent effort in developing such an electrochemical MLP (ec-MLP) that utilizes a hybrid scheme combining Wannier localization and polarizable electrode method to account for polarization of the interface [4]. The accuracy of the ec-MLP has been validated against AIMD simulation of electrified Pt water interface, reproducing the bell-shaped differential capacitive curve.

The ultimate test is of course being able to connect the simulation models to experiments under the same electrochemical conditions. The bridge in between is through spectroscopies. Envisioning the important role of spectroscopies, we have been developing AI accelerated methods for computing vibrational (IR, Raman and SFG) [5] and NMR [6,7] spectroscopies of electrochemical systems, so as to eventually be able to compare against experiments at the same level of complexity (e.g. composition, heterogeneity, disorder, as well as external condition). The hope is to combine in situ/operando characterizations to resolve the structures of highly complex materials, interfaces and even interphases in electrochemical devices.

References

[1] J.-B. Le, M. Iannuzzi, A. Cuesta, J. Cheng*, Determining potentials of zero charge of metal vs standard hydrogen electrode from DFTMD, Phys. Rev. Lett., 2017, 119, 16801.

[2] C.-Y. Li#, J.-B. Le#, Y.-H. Wang, S. Chen, Z.-L. Yang, J.-F. Li*, J. Cheng*, Z.-Q. Tian, In situ probing electrified interfacial water structures at atomically flat surfaces., Nat. Mater., 2019, 18, 697-701.

[3] J.-B. Le, Q.-Y. Fan, J.-Q. Li, J. Cheng*, Molecular origin of negative component of Helmholtz capacitance at electrified Pt(111)/water interface, Sci. Adv., 2020, 41, eabb1219.

[4] J.-X. Zhu*, J. Cheng*, Machine Learning Potential for Electrochemical Interfaces with Hybrid Representation of Dielectric Response, Phys. Rev. Lett. 2025, 135, 18003.

[5] Xianglong Du, Weizhi Shao, Chenglong Bao, Linfeng Zhang, Jun Cheng*, Fujie Tang*, Revealing the molecular structures of α-Al2O3(0001)-water interface by machine learning based computational vibrational spectroscopy, J. Chem. Phys., 2024, 161(12), 124702.

[6] Min Lin, Jingfang Xiong, Mintao Su, Feng Wang, Xiangsi Liu, Yifan Hou, Riqiang Fu, Yong Yang*, Jun Cheng*, A machine learning protocol for revealing ion transport mechanisms from dynamic NMR shifts in paramagnetic battery materials, Chem. Sci., 2022, 13, 7863.

[7] Qi You, Yan Sun, Feng Wang, Jun Cheng*, Fujie Tang*, Decoding the Competing Effects of Dynamic Solvation Structures on NMR Chemical Shifts of Battery Electrolytes via Machine Learning, J. Am. Chem. Soc. 2025, 147, 14667.

Thermodynamic Characterization of Electrochemical Interphases on Noble Metal Single-Crystal Electrodes Using Temperature-Dependent and Laser-Induced Techniques

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The thermodynamic characterization of the electrochemical interphase represents a fundamental tool for advancing the understanding of electron transfer and electrocatalytic processes at solid surfaces. Historically, thermodynamic analyses have played a crucial role in the early development of electrochemical double-layer theories, providing insights into interfacial phenomena. However, their application to well-defined solid single-crystal surfaces remains relatively limited. The measurement of capacitance and voltammetric profiles at varying temperatures provides valuable information on the entropic contributions of the interphase, particularly shedding light on the complex organization and reorientation of interfacial water molecules under the influence of the electric field. Traditional methods rely on globally changing the temperature of the electrolyte solution to probe these thermodynamic properties. In contrast, an advanced alternative involves the localized and rapid perturbation of the interfacial temperature using nanosecond pulsed laser irradiation in the visible spectrum. This technique induces a sudden temperature jump at the metal|solution interphase, enabling the capture of the electrochemical response on a submicrosecond timescale. The extremely fast time resolution of this laser-induced temperature jump method facilitates the decoupling of processes occurring on distinct kinetic scales: relatively slow charge-transfer adsorption phenomena such as hydrogen and hydroxyl adsorption, and the faster reorganization dynamics of the interfacial water network.

This approach has been successfully applied to platinum and gold single-crystal electrodes. The temperature coefficient of the double-layer potential obtained from these experiments directly relates to the net orientation of water dipoles at the interface, revealing potential-dependent water reorientation phenomena that are sensitive to the crystallographic orientation of the surface, and intimately related to the potential of zero charge. Furthermore, by combining temperature-dependent voltammetric and capacitance data with laser-pulsed measurements, the entropy of formation of the double layer and the absolute molar entropy of adsorbed species can be evaluated, offering molecular-level insights into adsorbate mobility and interactions.

In this communication, we will review the results of measurements conducted on solid noble metal single crystal electrodes involving temperature variations and the thermodynamic tools employed for their analysis.

References

[1] N. Garcia-Araez, V. Climent, and J. Feliu, “Potential-Dependent Water Orientation on Pt(111), Pt(100), and Pt(110), As Inferred from Laser-Pulsed Experiments. Electrostatic and Chemical Effects,” *J. Phys. Chem. C*, 113, 9290 (2009), doi: 10.1021/jp900792q.
[2] N. Garcia-Araez, V. Climent, and J. M. Feliu, “Analysis of temperature effects on hydrogen and OH adsorption on Pt(1 1 1), Pt(1 0 0) and Pt(1 1 0) by means of Gibbs thermodynamics,” *Journal of Electroanalytical Chemistry*, 649, 69 (2010), doi: 10.1016/j.jelechem.2010.01.024.

Dissecting the Electrochemical Response of the Double Layer into Spectroscopically Resolvable Molecular Dynamics

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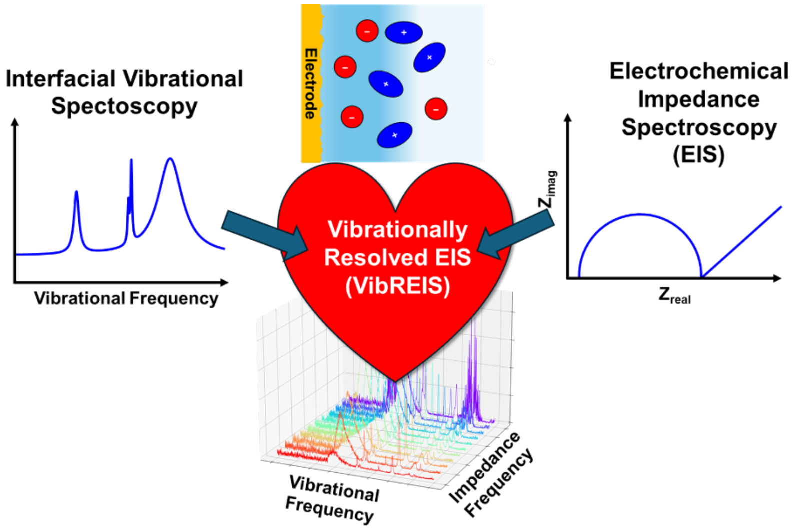
Dynamics of the electrochemical double layer (EDL) is crucial for understanding electrochemical phenomena. One of the widely used tools for this purpose is the electrochemical impedance spectroscopy (EIS), where the complex response of the EDL is recorded as a function of an oscillating potential. However, the EDL, even in relatively simple systems, has many components, with diverse and complex dynamics. EIS only records the aggregate response of the EDL. To better understand the individual response of molecular species, and more importantly the complex interplay between them, we combine EIS with electrochemical vibrational spectroscopy. We show that Vibrationally Resolved EIS (VibREIS) reveals the complex response the various components of an EDL composed of azide anions, cationic surfactants, and water. We discover unexpected results, for example a phenomenon akin to a “resonance”, where the response of azide has a preferred range of frequencies. Additionally, we observe that the surfactant, due to its large size can not keep up with potential oscillations beyond a threshold frequency, and delegates the job of screening the potential to the more agile azide. Finally, we show ion-correlated motion of the interfacial water. These phenomena are not directly inferable from EIS and is made visible only via VibREIS. We envisage further usage and expansion of the technique for dissecting the complexities of the interfacial environment.



Potential of zero (free) charge:
Why we should care

J. Liu[1], R. Kort[1], A. Hagopian[1], and K. Doblhoff-Dier[1]

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The potential of zero (free) charge is a fundamental quantity in electrochemistry. Right … That's what everybody says in their abstract. But why actually? Why *should* we care about the PZFC? Which changes occur in the double layer as we move away from zero charge? And what are the implications thereof for catalysis?

These are some of the questions that I will discuss based on ab-initio molecular dynamics simulations and the comparison thereof to spectroscopic [1] and electrochemical data [2].

Having motivated why we need to care about the PZFC, I will also discuss how to extract the PZFC from theory [3,4] and theory + experiment [5], and why the concept of "the" PZFC is oversimplified and how this can be verified in an theory – experiment collaboration.

References

[1] M.C.O. Monteiro†, L. Jacobse, A.M.V. Hagopian, V. Vonk, S. Chung, S. Louisia, A. Meinhardt, Ö. Alagöz, X. Deng, B. Roldán-Cuenya, K. Doblhoff-Dier†, M.T.M. Koper, A. Stierle; *Cation-surface interactions during electrocatalytic hydrogen evolution probed by Surface X-ray Diffraction*; submitted

[2] A. Hagopian*, S. Louisia*, K. Boterman, K. Doblhoff-Dier†, M.T.M. Koper†; *Molecular Insights into the Double-Layer Capacitance of Platinum Surfaces in Alkaline Media*; submitted

[3] A. Hagopian, M.T.M. Koper, K. Doblhoff-Dier†; *Assessing the Potential of Zero Charge in Ab Initio Molecular Dynamics Simulations*; submitted

[4] J. Liu†, K. Doblhoff-Dier†, M.T.M. Koper†; *Modelling the Double Layer of Polycrystalline Electrodes;* accepted at *ACS electrochemistry* (2026)

[5] N.L. Fröhlich*, J. Liu*, K. Ojha, K. Doblhoff-Dier†, M.T.M. Koper†;

[6] *Nature Chemistry* (2026) https://doi.org/10.1038/s41557-025-02063-9

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Electrosorption Valency and Capacitance of Weakly Adsorbed Cations in the Compact Double Layer

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Ion-specific effects in the compact (Helmholtz) layer have a critical influence on electrocatalytic activity and electrochemical energy storage. However, the microscopic thermodynamic origin of these effects, particularly for weakly adsorbing multivalent cations, remains poorly understood. In this study, we present an investigation of solvated cations at metal electrodes, employing density functional theory in conjunction with a hybrid implicit–explicit solvation scheme. In this scheme, the initial hydration shell is treated atomistically and embedded within a dielectric continuum. This framework captures the dilute, weak-adsorption limit, in which ions remain largely solvated near the surface and the compensating countercharge resides on the metal, with no diffuse layer present.

We compute integral Helmholtz capacitances for Na^+, K^+, Ca^{2+} and Mg^{2+} at Pt(111), Au(111) and Ag(111) from the interfacial potential drop generated by ion–electrode charge separation. Across all systems, the capacitances lie within the range of 10–20 $\mu F\ cm^{-2}$, which is consistent with the values observed for aqueous interfaces in experiments. A key finding is the emergence of two distinct concepts of ionic charge: the formal charge, which determines the compensating electrode charge, and the residual ionic charge after adsorption, as determined by Bader analysis. While alkali cations retain nearly their full charge, divalent cations exhibit substantial partial discharge to the metal. This partial charge transfer reduces the effective interfacial dipole and enhances the compact-layer capacitance.

Mapping the microscopic charge distribution onto a parallel-plate model gives effective dielectric constants of approximately 3-8, suggesting that screening in the compact layer is primarily driven by the electronic response of the metal and tightly bound interfacial water. This process involves minimal orientational contributions and shows only weak dependence on the choice of metal. In the absence of a diffuse layer, the electrosorption valency is equal to the negative of the partial charge transferred. These findings provide a clear, microscopic understanding of how ion identity affects capacitance.

These results establish a fundamental connection between partial charge transfer, interfacial dipole formation and compact-layer capacitance. This contributes to a thermodynamically consistent compact-layer description by relating a finite transferred charge to the corresponding interfacial potential drop and integral capacitance, while providing a microscopic explanation of ion-specific capacitance enhancement at transition-metal electrodes through charge redistribution, solvent polarization, and metal screening.

References

[1] F. Domínguez-Flores, A. Groß, W. Schmickler, J. Phys. Chem. C **129,** 9179 (2025)

[2] F. Domínguez-Flores, A. Groß, W. Schmickler, *J. Phys. Chem. C* **130**, 2475 (2026)

Magnetic Field Effects in the Electrochemical Double Layer

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Magnetic fields influence electrochemical systems through two principal mechanisms: the Lorentz force, $\mathbf{F}_{\boldsymbol{L}} = \boldsymbol{j} \times \boldsymbol{B}$, which drives magnetohydrodynamic convection when current density and field are non-collinear, and the magnetic field gradient force, $\boldsymbol{F}_{\boldsymbol{\nabla B}} = (1/2\mu_0)\chi_m c\nabla B^2$ which acts whenever orthogonal concentration and field gradients coexist. While their influence on the diffusion layer is well established [1], both forces have been dismissed at the double layer on energetic grounds — the magnetic energy of a paramagnetic ion in 1 T is five orders of magnitude below $k_B T$.

Nevertheless, uniform magnetic fields can significantly perturb double-layer structure in paramagnetic systems, modifying both double-layer capacitance and charge-transfer resistance by up to 50% at ~0.5 T [2]. This is interpreted as a magneto-wetting effect driven by Maxwell stress on concentrated paramagnetic radical anion clouds, shifting the outer Helmholtz plane by up to 0.25 nm, *a single interatomic distance*, with no change in intrinsic reaction kinetics. Co/Pt thin-film electrodes with perpendicular anisotropy generate field gradients of ~10^6–10^7 T/m directly at the electrode surface. This drives micro-convection in the diffuse double layer, modifying charge-transfer resistance and double-layer capacitance by 5–6%, again without altering intrinsic kinetics [3].

Neutron imaging shows macroscopic magnetically-driven redistribution of Gd^{3+} ions and suppression of double-diffusive salt-fingering instabilities, yet small-angle scattering reveals no field-induced molecular-scale ordering [4]. Rheological measurements further reveal unexpected low-frequency shear elasticity in confined paramagnetic solutions, pointing to collective interactions beyond conventional hydrodynamic descriptions [5], a challenge to the single-ion picture underlying most models. These questions are central to the development of Remedy's technology [6], based on the magneto-electrochemical separation of the rare earth elements.

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Cracking the interface problem: going deep and wide with (almost classical) analytical theory

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Generations of scientists have been fascinated by phenomena at electrified interfaces. Beyond scientific curiosity, understanding the microscopic region at the contact of an electrified metal surface with an electrolyte, known as electric double layer (EDL), is of foremost importance in biology, corrosion science, colloid science and electrocatalysis. In the latter context, theory and simulation are needed to shed light on the conditions in the microscopic region close to the catalyst surface, which are referred to generically as the local reaction environment (LRE). The LRE controls the capacitive response as well as the kinetics of electrocatalytic reactions.[1,2,3] Approaches towards elucidating the LRE must handle the interplay of metal electronic structure, adsorbates, solvent molecules, and ionic species, with all species and phenomena treated self-consistently as a function of electrode potential.[4] A hybrid quantum-classical approach that serves as a foundation for our efforts in this realm will be introduced and its capabilities in rationalizing capacitive and kinetic phenomena at electrochemical interfaces will be explained and demonstrated.[5] Ensuing from this approach, we have developed a model for supported electrocatalyst nanoparticles (NP).[6] It captures intertwined electronic and ionic equilibria in the three-component system of catalyst NP, support and electrolyte. Results of this model reveal how the support induces perturbations in local electronic and ionic charge densities at the surface of the NP that shape its capacitive response and electrocatalytic activity. The final part of the presentation shifts the focus towards a field-theoretic treatment of electron-ion correlations at interfaces, which is a variation on the method of image charges.[7] Taking EDL theory beyond the mean-field level, the approach achieves surprisingly close quantitative agreement with experimental capacitance data and resolves long-standing questions left unanswered by classical EDL theories. It unifies two important interface phenomena, viz. double-layer charging and electrosorption.

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A Step Towards FAIR Electrochemical Data: A Database of Cyclic Voltammograms for Metal Single-Crystals

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The study of metal single crystals by surface science and electrochemical approaches forms the basis of our fundamental understanding of atomic-scale processes on such electrodes. Furthermore, the knowledge gained from these systems is of high relevance to understanding processes on more complex catalyst materials found in applications. A key technique in elucidating potential-dependent atomic-scale processes on interfacial electrochemical systems is cyclic voltammetry. For well-defined single-crystal electrodes, the features in the cyclic voltammogram (CV) depend strongly on the experimental conditions and serve as a fingerprint of the electrode material and its surface crystallographic orientation. So far, experimental research is often limited to the investigation of individual systems, hampered by the complexity of the electrode preparation. Elucidating trends among materials with similar crystallographic orientations are often limited to computational approaches,[1,2] while equivalent experimental databases are scarce, even though thousands of experimental datasets exist (locked in figures of published articles).

In this work, we present an electrochemical database for interfacial electrochemistry, focusing on CV data for single-crystal model electrodes in aqueous and non-aqueous electrolytes.[3] We illustrate how CVs (mostly only available as traces in figures) and related metadata (scattered as plain text in manuscripts) are extracted and transformed into structured datasets enabling FAIR (findable, accessible, interoperable, and reusable) data handling, using a Python-based open-source framework.[4] Based on lessons learned from creating the database and related activities in the NFDI4Chem consortium,[5] we[6] suggest how electrochemical data could be reported in the future to improve its FAIR use. We also provide use cases of the database,[7,8] discussing what knowledge can be gained and to what extent it is relevant to quantify aspects related to the electric double layer (EDL) presented at the Seminar. Finally, possible further implementations and the combination of the database with computational approaches will be discussed.

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Interfacial Structure, Ion Transport, and Heat Generation in Electrified Solid/Liquid Interfaces

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Electrified Solid/Liquid Interfaces are essential in many fields, such as electrical energy storage, electrocatalysis, electroplating, capacitive deionization, and so on. Despite considerable studies on solid/liquid interfaces, the details of what would happen at electrolyte-electrode interfaces still require in-depth explorations, in particular, how heat would be generated during charging/discharging. During the last several years, we developed constant-potential molecular dynamics (MD) modeling to investigate the interfacial structure, ion transport, and heat generation in electrical double layers. Focusing on solid/liquid interfaces in supercapacitors, we examined solid/liquid interfaces systems with different electrodes and electrolytes, supported by experiment, to understand mechanisms of Interface formation and thus to help the design of electrochemical devices. The contents of this talk would include:

(1) Developing modeling techniques of constant-potential MD simulations, which presents the developed algorithm and code package of MD simulations for accurately mimicking capacitive systems.

(2) Exploring the influence of water impurity on ionic liquid (IL) interfaces, which expatiates water adsorption on electrode surfaces in contact with humid ILs and the possible strategy to reduce the water electrosorption at polarized electrodes.

(3) Studying the capacitance and charging dynamics of ILs in porous electrodes, which would show how nanoporous carbon and conductive MOFs as electrodes could achieve promising capacitive performance.

(4) Exploring the heat generation of interface formation in aqueous and IL electrolytes, which reveals that interface formation in aqueous electrolytes exhibits endothermicity under negative polarization and shows new complexity of endothermicity followed by exothermicity in ILs, regardless of electrode polarity.

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The electric double layer structure of bare and ad-atom modified stepped platinum electrodes

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The structure of the electric double-layer at platinum electrodes remains incompletely understood, even for the model Pt(111)/$HClO_4$ interface, which shows clear deviations from classical Gouy-Chapman-Stern theory [1]. While Pt(111) exhibits a true double-layer window (0.40 – 0.60 V_{RHE}) that enables direct measurement of double-layer capacitance, stepped Pt surfaces do not because hydrogen and/or hydroxyl adsorb at low-coordinated step sites across the entire potential range [2]. Here, we demonstrate that hydroxyl adsorption (OH_{ads}) exhibits fundamentally different behaviour depending on the step nature. On (110)-type steps, OH_{ads} is potential-independent within the nominal double-layer window, leading to decreasing capacitance with increasing (110)-step density due to suppression of the step Helmholtz capacitance [3]. In contrast, (100)-steps exhibit potential-dependent OH_{ads}, giving rise to a significant pseudocapacitance and an overall increase in capacitance with (100)-step density. These differences are corroborated by Parsons-Zobel (PZ) plot analysis: The PZ slope remains constant as a function of increasing (110)-density but decreases systematically with increasing (100)-step density. The dominance of the adsorption capacitance observed on (100)-step sites was also found to extend to heterogeneous polycrystalline Pt electrodes, where a larger capacitance in the (111) double-layer window was observed with an increasing proportion of (100)-facets [4]. To further probe the effect of step-site adsorption, we selectively passivated the step sites of stepped Pt single crystal electrodes by depositing Au* ad-atoms [5]. This modification suppresses step-specific adsorption processes, restoring predominantly electrostatic behavior for (100)-type stepped Pt surfaces and reversing the capacitance and PZ trends observed for bare stepped Pt surfaces. Overall, these findings demonstrate that step-site chemistry, and consequently the electrical double-layer structure, can be tuned to a remarkable degree of controllability through selective ad-atom modification and further highlights the importance of understanding these model catalysts at a fundamental level.

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Exploring how ionic correlations impact electric double layer formation and electrocatalytic activity

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Intermolecular forces play a central role in electric double layer formation, as electrostatic interactions generally attract oppositely charged counterions and repel like-charged co-ions from interfaces. This ion de-mixing leads to charge separation that screens interfacial potentials but incurs significant entropic penalties. Exploring how electrostatic and entropic influences balance to govern double layer properties, including potential gradients, ion distributions, and solvation, remains an active area of research, especially at high charge interfaces, where ion-ion correlations emerge. In this talk, I will focus on our work exploring how ionic correlations frequently play a defining role in sculpting electric double layer formation and electrocatalytic reactivity. I will present our work linking nanoscale structures, dynamics of ionic liquid-electrode interfaces to rates and selectivity of CO_2 reduction as a model for illuminating how collective ion assembly influences electrocatalytic activity. I will then discuss our recent discovery that co-ions can play defining roles in electrocatalytic reactions under the large applied biases inherent to most electrochemical systems, even when the bulk electrolyte is expected to behave classically. Further, I will explain how we leverage *in situ* interfacial spectroscopy to study ion surface assembly in parallel with kinetic analysis of electrocatalytic reactions to interrogate why co-ions can influence reactivity to a greater degree than counterions, contradicting classical predictions. I will also show how our results on co-ion modulation connect to CO_2 reduction, where like-charged co-ions play key roles in ionic liquid-mediated CO_2 conversion. By highlighting unifying themes across model systems, I will share our perspective for why working at the intersection of colloid science and electrocatalysis provides powerful tools to study electric double layer formation at charge-dense interfaces and opens new frontiers in modulating chemical reactions at solid-liquid interfaces.

Charging, Chemisorption, and Water Structure at applied potential conditions: Insights from Atomistic Simulations

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Interfacial thermodynamics and kinetics at electrified solid–liquid interfaces are governed by the atomistic structure and dynamics of the interface. Experiments such as cyclic voltammograms (CV), capacitance measurements, and temperature-jump measurements provide invaluable access to macroscopic response functions. They provide insights into charge–potential relations of the interface and their temperature dependence but are often difficult to directly relate to atomistic mechanisms. In this context, simulations play a crucial role in connecting microscopic structure to experimentally accessible observables.In my talk I will elaborate on a few key insights from theory connected with CVs and interfacial capacitances.

First, I will present a theoretical analysis of slow scan-rate CVs within a constant-potential framework, demonstrating how experimentally observed temperature-dependent response properties can originate from adsorption-induced, double-layer modifications. In this context I will clarify the interrelated nature of double layer recharging and Non-Nernstian CV position and shape changes, and report results from density functional theory calculations in implicit solvent environments on selected model systems [1].

While such simulations explain the effects of the double layer at a semiquantitive level, I will as well highlight their limitations at the example of the biased, pristine Pt(111)-water interface. Using ab-initio molecular dynamics (AIMD) simulations, I will quantify the importance of interfacial water structure, electronic and dynamical screeing as well as electronic spillover [2]. It is the combination of these three core ingredients that lead to the observed capacitance peak at Pt(111) which is not captured reliably in pure implicit models or common force fields. In contrast, I will demonstrate that all these factors can be described reliably at applied bias conditions either with AIMD or our recently developped machine-learned interatomic potential – RAZOR [3] – which promises to provide a viable pathway toward future simulations that consistently combine dynamic water response with surface reactions and electrosorption processes under applied potential conditions.

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Thermodynamic modelling of the electrode–electrolyte interface — Double-layer capacitance, solvation number, and validation

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A theoretical understanding of electrode–electrolyte interfaces is crucial for various electrochemical systems. A key quantity and investigation tool of the electrode–electrolyte interface is its potential-dependent double-layer capacity [1–3], which can be rigorously derived on the basis of non-equilibrium thermodynamics [4,5] and serves as a validation tool between theoretical and experimental studies. In this contribution, we sketch the derivation based on a general mixture theory which explicitly accounts for solvation effects [4], incompressibility [5], and concentration- as well as electric-field-dependent dielectric susceptibility [6], all of which contribute to the spatial structure of the double layer. We demonstrate that this framework yields both a qualitative and quantitative understanding of the double-layer capacity and provide insights from a broad validation study in aqueous as well as non-aqueous electrolytes [6]. The theory [5] additionally accounts for adsorption and partial de-solvation, yielding asymmetric capacity curves of strongly adsorbing ions [1,3]. We further address poly-crystalline surfaces [7] and outline current research on this topic.

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Anomalous charging of platinum seen by X-ray spectroscopy

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In this contribution, I will demonstrate how we can directly detect interfacial ions experimentally using soft X-ray absorption spectroscopy (XAS) and electrochemical quartz crystal microbalance. For this, we use mesoporous platinum, with a large ratio between the interfacial and bulk electrolyte in the pores. This allows an otherwise bulk-sensitive technique to provide quantitative data on the concentration and degree of hydration of cations and anions at the platinum electrolyte interface. We have used this methodology to track the interfacial anion and cation concentrations as a function of electrode potential, bulk ion concentration, pH, and anion and cation identity.

In electrolytes with non-adsorbing anions, we have studied three distinct surface adsorbate structures, H-covered, OH-covered, and oxide-covered platinum by varying the potential vs. PZC using a pH series at fixed potential vs. RHE (-0.05 V_{RHE}, 0.5 V_{RHE}, 1 V_{RHE}). For the H-covered surface, we find an interfacial cation concentration trend that is accurately captured using a basic modified Poisson-Boltzmann model. However, this is not the case for the OH and oxide covered surface, leading to non-intuitive trends. For example, we find that at pH 13, the Na^+ concentration increased when adsorbates changed from H (-0.05 V_{RHE}) to OH (0.5 V_{RHE}) and oxide (1 V_{RHE}), counterintuitive to capacitor models, which predict cation repulsion at higher potentials. At pH 12, we find a non-monotonic charging rate as a function of applied potential, with the lowest cation concentration in the “double layer” region where steps are OH-covered. In acidic media, we can also observe non-monotonic charging in the presence of sulfate adsorption, which carries a net negative charge that attracts cations. This shows how adsorbates reshape surface charge and the ions attracted, altering the local reaction environment.

The Breath of Solid-Liquid Interface during Electrocatalysis

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Electrified solid-liquid interfaces are central to energy and matter conversion in electrochemical systems[1], where intense local electric fields critically govern reaction kinetics[2]. Under realistic electrocatalytic conditions, the electrical double layer (EDL) is characterized by rapid charge transfer and far-from-equilibrium dynamics. While classic EDL models are derived under equilibrium and non-reactive conditions, failing to account for the molecular-level processes that emerge at reactive interfaces[3]. In this work, we develop an integrated experimental-computational framework to directly resolve the structure and dynamic evolution of the EDL under far-from-equilibrium conditions. We developed nanostructured platinum film electrodes that withstand elevated overpotentials and amplify infrared signals significantly, enabling high-sensitivity, time-resolved surface-enhanced infrared absorption spectroscopy (SEIRAS) measurements. This was complemented by machine learning-based molecular dynamics (MLMD) to capture nanosecond-scale interfacial charge fluctuations and solvent dynamics. Our results reveal a nonlinear, two-phase contraction of the inner EDL layer under cathodic polarization, which significantly intensifies the local electric field. We found an irreversible restructuring of interfacial water networks during cyclic potential modulation, and we define this phenomenon as “EDL breathing”. Our results reveal distinct temporal and structural evolution pathways of ions and interfacial water, establishing a quantitative framework for electrostatic potential variations and molecular reorganization at charged interfaces.

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Multiscale Modeling of Surface Heterogeneity and Adsorbates effects on Electrochemical Interfaces[1-3]

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Abstract: The surface of electrocatalysts typically shows (dynamic) surface heterogeneities, such as steps, kinks and valleys [4], and is often covered by adsorbates such as hydrogen (H) and hydroxyl (OH) [5]. These surface heterogeneities and adsorbates affect the electrocatalytic reaction activity and selectivity significantly [6]. However, the fundamental mechanisms underlying these structure-activity relationships, which are closely linked to the local reaction environment at the electrode/electrolyte interface, remain poorly understood.

The surface heterogeneity can be classified across different length scales, from the atomistic to the macroscopic level. At each scale, different physical effects dominate, and accordingly, different theoretical methods are required. In this work, we employ methods ranging from ab initio molecular dynamics (AIMD) simulations to continuum modeling to investigate electrochemical interfaces with varying degrees of surface heterogeneity, including stepped, mesoscopic rough, and polycrystalline surfaces.[4-5] At the microscopic scale, two fundamental interface properties, double layer capacitance and the potential of zero charge (PZC), are computed at the quantum level and directly compared with experiments. The results reveal that OH_{ads} at step sites quench the step dipole caused by Smoluchowski effect, leading to an increase in the PZC and explaining the experimentally observed reduction in the PZC–step density slope relative to the work function–step density slope. Furthermore, confinement of interfacial water at mesoscopic rough surfaces decreases local permittivity and raises the PZC, reducing the slope between PZC and work function. At the macroscopic scale, phase diagrams are constructed to identify when capacitance curves exhibit one or two minima and whether the potential of capacitance minimum aligns with the PZC. Overall, these findings highlight how heterogeneous surfaces, adsorbates, solvent molecules, and ions collectively shape electrochemical interfaces, leading to systematic deviations from classical theories, such as the Frumkin–Trasatti theory on the relation between PZC and work function [7].

Keywords: Multiscale modeling, surface heterogeneity, electrical double layer.

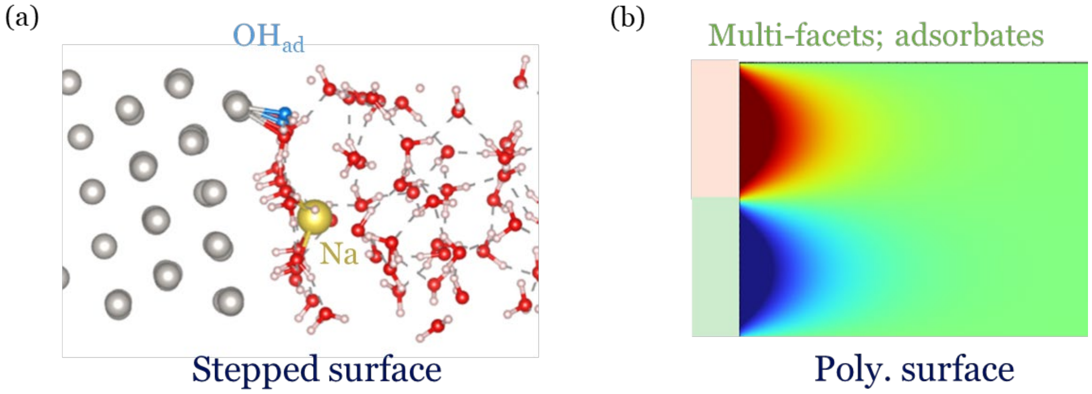

Figure 1. (a) Representative AIMD snapshots of Pt(553)/water interface, highlighting step-OH_{ad}-cation interactions; (b) schematic diagram for modelling the polycrystalline electrode as consisting of two distinct facets.

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Confinement Controlled Electrochemistry

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Single-entity electrochemistry (SEE) describes a recent trend in state-of-the-art electrochemistry applied to the investigation of individuals at a time. SEE is particularly appealing as it integrates different branches of modern electrochemistry and combines diverse fundamental approaches and techniques towards the ultimate limits of measurements. It provides powerful means to measure single cells, single particles, and even single molecules at the nanoscale through various well-defined interfaces. The confinement controlled interface significantly enhances electrical, and electromagnetic characteristics for electrochemical analysis, thereby greatly affecting the assay limitation and selectivity of single-entity measurement. Herein, we demonstrate how to achieve controllable nanoelectrochemistry through micro/nano interfaces and nanopore interfaces. We then present a fundamental understanding of how dynamic interactions control the features of the electrochemical interface and thus the stochastic and discrete electrochemical responses of single entities under nanoconfinement. Both stochastic collision electrochemistry and nanopore electrochemistry, as examples in this presentation, explore how these interactions alter the transient charge transfer and mass transport at the microscopic scale. Finally, we discuss further challenges and opportunities in SEE, ranging from the design of sensing interfaces to hybrid spectro-electrochemical methods, theoretical models, and advanced data processing.

X-ray scattering studies of the molecular structure of the aqueous electrolyte near platinum electrodes

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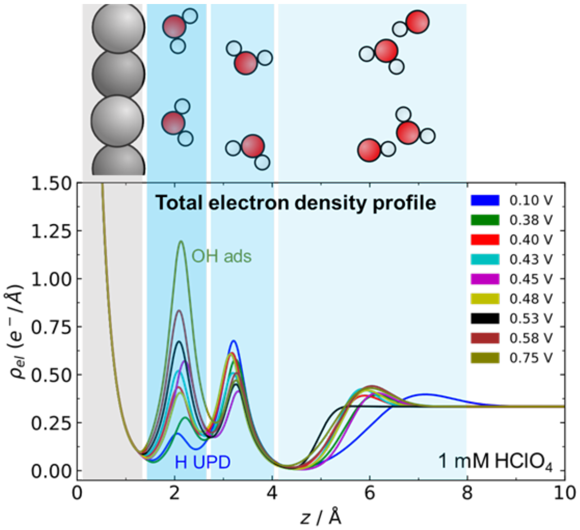
The Pt(111) surface is arguably the most studied system for fundamental studies of electrode-electrolyte interfaces. Recent electrochemical measurements found evidence of a double layer structure that strongly deviated from the traditional Gouy-Chapman-Stern model [1,2]. A structural influence of interfacial water has been proposed as a possible explanation for these deviations. Ab initio molecular dynamics indicate two layers of interfacial water molecules whose occupancy changes as a function of electrode potential [3,4]. Furthermore, the interfacial water structure is also linked to the well-known influence of cations on the electrocatalytic activity. In the talk, I will address these issues by direct studies of the molecular arrangement of interfacial water at Pt single crystal surfaces by surface X-ray scattering methods. In particular, I will show that using high-energy photons reliable quantitative data on the interface structure can be obtained that can be directly compared with molecular simulations.



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Thermodynamics of water-metal interface formation from DFT-MD Simulations

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Metal–water interfaces are central to many electrochemical, (electro)catalytic, and materials science processes and systems. However, our current understanding of their thermodynamic properties is limited by the scarcity of accurate experimental and computational data and procedures to determine the thermodynamics of metal-water interfaces.

In this contribution I will present the simulation of thermodynamic quantities for metal–water interface formation for a range of FCC(111) surfaces (Pd, Pt, Au, Ag, Rh, and PdAu) through extensive density functional theory based molecular dynamics and the two-phase entropy model. The results show that metal–water interface formation is thermodynamically favorable and that most metal surfaces studied in this work are completely wettable, i.e., have contact angles of zero. Interfacial water was found to have higher entropy than bulk water due to the increased population of low-frequency translational modes. The entropic contributions also correlate with the orientational water density, and the highest solvation entropies are observed for interfaces with a moderately ordered first water layer; the entropic contributions account for up to ~25% of the formation free energy. Water adsorption energy correlates with the water orientation and structure and is found to be a good descriptor of the internal energy part of the interface formation free energy, but it alone cannot satisfactorily explain the interfacial thermodynamics; *the interface formation is driven by the competition between energetic and entropic contributions.*

The results provide fundamental, atomistic understanding on the thermodynamics of metal-water. The insight can be used to develop, parameterize, and benchmark theoretical and computational methods for studying metal–water interfaces. Overall, our study yields benchmark-quality data and fundamental insight into the thermodynamic forces driving metal–water interface formation.

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How to measure the double layer capacitance of electrocatalytic interfaces?

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Capacitances, determined through electrochemical impedance spectroscopy (EIS) measurements play an important role in the characterization of the electrical double layer formed at the electrode/electrolyte interfaces. The lecture focuses on the following related issues:

(a) Methodological points: How to extract interfacial capacitance data from impedance spectra? What are the important properties of the interfacial capacitances? What are important experimental conditions?

(b) Double-layer capacitance is often found to be frequency dependent; a couple of typical examples will be shown. Where is the frequency dependence of capacitance coming from? What kind of theories can be used?

(c) What are the consequences of the non-uniform current distribution upon impedance spectra?

(d) Finally, dynamic EIS, a combination of cyclic voltammetry and EIS is presented. By this, slowly changing (e.g. unstable) systems can be studied.

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Probing the Electrified Solid–Liquid Interface with Surface Stress, Spectroscopy, and Mass Spectrometry

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Abstract

A central challenge in electrochemistry is connecting measurable thermodynamic and mechanical quantities of the electrified solid–liquid interface (such as capacitance, entropy, and surface stress) to the molecular-scale processes that govern reactivity and stability. Addressing this challenge requires experimental approaches that can resolve both interfacial thermodynamic response and interfacial chemistry under operating conditions.

In this talk, I will present ongoing efforts toward a broader operando metrology framework that leverages complementary approaches, including surface stress measurements, electrochemical mass spectrometry, and vibrational spectroscopy, to probe adsorption, interfacial structure, and reaction dynamics at electrode surfaces. Case studies ranging from CO adsorption on Pt to C–C coupling during CO electrolysis on Cu will be used to illustrate both the opportunities and the limitations of extracting mechanistic insight from complex operando datasets in the context of electrical double-layer phenomena.

I will also highlight limitations of current experimental strategies that must be addressed to enable further progress. More broadly, the future integration of these complementary metrologies may help disentangle contributions from charging, specific adsorption, and surface restructuring, and provide new insight into the roles of electrolyte identity and interfacial water organization in electrochemical systems.

Measurement of Enthalpy and Entropy of the Cobaltite-Water Interface

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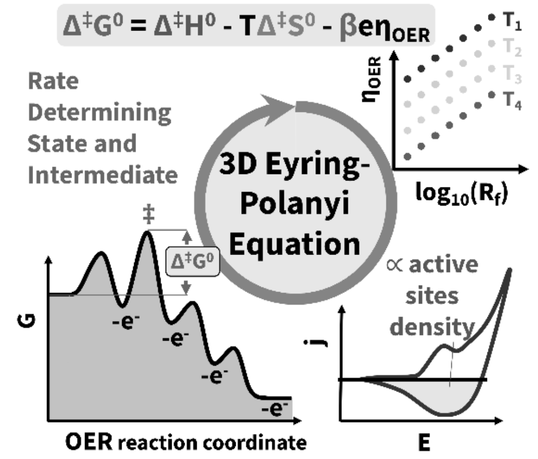

Enthalpy and Entropy of the rate determining state and intermediate of OER are obtained by fitting the 3D Eyring Polanyi equation. Our protocol can be readily extended to other electrocatalysts and electrocatalytic reactions.

Cobalt and its oxides are economically and strategically important materials with uses in batteries and catalysis, including the electrocatalysis of water/hydroxide oxidation by the oxygen evolution reaction (OER). The current assessment of electrocatalysts often relies on property-activity relationships relying on calculated thermodynamic parameters [1]. In contrast, experimentally determined thermodynamic parameters are rarely reported for electrocatalytic reactions including the OER. In my talk, I will introduce cobalt oxides used as electrocatalysts for the OER as well as their assessment based on calculated thermodynamic parameters and then focus on our experimental protocol for determining thermodynamic properties of the rate determining state and intermediate (RDSI) of the OER [2]. Cobalt oxide is investigated at pH 7 as a case study [3]. Two different approaches are employed: steady state polarization (SSP) that uses chronopotentiometry at different temperatures and current values, and potentiostatic electrochemical impedance spectroscopy (PEIS) at different DC voltages and temperatures. The data is used to fit a 3D plane from which entropy and enthalpy of the RDSI are obtained. The data analysis requires an appropriate filtering of the data. Hence, I discuss suitable figures of merit for establishing appropriate filtering criteria that are also valuable for Tafel analysis [1]. The values obtained for the cobalt oxide at PH 7 are 0.72 and −0.39 eV (at 298 K) for enthalpic and entropic contributions, respectively. The obtained values are reproducible for both approaches and consistent with literature. I will conclude by a brief outlook on the applicability of the protocol for electrocatalysis.

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Catalysis on High Entropy Alloys

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Abstract: The green transition requires discovery and development of new catalyst materials for sustainable production of chemicals and fuels. However, it is difficult to predict a material, which might have a high catalytic activity for a given reaction, therefore the development of catalysts up until now has been driven mainly by trial and error. It would increase the pace of development, if we could predict a range of promising materials or if we at least could understand the limitations of catalysis. In this context high entropy alloys offer a chemical space of possible materials where the composition can be smoothly varied and where the properties also might vary in a seamless manner. This is good news for catalysis as such a smooth space is easier to explore to determine the interesting regions in composition space. Furthermore, the highly heterogeneous nature of a high entropy alloy surface reveals fundamental effects, which are important for chemistry on surfaces in general, but are overlooked in the classic mean field view on catalysis.

Measuring the entropy of interface formation at Au(111)

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For a long time, detailed thermodynamic data on adsorbates was limited to mercury electrodes. Only in seminal works in the 90's Lipkowski et al. provided the first thermodynamic data for solid metal surfaces, i.e., for Au(111) [1]. Such data are essential to verify theoretical models of the solid/liquid interface.

Since then, the Au(111) surface is a very important model surface due to its nearly ideal polarizability and the high stability of gold in many electrolyte solutions.

Another fundamental quantity that provided important insight in the mercury/electrolyte interface was the entropy of formation of the interface [2]. Albeit several attempts to obtain this quantity also on solid electrodes, the only reliable method has been to use the temperature coefficient of the interfacial potential to measure the entropy of interface formation on Au and Pt surfaces [3,4].

In this contribution, we show an alternative method to obtain the entropy of interface formation using electrochemical microcalorimetry. We investigate the Au(111) surface in several electrolytes containing specifically adsorbing anions (SO_4^{2-}, Cl^-, Br^-, I^-). We found a universal behaviour for the potential dependence of the entropy of formation of the interface for all anions, which shifts in potential with their adsorption strength. Our results indicate strong entropic contributions of over 80 J mol^{-1} K^{-1} to the free enthalpy of the surface system [5].

Using different lattice gas models, we were able to qualitatively explain the observed entropy variations by considering pairwise repulsive dipole-dipole interactions within the quasi-chemical approximation. We further find a strong influence of cations on the entropy of interface formation in line with our thermodynamic model.

Finally, we will discuss our results with respect to other measurements of the entropy of interface formation and emphasize consequences of our results for the interpretation of the potential of maximum entropy.

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Large-scale atomistic simulations of battery materials and interfaces

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We are developing software for supercomputers for atomistic electrochemical simulations under operational conditions in order to capture the essential chemistry and physics of devices such as batteries but also provide the parameters needed for bridging atomistic with higher scale continuum simulations. Our developments are within the ONETEP program [1], which is based on a linear-scaling reformulation of density functional theory (DFT) that allows simulations of orders of magnitude more atoms than conventional DFT approaches, for more realistic models. In this talk, I will outline our developments, which include solvent and electrolyte models [2], and simulations at fixed voltage with respect to a computational reference electrode [3]. Also, I will describe our ongoing uses of the ONETEP linear-scaling framework combined with machine learning force fields to provide longer timescale simulations for processes such as the chemistry taking place during Solid-Electrolyte Interphase (SEI) formation – a very complex multi-component material crucial for battery operation. Finally, I will summarise recent applications of these tools to the process of lithium metal deposition on anodes and its competition with Li dendrite formation [4], one of the main mechanisms of battery degradation.

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Thermodynamics of the perfectly polarizable electrodes: complicating and less known issues

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This lecture aims to comment a number of uncertainties, misunderstandings, and little-known issues related to co-adsorption of ions and atoms.

For *equilibrium systems* supporting such co-adsorption (perfectly polarizable electrodes), thermodynamic description involves the notions of free and total electrode charges. Separation of the former is a matter of experimental determination of the *Gibbs adsorptions of ions*, which will be a matter of ad hoc discussion. Very closely interlinked issue will be accented as well: the *inversion of free charge* (induced by adatoms formation). The available direct data collected for highly dispersed platinum group metals in 1960s-70s will be discussed in respect to free charge vs. potential dependencies. Very rare and less complete data of this sort for iron group metals, copper, and carbon will be mentioned as well. Chapter [1] is recommended for navigation, which is a compressed (about 70 p.) version of never translated Frumkin's book "Potentials of zero charge". Many original articles closely related to the topic can be found in collection of Frumkin school articles [2].

Going to *non-equilibrium* situations, *electrocatalysis* on transition metals will be addressed in the context of *reaction layers*. We shall discuss to what extent equilibrium data can be helpful, and what is changed unavoidably because of formation of adsorbed reaction intermediates. In particular, the effect of organic adsorbates on the free electrode charge will be addressed. This consideration will be limited to reactions which occur in aqueous systems inside solvent stability window (hydrogen oxidation, organic fuels oxidation, oxygen reduction). Some comments on ionic adsorption outside stability window (oxygen and hydrogen evolution, carbon dioxide reduction) will be presented as well.

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Quantifying Electrical Double Layer Thermodynamics via 2D Periodic Density Functional Theory and Machine Learning Interatomic Potentials

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Density functional theory (DFT) provides the predictive power necessary to resolve the complex thermodynamics of the electrical double layer (EDL). However, standard implementations such as the Vienna *ab-initio* Simulation Package (VASP) employ 3D periodic boundary conditions (PBCs), which enforce charge neutrality. This constraint prevents the direct simulation of net-charged surfaces and introduces electrostatic artifacts that hinder the accurate determination of the potential of zero charge (PZC) and electrochemical capacitance.

In this work, we apply our recent implementation of 2D periodic boundary conditions within VASP [1], based on the Coulomb kernel truncation method, to compute the thermodynamic properties of the gold–water interface. Our approach computes the energies and forces for net-charged surfaces without the need for neutralising background charges or implicit solvation methods.

We first determine the electrochemical capacitance of the Au–water interface by training machine learning interatomic potentials (MLIPs) on a database of first-principles calculations generated under 2D boundary conditions. Using this benchmarked framework, we quantify how charged reaction intermediates modify the local EDL structure and shift the thermodynamic landscape by computing the adsorbate-induced changes in PZC and capacitance. Finally, we calculate the dipole moments of small molecules adsorbed on transition metal surfaces and rationalise these trends through a the Newns-Anderson framework. These dipole moments provide a physical basis for the capacitance shifts observed during chemisorption. Together, this integrated approach, combining 2D-DFT, MLIPs, and analytic modeling, establishes a robust framework for validating EDL thermodynamics and bridging the gap between electronic structure and macroscopic electrochemical observables.

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Electrochemical free energy barriers from first principles

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The calculation of electrochemical free energy barriers has been a longstanding challenge in computational electrocatalysis. Many important electrocatalytic reactions occur at electrified solid/liquid interfaces, whose complex structures and dynamics are challenging to describe in atomistic simulations. Among these is the potential-dependent reorganization of interfacial water, which is difficult to capture yet can in turn influence the reaction energetics. This challenge is compounded by the fact that standard density functional theory (DFT) calculations maintain a constant charge rather than potential in the simulation cell. Consequently, the model electrode potential can vary substantially during the simulation of an electrochemical reaction. To demonstrate one path forward, here we build upon a computational approach developed in our group that enables the determination of electrochemical free energy barriers under well-defined potential conditions. Specifically, we construct atomistic models of a solid electrocatalyst/liquid electrolyte interface (featuring explicit solvation) and obtain its dynamic structures from DFT-based ab initio molecular dynamics (AIMD) simulations. On top of this, we employ enhanced (umbrella) sampling to uncover the free energy profiles of elementary reaction steps, capturing both enthalpic and entropic contributions. We perform these simulations at several different surface charge conditions and, by sampling the varying work function along the reaction coordinate, we transform the resulting energetics from constant-charge (electronically canonical) to constant-potential (electronically grand-canonical) conditions. Using this approach, we explore the free energy profile of proton discharge at the Au(111) surface. We extract potential-dependent barriers and investigate the influence of different proton donors, including H^+ and H_2O to represent acidic and alkaline conditions, respectively.

EDL Structure at Potentials Significantly Deviated from the PZC

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While the electrical double layer (EDL) structure near the potential of zero charge (PZC) is well-documented, our understanding of the EDL under high polarization remains limited. Characterizing the interface far from the PZC poses significant experimental difficulties, yet bridging this gap is imperative. Contemporary research on electrocatalytic kinetics has increasingly focused on how the EDL modulates reaction pathways, often under conditions far removed from equilibrium. Despite extensive discussions on the interplay between EDL structure, reaction kinetics, and mass transport, the field lacks a fundamental description of the actual EDL structure in these potential regions.

To address this, we systematically investigated the EDL structure of alkali metal cations at potentials significantly negative to the PZC. We combined Polarization Modulation Attenuated Total Reflection Infrared spectroscopy (PM-ATR-IR) with in situ Electrochemical Atomic Force Microscopy (EC-AFM) to achieve a multi-dimensional characterization. The PM-ATR-IR analysis allowed us to track dynamic changes in interfacial water content, while EC-AFM provided direct probing of the layered structure. These combined results unveil the fundamental nature of the EDL far from the PZC, offering new insights into the correlation between interfacial water organization and charge distribution.

Electrocapillary Coupling – Surface Phenomena and Implications for Materials Behavior

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Surfaces often exhibit a strong coupling between their mechanical and their chemical or electrochemical state variables. The underlying materials parameter is an electrocapillary coupling constant, which is characteristic for the surface and for the electrode process. That parameter controls the local stress response to electric charging, the electric potential response to mechanical strain, and the strain-dependence of adsorption enthalpies. For selected model problems, there is excellent consistency between phenomenological description, experimental observation, and numerical simulation. Yet, a general predictive theory for the magnitude of the coupling constant remains elusive. One example relates to the work-function strain response of metal surfaces, which is governed by a small – and, hence, poorly predictable – difference between the numerically large strain-dependencies of Fermi energy and surface dipole. Irrespective of the missing theory, the local coupling phenomena are highly relevant for the electrode-potential strain response and for catalysis with strained surfaces. At the materials scale, the long-range nature of elastic interaction implies that the local surface stresses couple strongly into the bulk behavior. Analogously to the Laplace law for fluids, a generalized capillary equation for solids quantifies the relation between surface stress, microstructure, and the mean stress state of the bulk. Its consequences are exploited in actuation with high surface area solids. The coupled mechanics also underlies a strong size dependency in the phase transformation behavior during charging/discharging of electrochemical energy storage materials, such as lithium compounds or metal hydrides.

Understanding Cation effects in Alkaline Hydrogen Evolution Reaction: An Electrostatic Perspective

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Cation identity and concentration in alkaline electrolytes strongly influence electrocatalytic processes, yet their effects remain insufficiently understood. Taking hydrogen evolution reaction (HER) in alkaline media as a model system, variations in cation concentration induce complex, sometimes inverted, activity trends. Increasing cation concentration can either promote or inhibit electrocatalytic activity depending on cation identity, electrode material and solution pH [1]. These Janus-faced roles of cations challenge the current understandings of cation effects in electrocatalysis, which typically emphasize either promotional or inhibitory aspects.

The present work proposes a mechanistic rationale for the promoter-inhibitor transitions of cation effects and identifies cation position in the electric double layer (EDL) as the key factor governing this behavior. The theoretical framework that is introduced includes a refined EDL model that distinguishes two cation states: cations electrostatically attracted in the diffuse layer, and cations specifically adsorbed at the inner Helmholtz plane. Incorporating the electric field effect on water dissociation beyond the Frumkin correction, the model shows that the two cation states modulate the local electric field and thus HER kinetics in opposite ways, *i.e.*, specifically adsorbed cations suppress activity, while diffuse-layer cations enhance it. The observed inversions result from their competition, governed by cation size and adsorption strength [2]. The framework thus consistently explains the intricate effects of cations in alkaline HER electrocatalysis, and the insights gained will also be relevant to other electrocatalytic reactions at strongly negatively charged surfaces, such as CO_2 reduction.

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Abstracts of Posters

(in alphabetical order)

Solvent effects on the reaction entropy of an outer sphere electron transfer process

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Solvation plays an important role in electrochemical systems affecting interfacial structure, reaction thermodynamics and charge-transfer kinetics. While aqueous systems have been widely studied, solvation in organic solvents remain less well understood.

The redox couple $[Ru(NH_3)_6]^{2+}/[Ru(NH_3)_6]^{3+}$ is a classical example of an outer sphere electron transfer process and therefore well suited for studying solvent effects. Using electrochemical microcalorimetry [1], we determined the reaction entropy of this one electron transfer in water, methanol and DMSO. We analyzed the pronounced solvent-dependent differences in the framework of Y. Marcus' solvation model [2], which separates the solvation entropy into two contributions: (1) the strong immobilization of solvent molecules in the first solvation shell and (2) long-range electrostatic interactions (Born entropy).

We extended this approach to mixtures of DMSO and water to explore the composition dependence of the long-range and short-range entropy contributions.

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Dynamics of Au electrode surfaces probed by electro catalytic reactions

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While Au(111) single crystals often have an unreconstructed (1x1) surface, the reconstructed surface, known as the herringbone structure, is thermodynamically favored, but its formation is kinetically hindered at room temperature. Thermal annealing or low electrode potentials can induce the formation of the reconstructed surface, while specific adsorption of anions lifts the reconstruction. The reconstructed surface is more densely packed than the unreconstructed (1x1) surface. Therefore, lifting of the reconstruction leads to the formation of islands on the surface. Changes in the surface structure lead to differences in the catalytic activity. The hydrogen evolution reaction (HER) was used as a probe for the different surfaces and the potential-induced reconstruction.

In-situ scanning tunneling microscopy (STM) was used to image the Au(111) surface at various potentials. The well-known herringbone structure of the reconstructed surface was observed as well as the formation of islands after lifting of the reconstruction. The reconstruction kinetics at different potentials were investigated. The disappearance of the islands was observed while the structure of the potential-induced reconstructed surfaces differed slightly. The herringbone structure was formed at higher potentials, while parallel rows were formed at lower potentials.

Electrochemical investigations of Au(111) in 0.1 M H_2SO_4 and 0.1 M $HClO_4$ were conducted. Using the HER as a probe reaction, it was observed that the kinetics of surface reconstruction is potential-dependent. Furthermore, kinetic parameters of the reconstruction were investigated. It was found that the rate constant decreases at more negative potentials. The activation energy of reconstruction at different potentials was estimated.

Presently, similar investigations are performed with an Au(100) single crystal. It was found that the HER can be used here as a probe as well, enabling further research. Yet again, an STM study is planned to image the surface structures.

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Capillary rise of electrolyte-alkane mixtures between gold plates: wetting transition or electrocapillary effect?

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The transition from partial to complete wetting of binary liquid mixtures in contact with a third phase upon changing the system's temperature, i.e. wetting transition, is a well-documented phenomenon [1]. If one of the liquid phases is an electrolyte and the mixture is in contact with a conductive medium, the electrolyte-solid surface tension, and therefore the wetting properties of the system, can be controlled upon applying an electrical potential. To explore the possibility of a wetting transition controlled by electrical potential, we propose a completely novel approach by studying the capillary rise of an electrolyte-alkane binary mixture between two gold plates. Capillary rise of an electrolyte controlled by electrical potential – electrocapillarity - has been studied between dielectric plates [2] and can be explained by the Lippmann's equation. Our results present features that cannot be explained by an electrocapillary effect alone and using electrochemical impedance spectroscopy (EIS), we have conducted careful measurement of the system's capacitance to understand the nature of our observations.

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Comparing microcalorimetric and temperature-variation approaches for determining the reaction entropy of electrochemical reactions

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Measurements of the reaction entropy $\Delta_R S$ can provide valuable insights into the mechanisms of electrochemical processes at the electrode-electrolyte interface. Here we compare two approaches for its determination. Firstly, the reaction entropy can be accessed by measuring the reversibly exchanged heat with an electrochemical microcalorimeter [1]. Alternatively, the reaction entropy can be determined by measuring the temperature coefficient of the equilibrium cell voltage. Both approaches are applied for the determination of $\Delta_R S$ of the fast electron transfer reaction between $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ in aqueous solution.

Experimentally, the home-built electrochemical microcalorimeter [2] can be used to measure the small heat exchange at the interface upon a short current pulse with a sensitivity of a 1% change of a monolayer referred to the electrode surface. Temperature coefficients, on the other hand, can be measured by applying stepwise temperature changes either to one electrode (non-isothermal) or to the entire electrochemical cell (isothermal).

Both methods show similar entropy values of $-145\ J\ mol^{-1}\ K^{-1} \pm 10\ J\ mol^{-1}\ K^{-1}$. We explicitly discuss benefits, accuracy and reproducibility of each method. Furthermore, the influence of the entropy of transport $\Delta_T S$ is discussed based on entropy measurements in solutions with different supporting electrolytes.

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Confinement effect of cation on proton transport

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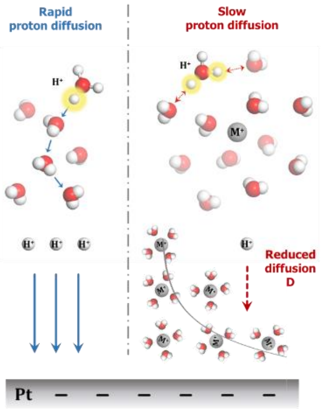
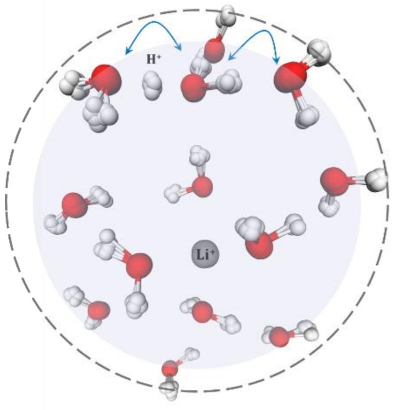
Protons, as one of the most fundamental and ubiquitous chemical reactants, play a pivotal role in both natural processes and modern energy conversion devices[1]. Over the past century, proton transport in pure water systems was established by Grotthuss mechanism, Eigen-Zundel structure, and the flowing delocalization between these, to understand the anomalously fast intrinsic diffusion and the molecular-level equilibrium and transfer structures[2,3]. However, in more complex electrolyte environments, the disturbed water hydrogen-bond network by electrolyte ions, and the uneven species distribution at interfaces pose significant challenges to understand the ion–water–proton interactions at interfaces and their dynamic impact on proton transport.

Here, we found a singular confinement phenomenon beyond classical electrostatic interactions between cations and protons in electrochemical measurements. The proton diffusion coefficient was reduced in alkali cation electrolyte and exhibited a distinct dependence on both cation species and concentration surprisingly. RP-AIMD simulations reveal the interactions among cations, water molecules, and protons. Protons exhibit a high spatial probability density around cations, which we term "proton confinement effect" of cations. Further spectroscopic evidence, combining the analysis of thermodynamic equilibrium states with reorientational dynamics, comprehensively analyzed the molecular-level picture of this phenomenon. The insights of structure and dynamic into cation–water–proton interactions provide a basis for a more comprehensive understanding of proton behavior and complex interactions between molecules at electrochemical interfaces.





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A thermodynamic origin of ion-specific adsorption at charged interfaces

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Ion-specific adsorption at charged interfaces and in confined spaces, where electric double layers (EDLs) usually overlap, strongly depends on ion–interface interactions, yet the thermodynamic origins of this behavior remain elusive. By integrating concentration-dependent adsorption isotherms obtained from atomic force microscopy (AFM) with molecular dynamics (MD) simulations, we resolve interfacial thermodynamics at molecular scale. We show that origin of forces driving adsorption behavior as a balance between electrostatic (ion-surface, ion-water and ion-ion) and entropic contributions, mediated by interfacial dielectric variations. In particular, ion hydration is treated here as quantitative descriptor that serves as the basis for evaluating thermodynamic observables. Orientational and translational pair correlations between ion-water and water-water pair are used to compute entropic contributions. Electrostatic interactions are approximated using a classical model of pairwise interactions at the interface. In this model the effective interfacial dielectric constant is the only unknown variable whereas other parameters (*e.g.,* pairwise distances, dipole orientations, interfacial water density), are fixed by atomistic simulations or experimental observations from sub-nm AFM imaging. Overall, we demonstrate that small or highly charged ions strongly perturb the interfacial water network, compressing its structure and imposing substantial entropic costs. These effects enhance dielectric screening near the interface, thereby reducing ion–surface interactions. In contrast, larger ions experience lower entropic penalties upon adsorption and significantly diminish dielectric screening through depletion of interfacial water, promoting charge inversion at the inner double layer induced by excessive adsorption of counterions (overadsorption).

Single-molecule detection of small molecules enabled by charge regulation at the solid–liquid interface of silicon nitride solid-state nanopores.

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Solid-state nanopores are promising tools for label-free single-molecule sensing, but the detection of small molecules remains challenging because of their weak electrical signatures. In this work, silicon nitride (SiNx) solid-state nanopores with diameters of 2 nm and 4 nm were used to detect perfluorooctanoic acid (PFOA) in 1 M LiCl at pH 8 and pH 4. By varying nanopore size and solution pH, we investigated how nanoscale confinement and solid–liquid interfacial charge regulation affect the sensing of small molecules. The results show that solution pH strongly influences the nanopore response to PFOA, likely through changes in the surface charge of SiNx and the ionization state of PFOA. In addition, measurements with different pore sizes reveal the importance of nanoscale confinement in small-molecule sensing. These findings demonstrate that interfacial charge regulation provides an effective strategy for improving the detection of small molecules in solid-state nanopores.

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DPχ: A Constant-Potential Machine-Learning Potential for Large-Scale Electrocatalysis

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Electrocatalytic interfaces span both femtosecond-to-second temporal scales and angstrom-to-micrometer spatial scales. Owing to its O(N^3) computational cost, ab initio molecular dynamics (AIMD) is typically limited to systems containing only hundreds of atoms over picosecond timescales, making it difficult to obtain equilibrated electric double layers (EDLs) and reaction free-energy landscapes under realistic conditions. Although conventional machine-learning potentials can greatly reduce the computational cost, their local descriptors neglect long-range charge transfer (LRCT) and nonlocal charge redistribution (NLCR), which limits their direct applicability to electrochemical systems. To address this issue, recent developments have focused on hybrid frameworks that combine explicit electrostatics with short-range neural networks. Depending on the charge representation, these approaches can generally be classified into atomic-charge (AC) and Wannier-center (WC) schemes. AC-based methods facilitate the imposition of conservation laws and locality constraints and can capture LRCT/NLCR to some extent, but their transferability remains uncertain. WC-based methods are more closely rooted in first principles and can accurately reproduce near-field electrostatics, yet they fix the electronic population on each atom and thereby suppress interatomic charge flow, which may lead to failure in metallic or conjugated systems.

Motivated by these limitations, we develop DPχ, a constant-potential machine-learning potential in which Bader-basin centroids (BCs), rather than Wannier centers, are used as the charge-representation nodes. In DPχ, the atomic charge is explicitly decomposed into two components: (i) a ″chemical″ component predicted by a neural network, and (ii) a ″conductor″ component that is restricted to metallic sites, satisfies the electroneutrality constraint, and responds self-consistently to the external field. During molecular dynamics simulations, the conductor component is solved on the fly using a Siepmann-Sprik-like polarizable electrode model, which adaptively redistributes charge between the working and counter electrodes and thus realizes constant-potential dynamics without explicitly imposing the Fermi level. Replacing WCs with BCs preserves the far-field electrostatic accuracy of the former while allowing fractional quantum charge transfer across metal-water interfaces, thereby overcoming the artificial restriction on interatomic charge flow inherent to WC schemes with fixed atomic electron numbers. Using the Pt(111)-H2O interface as a representative example, we show that DPχ can reproduce, at large scales, forces, interfacial potential drops, hydrogen evolution reaction barriers, and vibrational spectroscopic fingerprints in agreement with both experiment and first-principles calculations. DPχ therefore provides a practical route for predictive mechanistic studies of electrocatalysis under realistic electrochemical conditions.

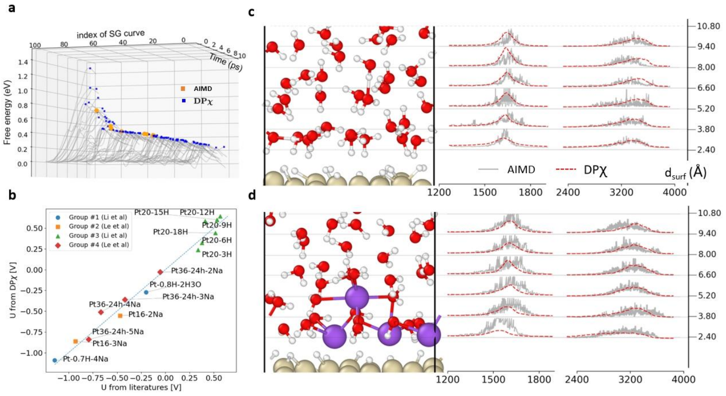

Fig. 1 (a) Reaction barriers from DPχ and AIMD . (b) Interface potential benchmarking: literature vs. DPχ. (c-d) Layer-resolved VDOS for acid and basic Pt111 around 0 V vs RHE: literature (gray dashed) vs. DPχ (red).

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Poisson-Boltzmann theory in practice

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This poster presents a double-layer model based on Poisson-Boltzmann theory, with an open-source implementation at github.com/lucasdekam/frumkin. The model incorporates dielectric saturation and finite ion size effects, and a simple boundary condition that allows the permittivity of the Stern layer to vary with the electric field. There are only three main parameters to choose: the distance of closest approach for ions, the limiting value for the permittivity of water at strong electric fields and the hydrated ion size. We show that for a single reasonable choice of these parameters, we can rationalize the following experimental data. (I) capacitance: the model predicts a correct camel shape with capacitance values in reasonable agreement with experiments [1], and shows that dielectric saturation plays an important role, in agreement with Ref. [2]; (II) XPS intensities of interfacial cations [3]: the model reproduces the experimentally observed saturation of the cation concentration at the interface; (III) kinetics: a kinetic model [4] incorporating a Frumkin correction from the Poisson-Boltzmann model fits recent experimental data [5], suggesting a Tafel-like law. These examples demonstrate that a simple continuum model, paired with an easy-to-use Python implementation, captures the essential physics of the double layer and provides a baseline to distinguish expected behavior from unexplained phenomena.

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Electronic and Ionic Charge Redistribution in Electric Double Layers under Curvature and Steric Constraints

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The understanding of the electrical double layer (EDL) has been established using well-defined, single-crystal electrodes. However, real electrochemical interfaces are polycrystalline, rough, and nanoporous. The surface heterogeneity resulting from steps, kinks, and edges creates distinct EDLs at the local level [1]. The spatial overlap of these layers redistributes the ionic charge across neighboring facets [2]. In nanoporous electrodes, finite ion size modifies this response further through steric confinement, and nonplanar pore walls introduce curvature-induced electronic inhomogeneity. Thus, elucidating the EDL in realistic electrodes necessitates moving beyond the planar, single-crystal model and incorporating surface heterogeneity, double-layer overlap, curvature, and steric constraints on an equal footing.

The present work demonstrates that the geometry of cylindrical pores can significantly alter the coupled electronic and ionic charging of silver electrodes immersed in nonadsorbing aqueous electrolytes. Within the Density Potential Functional Theoretical framework (DPFT), the work function increases with decreasing pore diameter due to curvature-induced electronic reorganization. However, the potential of zero free charge changes much more weakly because solvent dipoles partially screen this response. Steric confinement suppresses solvent density at the interface through ion enrichment, thereby strengthening the correlation between the PZFC and the work function compared to unconfined curved surfaces. This enhanced coupling results in more pronounced heterogeneity in charging between the pore interior and outer surface as pore diameter decreases. Consequently, the global PZFC no longer marks a unique cation-anion crossover point across the entire interface in small pores. Especially for a 1-nm pore, the differential capacitance curve develops two local minima, which are predominantly associated with the charging crossovers of the outer surface and the pore interior, respectively.

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Entropy Profiling of Hard Carbon/Na Metal Batteries with Stepwise Temperature Changes: Deciphering the Cell Voltage Response

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The entropy of the cell reaction of a battery as a function of the state of charge (SoC) provides valuable information on the ongoing electrochemical processes. It can be determined by measuring the temperature coefficient of the equilibrium cell voltage at a respective SoC, often called entropy profiling. In conventional entropy profiling experiments the temperature variations take more than ten minutes. [1,2] In contrast, we applied stepwise temperature changes to the electrochemical cell on the timescale of several seconds, which opened two perspectives. Firstly, the kinetics of the electrochemical processes during the readjustment of the new electrochemical equilibrium were reflected in the cell voltage response upon the fast temperature changes. In addition, the precision of the measurement was improved, e.g., by reducing the influence of baseline drift of the cell voltage.

In this study, we investigated the sodiation of hard carbon (HC), the common material for the negative electrode of sodium-ion batteries, at different SoCs.[3] Dependent on the SoC, characteristic features appeared in the cell voltage response on the temperature step. These features could be explained with a simple simulation of the cell voltage response including temperature gradients across the cell as well as Butler-Volmer type reaction kinetics for the processes at the HC and the Na metal electrode. Whereas for high SoCs of the HC electrode the sodiation process was fast, we found considerably delayed equilibration of the cell voltage at low SoCs, which we attribute to sluggish sodiation kinetics of HC at low SoCs.

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Impact of Electrolyte pH on the Morphology of Silver Electrodeposition Studied Using in-situ Transmission Electron Microscopy

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Control and regulation of the morphology of electrochemically deposited metal nanostructures is key for optimising applications including sensors, microelectronics and electrocatalysis. *In-situ* liquid phase transmission electron microscopy (TEM) can be used to monitor the evolution of both morphology and crystal structure at the nanoscale.[1] Commercially available electrochemically optimised chips (e-chips) can be employed to create an observable electrochemical cell environment within the vacuum of the electron microscope, thus growth, degradation mechanisms, and morphological changes can be visualised in real time.

Electrodeposition is frequently employed as it is a versatile, low-cost technique, that allows for direct attachment and subsequent growth of metal nanostructures on substrates. Deposition mass, thickness and morphology can be controlled by tuning the properties of the electrolyte solution, as well as the electrochemical parameters. In this work, we explore the impact of pH on the deposition mechanism and morphology of silver. Variations in morphology give rise to distinct crystallographic facets and exposed active sites, thereby influencing stability, active surface area and performance. Direct observation of these features by TEM is therefore critical to understanding how these are formed, in turn improving our knowledge of electrocatalysts.[2]

Herein, in-situ TEM was used to observe the growth regimes of different electrolyte compositions. To verify that the morphologies were not attributed to the confined geometry of the electrochemical cell or to adverse effects from the microscope (e.g., electron beam damage or radiolysis), complementary bulk-scale experiments were performed in the same electrolyte. . From this we were able to define a clear relationship between electrolyte composition, the expected electrochemically active deposition species and the resultant morphology.

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Scanning Impedance Microscopy under Potential Control to Probe Local Electrochemical Properties

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Electrochemical impedance spectroscopy (EIS) is among the most widely used electrochemical techniques for studying the electrochemical double layer and the kinetics of electrochemical reactions. In global EIS measurements, the observed results are averaged over the entire measuring area and may yield ambiguous or misleading interpretations, especially for non-uniform or heterogeneous samples.

The advantage of scanning electrochemical microscopy (SECM)- based techniques is that they allow EIS measurements to be conducted locally on the sample of interest. The acquired information corresponds to local variations in charge-transfer resistance, adsorption behavior, double-layer capacitance (C_{dl}), potential of zero charge (pzc), and apparent rate constants (k_{app}) on non-uniform materials.

The local EIS measurements are performed using a four-electrode SECM setup with independent potential control of the microelectrode tip and the catalyst sample in low-concentration aqueous electrolytes. Recorded EIS spectra were fitted with a physical equivalent electric circuit to examine local changes in electrochemical double-layer properties. The determined local C_{dl} and pzc of polycrystalline (pc) Au in 1 mM $HClO_4$ were found to be consistent with those of independently conducted global measurements, validating our methodology [1]. In addition, kinetic insights were examined by determining k_{app} of the oxygen reduction (ORR), nitrate reduction (NO_3RR), and hydrogen evolution (HER) reactions for a variety of samples. Au (pc) model systems were employed for the ORR, NO_3RR, and HER, while copper-gold (Cu/Au) and silver-gold (Ag/Au) monolayer systems, prepared via underpotential deposition (upd), were used to explore the NO_3RR and HER. The k_{app} dependency on the applied potential during the ORR aligns with the kinetics of the 2-electron reduction of O_2 on Au [1]. Furthermore, the results reveal higher site-specific activity during NO_3RR on Cu/Au and Ag/Au compared to pure Au, demonstrating the potential to guide the rational design of heterogeneous electrocatalysts in the future.

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Using electrochemical impedance spectroscopy to deconvolute (pseudo) capacitance from metal oxide interfaces

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The electric double-layer at the electrode-electrolyte interface is crucial for electrocatalytic reactions in electrochemical applications, such as water splitting. On metal oxide surfaces (α-Fe_2O_3, RuO_2 or Ni(Fe)OOH) in aqueous electrolytes, proton exchange between interfacial water and surface M-O(H) groups varies with pH and potential, giving rise to pseudocapacitive charging, intercalation, and charge transfer alongside classical EDL charging.

Using impedance spectroscopy, we deconvolute these parallel processes to reveal mechanistic insights. For α-Fe_2O_3(0001), the charge transfer resistance (R_{ct}) associated with adsorption pseudocapacitance decreases with Na^+ concentration but is pH-independent at a fixed Na^+ concentration, while the double-layer capacitance remains constant, indicating a compact Helmholtz-type layer with negligible diffuse contributions. This highlights that cations mediate the proton-coupled electron transfer (PCET) acid−base reactions.

In contrast, porous NiFeOOH exhibits ultrahigh capacitance and low R_{ct} due to cation intercalation, forming a confined EDL with diffusion-limited local charging. Acid-base and electrochemical equilibria cause counter-intuitive cation attraction at more positive potentials. We present some new distribution of relaxation times (DRT) data and pH-dependent studies near the point of zero charge on RuO2(110) where it is possible to measure R_{ct} under slower proton transfer conditions.

This work demonstrates how advanced impedance analysis can deconvolute “classical” and pseudocapacitive contributions to the EDL, revealing the interplay between proton adsorption, metal oxide oxidation, and cation-mediated charge transfer. Understanding these processes provides a foundation for correlating EDL formation on transition metal oxides with their electrochemical behaviour.

Influence of the electronics and cell resistances on electrochemical noise measurements

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Electrochemical noise is what we call fluctuations in current or potential around the average value in our measurements. These fluctuations occur for many different reasons, and in the field of electrochemistry are non-desirable. There are examples in the literature, connecting noise characteristics to the chemical reactions observed within a monolayer of molecules adsorbed onto an electrode[1][i]. In this poster we discuss one of the most crucial detail in noise measurements – the thermal (also called Johnson-Nyquist) noise of the resistive part of the system.

A common measurement setup can be often separated into two parts: the instrument, and the electrochemical cell. We compare two setups, one using a common potentiostat and another using a patch-clamp amplifier with a pre-amp headstage. Chronoamperometry using physical resistors is a quick evaluator of whether equipment can be used for electrochemical noise measurements, or its internal noise overwhelms the electrochemical shot noise coming from redox reactions. Thermal resistance of the electrochemical cell is more complex as it depends on ion diffusion, and electrolyte properties.

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Anion-Water and Hydroxyl Adsorption at the Pt(111) Interface: Influence of pH and Electrolyte Composition

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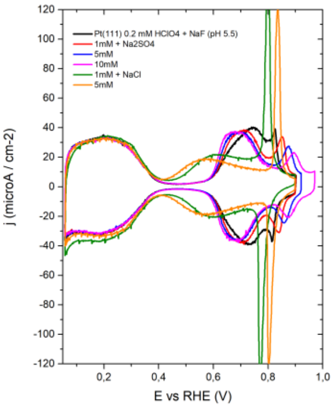
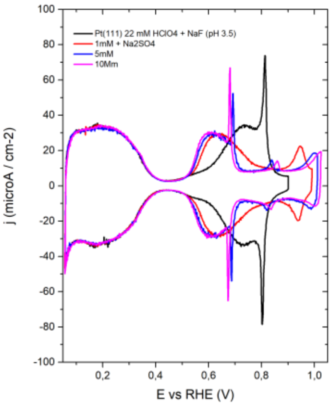
The study of anion adsorption processes occurring in association with H_2O molecules and hydroxyl (OH) coadsorption at the Pt(111) interface is essential for understanding electrocatalytic reactions in which this interplay may alter charge-transfer dynamics and facilitate specific reaction pathways, since H_2O acts as the universal oxygen-atom donor[1].
To elucidate the anion–H_2O-hydroxyl interaction, we investigated Cl^- and SO_4^{2-} anions in $HClO_4$ and CH_3-SO_3H solutions within the pH range $3 < pH < 6$ using cyclic voltammetry. The results indicate the existence of a balance between the adsorption energy of the specifically adsorbing anion (Cl^- or SO_4^{2-}) and that of the OH species originating from H_2O molecules that replace an adsorbed anion–H_2O ensemble[2].
On the one hand, experiments performed by varying the pH at a fixed Cl^- or SO_4^{2-} concentration show that increasing the pH shifts the onset of anion adsorption to higher potentials, while OH adsorption occurs at lower potentials, indicating that anion adsorption becomes weaker at higher pH. On the other hand, increasing the anion concentration at constant pH shifts the onset of anion adsorption to lower potentials and, consequently, the adsorption of OH occurs at higher potentials (see Figure below).This study contributes to a deeper understanding of interfacial phenomena and its influence on electrocatalytic processes.





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The effect of bias and temperature on interfacial water at **pristine** Pt(111) electrodes: Insights from atomistic MLIP simulations

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Electrode charge and temperature are key control parameters that determine the electronic and structural characteristics of the electrical double layer.

In this work, we employ the response-augmented machine-learning interatomic potential framework RAZOR (Response Analysis in z-Orientation) to model electrified Pt(111)/H_2O interfaces under finite bias conditions. RAZOR extends machine-learning interatomic potentials to charged systems by learning the first-order energy and force response to an applied bias. This approach enables robust atomistic simulations of electrified interfaces without the need to introduce explicit ions.

Using molecular dynamics simulations, we examine two observables of the interface: the work function and the connectivity of interfacial water, and how both respond to changes in charge and temperature.

This analysis provides molecular insight into the temperature-dependent electrical double layer behavior which can be probed by temperature-jump experiments. It further illustrates the capability of the RAZOR framework to link atomistic simulations with experimental observations.

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Surface Electrochemistry of the Au(111)/acetonitrile Interface: Formation of a Solvent Related Adsorbed Layer and its Implications for the Electrochemical Double Layer

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Studying the properties of the electrochemical double layer (EDL) at metal/non-aqueous solvent interfaces is important both technologically and for understanding the role of the solvent in the EDL. However, challenges with confidently identifying a double layer window and performing measurements with sufficient cleanliness have meant that understanding of these interfaces remains significantly less advanced compared to their aqueous counterparts.

Here we report electrochemical characterization of the Au(111)/acetonitrile interface in demonstrably clean conditions. Interestingly, cyclic voltammetry (CV) shows no Gouy-Chapman-Stern (GCS)-like capacitance minimum or concentration dependent behaviour. Instead, the non-catalytic potential window is dominated by an oxidative adsorption reaction which leads to the formation of an interphasial layer on the Au(111) surface. This layer forms due to the adsorption of acetonitrile, and also contains electrolyte ions. The presence of the adsorbed layer is confirmed by ex situ electrochemical characterization and X-ray photoelectron spectroscopy.

Our findings have several interesting implications about EDL structure. First, our results seem to contradict previous reports on this interface, which have shown qualitative alignment with GCS theory. This discrepancy may arise from the use of alternating current methods in these works, which might not fully capture the adsorption process. Interestingly, by accounting for an interphasial layer we can rationalize several unexplained issues in these works. Second, the ionic species in the adsorbed layer will participate in screening electric charge in the EDL. Having (part of) the charge contained in a surface confined layer may imply EDL properties fundamentally different from those observed at aqueous electrochemical interfaces. Third, we discuss the generality of interphasial layers for metal/non-aqueous interfaces by presenting CV characterization of various solvents and metals.

Machine-Learning-Accelerated First-Principles Simulations Reveal Ion-Correlated Structures at Concentrated Electrochemical Interfaces

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Understanding the microscopic structure of the electrical double layer in concentrated electrolytes remains a central challenge in electrochemistry. Recent experiments at metal–water interfaces have revealed anomalous capacitance behavior, non-classical screening lengths, and spectroscopic signatures suggesting multiple interfacial water states. These observations point to strong ion correlations and heterogeneous interfacial environments that remain difficult to fully capture within classical mean-field theories and conventional molecular dynamics simulations. Here we address the question: what is the real microscopic structure of the electrical double layer under concentrated electrolyte conditions? We employ large-scale molecular simulations based on machine-learned potentials trained to near first-principles accuracy, enabling atomistic simulations with both quantum-level fidelity and long time–length scales inaccessible to *ab initio* molecular dynamics. Our simulations reveal pronounced ion layering and strong ion–water correlations near the interface, including partially desolvated cation configurations involving shared hydration structures. These correlated arrangements generate spatially heterogeneous electric fields that induce distinct orientations and vibrational responses of interfacial water molecules, providing a microscopic picture consistent with emerging spectroscopic observations. The results highlight how quantum-level interactions and ion correlation effects reshape the classical picture of the electrical double layer, demonstrating the power of machine-learned simulations for resolving complex interfacial phenomena in concentrated electrochemical environments.

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Long-Range Ordered Pt Facets Govern Methane Electro-oxidation via Interfacial Solvent Dynamics

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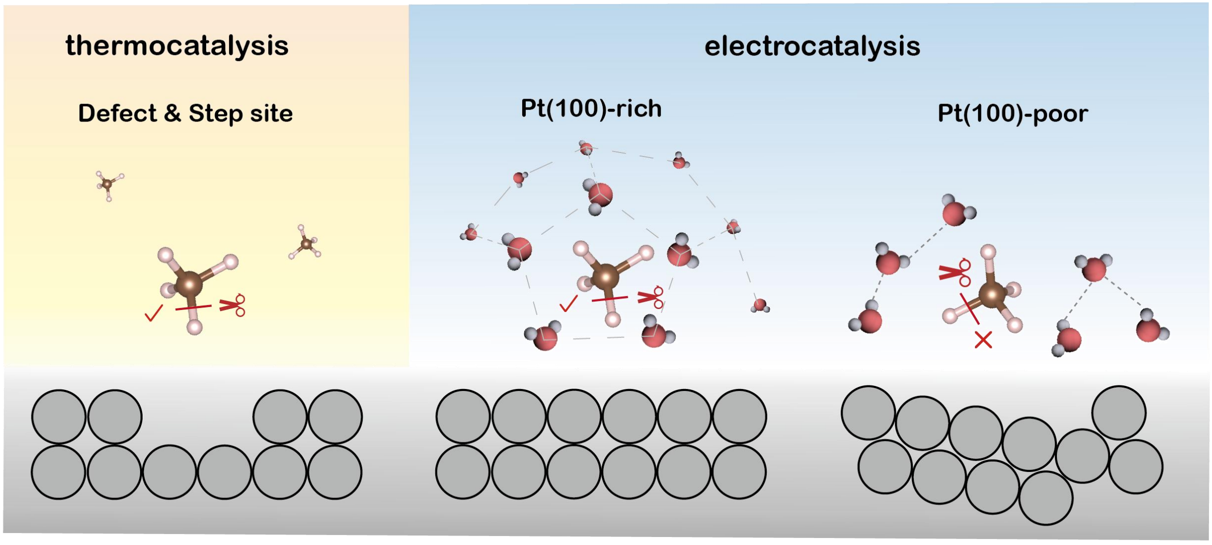
A fundamental distinction between electrochemistry and thermochemistry lies in the nature of the electrified solid-liquid interface, a unique environment that profoundly modulates reaction thermodynamics and kinetics. The Methane Oxidation Reaction (MOR)—often hailed as a "holy grail" in catalysis due to the high stability of the C-H bond — exemplifies this divergence. In contrast to thermal catalysis, which typically favors under-coordinated sites such as steps or defects, electrochemical MOR exhibits a distinct preference for long-range ordered Pt(100) terraces.

By constructing surfaces with varying Pt(100) domain sizes through both first-principles calculations and experiments, and probing interfacial water structures via Polarization-Modulated Infrared Reflection-Absorption Spectroscopy (PM-IRRAS) and Vibration Density of States (VDOS), we attribute this selectivity reversal to the fundamental physics of the electrified interface: the long-range order of the metal surface dictates the surface charge distribution, thereby defining the interfacial capacitance. This capacitance imposes strict constraints on the structural entropy of the interfacial water network, ultimately governing the selectivity and kinetics of key elementary steps.



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Linking Interfacial Water Structure to AFM Forces under Electrochemical Control

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Electrochemical reactivity is governed by the structure and polarization of the electrical double layer (EDL) at the electrode-electrolyte interface. Electrochemical 3D atomic force microscopy (EC-3D-AFM) has been used to map interfacial liquids with atomic scale resolution. However, a quantitative link between measured force and microscopic EDL structure remains nontrivial because the signal contains coupled contributions from hydration layering, ion specific adsorption, and electrostatics [1-3]. Prior work has demonstrated strong ion type and concentration dependence of hydration forces, including changes in the monotonic force background and the suppression or persistence of oscillatory layering depending on cation hydration strength [4-5].

Here we propose a simulation driven framework to recreate AFM measured forces from molecular dynamics (MD) and use this as a mechanistic basis for interpreting EC-3D-AFM on crystalline metal surfaces under potential control. The approach uses MD of aqueous electrolytes near a crystalline metallic surface to compute tip-sample forces as functions of position, ion identity, concentration, and electrode potential, enabling direct comparison to experimental force curves and 3D force maps. By correlating the sign and range of the monotonic background with orientation resolved water layering, we test whether the expected water orientation flip near the potential of zero charge (PZC) is reflected in the EC-3D-AFM force signal. This workflow aims to turn EC-3D-AFM force data into quantitative descriptors of interfacial polarization and may provide a route to relate the PZC directly to measured forces in realistic electrolyte environments.

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Probing Surface Structure and Vibrational Stark Effects in Ni Anodes with SERS during Alkaline OER

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Electrochemical water splitting is a key technology for the sustainable generation of hydrogen. However, the overall process is often limited by the sluggish kinetics of the oxygen evolution reaction (OER) at the anode. To reduce the reliance on noble-metal catalysts such as Ir and Ru, Ni-based catalysts have attracted considerable interest over the last decades, due to their abundance and promising catalytic performance. Operando Raman spectroscopy provides access to the surface structure of Ni anodes, typically believed to be NiOOH under OER conditions. In this work, we combine isotope-labeled surface-enhanced Raman spectroscopy (SERS) with density functional theory (DFT) calculations to challenge the commonly suggested presence of NiOOH in alkaline electrolytes. Furthermore, we investigate the influence of pH, applied potential, and the ionic strength of the near-surface electrolyte on the Raman response.[1]

Isotope-labeled Raman experiments reveal that the surface of Ni anodes does not contain any hydrogen atoms under OER conditions. Based on DFT calculations, the observed Raman bands can be assigned to NiO_2 rather than NiOOH. In addition, we investigate the influence of electrolyte properties such as pH, ionic strength, and the nature of cations (Li^+ to Cs^+). At low electrolyte concentrations, no significant influence of either the pH or the cations are observed in the Raman spectra. However, at higher ionic strengths (≥ 0.1 M), clear variations in the Raman spectra appear that resemble changes induced by increasing the applied potential. We interpret these spectral shifts as a vibrational Stark effect caused by cations located within the electrical double layer. These cations generate a local electric field that perturbs the vibrational modes of the surface structures in a manner analogous to the effect of the applied potential.

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Constant-Potential Kohn-Sham-Poisson-Boltzmann Theory for Electrified Metal-Solution Interfaces

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The electrical double layer (EDL) at the metal–solution interface, shown in Figure 1(a), is a nanoscale region where quantum-mechanical metal electrons interact with nearly classical electrolyte species. Herein, we developed one-dimensional (1D) and two-dimensional (2D) constant-potential Kohn–Sham–Poisson–Boltzmann (KSPB) theory [1], incorporating the exact kinetic energy of metal electrons to model the EDL. Using this framework, we self-consistently obtain the distributions of electron density, electrostatic potential, ion densities, and the double-layer capacitance. We then use the 1D KSPB model to benchmark orbital-free density–potential functional theory in terms of double-layer capacitance, as shown in Figure 1(b). Our results indicate that a significantly smaller gradient coefficient in the Thomas–Fermi–von Weizsäcker (TFvW) functional than the default value of 5/3 is more appropriate for modeling the EDL. For the 2D case, we investigate the effect of metal shape on the double-layer capacitance, as illustrated in Figure 1(c). We find that the peak in C_{dl} at lower potentials increases more prominently when the metal has a circular geometry.

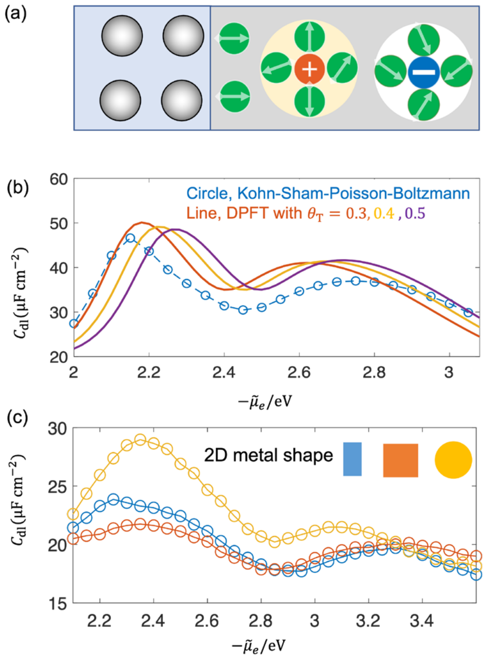

Figure 1 (a) schematic of the electrochemical interface consisting of a metal slab and an electrolyte solution, (b) comparison between the DPFT model with the TFvW functional and Kohn-Sham-Poisson-Boltzmann model in terms of the double-layer capacitance. Parameters used in calculation are as follows: $\bar{n}_{\mathrm{cc}} = 0.01$, $r_{\mathrm{s}} = 2.75$ Å, $r_a = 2.7$ Å, $r_c = 3.6$ Å, $n_{\mathrm{c,a}}^{\mathrm{bulk}} = 0.1$ M, $n_{\mathrm{s}}^{\mathrm{bulk}} = 55.6$ M, $p_s = 1.8$ D,$\epsilon_{\mathrm{op}} = \epsilon_{\mathrm{op}}^{\mathrm{M}} + \frac{(\epsilon_{\mathrm{op}}^{\mathrm{S}} - \epsilon_{\mathrm{op}}^{\mathrm{M}})}{2}\mathrm{erfc}\left(-\beta_{\mathrm{op}}(|X| - L_{\mathrm{M}})\right)$, $\epsilon_{\mathrm{op}}^{\mathrm{M}} = 3\epsilon_0$, $\epsilon_{\mathrm{op}}^{S} = 6\epsilon_0$, $D_{\mathrm{s}} = 0.5$ eV, $d_{\mathrm{s}} = 2a_0$, $\beta_{\mathrm{s}} = 1$, $L_{\mathrm{M}} = 20a_0$, $L_{\mathrm{S}} = 120a_0$.

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Cation Effects On Solvated Electron Generation

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Plasmonic materials can amplify electric fields, generate localized heating, and produce charged species with a limited lifetime when exposed to light, namely solvated electrons. These are highly reductive species, capable of catalyzing reactions relevant to sustainable chemistry. However, the yield of their generation from plasmonic nanoparticles is low, limiting their applicability. Therefore, it is important to identify the driving parameters behind their generation to improve it. Thus, probing the electrochemical activity of plasmonic nanoparticles under illumination is necessary to provide insights into the process.

This study explores the photoelectrochemical behavior of silver films under plasmonic excitation in four electrolyte systems, while varying the applied bias. We observe the generation of solvated electrons from silver films under plasmonic resonance conditions (λ = 385 nm). Furthermore, by varying the applied bias, we show that the photocurrent is consistent with the Brodsky-Gurevich model of electron photoemission. By varying the electrolyte cation, we also demonstrate the influence of the ionic environment on the photocurrent response. The photoemission increases for $K^+<Li^+<Na^+<Cs^+$. Finally, by comparing the photocurrent response across the four electrolytes, we reveal a correlation between electrolyte composition and efficiency, suggesting that electrolyte selection is crucial for efficient solvated electron generation.

Disentangling Temperature Effects in Proton Adsorption Barriers at Electrified Pt(111): Roles of Water Structure, Potential, and Vibrational Free Energies

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Proton adsorption at electrified metal–water interfaces is governed by a delicate interplay between electrode potential and interfacial water structure. Reaction barriers are often evaluated using idealized, ice-like solvent models at zero K, neglecting the complexity and thermal disorder of realistic interfaces. To bridge the gap between zero K models and finite temperatures, we sample interfacial water structures from ab initio molecular dynamics (AIMD) simulations. For each interfacial water structure, we run nudged elastic band (NEB) calculations in a quasi-static water environment, comparing barriers from thermally fluctuating ensembles to those obtained with ordered, ice-like overlayers. Further, we investigate the differences in the commonly used vibrational free energies—obtained from Hessian calculations—between ice-like and disordered water structures. In our comparison, we focus our analysis on the local coordination environment of the reacting H_2O/H_3O^+ species, quantifying how variations in hydrogen-bond arrangements and interactions with neighbouring water molecules influence the adsorption barrier, and how the barrier responds to changes in applied potential. With our combined approach of vibrational free-energy evaluation and disordered water structures, we aim to understand the gap between zero K barriers and dynamically sampled barriers. This perspective may help guide more realistic modelling of electrocatalytic processes under operating conditions.

Benchmarking QM/RISM method for the Au–Electrolyte Interface

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Modeling the electrical double layer at the electrode–electrolyte interface remains a major challenge in computational electrocatalysis. Owing to the typical size and complexity of these systems, ab initio molecular dynamics (AIMD) simulations are generally prohibitively expensive. As a result, combined QM/implicit approaches are often employed, in which the electrode and reactive species are treated at the DFT level, while the electrolyte is described by an implicit model. The most widely used implicit electrolyte model is the Poisson–Boltzmann framework and its variants, in which the solvent is represented as a dielectric continuum and the ions as continuous charge distributions. The reference interaction site model (RISM) has emerged as a less coarse-grained alternative. It is based on the molecular (rigid-body) Ornstein–Zernike equation and enables the calculation of particle–particle correlation functions for the electrolyte surrounding the explicit QM region. In this contribution, we investigate the capabilities and limitations of the QM/RISM [1] approach in its recently developed dielectrically consistent variant (DRISM) [2] for modeling the electrode–electrolyte interface. As a test system, we consider an Au electrode in contact with aqueous NaCl. We compare density profiles, differential capacitance, and adsorption energies, as well as their dependence on the electrode potential. We show that these properties are strongly influenced by the Lennard-Jones parametrization. In particular, by introducing pair-specific parameters for the solute–solvent interactions instead of relying on the commonly used Lorentz–Berthelot mixing rules, we increase the flexibility of the model. Our results demonstrate that, despite the intrinsic limitations of implicit approaches, there is still substantial room for improvement through modified pair-potential functional forms and parametrization.

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Double Layer Capacity at Pt(111) Electrode in Near-Neutral Electrolytes

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A detailed understanding of the electric double layer (EDL) structure is essential for describing the electrode/electrolyte interface, which underpins many electrochemical processes[1]. The charge stored at this interface strongly influences the structure of the EDL. This stored charge is governed by the potential of zero charge (PZC) and the differential double-layer capacitance (C_{dl}). However, determining these parameters for hydrogen-adsorbing metals such as platinum remains challenging and becomes even more complex at near-neutral pH.

Using buffered solutions containing non-specifically adsorbing anions (perchlorate and fluoride), we have shown that it is possible to obtain thermodynamically reversible voltammetric profiles up to pH 6[2]. Integration of the voltammetric currents, combined with CO charge displacement experiments and a non-thermodynamic extrapolation, allows determination of the potential of zero free charge (PZFC) at different pH values. For the determination of C_{dl}, we employ a thermodynamic method based on the work of Frumkin and Petrii[3] and later applied by Garcia-Araez et al.[4] in the range $1 \leq pH \leq 3$, extending it here to pH values close to 6. Analysis of the C_{dl} vs. charge curves reveals three main peaks, which likely correspond to solvent reorientation, the onset of OH adsorption, and the completion of the OH adlayer. The C_{dl} values obtained using this approach are compared with those reported by Pajkossy[5] and Koper[6] using other methods.

Knowledge of these fundamental properties improves our understanding of the EDL and could guide the rational design of electrode–electrolyte interfaces.

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Concentration dependent entropy determination for sodium deposition

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Sodium metal is a promising negative electrode material for future battery systems due to its high abundance, low cost, and high capacity. However, the deposition of Na at room temperature is accompanied by several issues, such as poor interfacial stability and non-uniform deposition, resulting in poor reversibility.[1] Therefore, a fundamental understanding of the deposition process from non-aqueous solvents, such as ethers and carbonates, is desirable.

In this study, electrochemical microcalorimetry was used to investigate the deposition of Na from electrolyte solutions of varying concentrations. The method allows the determination of the reversibly exchanged heat at a single sodium metal electrode during the deposition and dissolution of sodium. This quantity provides direct access to the reaction entropy. Since the reaction entropy of sodium deposition is strongly governed by the desolvation of Na^+ ions,[2] its concentration dependence can give insights into the ion-solvation environment.

Generally, a decrease in reaction entropy for Na deposition with decreasing Na^+ concentration is observed. The measured entropy differences for Na deposition between 1 M; 0.1 M and 0.01 M $NaPF_6$/PC electrolyte solutions without additive agree with the theoretically expected values from dilution. We found no indications of ion-pairing effects on the reaction entropy. Upon addition of 5 wt.% fluoroethylene-carbonate (FEC) an increase in reaction entropy is observed across the entire investigated concentration range studied in comparison to the FEC-free electrolyte solutions. This suggests the presence of FEC in the first solvation sheath of Na^+. Furthermore, the difference in reaction entropy for Na deposition from 1 M and 0.1 M $NaPF_6$/PC+FEC solutions is smaller than expected from pure dilution, which might point to the presence of ion-pairs in the 1 M solution. For lower concentrations $\leq$ 0.1 M the difference of the reaction entropy agrees well with the theoretically expected value from dilution, suggesting a negligible amount of ion-paring in the 0.1 M $NaPF_6$/PC+FEC solution.

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Electron Redistribution Between Coadsorbed Species at the Electrochemical Interface

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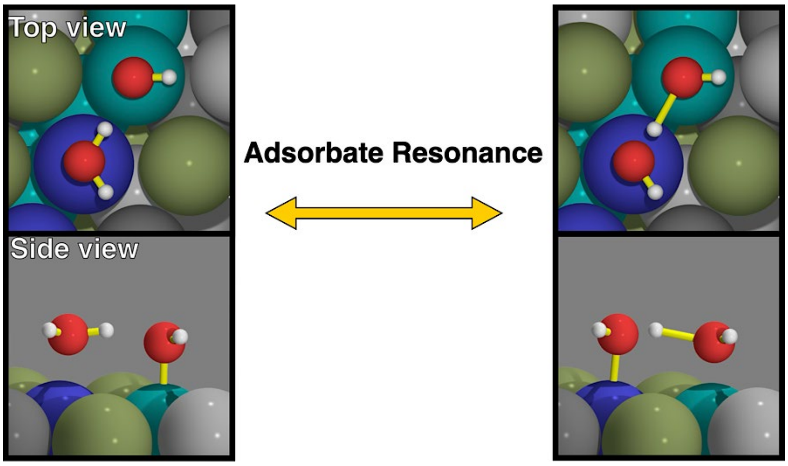

Part A

We explore how water and hydroxyl species interact when coadsorbed on metallic surfaces. Using density functional theory (DFT) calculations on thousands of high-entropy alloy (HEA) slabs, we identify conditions under which water forms covalent bonds with the surface. This behavior is linked to directional hydrogen bonding with adjacent hydroxyl, enabling electron redistribution between water and hydroxyl through enantiomer-like resonance structures. We have coined this phenomenon adsorbate resonance.

Part B

Building on the insights from **Part A**, we examine the coadsorption of sulfate and water at the Au(111)-electrolyte interface. Combining ab initio molecular dynamics and static DFT calculations with previous STM studies, we show that the initial formation of ordered sulfate chains - prior to the full disorder-to-order transition - is contingent on water coadsorption and associated electron redistribution. These findings provide a deeper understanding of the cooperative interactions between adsorbates in evolving interfacial structures.

The Computational Cation Electrode: A Case Study on CO2RR

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The electrochemical reduction of CO_2 offers a promising route to store renewable energy in chemical bonds while generating valuable products. Over the past decade, electrolyte cations have emerged as key players in governing CO_2 reduction activity and selectivity. Despite their recognized importance, computational treatments of cation effects remain inconsistent across studies. In this contribution, a computational cation electrode framework that establishes a coherent and transferable reference state for metal cations in Density Functional Theory (DFT) will be presented. We show that the reference state can have a significant effect on the energetics of CO2RR intermediates and we will suggest strategies for selecting appropriate bulk states for the computational cation electrode.

The influence of the Electric-Double layer and Cathodic Bias on the Ultrafast Dynamics of Silver Nanoparticles

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Transitioning the chemical industry away from fossil-derived feedstocks is critical for achieving net-zero emissions by 2050. Photoelectrochemical reduction utilizing plasmonic nanoparticle antennas represents a promising pathway for this process, particularly for its ability to tune product selectivity. Previous studies have demonstrated that illuminating AuNP@glassy carbon photoelectrodes can dramatically alter reaction pathways, shifting selectivity from carbon monoxide (generated under standard electrochemical conditions) toward more complex products like methanol[1].

However, the fundamental mechanisms governing these shifts remains unknown; specifically, the influence of applied bias potentials on the ultrafast dynamics of the localized surface plasmon resonance (LSPR) is poorly understood. In this work, we employ in situ transient absorption spectroscopy to investigate the carrier dynamics of silver nanoparticles under cathodic bias and varying electrolyte compositions.

Contrasting with conventional electrostatic models[2], we observe a distinct red-shift of the plasmon resonance upon the application of a cathodic bias, accompanied by a significant increase in the electron-phonon coupling lifetime. Furthermore, experiments wherein we vary the cations and thus the structure of the electric double layer[3], reveal spectral shifts dependent on the electrolyte-interface environment, indicating a large influence of the electrical double layer on the plasmon resonance. Additionally, the electron-phonon coupling lifetime is also influenced by the structure of the double layer. These experiments provide new insights on how the solid-liquid interface influences the plasmonic resonance and the generation of hot-charge carriers and offer a blueprint for engineering improved plasmonic photo-electro catalysts.

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First Steps Matter Most: Free Energy Barriers of the Volmer Step in Hydrogen Evolution at Pt(111)

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The Hydrogen Evolution Reaction (HER) plays a central role in hydrogen-based energy conversion. The initial Volmer step, involving proton adsorption at the electrode interface, is key to understanding reaction kinetics and the influence of pH. Conventional approaches to estimating barrier heights based on density-functional theory are limited by the need for reduced system sizes and short simulation times, which restrict statistical sampling and hinder fully converged free-energy calculations, particularly when solvent reorganisation is involved.

Here, we explore machine-learned interatomic potentials (MLIPs) combined with enhanced sampling techniques to gain more comprehensive insight into the reaction mechanism and barrier for the Volmer step at Pt(111) in dynamically described interfacial water and under alkaline conditions. Using collective variables that capture solvent reorganisation, we aim to account for dynamic environmental and solvent effects that are difficult to access with standard sampling.

We further investigate the applicability of the RAZOR (Response Analysis in z-ORientation) framework [1] to quantify how the interfacial water-structure response, and the barrier evolve under electrode charging/applied bias. Together, these approaches provide a pathway toward more consistent and physically grounded modelling of HER across different pH conditions.

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Probing Nafion structure at Electrified Pt Interfaces via in-situ Polarization-Modulated Infrared Spectroscopy

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In electrochemical energy-conversion devices, membrane-electrode assembly (MEA) interfaces govern the reaction kinetics and mass transport efficiency. In low-temperature MEAs, Nafion stands out as the benchmark proton-conducting ionomer, combining high proton conductivity with robust chemical/mechanical stability. However, classic electrical doble layer (EDL) models developed for electrode–electrolyte solution interfaces fail to adequately describe

Nafion–electrode interfaces, owning to the complexity of Nafion structure and its weak interaction with electrodes. To figure out this, it is both challenging and essential to probe the intricate Nafion structure at electrified interface and to detect the subtle Nafion–electrode interactions. In this work, we constructed a Nafion-covered Pt single-crystal electrode interface and implemented in-situ electrochemical polarization-modulated infrared reflection-absorption spectroscopy (PM-IRRAS) with superior surface sensitivity to elucidate the structural evolution of adsorbed Nafion at the electrified electrode interface. A key vibrational signature at 1320 cm^{-1}, assigned to the vs(S=O) stretching mode of the sulfonic group, was uniquely observed across a broad potential window only when the electrode surface was present. This provides direct evidence of the profound influence exerted by the electrode surface on Nafion adsorption. Furthermore, the enhanced characteristic bands when adsorbed on the surface metal corresponding to the symmetric stretching of ether groups (C-O-C, 970 cm^{-1} and 980 cm^{-1}) and the sulfonate group (-SO3-, 1060 cm^{-1}) were clearly observed. These findings offer critical spectroscopic insights into the molecular orientation and interaction mechanisms of Nafion at electrified interfaces, establishing a mechanistic foundation for the rational design of high-performance MEA.

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Machine-Learning Assisted Determination of Reaction Paths for Electrocatalytic Reactions

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The ongoing search for novel catalysts remains central to improving the efficiency and accessibility of green energy. Many methods applied today in both theoretical and experimental catalysis rest on the assumption that we know with certainty which catalytic reaction path is taken. However, this is far from always true.

For reactions with several possible intermediates, the network of potential reaction mechanisms can quickly grow highly complex. [1]

We propose a Gaussian Process machine learning model with Bayesian optimization, utilized in tandem with kinetic Monte Carlo (KMC) simulations of electrocatalytic reaction surfaces.

It is our goal to use this ML-model to fit the rate constants of elementary catalytic events directly to experimental electrocatalytic datasets, thereby allowing the data itself to show which reaction path is most consistent with the observed behaviour.

We are currently using the model to fit rate parameters to electrocatalytic CO oxidation on polycrystalline platinum and palladium electrodes. [2]

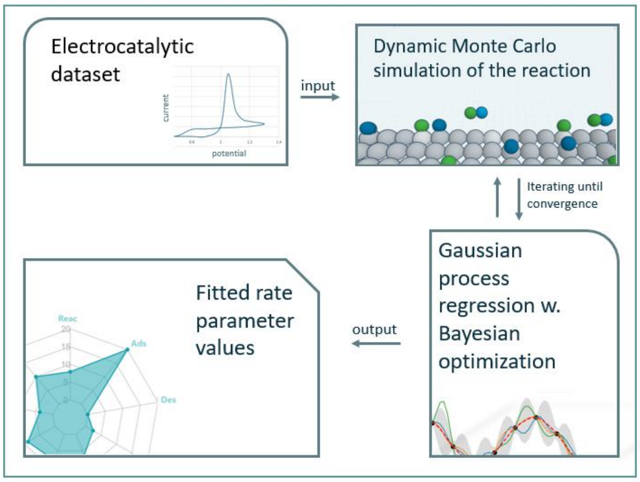

Figure 1: The workflow of our proposed Machin Learning model, used for fitting rate constant parameters to experimental datasets.

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3D porous model systems for electrocatalysis

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The use of porous metal as catalysts is promising to achieve a high activity, because of their high specific surface area. The surface area scales inversely with pore size and a higher surface area should result in higher current densities[1]. However, decreasing the pore size strongly influences the mass transport of different species like ions, solvent molecules and dissolved gases due to nanoconfinement. These effects of nanoconfinement are not yet well understood fundamentally. [2].

Using hard and soft templating strategies and electrodeposition, we synthesized well-defined (meso)porous materials with uniform pore sizes ranging from 18 nm to 370 nm, using well-known CO_2RR electrocatalysts like Ag and Au.(Figure 1) Such an ordered porous structure will act as a model system to achieve a fundamental understanding of the effects of nanoconfinement on the transport of different electrolyte species and the effect of nanoconfinement on physical properties such as solubility[3]. During CO_2 reduction, remarkable effects of pore sizes on catalytic activity and selectivity can be seen in the preliminary results[2]. The fundamental understanding obtained about the effect of nanoconfinement and transport of electrolyte species in the nanopores will help in better design of porous electrocatalysts and achieve higher current densities.

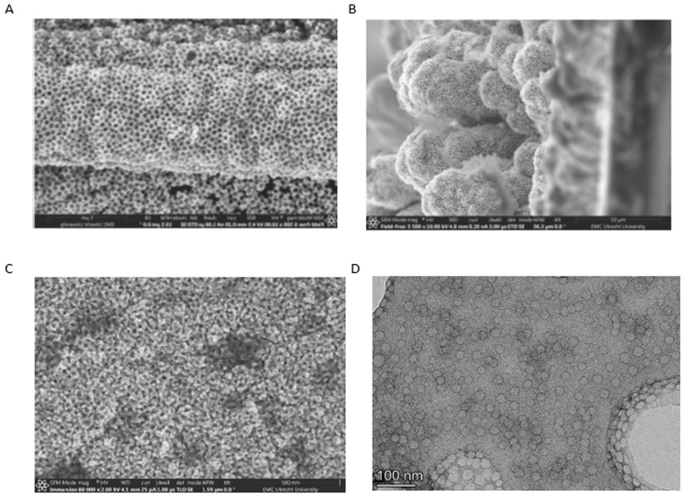

Figure 1: Electron Microscopy images of the order porous electrodes. A) Top-view SEM image of porous Ag(370 nm) on carbon paper. B)Cross-sectional SEM image of porous Ag. C) Top-view SEM image of mesoporous Au (18 nm) on Ag foil. D) TEM image of the micelle

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Raman Scattering Measurement of Single Nanoparticle Collision

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Understanding chemical processes at electrified solid–liquid interfaces is essential for elucidating electrochemical energy conversion and catalytic reactions. However, conventional ensemble measurements obscure the intrinsic heterogeneity of nanoscale interfaces, particularly during dynamic electrochemical events.

Single nanoparticle collision electrochemistry provides a powerful approach to probe the behavior of individual nanoparticles at ultramicro- or nanoelectrodes under electrochemical confinement[1]. This technique enables *real-time* observation of electrochemical reactions occurring within the electron-transfer region during nanoparticle impacts, revealing particle-to-particle variations in properties such as size[2], catalytic activity[3], and electronic structure[4]. Nevertheless, directly probing interfacial molecular species and ligand distributions during the collision process remains challenging.

Here we report an optical–electrochemical platform that integrates single nanoparticle collision electrochemistry with surface-enhanced Raman spectroscopy (SERS) to probe molecular processes at electrified interfaces. When a plasmonic nanoparticle collides with a plasmon-active substrate, a transient nanogap forms, generating intense electromagnetic "hot spot" that strongly amplify Raman signals from molecules confined within the gap.

This approach enables in situ Raman detection of interfacial molecules during individual nanoparticle collision events. By analyzing the evolution of Raman peak positions and intensities, we obtain molecular-level information on ligand distributions on nanoparticle surfaces and dynamic changes of interfacial species during electrochemical processes. The method provides a new route for probing heterogeneous electrochemical interfaces at the single-particle level and offers insights into nanoscale interfacial chemistry relevant to electrocatalysis and energy-related systems.

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Density-Potential Functional Theoretic (DPFT) Schemes of Modeling Reactive Solid-Liquid Interfaces

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Simulating electron transfer at reactive solid-liquid interfaces under constant electrochemical potentials of the constituents (electrons, ions, solvent etc.) is crucial to understanding the formation, function and failure of electrochemical devices and beyond. Albeit being sufficiently accurate in describing breaking and formation of chemical bond at solid surfaces, existing methods based on Kohn-Sham density functional theory (DFT) are unsatisfactory in system consistency, namely, simulating the solid-liquid interface under grand-canonical conditions, as well as in scaling up the simulation due to its high computational cost. To improve the system consistency and computational efficiency, we develop density-potential functional theoretic (DPFT) [1][2] schemes out of first principles. The proposed DPFT transforms an all-atom, Kohn-Sham DFT description of the nonreactive electrolyte solution into a coarse-grained, field-based description, while retaining a Kohn-Sham DFT description for the reactive subsystem.

Here, we present an in-house MATLAB implementation of DPFT with Kohn-Sham DFT description for metal electrons[3]. For the electrolyte solution, not only considering the Colomb interaction, but steric potentials are also introduced for the short-range interactions between ions. With steric potentials, the double layer capacitance is suppressed when the electrode is highly charged and captures the ion crowding effects.

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Towards a DFT-based Workflow to Simulate Competitive Adsorption of Electrolyte Species at a Pt Electrode

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Electrochemical hydrogen conversion devices will be essential components of a future energy economy. Technologies under development include polymer electrolyte fuel cells and water electrolyzers. Within such devices, vital reaction processes occur at microscopic catalyst-ionomer interfaces in the catalyst layers. However, it is unclear if adsorbing ionomer molecules on the catalyst surface could block reaction sites and thus reduce the device performance [1]. This concerns not only Nafion, a widely used perfluorinated sulfonic acid (PFSA) ionomer, but also new fluorine-free ionomer materials that are under development to alleviate environmental concerns [2].

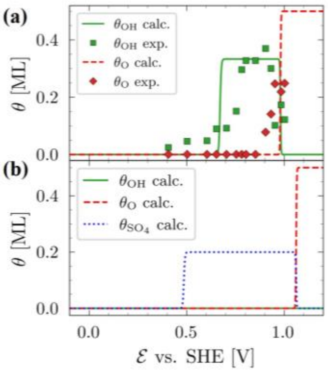

Figure 1: (a) Calculated coverages (solid and dashed lines) of oxygenated adsorbates, in comparison with experimental literature data (symbols, derived from Ref. [3]). (b) Calculated coverages including sulfate adsorption.

Our objective is to rationalize the interplay of competing adsorption processes in the catalyst layer. For this purpose, we have devised a computational workflow to calculate the catalyst surface coverage with adsorbing electrolyte species as function of electrode potential. The DFT-based approach combines a grand-canonical treatment of changes in electronic surface charge and the computational hydrogen electrode (CHE) referencing scheme, a hybrid explicit–implicit aqueous solvation model, and a statistical approach to calculate mixed, potential-dependent coverages of the electrode with different adsorbates. As validation and demonstration cases, we consider the electrochemical adsorption of oxygenated species at a Pt(111) surface (see Figure 1(a)), and the competing adsorption between them and sulfate anions, also at Pt(111) (Figure 1(b)). Simulated surface coverages as a function of the applied potential show a very good agreement with experimental reference data, paving the way towards consideration of other combinations of catalyst and ionomer. As an overall outcome of these explorations, we aim to unravel correlations between chemical nature and interfacial reactivity of novel ionomer materials for highly performing and sustainable hydrogen technologies.

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Correlating electric double layer structure and electrochemical plasmonics of nanoparticles: a theoretical study

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Electrochemical plasmonics enables in-situ optical probing and modulation of electrochemical interfaces. Experiments have revealed that localized surface plasmon resonance (LSPR) in metal nanoparticle-solution systems is sensitive to surface charge, morphology, electrolyte composition and chemisorption. [1-3] However, resolving nanoscale interfacial structures from the measured LSPR is rarely practiced. Herein, we report on a nonequilibrium density-potential functional theoretical (DPFT) approach to enable LSPR simulations under realistic conditions; coupled electron-ion-solvent interactions are considered under a terahertz electromagnetic perturbation. The DPFT model successfully captures both nanoparticle size and solvent permittivity effects. Going beyond the uncharged interfaces, the DPFT model allows to investigate electrode potential effects; a blueshift at more positive potentials is associated with a steeper electron density gradient at the interface. This indicates that the plasmon peak position is primarily governed by electron spillover distribution rather than the total electron density. The DPFT framework contributes to establishing a quantitative relationship between electrical double layer structure and plasmonic resonance.

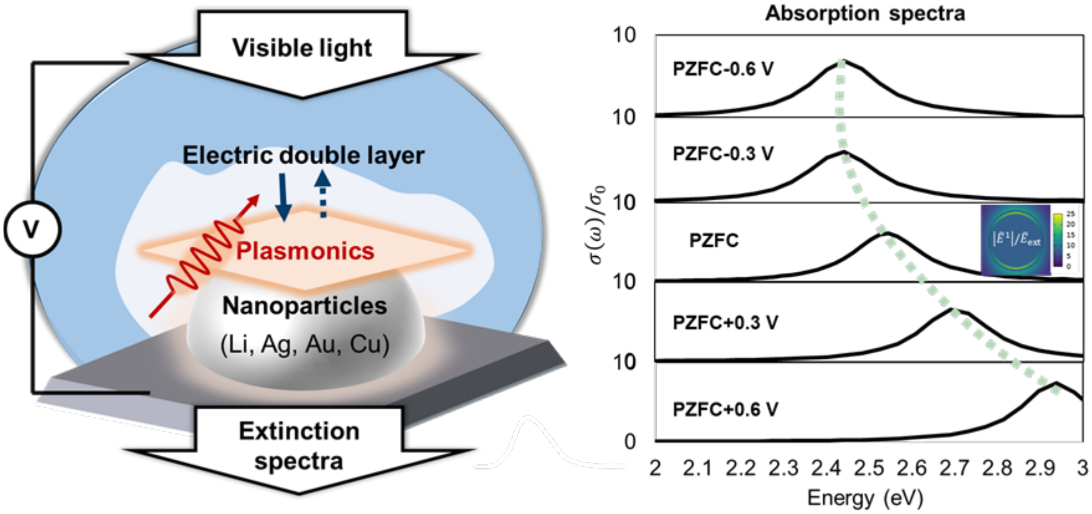

Figure 1. (left) Schematic illustration of the nonequilibrium DPFT framework for electrochemical plasmonics. (right) The effects of electrode potential on absorption spectra obtained by the DPFT model for the system of a silver nanoparticle immersed in a dilute solution. (inset) Enhanced electric field at resonance frequency.

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Potential of Zero Stress of Solid-Liquid Interfaces

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Surface stress bridges electrical, chemical and mechanical aspects of solid-liquid interfaces, while fundamental understanding of surface stress, even in absence of interfacial reactions, remains elusive. Various potential dependencies of the surface stress on solid-liquid interfaces have been reported experimentally, while their microscopic fundamental origins remain largely controversial. Herein, aiming at understanding how metal electrons and interfacial water influence the surface stress, we employ a semiclassical, hybrid density-potential functional theory (DPFT) to calculate the surface stress under constant-potential conditions. Distinct surface stress behaviors, including monotonically increasing, monotonically decreasing, and nonmonotonic behaviors, can be rationalized with different dependencies of water adsorption on the elastic strain. We define the potential of zero stress (PZS) to characterize the stress-neutral state and discuss its relationship with the potential of zero charge.

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Reactive electrical double layers under confinement: insights from atomistic to continuum

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The comprehension of the behaviour of reactive electrical double layers (EDLs) under nanoconfinement is of fundamental interest for the advancement of electrochemical energy conversion and storage[1]. The employment of nanoporous materials in these applications is a matter of particular note, due to the fact that these materials possess an exceptionally high specific surface area, a feature which facilitates enhanced reaction rates and charge storage. However, a comprehensive mechanistic understanding of how confinement alters the EDL structure and reactivity remains to be elucidated.

In this study, Pt nanopores are examined as a model system, considering their high (electro-)catalytic activity in fuel cell reactions (e.g., oxygen reduction reaction). The mesoscopic Pt nanopore/electrolyte EDL is described via continuum modelling, in which the chemisorption processes are included in boundary conditions. In particular, the continuum model incorporates findings from previous *ab initio* molecular dynamics simulations[2], which have highlighted the influences on interfacial structures and potential originating from intricate interplay between water and adsorbates. The present study elucidates the manner in which the EDL structure and charging behaviour vary with pore size and electrochemical conditions, by accounting for these atomistic insights within a continuum model. This modelling approach can be extended to heterogeneous materials, such as carbon nanotube-supported metal nanoparticles, providing valuable insight for the rational design of complex, confined electrochemical environments.

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