

Solid-Water Interfaces at the Molecular Level

805. WE-Heraeus-Seminar

25 February – 01 March 2024

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 805. WE-Heraeus-Seminar:

Solid-water interfaces are ubiquitous both in nature and technology. For example, mineral-water interfaces are at the heart of fundamental processes taking place in nature, including weathering, dissolution and growth of rocks, biomineralization as well as buffering of the seawater pH value. Likewise, numerous industrial and everyday life processes involve solid-water interfaces, in fields ranging from seawater desalination and incrustation inhibition to electrochemistry and catalysis.

A comprehensive understanding of these processes requires elucidating the interfacial structure, chemical composition and charge distribution at the molecular scale. So far, however, many fundamental details of the interface remain unknown. Moreover, solid-water interfaces are often modelled using continuum theories, which will break down at the interface. Very recent advances in experiment and theory now enable to gain unprecedented insights into solid-water interfaces and elucidate molecular-level mechanisms at play.

In this seminar, we will bring together renowned experts and young investigators in an open and an inspiring atmosphere to foster in-depth discussions. Recent advances in experimental and theoretical approaches for studying solid-water interfaces will be presented. We will discuss implications for understanding molecular-level mechanisms in fields such as biomineralization, ice nucleation as well as electrochemical applications.

Scientific Organizers:

Prof. Dr. Angelika Kühnle, University of Bielefeld, Germany
E-mail: kuehnle@uni-bielefeld.de

Prof. Dr. Frieder Mugele, University of Twente, the Netherlands
E-mail: f.mugele@utwente.nl

Introduction

Administrative Organization:

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Mojca Peklaj

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Registration:

Mojca Peklaj (WE Heraeus Foundation)
at the Physikzentrum, Reception Office
Sunday (17:00 h - 21:00 h) and Monday morning

Program

Program

Sunday, 25 February 2024

17:00 – 21:00 Registration

18:30 *BUFFET SUPPER and informal get-together*

Monday, 26 February 2024

08:00 *BREAKFAST*

08:50 Scientific organizers **Welcome words**

09:00 – 10:00 Marie Gaigeot **Modeling Aqueous Interfaces**

10:00 – 11:00 Elias Nakouzi **Interfacial Solution Structure Controls
Pathway and Dynamics of Particle
Attachment, Aggregation, and Self-
assembly**

11:00 – 11:30 *COFFEE BREAK*

11:30 – 12:30 Ellen Backus **Reactions at the Solid-water Interface**

12:30 – 12:40 **Conference Photo** (in front of the lecture hall)

12:40 – 14:00 *LUNCH BREAK*

Program

Monday, 26 February 2024

14:00 – 15:00	Eric Borguet	Hydrogen Bonding and Ultrafast Dynamics at Aqueous-oxide Interfaces
15:00 – 16:00	Bernhard Reischl	Atomistic Simulation of Heterogeneous Nucleation on Mineral Surfaces
16:00 – 16:30	<i>COFFEE BREAK</i>	
16:30 – 17:30	Remco Hartkamp	Do Surface Reactions Perturb the Electric Double Layer Structure?
17:30 – 17:45	Stefan Jorda	About the Wilhelm and Else Heraeus Foundation
17:45 – 18:30	Discussion Session 1 <i>(discussion leader Adam Foster)</i>	
18:30	<i>DINNER</i>	

Program

Tuesday, 27 February 2024

08:00	<i>BREAKFAST</i>	
09:00 – 10:00	Andrea Auer	Visualizing Electrified Solid-liquid Interfaces
10:00 – 11:00	Philipp Rahe	High-resolution Real-space Imaging of a Mineral Surface: Water Adsorption on Calcite(104)-(2×1)
11:00 – 11:30	<i>COFFEE BREAK</i>	
11:30 – 12:30	Igor Siretanu	Local Surface Charge, Ions and Water Structuring at Solid-electrolyte Interfaces: Insights from AFM Spectroscopy
12:30 – 14:00	<i>LUNCH BREAK</i>	
14:00 – 15:00	Discussion Session 2 <i>(discussion leader Ricardo Garcia)</i>	
15:00 – 16:00	Poster flash	
16:00 – 16:30	<i>COFFEE BREAK</i>	
16:30	Poster Session 1	
18:30	<i>DINNER</i>	

Program

Wednesday, 28 February 2024

08:00	<i>BREAKFAST</i>	
09:00 – 10:00	Olaf Magnussen	X-ray Scattering Studies of the Molecular Structure at Electrochemical Interfaces
10:00 – 11:00	Frank Heberling	Chemical-thermodynamic Models for Mineral-water Interfaces, from Free Surfaces to Nanoconfined and Nanostructured Systems
11:00 – 11:30	<i>COFFEE BREAK</i>	
11:30 – 12:30	Thorsten Geisler-Wierwille	Real-time, In-situ Investigations of Glass-water Reactions at the Micrometer Scale by Fluid-cell Raman Spectroscopy
12:30	<i>LUNCH BREAK</i>	
14:00 – 18:00	Excursion	
18:30	<i>HERAEUS DINNER</i> (social event with cold & warm buffet with complimentary drinks)	

Program

Thursday, 29 February 2024

08:00	<i>BREAKFAST</i>	
09:00 – 11:00	Poster session 2	
11:00 – 11:30	<i>COFFEE BREAK</i>	
11:30 – 12:30	Discussion in small groups	
12:30 – 14:00	<i>LUNCH BREAK</i>	
14:00 – 15:00	Ester Alarcón Lladó	Understanding and Controlling Nanoscale Processes at Metal Electrodes with Electrochemical AFM
15:00 – 16:00	Hendrik Bluhm	Interplay of Ions and Surfactants at Liquid-vapor Interfaces
16:00 – 16:30	<i>COFFEE BREAK</i>	
16:30 – 17:30	Benjamin Murray	Ice in the Earth's Atmosphere
17:30 – 18:30	Discussion in small groups	
18:30	<i>DINNER</i>	

Program

Friday, 01 March 2024

08:00	<i>BREAKFAST</i>	
09:00 – 10:00	Denis Gebauer	Dense Liquid Minerals: Mechanisms and Applications
10:00 – 11:00	Discussion Session 3 <i>(discussion leader: Jim DeYoreo)</i>	
11:00 – 11:30	<i>COFFEE BREAK</i>	
11:30 – 12:30	Scientific organizers	Closing
12:30	<i>LUNCH</i>	

End of the seminar and departure

Posters

Poster List

Vincenzo Alagia	Probing Electrolytes' Impact on the Formation of Interfacial Layers during Olivine Dissolution
Christian Aleff	Nucleation Activity of Molecular Ice Nucleators of Natural Origin
Dilafuz Allanazarova	Exploration of the Nucleation of Trisilver Citrate
Leo Sahaya Daphne Antony	Nanoscale Adhesion Force Heterogeneities at Electrochemical Interfaces
Philipp Begemann	Ambient Scanning Probe Microscopy with qPlus Sensors
Maël Brulé	Resolving the Surface Structure and Hydration Layer Structure of Model Copper/Halides CO ₂ RR Catalysts by in Situ AFM
Alper Tunga Celebi	Role of Surface Cation and Ion Concentration on the Adsorption Behavior at Water-mica Interfaces
Tobias Dickbreder	Atomic Structure of K-Feldspar Microcline (001) and its Interaction with Water
Martijn Dijkhuizen	In Situ AFM Study of Electrocatalytic Active Faceted Platinum Nanoparticles Produced by Solid-state Dewetting
Kim Noelle Dreier	Indications of Reconstruction at μm -Scale as a Possible Stabilization Mechanism of Polar, Ice Nucleating Silver Iodide Surfaces
Jonas Heggemann	The (2x1) Reconstruction of the Calcite(104) Surface

Poster List

Lisa Hirsch	Determination of the Reaction Volume of the Underpotential Deposition of Cu and Ag on Au(111)
Bahram Hosseinimonjezi	Quartz Crystal Microbalance (QCM): A Useful Tool for Understanding Complex Interactions in Interfacial Processes
Farzin Irandoost	Tip Classification in High-resolution AFM Imaging in Liquids
Alexei Kiselev	IR Study of D2O Adsorption on Alkali Feldspar
Antonia Köhler	Charged Surfaces: Hydration Layer Mapping at the Au(111) Electrode Surface
Ruerd Kroon	Influence of Ionic Concentration on the Electrochemical Solid-liquid Interface of Gold
Diana Mendez Arvelo	Interfacial Layering of Hydrocarbons on Pristine Graphite Surfaces Immersed in Water
Shurui Miao	Role of Interfacial Water and Specific Ion Effects in Carbon Mineralisation
Shilpa Mohanakumar	Exploring Additive-Mediated Surface Alterations in Olivine for Enhanced Reactivity in Carbon Capture
Swetha Nair	Modeling of Electrical Fluctuations Next to an Electrode to Probe the Properties of Interfacial Electrolytes
Vahid Nasirimarekani	Pattern Formation at the Dynamic Interface of an Evaporating Droplet

Poster List

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|-------------------|---|
| Matteo Olgiati | Towards Understanding Interfacial Thermodynamics: Visualising and Quantifying Competitive Adsorption on Muscovite Mica with AFM |
| Franziska Sabath | Water Arrangement at the K-Feldspar Microcline (001)-Water Interface |
| Finn Schröter | In Situ Surface X-ray Diffraction Studies of the Electrochemical Double Layer on Pt(111) |
| Johanna Seidel | Real-time X-ray Scattering Study of Ice Nucleation on Natural Feldspar |
| Chinmay Shukla | Towards High Efficiency Photocatalyst Materials: In Situ Characterization of Faceted SrTiO ₃ Nano-particle-electrolyte Interfaces by Atomic Force Microscopy |
| Shiraz Tanklevsky | Interaction of Water Vapor with Heavily Reduced TiO ₂ (110) |
| Juntao Yang | C-C Bond Cleavage in the Electrooxidation of 2,3-Butanediol Controlled by an Ionic Liquid Modifier |
| Yuke Yang | Detection of Surface Intermediates for Oxygen Evolution on Hematite Using Operando Sum Frequency Spectroscopy |

Abstracts of Lectures

(in alphabetical order)

Understanding and controlling Nanoscopic Processes at metal electrodes with electrochemical AFM

L.S.D. Antony,¹ M. Aarts,^{1,2} L. Monin,¹ E. Alarcon-Llado^{1,3}

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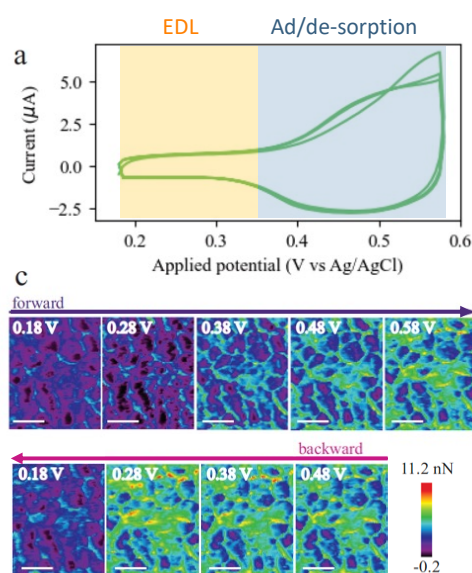
³University of Amsterdam, HIMS, Amsterdam, Netherlands

One of the challenges in achieving the energy transition is the conversion and storage of sustainable energy. Electrolysers can solve this issue as they convert green electricity to energy-rich compounds such as hydrogen, hydrocarbons or alcohols produced from water and CO₂. To make electrolyzers a scalable deployable technology we must find earth-abundant materials that are efficient and stable electrocatalysts, as only precious metals fulfill these requirements so far. But why/how are these good?

One of the most important bottlenecks is the lack of a fundamental understanding of nanoscopic processes that control charge transfer at the solid-electrolyte interface. In recent years, more and more evidence emerge on the intertwining of electrode inhomogeneities, local electrolyte structure and ion distribution, which all affect the nanoscopic electrochemical processes. All these are difficult to infer from macroscopic measurables. Electrochemical scanning probes are powerful tools to measure of the properties of solid-liquid interfaces, from local EDL build-up times to high-resolution 3D imaging interfacial water arrangement.

In this work we simultaneously probe the water structure and catalyst surface with nanometer resolution as the potential is swept across the EDL formation and adsorption/desorption of sulfite ions. We take advantage of the link between interfacial energy and adhesion forces to map entropic changes in the interfacial water as a function of bias and other electrochemical conditions. We reveal that the water structure on even a simple Au film is highly inhomogeneous and dynamic. We infer that areas with a tight water structure will have a higher entropy penalty for the OER.

Understanding and controlling these nanoscale phenomena provide us with many fascinating challenges, of direct relevance not only in energy storage but also other fields like nanomaterial fabrication.



References

- [1] Antony et al., 10.26434/chemrxiv-2023-7fcl8-v2
- [2] Aarts et al., Nanoscale Advances 4, 1182 (2022)

Visualizing electrified solid-liquid interfaces

A. Auer^{1,2}

¹*Institute of Physical Chemistry, University of Innsbruck, Austria*

²*Institute of Experimental and Applied Physics, University of Regensburg, Germany*

To design efficient electrochemical interfaces for sustainable energy conversion, it is crucial to resolve the molecular structures of the electric double layer, where inevitably all electrocatalytic reactions take place. While most current electrochemical scanning probe microscopy approaches are successfully employed to study the structural evolution of an electrode surface even under reaction conditions [1], they are largely insensitive to the solvent structure formed at the liquid side. In contrast, high-resolution atomic force microscopy (AFM) has been shown to be able to visualize the vertical arrangement of water molecules in the direction normal to the surface, see e.g., [2]. However, only very few reports exist with potential control in an operating electrochemical cell. We recently developed an electrochemical frequency-modulation AFM that can be simultaneously performed with scanning tunneling microscopy (STM) using stiff self-sensing quartz cantilevers (qPlus sensors) [3,4]. This allows us to locally image both the vertical layering of the interfacial solvent and the lateral structure of the electrochemical double layer in great detail.

In this talk, I will briefly introduce the state-of-the-art of electrochemical scanning probe microscopy including the possibilities given by qPlus force sensors and discuss a couple of examples from our recent work on well-defined single crystals. These include investigations of a Au(111) electrode in various aqueous electrolytes that reveal a distinct potential-dependent, oscillatory frequency shift modulation in z-direction. Depending on the applied potential, the charge of the electrode and the type of ions, we attribute these oscillations to water and/or ion layering close to the electrode, which we can correlate with atomistic molecular dynamics simulations.

References

- [1] A. Auer, M. Andersen, E.-M. Wernig, N.G. Hörmann, N. Buller, K. Reuter and J. Kunze-Liebhäuser, *Nat. Catal.* **3**, 797–803 (2020).
- [2] T. Fukuma and R. Garcia., *ACS Nano.* **12**, 11785–11797 (2018).
- [3] F.J. Giessibl, *Rev. Sci. Instrum.* **90**, 011101 (2019).
- [4] A. Auer, B. Eder and F.J. Giessibl, *J. Chem. Phys.* **159**, 174201 (2023).

Reactions at the solid-water interface

Ellen H.G. Backus¹

¹*University of Vienna, Faculty of Chemistry, Institute of Physical Chemistry, Vienna, Austria*

Upon contact with water solids could undergo spontaneous reactions varying from deprotonation to dissolution. For minerals, this dissolution plays a crucial role in geochemistry and could be enhanced as water is often not in static contact but flowing. Besides spontaneous reactions, also external triggers like light could induce interfacial reactions relevant in for example catalysis. In this talk we will discuss one example of each.

In the first part of the talk we will study the dissolution and surface adsorption processes of magnesium oxide (MgO) under static and flowing condition. To monitor the interface sum-frequency generation (SFG) spectroscopy is used. This technique is capable of retrieving vibrational information of selectively interfacial molecules even if bulk amounts of liquid are present at the interface and can be performed with flowing and static liquid at the interface. We use the O-H stretch vibration of the water molecules as a marker in this talk and observe that for MgO the surface chemistry is dominated by acidic mediated surface dissolution.

In the second part of the talk photocatalytic water dissociation at the interface between water and titanium dioxide (TiO₂) will be studied as example of a light induced reaction at the solid-liquid interface. In these experiments the TiO₂ thin film is excited with a short UV pulse mimicking the sun light. Subsequently, the O-H stretch vibration of the interfacial species are monitored with SFG on a subpicosecond timescale. Our data show that the surface charge changes on ultrafast timescales upon excitation resulting in reorientation and partly dissociation of the water molecules on tens of ps timescales. These UV-pump SFG-probe data illustrate the first steps towards following the photo-induced dissociation of water at the TiO₂ interface in real-time. [1]

References

- [1] E.H.G. Backus et al., *Angew. Chem. Int. Ed.*, accepted (2024)

Interplay of ions and surfactants at liquid-vapor interfaces

Hendrik Bluhm

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Liquid-vapor interfaces are abundant in nature and play a major role in such important processes as the sequestration of carbon dioxide by the oceans and the uptake and release of trace gases by aqueous aerosols.[1] These interfaces feature similar phenomena as liquid-solid interfaces, in particular the formation of electric double layers. The double layer properties are strongly affected by the presence of surfactants at the solution-vapor interface, which are ubiquitous in nature. Many surfactant molecules possess charged hydrophilic groups, which influence the propensity of ions for the interface through electrostatic interactions.

In this talk the general strategies for the investigation of these interfaces using X-ray photoelectron spectroscopy will be presented, including the preparation of solution-vapor interfaces for investigations under vacuum conditions [2] and the analysis of concentration profiles and details on the chemical nature of the surface-active species as a function of, e.g., solution pH and solute concentrations.[3-5] We also discuss to which degree the results of investigations on liquid-vapor interfaces can be applied to a deeper understanding of the molecular details of the solid-vapor interface.

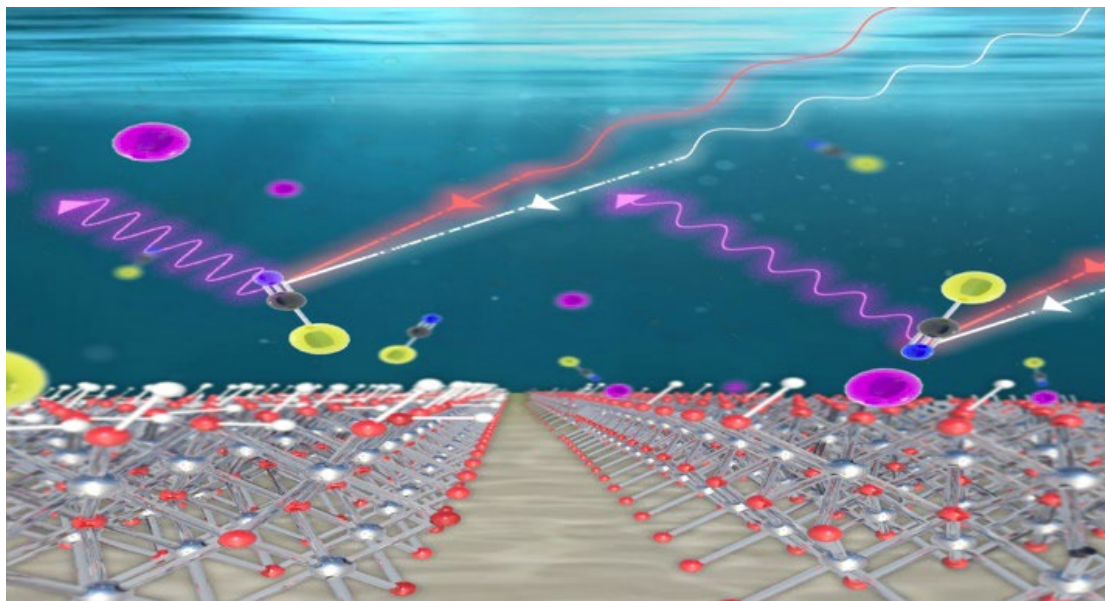
References

- [1] B.J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.* **11**, 7760 (2009).
- [2] R. Dupuy et al., *J. Chem. Phys.* **154**, 060901 (2021).
- [3] R. Dupuy et al., *Phys. Chem. Chem. Phys.* **24**, 4796-4808 (2022).
- [4] R. Dupuy et al., *Phys. Rev. Lett.* **130**, 156901 (2023).
- [5] C. Richter et al. *ACS Symposium Series* **1396**, 39 (2021).

Hydrogen bonding and ultrafast dynamics at aqueous-oxide interfaces

Eric Borguet

Department of Chemistry, Temple University, Philadelphia PA 19122, USA



Abstract

Interfacial water structure is key to diverse chemical and physical processes, including many of environmental and geochemical relevance. It can be probed by vibrational sum-frequency generation (vSFG) spectroscopy as well as ultrafast time-resolved vSFG. Combined with computational tools, such as molecular dynamics simulations, a microscopic understanding of interfaces can be approached. Our experiments show that in the absence of surface charge (pH 2), water at silica surfaces exhibits significantly slower OH stretch vibrational relaxation (~ 600 fs) compared to bulk water. However, at charged silica surfaces (e.g., pH 6), bulk-like fast dynamics (~ 200 fs) are observed at low ionic strength. This decelerates to ~ 600 fs with the addition of NaCl. In parallel, vSFG results demonstrated that silica interfacial water structure is most sensitive to ions at pH=6-8, correlating with the known salt and pH dependence of silica surface reactivity. Consequently, it is unclear whether the observed slowing of the vibrational dynamics is due to the reduction in the Debye length, or because of changes in the local hydrogen bonding environment caused by the electrolyte and how this might depend on the identity of the ions or the solid surface. The combination of molecular dynamics simulations with spectroscopic and time-resolved vSFG experiments on aqueous Al_2O_3 interfaces, along with the use of a molecular probe (SCN^-), sheds light on the ongoing debate on the role of ions in interfacial water structure and the hydrogen bonding network, as well as whether the observed behavior is specific to silica/water interfaces or can be generalized to other aqueous interfaces.

Moderated discussion (theory)

A.S. Foster¹

¹Aalto University, Helsinki, Finland

Following the spirit of WE-Heraeus Seminars, the seminar is planned to give plenty of opportunities for discussions both in plenum and in small groups. To this end, we include long breaks for informal exchanges as well as slots for moderated discussion on the core topics of the meeting. These moderated discussions will be led by experienced researchers from the field. The discussion leaders have been asked to initiate the discussion by providing an informal summary of the respective session, including their own perspective of exciting open questions.

Modeling aqueous interfaces

Marie-Pierre Gaigeot

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²Institut Universitaire de France (IUF), 75005 Paris, France

In this tutorial, I will review the current state-of-the-art of molecular dynamics simulations (ab initio DFT-MD, classical MD) that are applied to solid/liquid water interfaces. I will focus on the strengths and limitations of the methods, on their applicability to diverse molecular systems and conditions that can be encountered in experiments (for instance pH, concentration in electrolytes, surface potential ...), and their applicability for extracting certain properties of interest that can be measured experimentally (for instance, spectroscopies). All of these will hopefully trigger discussions and directions for future theoretical works, including machine learning types of methods.

Dense Liquid Minerals: Mechanisms and Applications

D. Gebauer¹

¹*Institute of Inorganic Chemistry, Leibniz University Hannover, Hannover, Germany*

Liquid mineral precursors have been studied since their discovery almost 25 years ago [1,2]. It has been demonstrated that their properties offer several advantages in materials synthesis [2], for example, the ability to infiltrate small pores, the production of non-equilibrium crystal morphologies, or mimicking textures from biominerals. Indeed, dense liquid minerals may be key to better understand biomineralization processes as a chemical Medusa, which was originally coined by Mann [3], turning soft matter into stone. However, in artificial syntheses, their potential has never been fully tapped, largely due to the lack of efficient and scalable synthesis protocols. The reason for this, in turn, has been the limited understanding of the formation mechanism of these rather elusive mineral precursors.

Here, we introduce a basic theoretical framework for dense liquid mineral formation, and illustrate the explanatory and predictive power of the so-called pre-nucleation cluster pathway [4]. Based on the improved mechanistic understanding, a “scalable controlled synthesis and utilization of liquid-like precursors for technological applications” (SCULPT) method was developed [5]. With it, for the first time, a dense liquid precursor phase could be isolated on a gram scale. While, e.g., magnesium ions and concrete superplasticizers allow optimizing SCULPT for specific demands, the stabilizing role of polycarboxylates is crucial. Colloidal stabilization of dense liquid calcium carbonate precursors leads to bicarbonate entrapment resulting in local stoichiometric mismatches in solid amorphous calcium carbonate (ACC) [6]. This explains its pronounced stabilization against crystallization, but the history as a colloid also gives rise to the formation of mobile water environments, rendering ACC electrically conductive. While this rather surprising property may be utilized in electrochemical devices in the future, it is evident that dense liquid minerals have become promising candidates for calcium carbonate-based, CO₂-neutral cements.

References

- [1] L.B. Gower, D.A. Tirrell, *J. Cryst. Growth* **191**, 153–160 (1998)
- [2] L.B. Gower, *Chem. Rev.* **108**, 4551–4627 (2008)
- [3] S. Mann, *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry* (Oxford University Press, New York, 2001)
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- [6] M.B. Gindele, S. Vinod-Kumar, J. Rochau, D. Boemke, E. Groß, V. SubbaRao Redrouthu, D. Gebauer, G. Mathies, *Nat. Commun.* **15**, 80 (2024).

Real-time, *in-situ* investigations of glass-water reactions at the micrometer scale by fluid-cell Raman spectroscopy

T. Geisler, M. B. K. Fritzsche, L. Dohmen, G. Trapp-Müller, M.I. Lönartz and Christoph Lenting

¹ *Institute of Geosciences, University of Bonn, Germany*

Glass-water reactions are often characterized by the formation of silica-based surface alteration layers (SAL) that complexly affect the dissolution behavior of the glass [1-3]. Despite numerous sophisticated experimental studies, there is still an intensive debate about how these alteration layers form and about the rate-limiting reaction step(s) [1,2]. Most of these experiments, however, delivered chemical, structural, phase and textural information only after the sample has been cooled down to room temperature, dried, and mechanically sectioned before analysis. To overcome such drawbacks, we have developed fluid-cell hyperspectral Raman spectroscopy (FC-CHRS) [3]. FC-CHRS thereby provides a wealth of spatially- and time-resolved information about phase assemblage, chemistry, and structure, as well as the concentration of aqueous species while the reaction is proceeding. Here, we report on FC-CHRS experiments with borosilicate glasses at temperatures between 70 and 90 °C that provided unprecedented real-time insights into reaction and transport processes during aqueous silicate glass corrosion. For instance, the formation of a several micrometer-thick water-rich zone between a silica-based SAL and the underlying glass, interpreted as an interface solution, was detected, as well as pH gradients at the glass surface and within the SAL. Moreover, by replacing the solution with a deuterated solution, it was observed that water transport through the SAL obeyed Fickian diffusion at pH values near 8, but anomalous diffusion at lower and high pH values. In summary, the *in-situ* data are not at all in accordance with a traditional diffusion-controlled glass leaching model [1] neither under basic nor at acidic pH conditions. Instead, the data supports an interface-coupled dissolution-precipitation (ICDP) process for SAL formation during glass corrosion [2,3]. Recently, however, it has been shown that an interdiffusion zone can form in front of an ICDP front in the glass when the movement of the ICDP front slows down due to transport limitations, so that interdiffusion in the glass becomes faster [2]. In general, FC-CHRS experiments open up new avenues of investigating glass-water reactions, but also other solid-water reactions, with the possibility of following specific sub-processes in real time with the aid of stable isotopes.

References

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Do surface reactions perturb the electric double layer structure?

R. Hartkamp¹

¹*Process and Energy, Delft University of Technology, Leeghwaterstraat 39, 2628 CB, Delft, The Netherlands*

Detailed insight into the local structure and transport properties of an electrolyte solution in contact with a solid surface is hard to obtain. Experimental techniques are often either limited in their accessible resolution or their interpretation relies on models and assumptions that may break down on the molecular scale or are invalid under the local interfacial fluid conditions. Continuum-based modeling typically also relies on a priori knowledge or assumptions pertaining to electric double layer properties, whereas the outcomes of molecular simulations hinge entirely on a good description of atomic interactions. In this lecture, we look at how we can address this challenge.

Furthermore, we will explore to what extent surface reactions can perturb the electric double layer structure and consequently fluid transport along or perpendicular to the surface. We will analyze two case studies: first, a nanoconfined liquid at chemical equilibrium with the surface [1], and second, a system in which electrochemical conversion takes place at an electrode surface [2]. These two cases are characterized by different length scales, different transport mechanisms, and different simulation techniques will be used to study them.

References

- [1] M.F. Döpke, F. Westerbaan van der Meij, B. Coasne, and R. Hartkamp, *Phys. Rev. Lett.* **128**, 056001 (2022)
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Chemical-thermodynamic models for mineral-water interfaces, from free surfaces to nanoconfined and nanostructured systems

Frank Heberling, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

Electrostatic surface complexation models (SCMs) provide a framework to describe chemical reactions and electrostatic conditions at mineral-water interfaces. In this presentation the fundamentals of electrostatic SCMs will be explained. The power of SCMs to integrate a broad variety of information, ranging from molecular scale experimental and theoretical insights to macroscopic measurements, into one quantitative modelling framework will be highlighted. As an example, the equilibrium speciation at the calcite-water interfaces will be introduced (Heberling et al. 2021) and new developments in that system will be discussed (Söngen et al. 2021; Zarzycki 2023).

Classical SCM approaches are limited to flat, free surfaces (i.e. semi-infinite systems, where the electrostatic potential decays to zero in solution). The charge regulation approach enables simulations of surfaces interacting on the nanoscale (Gil-Díaz et al. 2021; Heberling et al. 2023). It allows to assess the surface chemistry in nanoconfined systems as well as electrostatic forces and the osmotic pressure between charged surfaces. The basics of the charge regulation approach will be introduced, and it will be shown how it can e.g. be used for an improved quantification for tip-sample interactions in atomic force microscopy. New developments that extend the capabilities of charge regulation models beyond the 1D interaction of two flat interfaces to interactions of multiple surface segments in 2D or 3D for simulations of nanostructured or heterogeneous surfaces will briefly be introduced.

References

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X-ray scattering studies of the molecular structure at electrochemical interfaces

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Interfaces between metal electrodes and aqueous electrolyte solutions play a central role in electrochemical energy technology. In-depth understanding of electrochemical reactions is intimately connected with understanding the structure, dynamics, and properties of the electrode-electrolyte interface on the molecular scale. Recent experimental and theoretical studies provide evidence that this interface is considerably more complex than described by traditional double layer theories. In the talk, I will show how the structure and dynamics of water and ions near the electrode surface can be probed by X-ray scattering methods. I will specifically address the interface structure at Pt single crystal surfaces, which is a topic of great current interest. First, the liquid structure in the double layer regime will be discussed, where current experiments and AIMD calculations indicate a complex Pt-water interaction. Second, the interaction of solution species with the surface under Pt oxidation conditions will be described.

Ice in the Earth's atmosphere

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The formation of ice in the Earth's atmosphere is of central importance to clouds, climate, the hydrological cycle, and consequently, life on Earth. Since water has a remarkable propensity to supercool well below ice's melting point, cloud water frequently exists in a supercooled liquid state. When in this metastable state, clouds are susceptible to the formation of ice in the presence of special particles that can heterogeneously nucleate ice. The nucleation of ice triggers profound changes in clouds through a cascade of microphysical processes, altering their radiative properties and shortening their lifetime. At the heart of these changes are poorly understood nanoscale sites on aerosol particles that are themselves only 100s nm to a few microns in size that can nucleate ice [1,2].

While a range of atmospheric aerosol particle types have been shown to nucleate ice, mineral dusts derived from the Earth's surface are thought to be one of the most important ice-nucleating particle (INP) types on a global scale. The majority of atmospheric mineral dust is emitted from the African and Asian deserts, but mineral dust is also emitted from agricultural sources and glacial valleys. This mineral dust is transported globally, even to the poles and to the upper troposphere where cirrus clouds form.

The global climate modelling community is only just starting to include mineral dust ice nucleation in their models, and this is raising questions on how to best represent mineral dust's ice nucleating properties. These models need physically realistic, but simple parameterisations. At present, most of our understanding of the ice nucleating ability of mineral dust is empirically based, but we really would prefer a more fundamental basis to our parameterisations, ideally based on a fundamental model. Nucleation is known to be a stochastic (therefore time dependent) process that often occurs at specific sites. These sites have a massive diversity in terms of their ice nucleating activity (temperature at which they trigger freezing). Representing both time dependencies and site diversity in climate models is too expensive, hence simplifications must be made. In this presentation I will summarise these different approaches and present the detailed experiments that have been done by ourselves and others in the community that are feeding into this debate.

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Interfacial solution structure controls pathway and dynamics of particle attachment, aggregation, and self-assembly

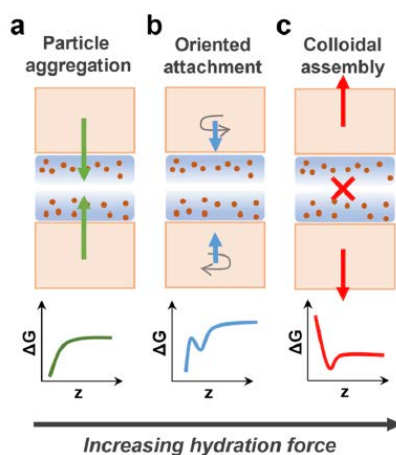
E. Nakouzi,¹ J. Prelesnik,² R. Alberstein,² P. Butreddy,¹ J. Heo,¹ S. Zhang,^{1,2} S. Kerisit,¹ N. Rampal,³ T. Liu,³ L. Liu,¹ G. K. Schenter,¹ J. Chun,¹ A. G. Stack,³ J. J. De Yoreo¹

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Solid-liquid interfaces are central to a range of interesting phenomena including catalysis, heterogeneous nucleation, water desalination, charge transfer, and biomolecular assembly. Despite this ubiquity, key aspects of the underlying physical origins of interfacial solution structure and the associated hydration forces have remained elusive. Using a combination of three-dimensional atomic force microscopy, light and neutron scattering, molecular dynamics simulations, colloidal theory, and other tools, we establish a connection between molecular-scale descriptors of the interfacial structure and the hydration force. Specifically, we observe that stronger networks of solution structure result in stronger hydration forces as they are displaced by incoming particles. We present four case applications for this interpretation:

- 1) Biomolecules can assemble on top of hydration layers instead of directly adsorbing at crystal interfaces, influencing the assembly patterns.
- 2) The rate of particle aggregation decreases by several orders of magnitude at extreme ionic strength where hydration forces dominate.
- 3) Solvents with stronger hydrogen bonding produce stronger solvation forces, resulting in solvent-specific pathways for particle attachment.
- 4) The incorporation of nanoparticles in growing crystal lattices is controlled by specific ligand-surface interactions and the ability to penetrate hydration layers.

These results demonstrate how molecular-scale structure influences the scaling, magnitude, and outcome of hydration forces, which will enable the prediction of particle attachment, assembly, and aggregation, with a broad relevance on a multitude of other interfacial phenomena.



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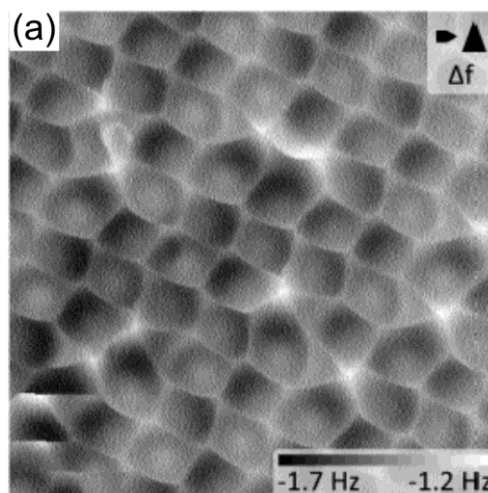
High-resolution real-space imaging of a mineral surface: Water adsorption on calcite(104)-(2×1)

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Calcium carbonate (CaCO_3), in particular the most stable polymorph calcite, is among the most abundant minerals in the earth's crust and of key relevance in natural and biological processes [1] such as dissolution-precipitation, weathering, the purification of potable water, or biomineral growth.

Here, the properties of the calcite(104) surface in pristine and water-covered state are studied at the atomic scale using low-temperature non-contact atomic force microscopy (NC-AFM). First, a brief introduction into the methodology of high-resolution NC-AFM experiments with functionalized tips is given and the particular contrast pattern on calcite(104) when imaged with a carbon monoxide (CO)-terminated tip is discussed [2]. From a comparison with simulations based on the probe particle model [3], a consistent interpretation of the imaging contrast is achieved [2]. Next, the structure and symmetry properties of the calcite(104) surface are investigated and strong evidence is given for the presence of a (2×1) reconstruction [2]. Finally, the focus is set on the adsorption properties of water [4,5]. From high-resolution imaging (see figure), the adsorption geometries of single water molecules are established from real-space observation. Interestingly, a lifting of the surface reconstruction as a result of the water-surface interaction is identified.



Constant-height NC-AFM image of the water/calcite(104)-(2×1) surface acquired with a CO tip. [5]

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Atomistic Simulation of Heterogeneous Ice Nucleation on Mineral Surfaces

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Water freezes homogeneously only at temperatures below -38 °C, while ice nucleation at higher temperatures occurs heterogeneously, with the help of a surface or seed particle. Heterogeneous ice nucleation therefore plays a major role in many natural or technological processes, such as the formation of ice and mixed-phase clouds, which have very different properties compared to clouds consisting of liquid droplets, which impacts both, our weather and climate. Ice clouds form on ice nucleating particles (INPs) such as mineral dusts or organic matter, but a detailed understanding of the microscopic nucleation mechanism is still missing. In classical heterogeneous nucleation theory, the free energy barrier to homogeneous nucleation is simply reduced by a geometric factor which depends on the different bulk surface tensions at the triple interface of water, ice, and the “surface”. Recent experimental advances using TEM and AFM have proven the existence of specific active sites on mineral surfaces where the nucleation happens. However, limits in spatial and, more importantly, temporal resolution hinder the direct observation of the atomistic nucleation mechanism in experiments. While the nanometer length scales of these processes are well suited for atomistic simulations, the time scales on which nucleation typically occurs often exceed what can be reasonably achieved in unbiased molecular dynamics simulations, even for very ice nucleation active systems.

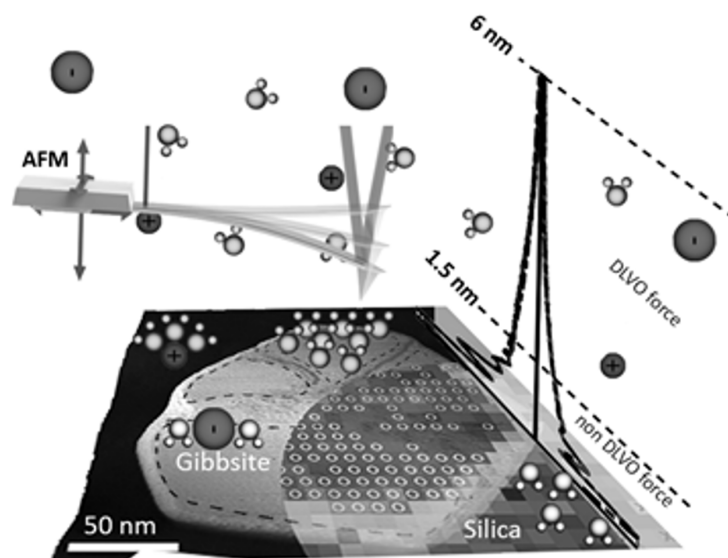
In this lecture I will give a short overview of atmospheric heterogeneous ice nucleation and highlight some recent experimental studies revealing the existence of active sites for ice nucleation on different mineral surfaces. I will present state of the art atomistic simulations of ice nucleation at different crystal surfaces and discuss the complex relationship between surface chemistry and topography, the hydration layer structure at the interface and the ice nucleation activity. I will discuss the details of simulation setups and present ways to tackle the timescale issue by either performing seeded molecular dynamics simulations or applying biased sampling techniques, such as forward flux sampling.

Local surface charge, ions and water structuring at solid-electrolyte interfaces: Insights from AFM Spectroscopy

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Understanding the structure and function of solid-liquid interfaces in ambient aqueous electrolytes of variable composition (pH and specific electrolyte ions) is essential for the development of nanomaterials for various applications, including crystal growth, mineral dissolution and reprecipitation, CO₂ capture by carbonation, biosensing, colloidal stability and self-assembly, and improved electro- and photoelectrocatalytic water splitting for storage of renewable electricity. In this contribution, I will give an overview of the insights that we have gained using in situ Atomic Force Microscopy (AFM) measurements on the structure of the electric double layer and the resulting nano-scale interaction forces. I will illustrate the potential of dual-scale AFM spectroscopy and imaging with adapted AFM tip sizes and discuss aspects of surface charge, ion adsorption, hydration, and electrostatic forces for a variety of heterogeneous systems ranging from clay minerals to metal/semiconductor catalyst nanoparticles [1-4].



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Abstracts of Posters

(in alphabetical order)

Probing electrolytes' impact on the formation of interfacial layers during olivine dissolution

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Olivine (magnesium iron silicate) is a prime contender for CO₂ mineralization in aqueous environments via natural weathering or industrial processes. It has been reported, however, that upon its dissolution, a silica and iron rich alteration layer gets formed, which can slow down the chemical reactions at the mineral-electrolyte interface (1). Despite extensive research, the interfacial layer's nature and variability remain to be clarified. Sulfuric acid is known to expedite olivine dissolution; however, there is conflicting evidence regarding the role of iron oxidation in the passivation of the dissolution reaction (2).

To get more insight into the interfacial layer formation process during olivine dissolution, we used Energy Dispersive, Raman, X-Ray Photoelectron Spectroscopies and Scanning Electron Microscopy. We monitored the dissolution kinetics and interfacial layer formation in sulfuric, hydrochloric, and nitric acid at varying pH levels. An interfacial layer primarily consisting of Iron (III) oxides was observed when dissolving olivine in H₂SO₄ upon reaching pH 3, while in all other cases no interfacial layer was observed. Despite the layer formation, H₂SO₄ still dissolves olivine considerably faster than both HCl and HNO₃, suggesting that eventual passivation mechanisms influence the reaction rate less than the electrolyte chemistry.

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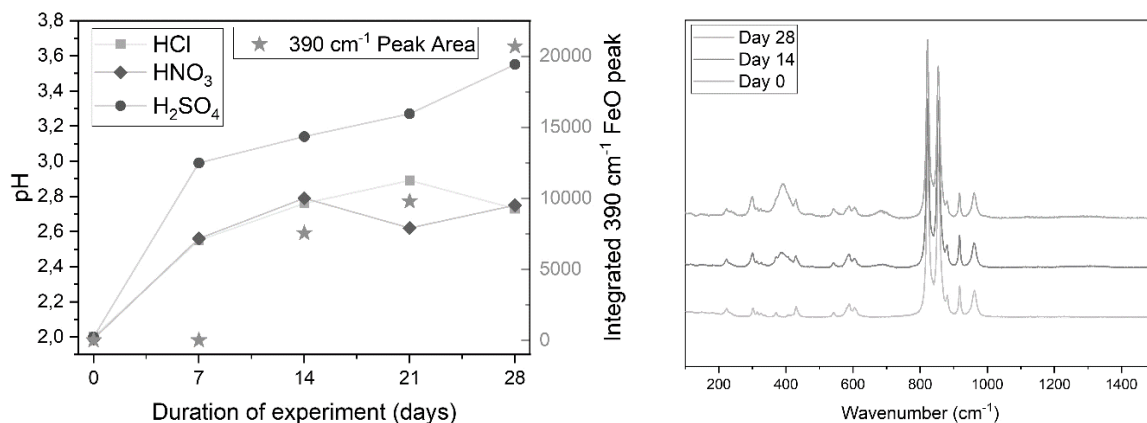


Fig.1 – (a) pH evolution of the electrolytes during dissolution compared with the integrated area of the 390 cm⁻¹ Raman peak of FeO(OH); (b) evolution of the representative Raman spectrum of olivine dissolving in H₂SO₄.

Nucleation activity of molecular ice nucleators of natural origin

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While extensive studies of ice nucleators (INs) of natural origin have revealed that a multitude of different species impact atmospheric ice nucleation processes, information about the properties of these IN is in many cases still scarce. As these processes have a profound impact on precipitation and climate by way of changing cloud properties, more information on the origin of the responsible IN's nucleation activity is therefore required.

We investigated several naturally occurring substances such as pollen, lichen or proteins, all of which are considered to be of relevance through their ubiquity in nature as well as their high ice nucleation activity^[1,2]. In our studies, we focused on the molecular properties of the different INs, as for example several studies have suggested polysaccharide molecules to be the ice nucleation active species in some pollen^[3]. We extended these investigations by examining the ice nucleation characteristics of different species of these molecular INs. For this purpose, we applied two different optical freezing arrays – the microliter droplet BINARY and nanolitre droplet nanoBINARY setups – for simultaneous ice nucleation measurement of many samples over a wide temperature range extending towards the homogenous ice nucleation temperature of water at about -37 °C ^[4,5]. In order to characterize the underlying molecular IN at play, we conducted ice nucleation measurements after varying sample preparation methods, such as e.g. heat denaturation or size exclusion filtration.

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Exploration of the nucleation of trisilver citrate

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For many years, silver-based materials have been used in versatile applications due to their unique physical and chemical properties (i.e., optical, magnetic, electrical, antimicrobial, or chemical properties) [1], such as investigation of the mechanism of trisilver citrate formation has attracted great attention. The chemical method of trisilver citrate generation is one of the most widely used ones, due to its simplicity, low cost, etc. The potentiometric titrations carried out in solution allow for controlling the simultaneous formation and growth of solids using metal precursors, reducing agents, stabilizing agents, and pH. However, many questions related to the early stages of formation, and the precise solubility product of trisilver citrate are not known yet [2]. Firstly, it is not clear whether nucleation occurs according to the notions of classical nucleation theory, two-step nucleation, or the pre-nucleation cluster pathway. While there is some evidence for the latter the composition of putative trisilver citrate prenucleation clusters remains elusive. Moreover, it is unclear whether an adaptation of classical nucleation theory for reactive nucleation is possible for this system. Importantly, changes in the different concentrations of the reducing and surfactant agent affect the early stages of nucleation, the size of silver nanoparticles, and the size and shape of pure nanoparticles, but their exact mechanistic roles remain unclear [3,4]. Potentiometric titrations in combination with turbidity electrode, and Ag-ion selective electrode at pH-constant titration can allow quantitative determination of the free and bound amounts of the precursor species. In this context, we investigate the nucleation of trisilver citrate by potentiometric titrations at seven different pH conditions (between 5.0 and 8.0), as well as the determination of the solubility product of trisilver citrate.

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Nanoscale adhesion force heterogeneities at electrochemical interfaces

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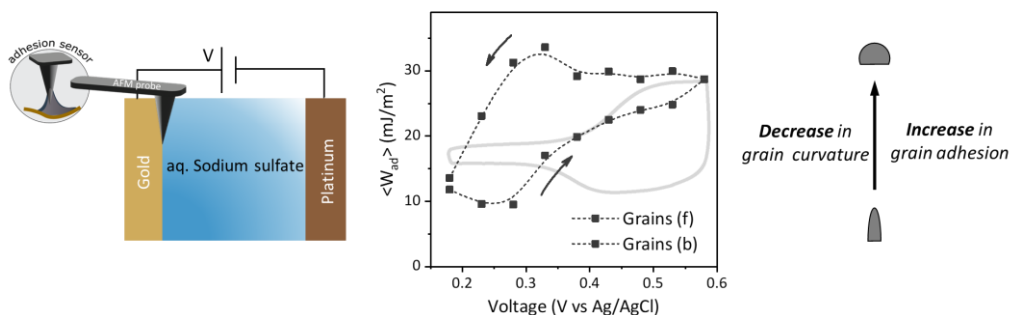
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Electrochemical solid-liquid interfaces (SLI) play a significant role in dictating charge transfer dynamics and selectivity of reactions at any given electrochemical interface. Probing the structure and arrangement of interfacial ion and solvent molecules in-situ with nanoscale resolution is crucial to understand the SLI and develop efficient electrocatalysts. In this contribution, I will highlight the use of Electrochemical atomic force microscopy (EC-AFM) as an interfacial force sensor to map the interfacial adhesion forces in addition to the local topography of the electrode under applied bias. As the electrode surface charge is tuned by applied bias, the local SLI structure is modulated, leading to quantifiable changes in the adhesion forces mapped by the EC-AFM. Adhesion forces extracted from the AFM retract curves provide direct insights into the interfacial energy associated with the molecular arrangement of the SLI.

I will discuss the presence of adhesion force inhomogeneities on the SLI when a (111) textured polycrystalline gold electrode is immersed in the neutral electrolyte solutions (Na_2SO_4 or NaCl). These inhomogeneities are indicative of local differences in the SL interfacial energy. At the potentials corresponding to the anion adsorption on the gold electrode, the measured adhesion force (SLI interfacial energy) increases. We observe the presence of potential-induced hysteresis of adhesion forces as the potentials are cycled from low to high values and back. The potential dependent adhesion force hysteresis varies based on the adsorbed anion (sulphate or chlorine ion). A force minimum is observed before the onset of the anion adsorption, which we attribute to the point of zero charge as the surface charge switches from negative to positive and the interfacial energy is at the minimum.



Ambient scanning probe microscopy with qPlus sensors

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As an undergraduate student, the notion of resolving individual atoms with a machine barely larger than a paperback book, by scanning a sharp tip attached to a quartz oscillator across a sample surface, seemed far-fetched. However, my recent foray into atomic force microscopy (AFM) has convinced me otherwise. Within a few weeks of working with AFM, I achieved atomic resolution with a sensor and tip I built myself. In our research group, we specialize in frequency-modulation AFM (FM-AFM), employing a custom-built Orpheus II microscope [1]. This setup is centered around the self-sensing qPlus sensor, which enables us to oscillate a sharp tip near a sample and detecting minute changes in the resonance frequency to gauge surface interactions. Remarkably, even under conditions relevant to both electronic devices and biological samples, we consistently attain atomic resolution. I present experimental data on diverse surfaces like muscovite mica and the ionic crystal KBr to exemplify this.

Our recent exploration into imaging biological specimens in liquid environments has presented challenges, notably heightened noise levels. Leveraging the advantages of the qPlus sensor, we have managed to achieve approximately 10nm spatial resolution of S-Layer protein structures [2]. This feat relies on the increased stiffness of the qPlus sensor and the high flexibility of the qPlus sensor in accommodating tips with varying length and material composition [3].

Moving forward, our focus lies on refining measurements at ambient conditions and enhancing spatial resolution when imaging biological samples in liquid environments.

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Resolving the surface structure and hydration layer structure of model copper/halides CO₂RR catalysts by *in situ* AFM

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The CO₂ electroreduction reaction (CO₂RR) is of great interest for renewably-driven CO₂ conversion into fuels and value-added chemicals. Copper (Cu) stands out as the sole metal capable of converting CO₂ into C₂₊ products, including ethylene and ethanol. However, the rational design of selective and active electrocatalysts is hindered by lacking nano- and atomic-scale surface structure information derived in relevant electrolytes under operating conditions. Both resolving the catalyst surface structure^{1,2} and gaining complementary insights into the structure of the electrolyte (cations, water layers, ...) near the surface is critical. Metal cations have proven to be essential for CO₂RR³ and controlling the electrolyte cation composition enables tuning catalytic properties⁴. Moreover, synergistic effects between metal cations and halides anions have been shown to enhance the CO₂RR performance of Cu⁵, while the underlying mechanisms remain a topic of debate.

First, we resolve the surface reconstructions occurring on Cu(100) during CO₂RR for a wide range of reductive potentials, down to -1 V_{RHE}. We reveal the dynamically evolving monoatomic step upon reduction of oxidized Cu surface, transitioning from round to square to round edges after a reducing potential step. At -1 V_{RHE}, we observe the formation of aggregates and clusters of various sizes, highlighting the dynamic nature of the catalytic interface. Second, following our previous work exploring the impact of halides on the surface structure of Cu(100) under CO₂RR conditions, we assess the synergistic influence of halide anions with the cation type on the Cu(100) hydration layer structure at open circuit potential (OCP), using 3D AFM. At OCP, we show different coverages of mixed halides/hydroxide adsorbate phases and hydration layer ordering both vertically and in plane, likely related to OH ... H₂O hydrogen bonds. We finally discuss the perspective of scanning probe microscopy for nanoscale catalysis and how these findings contribute to rationally innovate state-of-the-art energy conversion materials.

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Role of surface cation and ion concentration on the adsorption behavior at water-mica interfaces

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Adsorption of ions at the solid-liquid interface is central to many natural processes and applications such as corrosion of metals, electrochemical energy storage, and swelling of clays. In these processes, the composition of electrolyte has a profound influence on the structure, dynamics and energetics of the ions and water at interface. Atomistic simulations are practical to properly explore cation-specific effects and concentration-dependence at molecular level. We perform molecular dynamics (MD) simulations to examine the ion adsorption, hydration and electric double layer structures, and ion transport behavior in aqueous electrolytes (Cs^+ , Li^+ , and Ca^{+2} ions) confined between two negatively charged mica surfaces. Our simulation results show that Cs^+ ions have the most prominent screening effect at the surface, indicating a stronger ion adsorption compared to Li^+ and Ca^{+2} ions at the same concentration. Interestingly, the number of adsorbed Cs^+ ions exceeds the surface charge of mica. This refers to a phenomenon called as “overscreening”. As a result, the surface becomes positively charged, and the diffuse layer of EDL becomes co-ion dominated. However, this is not the case for Li^+ and Ca^{+2} which they attach less strongly to the surface and undercharge the mica. These ion adsorption directly affects the water structures. Although there are less Li^+ ions at the surface compared to Cs^+ , more water molecules come near to the surface from the center of the channel for Li case. Water molecules can go through between adsorbed Li^+ layer and the surface, strongly hydrating Li^+ ions whereas this is not possible for Cs^+ . These indicate that hydration is the driving force in Li solution while surface forces are dominant in Cs case. By assessing the competitive behavior of charged species at the surface, the adsorption coverage is quantified as a function of ion concentration. Cs^+ coverage significantly increase with the increase of concentration while a linear but less prominent increase is obtained for Li^+ adsorption. On the other hand, increased ion concentration shows a negligible influence on the Ca^{+2} coverage. MD simulation results highlighting the ion adsorption as a function of ion type and concentration is critical to understand the interfacial thermodynamics directly from high resolution atomic force microscopy imaging.

Atomic Structure of K-Feldspar Microcline (001) and its Interaction with Water

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Ice nucleation plays a fundamental role in the formation of mixed-phase and ice clouds and, thus, the understanding of ice nucleation is essential for the development of more reliable climate models. Most ice nucleation in the atmosphere is heterogeneous caused by ice nucleating particles such as mineral dusts or organic aerosols. In this regard, feldspar minerals have gained great interest recently as they are found to be one of the most important ice nucleating particles under mixed-phase cloud conditions. Recent scanning electron microscopy studies have shown that ice nucleation on the (001) and (100) cleavage planes of K-rich feldspars predominantly takes place at step edges and pores. Moreover, the formation of ice crystals on feldspar surfaces has been observed by video and atomic force microscopy on the micrometer scale. The mechanism by which feldspar minerals facilitate ice nucleation, however, remains elusive. An in-depth understanding of the atomic-scale structure of feldspar mineral surfaces is mandatory for unravelling the origin of this exceptional ice nucleation ability. In this respect, it is especially crucial that experimental studies on the atomic-scale surface structure of feldspar minerals are sparse. Here, we present atomic force microscopy images of K-feldspar microcline (001) taken in ultrahigh vacuum. On the nanometer scale, we find that our microcline samples exhibit a rich microstructure with a high density of step edges and other surface features. On the atomic scale, our AFM data reveal features consistent with a hydroxyl-terminated surface. This finding suggests that water in the residual gas readily reacts with the surface. Indeed, corresponding density functional theory calculations confirm a dissociative water adsorption. These insights into the surface structure at the nanometer and atomic scale will contribute to understanding the excellent ice nucleating ability of feldspar minerals.

In Situ AFM study of electrocatalytic active faceted platinum nanoparticles produced by solid-state dewetting

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The hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) are the foundation stones of the renewable hydrogen economy and are core to the transition towards a sustainable carbon-neutral economy. Recently, it has been suggested that the interfacial water structure and electric double layer play a crucial role in the hydrogen evolution rate of the model catalyst Pt (111) surface¹⁻³. In this study, using electrochemical atomic force microscopy (EC-AFM), we investigate the effects of fluid composition (pH and specific electrolyte ions) and applied potential on hydration forces and the surface structure of faceted platinum nanoparticles.

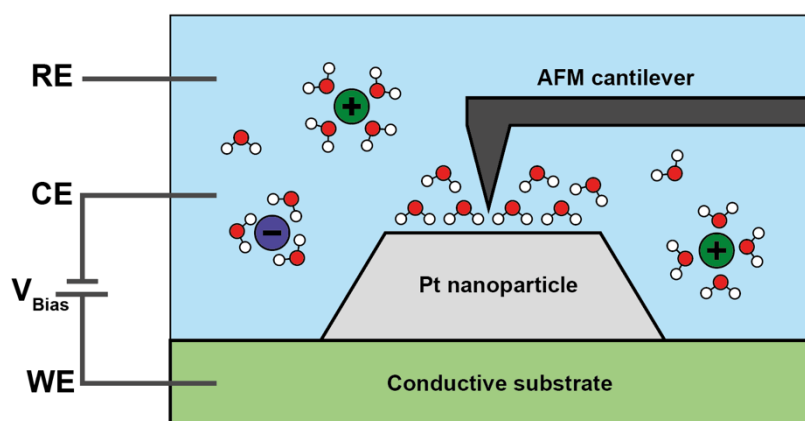


Figure: Experimental setup sketch of the EC-AFM system

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Indications of Reconstruction at μm -Scale as a Possible Stabilization Mechanism of Polar, Ice Nucleating Silver Iodide Surfaces

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The characteristics of ice-nucleating particles (INPs) are important due to their high relevance for weather processes and climate in general. Especially in clouds, INPs have a significant influence by initiating the formation of ice and thereby changing the cloud's radiative properties. In this context, a prominent example of an INP is silver iodide (AgI), which nucleates ice at temperatures up to $-4\text{ }^{\circ}\text{C}$. A common explanation for this extraordinary IN efficiency is a particularly small lattice mismatch between the basal plane of ice Ih and the relevant AgI surface. However, the AgI planes are polar surfaces and, therefore, thermodynamically unstable. Generally, surface reconstruction or an adsorption of charged species are possible stabilization mechanisms. In either case an alteration in the surface structure of AgI is expected, which questions the aforementioned explanation. Results of atomic force microscopy (AFM) measurements of the polar AgI surfaces in water and ethanol did not show any sign of surface reconstruction on the atomic scale [1]. In contrast to that, μm -sized AFM images at the AgI-water interface showed triangular facets that might be an indication of surface reconstruction on a larger scale, considering that a triangular reconstruction was also observed as a favorable stabilization mechanism for the polar, zinc-terminated (0001) surface of zinc oxide [2].

Here, we present AFM experiments on the μm -scale at the AgI-water and AgI-alcohol interface. Both cases showed distinct triangular facets. Additionally, terraces with gaps and canal-like structures were observed at the AgI-alcohol interface under conditions for reduced ion adsorption. As the obtained results provide further indications of reconstruction, they represent an important advance in understanding the stabilization of polar AgI surfaces and thus of the mechanism of ice nucleation.

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The (2x1) reconstruction of the calcite(104) surface

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Calcite, the most stable polymorph of calcium carbonate (CaCO₃), is an abundant mineral in the Earth's crust [1]. The interaction between the (104) face, the most stable cleavage plane of calcite, and water is of utmost importance [2,3]. Consequently, the surface has intensively been studied with a plethora of methods. Still, there have been conflicting reports in literature concerning the surface structure of the pristine calcite(104) surface. In particular, a (2x1) reconstruction and a row-pairing reconstruction have been found [4,5] that are both not in agreement with the structure of the bulk-truncated (1x1) structure of calcite [6].

In this contribution, the microscopic geometry of the pristine calcite(104) surface is investigated by a combination of high-resolution atomic force microscopy (AFM) data at 5 K, density functional theory (DFT), and AFM image calculations. From a comparison between the experimental AFM images and AFM image calculations, strong evidence is given that the pristine calcite(104) surface expresses a (2x1) reconstruction and further contains a glide plane symmetry element with axes of glide plane symmetry located along the carbonate group rows [7]. Most importantly, it is demonstrated that the adsorption of carbon monoxide (CO) molecules on calcite(104) is influenced by this reconstruction as two different adsorption geometries are identified for CO.

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Determination of the reaction volume of the underpotential deposition of Cu and Ag on Au(111)

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The reaction volume of processes at the electrochemical interface is determined by the intrinsic volume change of the participating ions as well as by the variation of the electrostriction of solvent molecules in the high electric fields in the solvation shell or in the electric double layer. Thus, the reaction volume of electrochemical reactions contains valuable information on the processes themselves as well as on the participation of solvent. However, for electrochemical surface reactions data on the reaction volume is quite limited. [1-3]

We address this thermodynamic quantity by measuring the pressure dependence of the electrode's equilibrium potential. With a specifically designed cell we apply pressure pulses of moderate amplitude (5 bar) and durations of several seconds. From the change of the equilibrium potential with the applied pressure ($\Delta\phi/\Delta p \lesssim 20 \mu V/\text{bar}$) we directly calculate the reaction volume of the ongoing electrode process. For (111)-textured Au-films in $\text{CuSO}_4/\text{H}_2\text{SO}_4$ as well as $\text{Ag}_2\text{SO}_4/\text{H}_2\text{SO}_4$ the reaction volume has been determined for different surface states including a Cu (or Ag) covered Au surface, coadsorption states or fully sulfate covered Au.

Within the Cu UPD region, the reaction volume approximately maintains the value of Cu bulk deposition ($18 \text{ cm}^3/\text{mol}$). Deviation indicate coadsorption of sulfate and copper. At more positive potentials where solely the adsorption of sulfate takes place, the reaction volume decreases to $0 \text{ cm}^3/\text{mol}$ for a fully sulfate covered surface, showing that in the latter case the solvation state of sulfate does not change during adsorption. Within the Ag UPD, Δ_{RV} equals the value of Ag bulk deposition ($13 \text{ cm}^3/\text{mol}$) at the Ag UPD peaks, but also varies at potentials between them.

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Quartz Crystal Microbalance (QCM): A useful tool for understanding complex interactions in interfacial processes

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The Quartz Crystal Microbalance (QCM) is an elegant tool for studying and better understanding the complexity of interfacial processes like (ad)sorption and formation of layers on surfaces, and may even offer remarkable insight into material interactions at the molecular level.

The ability of QCM to monitor minor changes in mass on the sensor surface with high sensitivity allows us to study dynamic phenomena such as adsorption, desorption, and layer formation in real-time. This technique proves especially elegant in investigations of the complex interactions involved in (ad)sorption processes, where multiple factors influence the binding of molecules to surfaces. By providing quantitative data on mass changes, QCM enables us to analyze the kinetics, thermodynamics, and structural aspects of the sorption processes, offering a comprehensive understanding of the mechanisms involved.

In this study, valuable experience was gained by investigating the nucleation and growth process during the formation of Metal-Organic Frameworks (MOFs) as both powder and thin films on substrates. The size and morphology of the MOF crystals play a crucial role in determining their applicability in various fields. For this purpose, controlling the solid-liquid interface conditions, such as modulating solvent polarity or using additives and optimizing the reaction parameters, is important. The above parameters can impact nucleation and growth processes by influencing the coordination behavior of metal ions and linkers, result in the formation of smaller or larger particles and even lead to the creation of a dense and homogeneous layer on the substrate. More recently, we evaluated the potential use of QCM in typical (ad)sorption processes, with the ultimate goal to develop robust thermodynamic models based on structural characterizations and mechanical understanding. Initially, we explored NaCl interactions with Si-QCM and Au-QCM surfaces and subsequently plan to investigate Eu adsorption under different salinity conditions and ultimately, also in the presence of other trivalent cations (in particular Al³⁺).

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TIP CLASSIFICATION IN HIGH-RESOLUTION AFM IMAGING IN LIQUIDS

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Abstract

AFM imaging in liquids is not just a direct reflection of the water hydration layers but is majorly affected by the scanning height and tip. As a result of this dependency, imaging of the same crystal surface might end up with different 2D maps [1, 2].

In this work, we are developing a workflow to identify diverse contrast patterns resulting from AFM scanning height and tip dependency. Initially, our model clusters the latent space summarisation of images in large experimental datasets, based on the similarity in their contrast patterns. Finally, it compares and assigns the clusters to relevant free energy simulations based on scanning height and tip. Two key factors to the success of this mission are selecting a sensitive latent vector to the contrast patterns and, implementing a robust benchmark for clustering reliability.

Notably, a statistical analysis on Fourier transforms peaks as image descriptors, aided by tSNE and K-means clustering shows promise in qualitative evaluation. However, developing a quantitative method for evaluating the results on large datasets remains a priority. To this end, we are developing a method for lattice vector extraction out of experimental data, which promises to make quantitative benchmarks available for periodic crystal images. In addition to being used as a benchmark tool, a set of extracted lattice vectors holds the potential for being used as an alternative way of describing images containing periodic patterns.

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IR study of D₂O adsorption on alkali feldspar

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Due to its ubiquitous presence in the Earth's crust, alkali feldspar is an important constituent of airborne mineral dust aerosol and thus plays a major role in the nucleation and growth of atmospheric ice particles. The presence of ice particles in the atmosphere has a strong influence on a variety of processes such as radiative heat transfer, formation and evolution of clouds, precipitation and absorption of trace gases. Some alkali feldspars have attracted researcher's attention due to their particularly high ice nucleation (IN) activity. This phenomenon has been recently ascribed to structural similarities of the ice (101 $\bar{0}$) prism planes and the (100) planes of alkali feldspar [1]. However, since the (100) plane does not exhibit crystallographic match to ice I_h, a layer of hydroxyl groups on the surface of feldspar is required to minimize the interfacial energy and thus create beneficial conditions for ice nucleation. The structure of this hypothetical hydroxyl layer under realistic environmental conditions is not known and has to be derived from measurements.

In this study, we investigate the structure of D₂O water adsorbed on the (001) and (010) planes of alkali feldspar using the UHV IR Reflection Absorption Spectroscopy (IRRAS) [2]. We compare the IRRAS spectra obtained for two distinctly different K-feldspar specimen: gem-quality K-rich orthoclase and structurally complex microcline perthite, varying the amount of adsorbed water and deposition temperature in the range between 118 K and 250 K. By characterizing the ice nucleation from water vapor (i.e., deposition mode nucleation) at cold temperatures (118 - 150 K) on a range of K-feldspar samples, we find direct evidence that ice nucleation efficiency of K-feldspar samples is related to the structural symmetry and orientation of surfaces. These findings are supported by direct measurements of the IN efficacy of feldspar specimens performed with a droplet freezing array setup [3].

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Charged Surfaces: Hydration Layer Mapping at the Au(111) electrode surface

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Interfacial water plays an important role in many fields, including electrochemistry and catalysis. In most cases the solid electrode surface is charged, affecting the hydration structure of interfacial water. Currently, many fundamental processes at the electrode-electrolyte interface are still poorly understood. An ideal method for investigating the hydration structure at the molecular level is three-dimensional atomic force microscopy (3D-AFM). Here, we present 3D-AFM data unravelling the hydration structure at the Au(111) surface. Furthermore, the development of an electrochemical setup that allows for hydration layer mapping under potential control is described. It is based on the 3D-AFM setup, additionally equipped with a working-, counter- and reference-electrode connected to a potentiostat. In future, this setup should be capable to map the electrode-electrolyte interface under potential control.

Influence of ionic concentration on the electrochemical solid-liquid interface of gold

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Electrochemistry in fluids happens mostly at the solid-liquid interface. Therefore it is of vital importance to know what is happening at the surface of the electrode. A deeper understanding of the solid-liquid interface could greatly improve electrochemical reactions and catalysts. In this work, I show the use of an Atomic Force Microscope (AFM) to study the interfacial forces on an electrode under applied bias. Using the AFM, the local topology and adhesion forces of polycrystalline Au electrodes in Na₂SO₄ electrolyte solutions can be measured. We use this technique to study the adsorption of the sulphate anions on the gold surface. By varying the applied bias, the level of sulphate adsorption changes. At the potentials corresponding with sulphate adsorption, the adhesion forces measured in the AFM increase due to the solid-liquid interfacial energy increasing. We observe hysteresis in the adhesion forces when cycling the applied bias from low to high potentials and then back. When changing the ionic concentration of the Na₂SO₄ electrolyte the overall adhesion values decrease.

Interfacial layering of hydrocarbons on pristine graphite surfaces immersed in water.

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Interfacial water participates in a wide range of phenomena involving graphite, graphite-like and 2D material interfaces. Three dimensional AFM (3D AFM) is an advanced Atomic Force Microscopy technique which allows to image the organization of liquid molecules above a solid surface with sub-nm resolutions^{1,2}. In this work, 3D AFM was applied to follow in real-time the evolution of graphite-water interfaces. Pristine graphite surfaces in water showed the presence of hydration layers characterized by a distance of 0.3 nm^{3,4}. Those layers were short-lived. After several minutes, the interlayer distance increased to 0.45 nm. This distance of 0.45 nm characterizes the layering of predominantly alkane-like hydrocarbons and it is comparable to the values that have been measured on graphite surfaces immersed in organic solvents such as hexane or pentadecane⁴. Molecular dynamics calculations supported the experimental observations. Free-energy considerations show that the replacement of water by alkanes is a spontaneous process⁵.

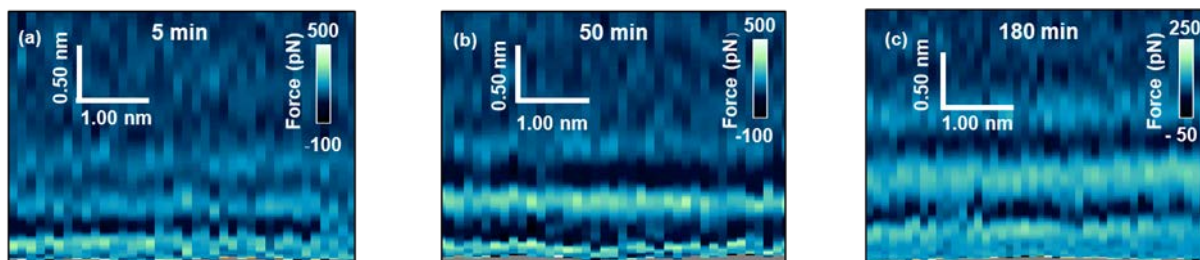


Figure 1. Time evolution of 2D force maps (x,z) of graphite-water interfaces extracted from 3D AFM volume images.

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Role of Interfacial Water and Specific Ion Effects in Carbon Mineralisation

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The latest IPCC report shows that reducing greenhouse gas emissions alone will not be enough to prevent climate disasters.[1] Rapid carbon mineralisation emerged as a promising candidate for long-term carbon sequestration. This process involves dissolved CO₂ reacting with various naturally abundant ions such as Mg²⁺ and Ca²⁺ within porous basaltic minerals.[2] However, its molecular mechanism remains largely unknown due to the lack of direct experimental data probing structures and forces near the solid-liquid interface.

Recent work has suggested that many minerals including calcite display nonclassical crystal growth.[3,4] Aligned aggregation of particles ranging from multi-ion complexes to nanocrystals is now recognised as a pathway of crystallisation. However, many mysteries remained, such as the sensing and alignment of particles over very long distances and the draining of solution during aligned attachments. These phenomena and the nonclassical crystallisation mechanism are likely closely related to the ordering of the water near the particle surface.[3] Our work uses dynamic light scattering and surface force balance (SFB) to monitor the bulk behaviour of mineral nanoparticles and the structure of solutions near the solid-liquid interface. The SFB can directly measure free energy of interaction with a resolution of $\sim 10^{-6}$ J/m², and with a spatial resolution of 0.1 nm, both required to resolve the role of interfacial water. We have studied the solution structure and how it modulates particle-particle interactions as a function of ionic strength and salt composition. This work provides key experimental results and molecular insights for the rational design and optimisation of carbon capture processes based on mineralisation.

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Exploring Additive-Mediated Surface Alterations in Olivine for Enhanced Reactivity in Carbon Capture

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Olivine, a magnesium silicate mineral, stands as a promising candidate for CO₂ sequestration and capture, either through natural weathering or industrial conversion processes. A silica-rich layer formed on the mineral surface during dissolution at the mineral-electrolyte interface poses a challenge, slowing down the ion exchange with the solution. A precise mechanistic understanding of the formation and properties of these layers, and their connection to the dissolution process, remains elusive, necessitating a thorough investigation to unveil the underlying mechanisms.

In this study, we probe the potential of oxalic acid as an additive to accelerate the release of Mg²⁺ ions, thereby suppressing the formation of inhibitory silica layers. The impact of oxalic acid on the dissolution process is systematically examined in two distinct systems: olivine pebbles dissolving in H₂SO₄ and HCl at varying pH levels. The quantification of Mg²⁺ ions released during dissolution, both in the presence and absence of oxalic acid, is carried out using Fluorescence Lifetime Imaging Microscopy (FLIM) with a Mg-responsive dye. With Confocal Raman Microscopy (CRM) we investigate the evolution of the interfacial layer to discern its porosity and thickness, specifically in relation to ion release and correlate with FLIM data. Our findings demonstrate that oxalic acid significantly increases the release of Mg²⁺ ions. This is further corroborated by an observed enrichment of Si in the bulk solution. The study delves into the nuanced behavior of the additive under different acid systems and varying conditions, providing valuable insights into the intricacies of olivine reactivity enhancement for CO₂ sequestration.

Modeling of electrical fluctuations next to an electrode to probe the properties of interfacial electrolytes

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In electrochemical processes, fluctuations in physical quantities are commonly regarded as noise, which needs to be minimized relative to the signal. The charge exchange at the electrode-electrolyte interface drives chemical transformations, forming the basis for crucial technologies. Through molecular simulations, we explore the connection between solvent polarization fluctuations around a solute near an electrode, electron transfer kinetics (Marcus theory), and how these fluctuations manifest in electrode charge fluctuations^{1,2,3}. The electrode's metallicity, indicative of its electronic structure, influences electron transfer kinetics⁴. This metallic character is encapsulated by the Thomas-Fermi screening length (l_{TF}) within the electrode^{5,6}. Molecular simulations in the constant-potential ensemble, incorporating l_{TF} ⁷, have revealed its role in interfacial thermodynamics, elucidated through the charge distribution within the electrode⁸.

To investigate the charge distribution induced on the surface by a single ion at varying distances from the electrode (d)⁹, classical molecular dynamics (MD) was employed for an ion adjacent to a tunable metallicity graphite electrode in vacuum and water. Analyzing 2D and radial charge distributions, we explored the impact of distance (d), screening in the metal (l_{TF}), and solvent (ϵ_r). This initial exploration sets the stage for understanding the collective influence of these factors on the "vertical energy gap," a key determinant of electron transfer reactions. The MD results were compared to continuum electrostatics predictions, affirming the significance of the proposed effective length's long-range behavior, incorporating d , l_{TF} , and ϵ_r . Additionally, we emphasized the role of periodic boundary conditions and the solid lattice's atomic structure, particularly the significance of the "Jellium edge."

This work is part of the ERC project SENSES (grant No. 863473). Project website: <https://benrotenberg.github.io/erc-senses/>

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Pattern formation at the dynamic interface of an evaporating droplet

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Liquid-liquid phase separation (LLPS), which occurs in both organic and inorganic macromolecules, leads to certain pattern formation in a liquid phase. How a dynamic interface between liquid and air can lead to the formation of macroscopic patterns of polymer aggregates is not questioned. I studied the pattern formation of organic and inorganic macromolecules in an evaporating droplet with a dynamic interface to understand the pattern formation of these macromolecules in the droplet. I observed that by adjusting the polymer concentration, a very unique and regular lattice pattern forms. Through various experiments, I was able to show that this pattern is due to the salt depletion effect, which leads to a solutal Marangoni flow and aggregation of the macromolecules at the interface.

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Towards understanding interfacial thermodynamics: visualising and quantifying competitive adsorption on muscovite mica with AFM

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Given its peculiar crystal structure and inherent surface charge, the (001) plane of muscovite mica has served as an excellent model system to study the hydration and electric double layer (EDL) forces at solid-liquid interfaces [1]. So far, force spectroscopies, which measure along the direction perpendicular to the surface, as well as molecular dynamics (MD) simulations, have demonstrated a certain ion-specificity towards the strength of hydration forces on mica surfaces [2-5]. These deviations are mainly attributed to the different properties of individual ions (e.g., hydration shell, size, valency, etc.), which ultimately determine their adsorption character on mica, as well as the interfacial hydration structure [5]. Nevertheless, lateral distribution and arrangement of cations adsorbed on mica was experimentally investigated only to a lesser extent [6], although unravelling the ions' organisation directly at the surface is crucial to elucidate the structure and properties of EDLs.

In the present contribution, we discuss how high-resolution atomic force microscopy (AFM) imaging enables us to visualize the lateral distribution of individual mono- and multi-valent ions on the surface of mica. Thanks to this approach, we are able not only to resolve the crystal structure of mica immersed in aqueous solution, but also to transiently picture the population of adsorbed ions from the salt-rich solutions at different concentrations. By using an automated triangulation algorithm, the ion adsorption coverage as a function of concentration can be quantified in a first order approximation. This methodology highlights the possibility to outline a certain competitive behaviour of charged species at the surface. Understanding such competition as a function of type and concentration of ions allows us to unravel the interfacial thermodynamics directly from AFM data, which has been so far mainly exclusive to MD simulations. To further support our findings, we use surface force apparatus and MD simulations to characterise the structure and mechanical properties of EDLs on mica for different cation species.

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Water Arrangement at the K-Feldspar Microcline (001)-Water Interface

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Microphysical properties of clouds, which also affect global climate, depend on whether cloud droplets are liquid or frozen. Cloud droplets often freeze heterogeneously in the presence of an ice nucleating particle (INP), such as mineral dusts. Here, potassium rich feldspar particles are of particular relevance, due to their abundance in the atmosphere and their excellent ice nucleating abilities at low supercooling. Recent experimental studies on the micrometer scale have shown that surface defects such as steps and pores can act as active sites for ice nucleation. Additional density functional theory studies at the feldspar-water interface disclose an inconsistent picture. Some studies observe no evidence of an ice-like structure, while another work could identify an ice-like structure in the second water layer. Therefore, investigations of the feldspar-water interface on the atomic scale are necessary for unravelling the origin of the outstanding ice nucleation efficiency of K-feldspars. Here, we present two- (2D) and three-dimensional (3D) atomic force microscopy (AFM) images on the atomic scale taken at the microcline (001)-water interface. The 2D AFM images reveal patterns with unit cell dimensions, which are in excellent agreement with the unit cell of the underlying microcline (001) surface. 3D AFM measurements unravel a hydration structure with three hydration layers normal to the surface. Based on molecular dynamics simulations, we propose that the AFM measurements show the second and higher water layers, while the first layer is hidden in the repulsive region close to the surface. The water molecules in the second water layer appear rather mobile and are not localized on well-defined sites. Our 2D and 3D AFM measurements at the microcline (001)-water interface show no evidence of an ice-like structure.

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In situ surface X-ray diffraction studies of the electrochemical double layer on Pt(111)

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The molecular structure of the electrochemical double layer is an important fundamental topic in interfacial electrochemistry. In the measurements presented here, we investigated the properties of the electrochemical double layer on Pt(111) in aqueous electrolyte solution via in situ surface X-ray diffraction (SXRD), a technique that is well-established for single crystal studies [1,2].

Platinum electrodes are widely used as electrocatalysts, for example as cathodes in fuel cells due to their high ORR reactivity. The single-crystalline Pt(111) surface, which is a well-studied model system, is especially interesting for studies of the electrochemical double layer. Recent electrochemical measurements revisited this system and found evidence for a double layer structure that strongly deviated from the traditional Gouy-Chapman-Stern model and indicated a complex structural influence of water [3,4]. The water structure within the electrochemical double layer is also of major interest in computational studies. For non-adsorbing, aqueous electrolyte the electrode surface charge can be partly compensated by a layer of oriented water molecules due to their dipole moment. For potentials around the potential of zero charge (PZC), a potential-dependent orientation of water molecules with respect to the electrode surface was suggested [5,6].

To investigate the arrangement and orientation of the water molecules near the Pt(111) surface we used in situ SXRD methods, focusing on X-ray reflectivity (XRR) and crystal truncation rod (CTR) analysis. The experiments were performed at beamline ID31 of the European Synchrotron Radiation Facility. We will report results on the water structure in the double layer obtained in perchloric acid at potentials around the PZC.

We gratefully acknowledge financial support by the BMBF via 05K19FK3 and 05K22FK1 and the Deutsche Forschungsgemeinschaft via project no. 418603497.

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Real-time X-ray scattering study of ice nucleation on natural feldspar

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Cloud ice is of great importance for the earth's weather and climate system as it drives the formation of precipitation and affects the radiation budget. The ice formation happens mainly via the heterogeneous formation mechanism, whereby aerosols such as mineral dust act as ice nucleating particles (INP) initiating the freezing process. The most ice active constituent of mineral dust is feldspar, especially perthitic Alkali feldspar with a complex microstructure in form of sodium-rich and potassium-rich exsolution lamellae. Such feldspar is naturally formed during the cooling process after the magmatic and metamorphic crystallization at high temperatures above 500 °C. Surface defects like cracks or cavities are thought to be responsible for the high ice nucleation ability. At the molecular level, however, the ice nucleation mechanism itself is not yet well known. A detailed understanding is essential to assess the role of feldspar in cloud formation and precipitation processes. Using the technique of X-ray diffraction at a synchrotron facility, we want to conduct in situ measurements of the ice nucleation process from the vapor phase on natural potassium-rich and perthitic feldspar cleaving surfaces (001) and (010). Thereby, each sample will be exposed to a temperature and humidity controlled air environment simulating the real atmosphere. With our laboratory experiments we aim to discover the role of adsorbed or liquid water in pores and cavities and whether ice grows in a predictable manner regarding the crystal orientation.

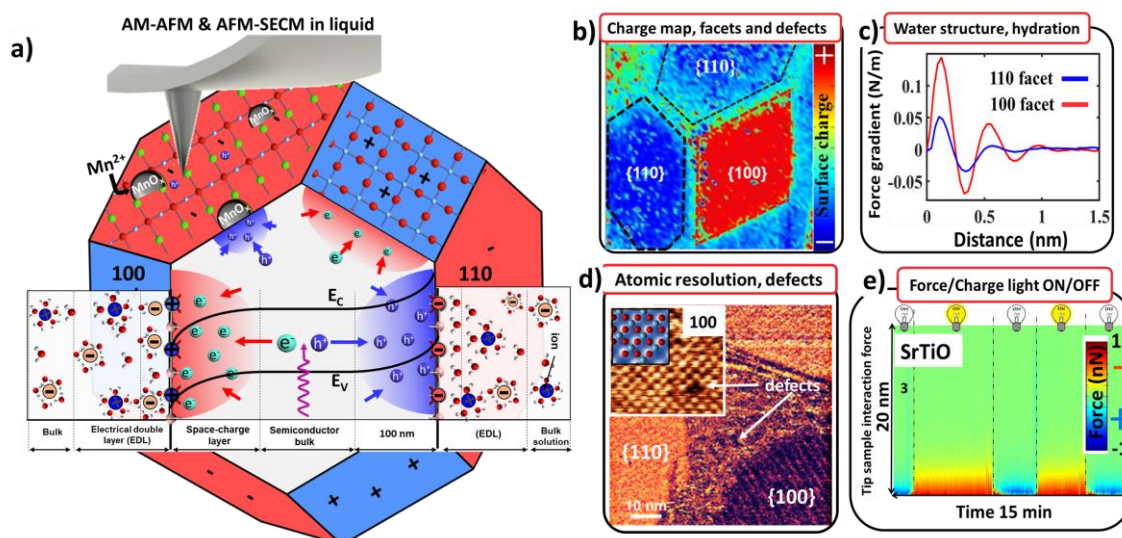
Towards high efficiency photocatalyst materials: *In situ* characterization of faceted SrTiO₃ nano-particle-electrolyte interfaces by Atomic Force Microscopy

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Anisotropy of shape and surface properties determine the functionality of faceted nanoparticles in various contexts including facet selective colloidal self-assembly, crystal growth, biosensing, improved photo/electrocatalytic activity and enhanced selective cellular and ions uptake. The characteristic anisotropy, surface properties and function of solid-liquid interfaces of crystalline faceted nanoparticles are believed to be essential for their performance but remains poorly understood and difficult to characterize and quantify. We use dual scale Atomic Force Microscopy to measure electrostatic and hydration forces of faceted SrTiO₃ nanoparticles in aqueous electrolyte at variable pH. We demonstrate (i) the ability to quantify strongly facet-dependent surface charges yielding isoelectric points of the dominant {100} and {110} facets that differ by as much as 2 pH units, ii) fluids composition controlled facet-dependent accumulation of oppositely charged (SiO₂) particles, and iii) that atomic scale defects can be resolved but are in fact rare for the samples investigated [1]. Atomically resolved images and facet-dependent hydration structure suggest a microscopic hydration and charge generation mechanism [1].



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Interaction of water vapor with heavily reduced $\text{TiO}_2(110)$

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Reducible transition metal oxides such as TiO_2 are promising candidates for various applications such as CO_2 reduction, hydrogen production from H_2O splitting and pollutant degradation. Reducible oxides become rich in complex defects such as kinks, steps, oxygen vacancies, etc., when annealed at high temperatures at low base pressures. Such defect sites are typically the preferred adsorption sites of reactant gas-phase molecules and the active sites for various reactions. Understanding the interface chemistry of H_2O adsorption on such heterogeneous oxides is a long-time scientific interest in catalysis research. However, due to the combination of highly complex atomic structure and scarce availability of suitable techniques, a molecular-level understanding of the processes occurring at the interface between the H_2O vapor and the oxides at ambient pressure (e.g., >20% relative humidity (RH)) and temperature (e.g., room temperature) is lacking. We studied the effect of varying H_2O vapor pressure (i.e., RH) on a highly reduced, defect-rich, and reconstructed $\text{TiO}_{2-x}(110)-(1\times 5)$ surface. In addition to atomic force microscopy (AFM) images, low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) confirm the existence of a heavily reduced and reconstructed (1×5) surface. Ambient pressure AFM (AP-AFM) shows two different regions on the reduced TiO_{2-x} surface, with relatively high and low defect densities. At 20% and 50% RH, these two regions behave differently during imaging both in soft-tapping mode (higher force) and in non-contact mode (lower force). We observe phenomena such as formation of mobile water clusters on the surface, strong adhesion forces between the tip and the sample, and structural damage in TiO_{2-x} while scanning with intermittent contact, which only take place in humid conditions.

C-C Bond Cleavage in the Electrooxidation of 2,3-Butanediol Controlled by an Ionic Liquid Modifier

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In heterogeneous catalysis, ionic liquids (ILs) are used as chemical modifiers to control selectivity. In our work, we aim to apply the same concept to electrocatalytic systems.^[1]

As a model reaction, we studied the electrooxidation of 2,3-butanediol on the low-index Pt(111), Pt(100) and Pt(110) surfaces in an acidic environment. We used the IL 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C₂C₁Im][OTf]) dissolved in an aqueous electrolyte as a catalyst modifier. The reaction mechanisms were investigated by electrochemical infrared reflection absorption spectroscopy (EC-IRRAS). The oxidation of 2,3-butanediol is highly structure dependent. On all three surfaces, the two products formed are acetoin and diacetyl, i.e. either one or two alcohol functionalities are oxidized. However, we observe distinct features on the different surfaces with respect to activity, potential window of oxidation, and selectivity. Only the Pt(100) surface is active towards C-C bond cleavage. The latter reaction leads to the formation of CO_{ads} and poisoning of the catalyst. Modification of this surface by addition of the IL leads to an increase of the selectivity for acetoin from 51% to 78% (at 1.1 V_{RHE}). In addition, C-C bond cleavage is suppressed, no CO is formed, and the surface remains active for the target reaction. We attribute these effects to the reversible and structure dependent adsorption of the [OTf]⁻ anions on the Pt surfaces. Our results demonstrate the potential of ILs to control selectivity in electrocatalytic reactions.^[2]

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Detection of surface intermediates for oxygen evolution on hematite using operando sum frequency spectroscopy

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Photoelectrochemical water splitting is a promising technique for converting solar energy into hydrogen fuel. As a photoanode material hematite ($\alpha\text{-Fe}_2\text{O}_3$) is widely studied for oxygen evolution reaction (OER) due to its abundance, stability, non-toxicity, etc. However, the mechanism of OER on hematite that limits its performance is still undetermined. There is still controversy over single- and multi-hole mechanisms depending on the samples and electrolytes. Operando attenuated total reflectance infrared spectroscopy (ATR-IR) is commonly used to detect surface intermediates at the hematite/electrolyte interface.[1,2] However, ATR-IR gets interference from other species on either the solution or the solid side that is resonant at similar photon energies. Other methods to probe the OER mechanism are indirect and thus possible control of the mechanism by the change in the sample is difficult to infer. Vibrational sum frequency spectroscopy (VSFS) is an interface-specific technique that allows the direct observation of intermediates. By the potential dependent (dis)appearance of a succession of intermediates such as Fe-OH, Fe=O, and Fe-OOH, we demonstrate unambiguously a single-hole mechanism is operative. Additionally, there is a bias-dependent surface phonon mode at around 650cm^{-1} due to lattice distortion, which may be related to the polaron formation and transport. Because of femtosecond pulses in the VSFS measurement, this work also suggests a path toward resolving chemical dynamics on ultrafast timescales.

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