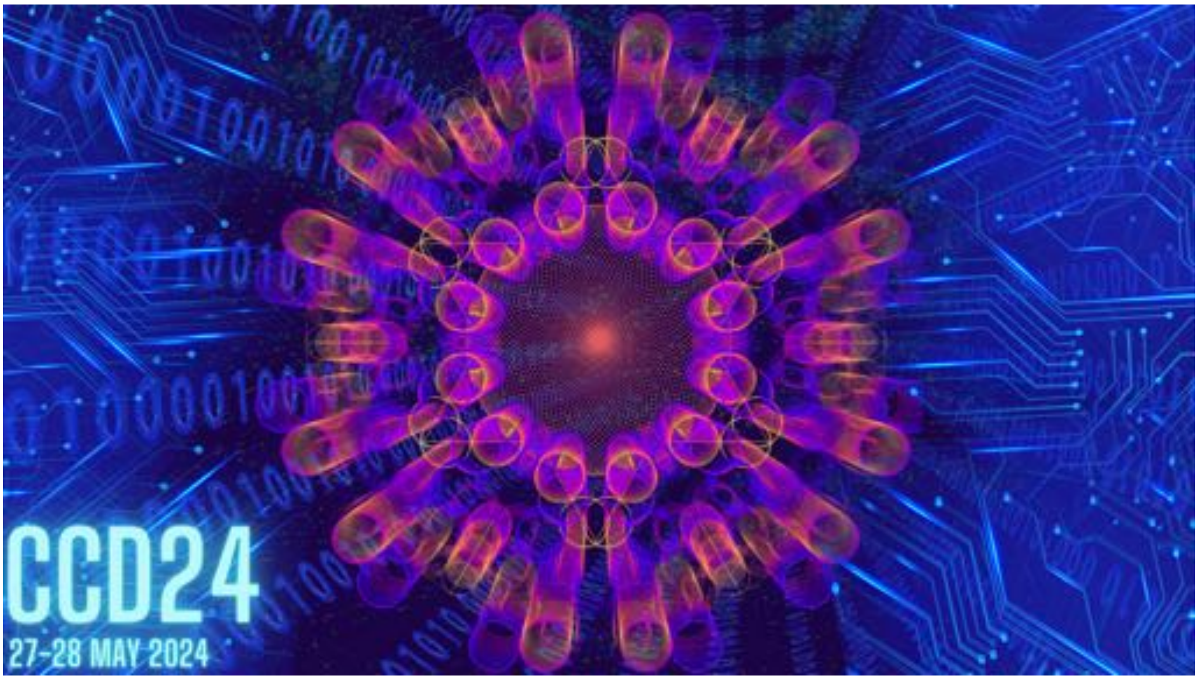
Computational Chemistry Days 2024

27.–28.5.2024, University of Jyväskylä



Book of Abstracts

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About

Computational Chemistry Days

CCD is an annual event showcasing Finnish computational chemistry research. The event provides an opportunity for students and young researchers in the field to network and present their work.

The themes of this year's event CCD24 comprise (a) the modeling of **catalysis and materials**, (b) the modeling of **biomolecules and soft matter**, and (c) the usage of **machine learning** in chemistry research.

Invited Speakers

Five speakers are scheduled to give invited talks at CCD24: Hanna Vehkamäki (HU), Maria Sammalkorpi (Aalto), Miguel Caro (Aalto), Berk Hess (KTH), and Georg Kastlunger (DTU). In addition, we can enjoy listening to 16 contributed talks and seeing 29 poster presentations. The number of participants is 93.

Organizing committee

Department of Chemistry, Nanoscience Center

Karoliina Honkala
Ville Korpelin
Bhumi Baraiya
Marko Melander
Minttu Kauppinen
Aku Lempelto
Hanan Ibrahim
Lorenzo Alonso Gómez
Gerrit Groenhof
Maryam Sabooni
Rasmus Ikonen
Toni Kiljunen
Laura Laverdure
Timo Weckman

Timetable

Monday, 27 of May

12:15	**Welcome remarks**		
12:30–13:00	IS	**Georg Kastlunger** Technical University of Denmark	On the interplay of potential and the reaction environment in the electroreduction of CO_2 and biomass
13:00–13:20	CT	**Omar Lopez-Estrada** Queen's University	Insights into the overall water splitting reaction by monodispersed Fe–Co–Ni–P electrocatalyst
13:20–13:40	CT	**Laura Laverdure** University of Jyväskylä	DFT insights on gold catalyzed sugar oxidation
13:40–14:00	CT	**Bhumi Baraiya** University of Jyväskylä	Isobutene formation from syngas over m-$ZrO_2(\bar{2}12)$ catalyst: A DFT mechanistic and kinetic study
14:00–14:30	**Coffee**		
14:30–15:00	IS	**Hanna Vehkamäki** University of Helsinki	Tackling the chemical complexity in atmospheric new-particle formation
15:00–15:20	CT	**Stephen Ingram** University of Helsinki	Ruptures in mixed monolayers under tension and supercooling: A molecular dynamics study
15:20–15:40	CT	**Maria Dimitrova** University of Helsinki	Magnetic properties calculated using the Ampère–Maxwell law
15:40–16:00	CT	**Annika Lehmann** University of Jyväskylä	Completing the series: The dimeric dialuminene $^{iPr8}AlAlAr^{iPr8}$ ($Ar^{iPr8} = C_6H$-2,6-(C_6H_2-2,4,6-$iPr_3)_2$-3,5-iPr_2)
16:00–16:20	CT	**Oleksii Zdorevskyi** University of Helsinki	Long-range charge transfer in respiratory complex I: Insights from multi-scale molecular dynamics simulations
17:00–19:00	**Poster session with drinks**		

IS: Invited Speaker, **CT**: Contributed Talk

Tuesday, 28 of May

9:00–9:30	IS	**Maria Sammalkorpi** Aalto University	Computer simulations, spider silk-like designer proteins, and itsy bitsy steps toward responsive polymeric materials
9:30–9:50	CT	**Adam Harmat** Aalto University	Computational modelling driven biosynthetic protein materials design
9:50–10:10	CT	**Kourosh Hasheminejad** Aalto University	A computational take on designing self-assembling block copolymer films
10:10–10:30	CT	**Alex Bunker** University of Helsinki	Polymer coatings for drug delivery nanoparticles: Molecular dynamics simulation as design tool
10:30–10:50	**Coffee**		
10:50–11:10	CT	**Sasikaladevi Assa Aravindh** University of Oulu	Tuning the properties of Janus van der Waals hetero structures by varying interface terminations
11:10–11:40	IS	**Berk Hess** KTH Royal Institute of Technology	Accelerating conformational transitions in molecular simulations
11:40–13:00	**Lunch**		
13:00–13:30	IS	**Miguel Caro** Aalto University	Atomistic machine learning for materials modeling
13:30–13:50	CT	**Patricia Hernández León** Aalto University	Efficient many-body representation of atomic environments for machine learning based models and beyond
13:50–14:10	CT	**Max Veit** Aalto University	Incorporating explicit electrostatic interactions in machine learning atomistic simulations
14:10–14:30	CT	**Mario Mäkinen** Aalto University	Modelling the growth of zincone ALD/MLD hybrid thin films using DFT
14:30–14:50	CT	**Ouail Zakary** University of Oulu	Modeling porous liquids with machine-learning-assisted molecular dynamics
14:50–15:10	CT	**Kameyab Raza Abidi** University of Jyväskylä	Atomically thin metallenes are nanoscale amoebae
15:15	**Conclusion**		
15:30	**End of Program**		

IS: Invited Speaker, **CT**: Contributed Talk

Talks

Monday 27th

IS

Computational Chemistry Days 2024

On the interplay of potential and the reaction environment in the electroreduction of CO_2 and biomass

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The atomistic understanding of complex reaction mechanisms in electrocatalysis aids not only the discovery of improved catalytic materials but also the choice of ideal reaction environments for tailored products.

In my talk, I will present density functional theory-based studies on electrocatalytic reaction mechanisms with a special focus on electrochemical $CO_{(2)}$ reduction and biomass valorization. I will describe how the combination of constant-potential DFT approaches and transition state theory-based considerations allow us to explicitly study the potential, pH and electrolyte dependence of multistep reaction networks relevant for the green transition [1].

Further, I will discuss general trends in the kinetic characteristics of the competing elementary reactions in electrocatalytic reductions and their consequences on the potential and pH response of the product selectivity [2,3].

[1] G. Kastlunger *et al.*, Using pH dependence to understand mechanisms in electrochemical CO reduction, *ACS Catal.* **2022**, *12*, 4344–4357.

[2] G. Kastlunger, H. H. Heenen, and N. Govindarajan, Combining first-principles kinetics and experimental data to Establish guidelines for product selectivity in electrochemical CO_2 reduction, *ACS Catal.* **2023**, *13*, 5062–5072.

[3] S. Liu *et al.*, Unraveling the reaction mechanisms for furfural electroreduction on copper, *EES Catalysis* **2023**, *1*, 539–551.

Insights into the Overall Water Splitting Reaction by monodispersed Fe–Co–Ni–P Electrocatalyst

Omar López-Estrada,[a] Lakshya Kumar, [b] and Bindu Antil, [b] Ankur Kumar, [b] Manash R. Das [c] Samira Siahrostami [d] Sasanka Deka [b]

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Nonprecious transition-metal phosphide (TMP) $Fe_{0.5}CoNi_{0.5}P$ nanoparticles were developed as efficient electrocatalysts for water splitting. This catalyst exhibited exceptional performance in both hydrogen and oxygen evolution reactions (HER and OER), surpassing commercial counterparts in an electrolyzer setup. Mechanistic analyses revealed surface reconstruction induced by KOH, enhancing catalytic activity. The synthesis method employed resulted in densely-packed spiky-ball particles, contributing to superior performance [1].

Computational density functional theory (DFT) simulations were conducted to elucidate the underlying mechanisms. DFT modeling of various $Fe_xCo_yNi_zP$ compositions revealed insights into their structural and electronic properties. Pourbaix diagrams were employed to analyze surface oxidation states during the OER, providing a comprehensive understanding of the stability landscape. Additionally, utilizing the computational hydrogen electrode, we evaluated the activity of different catalyst compositions, demonstrating that $Fe_{0.5}CoNi_{0.5}P$ exhibits the lowest theoretical overpotential, indicative of superior performance in OER. Our computational investigations further explored into the HER mechanism on the catalyst surface, confirming $Fe_{0.5}CoNi_{0.5}P$ as the most efficient catalyst (Figure 1).

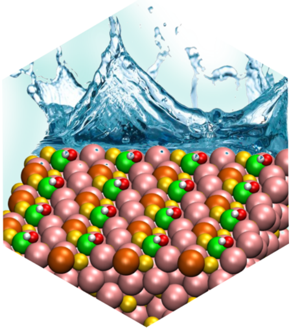

Figure 1: $Fe_{0.5}CoNi_{0.5}P$ water splitting catalyst

[1] L. Kumar et al. *ACS Appl. Mater. Interfaces* **2023**, *15*(47), 54446-54457.

DFT insights on gold catalyzed sugar oxidation

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Electrocatalytic oxidation (ECO) of polyols derived from biomass on gold (Au) catalysts holds significant promise for clean energy and chemical production. Experiments have shown that activity and selectivity toward ECO products depend not only on the catalyst but also on the electrode potential and the pH. A previous computational study established the relevant OH_{ads} coverage for a given set of pH and potential on Au(111) and its effects on glycerol oxidation. [1] Here, we present the results of our investigation into the intricate mechanisms underlying glucose and xylose oxidation on Au(111). In agreement with our previous study, [1] we show that the OH_{ads} surface coverage as well as the applied potential are critical factors in determining the most favorable reaction paths. In addition to promoting sugar adsorption, the presence of OH_{ads} facilitated the initial proton-coupled electron transfer in the oxidation mechanism leading to gluconic or xylonic acid. While surface-mediated tautomerization to fructose and xylulose is competitive with the oxidation reaction on the bare surface at low potential, the products from this undesirable competing reaction are minimized in the presence of OH_{ads} as well as higher oxidative potentials. [2] Our findings underscore the importance of comprehensive computational modeling to accurately predict electrocatalytic behavior, particularly emphasizing the necessity to account for pH, potential, and coverage effects.

[1] A. M. Verma, et al. *ACS Catal.* **2022**, *12*, 662.
[2] J. P. Oña, et al. *ACS Catal.* **2024**, *14*, 1532.

Isobutene Formation from Syngas over *m*-$ZrO_2(\bar{2}12)$ Catalyst: A DFT Mechanistic and Kinetic Study

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Isosynthesis mechanism (aldol condensation vs. ketonization) over a range of zirconia-based catalysts to produce isobutene (i.e., an intermediate for the selective production of jet fuel range hydrocarbons) is still a topic of discussion and it has regained interest due to a demand for selective renewable feedstock conversion routes [1]. To understand the role of Lewis acid-base pairs (Zr^{4+}-O^{2-}) of *m*-$ZrO_2(\bar{2}12)$ model catalyst in the selective formation of isobutene, thermodynamics, and kinetics of the proposed isosynthesis mechanism, the vdW-corrected DFT calculations were carried out with the GPAW simulation code [2]. The undercoordinated sites of the modeled catalyst were found to promote the conversion by assisting the CO hydrogenation and H_2 dissociation. The DFT results indicated that the combination of unsaturated acid-base edge sites promotes the C-C coupling (C_1-C_n, n = 2, 3..) for the chain growth of C_2 to C_3 species & chain branching of C_3 to i-C_4 compounds [3]. At the same time, the irreducibility of the catalyst could hinder the ketonization pathway to produce isobutene from syngas. The potential energy surface scan revealed that faster carbonylation of methyl compared to methyl-to-methylene conversion (rate-limiting step) might be the reason for avoiding excess methanation in the process. This computational study demonstrates the role of the Lewis acid−base pair (often relevant in experimental studies) in the active and selective reaction of syngas-to-isobutene conversion through cross-aldol condensation.

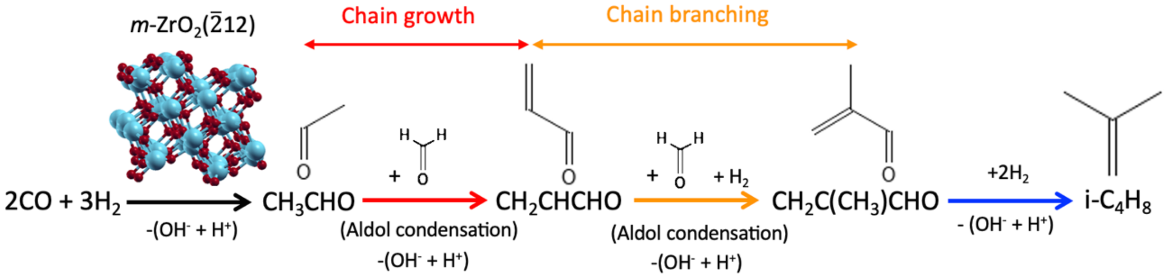

Figure 1: Formation path of isobutene from syngas conversion.

[1] Wu X. *et al. Fuel* **2019**, 243, 34–40.
[2] Enkovaara, J. *et al. J. Phys.: Condens. Matter* **2010**, 22, 253202.
[3] Maruya, KI. *et al. J. Organomet. Chem.* **1998**, 551, 101–5.

IS

Tackling the chemical complexity in atmospheric new-particle formation

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Human perturbations of the atmosphere have resulted in two of the greatest environmental challenges of our time: climate change and air pollution. A key process in both challenges is aerosol formation: the poorly understood conversion of gaseous matter into the condensed phase initiated by radical reactions and molecular clustering. In the atmosphere, aerosol formation involves an extremely large number of predominantly organic chemical species and processes, many of which are even individually difficult to measure or model.

In the Research Council of Finland Centre of Excellence VILMA, we are tackling this chemical complexity using a large variety of computational and experimental tools. On the chemistry side, we characterise the reaction pathways leading to the least volatile (and thus most effectively aerosol-forming) compounds using quantum chemical reaction dynamic tools, in collaboration with mass spectrometric experiments [1,2]. Information from these studies are then encoded in automated reaction mechanism generators, which can produce vast datasets containing up to millions of representative low-volatility products [3]. Their likely condensation behaviour be roughly estimated by computing their saturation vapor pressures using novel machine-learning based approaches [4]. More accurate descriptions of aerosol formation require explicit simulations of the clustering physics, which can also be done using quantum chemistry methods – but only for a very small subset of the vast combinatorial phase space of possible molecular clusters. AI-based tools are thus urgently needed also for efficiently predicting cluster stabilities based on the chemical identities of the clustering molecules.

[1] F. Bianchi, T. Kurtén, M. Riva, C. Mohr, M. P. Rissanen, P. Roldin,T. Berndt, J.D. Crounse, P. O. Wennberg, T.F. Mentel, J. Wild, H. Junninen, T. Jokinen, M. Kulmala, D.R. Worsnop, J. Thornton, N. Donahue, H. G. Kjaergaard, and M. Ehn. Chemical Reviews 2019, *119*, 3472.
[2] O. Peräkylä, T. Berndt, L. Franzon, G. Hasan, M. Meder, R. Valiev, C. Daub, J. G. Varelas, F. M. Geiger, R. J. Thomson, M. Rissanen, T. Kurtén, T and M. Ehn. Journal of the American Chemical Society 2023, *145*, 7780.
[3] V. Besel, M. Todorović, T. Kurtén, P.Rinke and H. Vehkamäki. Scientific Data 2023 *10*, 450.
[4] E. Lumiaro, M.Todorović, T. Kurtén, H. Vehkamäki, and P. Rinke: Atmospheric Chemistry and Physics 2021, *21*, 13227.

Ruptures in Mixed Monolayers Under Tension and Supercooling: A Molecular Dynamics Study

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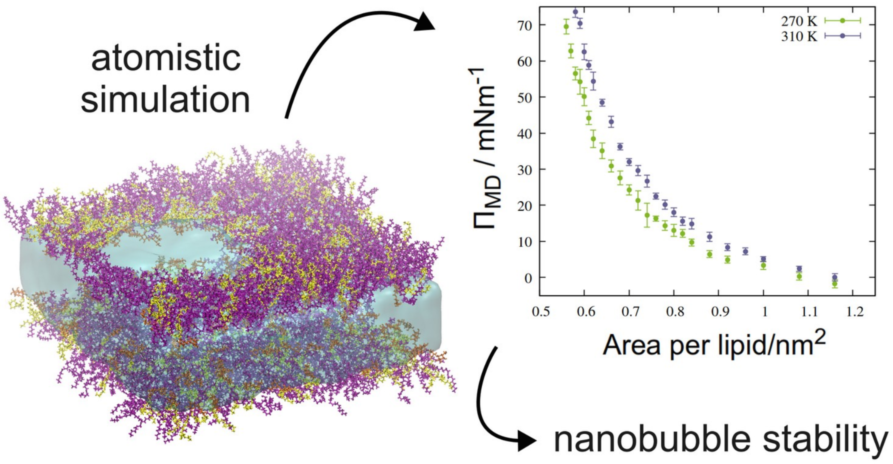
Mixed phospholipid and glycolipid monolayers likely coat the surfaces of pressurised gas nanobubbles within the hydraulic systems of plants. The lipid coatings bond to water under negative pressure and are thus stretched out of equilibrium [1]. In this work, we have used molecular dynamics simulations to produce trajectories of a biologically relevant mixed monolayer, pulled at mild negative pressures (-1.5 to -4.5 MPa). Pore formation within the monolayer is observed at 310 K, and proceeds as an activated process once the lipid tails fully transition from liquid condensed/liquid expanded (LC/LE) coexistence to the liquid expanded phase. Pressure:area isotherms showed reduced surface pressure under slight supercooling (T = 270 K) at all observed areas per lipid. Rayleigh-Plesset simulations [2] were used to predict evolving nanobubble size using the calculated pressure : area isotherms as dynamic surface tensions. We confirm the existence of a second critical radius, with respect to runaway growth, above the homogeneous cavitation radius.



[1] H J Schenk et al., *Plant Physiology.* **2017**, *173(2)*, 1177.
[2] P Marmottant et al., *J. Acoust. Soc Amer.,* **2005**, *118*, 3499.

Magnetic properties calculated using the Ampère-Maxwell law

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The Ampère-Maxwell law defines the classical relationship between a magnetic field and an electric current in a circuit. It turns out that the equation is applicable to quantum chemistry calculations of the magnetically induced current density (MICD) from the induced magnetic field in a molecule placed in an external magnetic field. Typically, MICD is calculated using the nuclear magnetic shielding tensor. In our recent studies, we have shown that it is possible to calculate the shielding tensor components on a loop to obtain the total MICD of a molecule or to accurately quantify the strength of the flux of a current-density vortex.[1,2,3]

The total MICD can be obtained by defining an integration plane originating at the centre of the molecule and extending to infinity above, below and away from the centre.[1] Traditionally, the net current strength is calculated by integrating the MICD on points lying on the plane. Instead, we have calculated the nuclear magnetic shielding tensor on the closed loop defined by the perimeter of the integration plane.

The current-density field usually consists of multiple vortices. The zero points in the field define the stagnation graph (SG) of the MICD. We have performed thorough analyses of the SG in a series of molecules, and we have calculated the nuclear magnetic shielding tensor on the stagnation lines.[2,3] This approach allowed us to accurately assign the strength of each vortex, which is in contrast with the traditional approximate method of integrating the MICD on a series of 2D grids.

Figure 1: The two vortices in the magnetically induced current-density field of LiH.

[1] R. F. J. Berger, M. Dimitrova, R. T. Nasibullin, R. R. Valiev, D. Sundholm. *PCCP* **2021**, *24*, 624.
[2] R. F. J. Berger, M. Dimitrova. *PCCP* **2022**, *24*, 23089.
[3] R. F. J. Berger, M. Dimitrova. *(submitted)* **2024**.

Completing the Series: The Dimeric Dialuminene ^{iPr8}AlAlAr^{iPr8} (Ar^{iPr8} = C_6H-2,6-(C_6H_2-2,4,6-iPr_3)$_2$-3,5-iPr_2)

Annika Lehmann,[a] Joshua D. Queen,[b] Kari Rissanen,[a] Heikki M. Tuononen,[a*] and Philip P. Power[b*]

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Low-valent main group compounds have generated much interest as they often show facile reactivity towards small molecules and can be used as building blocks for systems with main group atoms in unusual bonding environments. Of the group 13 elements, low-valent Al species are challenging to isolate because of higher reactivity and tendency to disproportionate compared to the compounds of their heavier congeners. Although the use of sterically demanding ligands, such as terphenyls, have allowed the realization of one-coordinate diyl compounds of the form TerE: (E = Ga, In, Tl; Ter = terphenyl ligand), analogous Al(I) species were unknown until the isolation and characterization of ^{iPr8}ArAl: (Ar^{iPr8} = C_6H-2,6-(C_6H_2-2,4,6-iPr_3)$_2$-3,5-iPr_2) in 2020.[1] In similar fashion, the dimeric dimetallenes, formally represented as TerE=ETer, are currently known for all but the lightest of group 13 metals Al. Herein, we present the characterization of the dialuminene ^{iPr8}ArAlAlAr^{iPr8}, a missing species in the series of group 13 dimetallenes.[2] The compound shows facile reactivity towards hydrogen and ethylene at room temperature and DFT calculations were used to elucidate the associated reaction mechanisms. The results show that even though ^{iPr8}ArAlAlAr^{iPr8} is the only reactive species with dihydrogen, its dissociation to ^{iPr8}ArAl: (Figure 1) opens up two reaction routes with ethylene that lead to different outcomes.

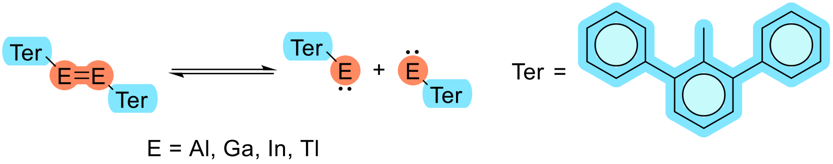

Figure 1: Monomer-dimer equilibrium between group 13 diyls and respective dimetallenes.

[1] Queen, J. D.; Lehmann, A.; Fettinger, J. C.; Tuonomen, H. M.; Power, P. P. The Monomeric Alanediyl :AlAr^{iPr_8} (Ar^{iPr_8} = C_6H-2,6-(C_6H_2-2,4,6-$^iPr_3$)$_2$-3,5-$^iPr_2$): An Organoaluminum(I) Compound with a One-Coordinate Aluminum Atom. *J. Am. Chem. Soc.* **2020**, *142* (49), 20554–20559.

[2] Lehmann, A.; Queen, J. D.; Rissanen, K.; Tuononen, H. M.; Power, P. P. The Dimeric Dialuminene ^{iPr8}AlAlAr^{iPr8} (Ar^{iPr8} = C_6H-2,6-(C_6H_2-2,4,6-iPr_3)$_2$-3,5-iPr_2). *Manuscript in preparation.*

Long-range Charge Transfer in Respiratory Complex I: Insights from Multi-scale Molecular Dynamics Simulations

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Molecular function of respiratory complex I (NADH:ubiquinone oxidoreductase) has remained one of the most controversial problems in bioenergetics. This large molecular machine (up to 1 MDa in some organisms) utilises the energy from NADH oxidation and quinone reduction for the pumping of four protons across the inner mitochondrial membrane. Being spatially separated by ca. 200 Å, it is not completely understood how these charge transfer processes are coupled together. In our work, we address this question by employing microsecond-long classical molecular dynamics (MD) in combination with state-of-the-art hybrid quantum-mechanical/molecular-mechanical (QM/MM) free energy calculation methods.

Our simulations on the high-resolution structures of respiratory complex I from yeast [1], and mammalian species [2,3] reveal the mechanistic details of the long-range charge transfer processes in various catalytic regions of the enzyme. Particularly, we show that the protons can travel along the membrane-bound subunits parallel to the membrane [4], coupling the redox reaction to the proton pumping site(s). Also, we underline the importance of the partially reduced and partially protonated quinone species in the catalytic cycle of respiratory complex I, and how electron transfer between two quinone ligands facilitates redox catalysis [3].

Our findings challenge the current models of redox-coupled proton transfer by respiratory complex I and have far-reaching implications in understanding complex I-associated metabolic disorders on the atomistic scale.

[1] K. Parey, J. Lasham et al., *Sci. Adv.* **2021**, 7, eabj3221.
[2] J. Gu et al., *Nat. Struct. Mol. Biol.* **2022**, 29, 172.
[3] Y.-C. Shin et al., *bioRxiv* **2024.**
[4] O. Zdorevskyi et al., *Chem. Sci.* **2023**, 14, 6309.

Tuesday 28th

IS

Computer simulations, spider silk-like designer proteins, and itsy bitsy steps toward responsive polymeric materials

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In this talk, I provide a brief overview to our recent modelling efforts on polymeric materials, especially materials based on biosynthetic spider silk-like proteins and polymer coatings with advanced functionalities. The focus is on some of our recent simulations work to connect the molecular level design of the polymeric components to the materials response, extracting the mechanisms behind the experimentally observed materials response, and in interpreting the experimentally observed changes and trends. I discuss the interplay of experimental characterization and particle-based modelling approaches at multiple length and time scales in understanding and designing these materials.

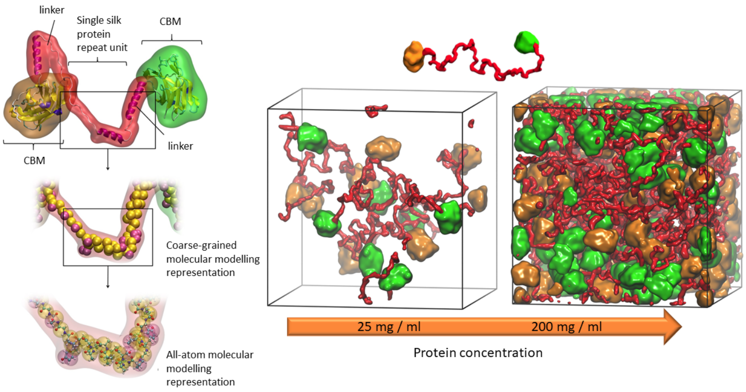

Figure 1: Particle-based modelling approaches to protein materials at multiple length and time scales, here a biosynthetic silk-like protein and its water solutions. Images: Dr. Piotr Batys.

[1] D. Tolmachev, M. Malkamäki, M. B. Linder, and M. Sammalkorpi, *Biomacromolecules* **2023**, *24* (12), 5638.
[2] D. Fedorov, N. Roas-Escalona, D. Tolmachev, A. L. Harmat, A. Scacchi, M. Sammalkorpi, A. S. Aranko, M. B. Linder, *Small* **2023**, 2306817.
[3] L. Lemetti, A. Scacchi, M. B. Linder, M. Sammalkorpi, and A. S. Aranko, *Biomacromolecules* **2022**, *23* (8), 3142.
[4] P. Batys, D. Fedorov, P. Mohammadi, L. Lemetti, M. B. Linder, and M. Sammalkorpi, *Biomacromolecules* **2021**, *22* (2), 690.
[5] K. Hasheminejad, A. Scacchi, S. Javan Nikkhah, and M. Sammalkorpi, *Applied Surface Science* **2023**, *640*, 158324.
[6] A. Scacchi, K. Hasheminejad, S. Javan Nikkhah, and M. Sammalkorpi, *Journal of Colloid and Interface Science* **2023**, *640*, 809.

Computational modelling driven biosynthetic protein materials design

Adam L. Harmat[a,b], Dmitry Tolmachev[a,b], Alberto Scacchi[b,c], Markus B. Linder[b,c], and Maria Sammalkorpi[a,b]

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[b] Academy of Finland Center of Excellence in Life-Inspired Hybrid Materials (LIBER), Aalto University, Espoo, Finland
[c] Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland
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Condensate formation, i.e. liquid-liquid phase separation (LLPS) of protein solutions in living cells is an established assembly step associated with basic biological cell function and several pathological conditions. These include, e.g., Alzheimer's disease, amyotrophic lateral sclerosis, and Parkinson's disease [1]. LLPS is also an intermediate step in the formation of advanced biobased materials, such as amyloids, mussel feet adhesives, squid beaks or silk-like fibers. Protein structural materials exhibit exceptional mechanical properties whilst being biodegradable and lightweight. The rational design of protein condensates is necessary for understanding LLPS and paving the way for engineered biosynthetic protein materials.

To this purpose, we investigate engineered silk-like proteins using computational modelling to explore molecular level interactions and their implications on LLPS as observed in experiments [2,3]. Silk-like proteins have two folded domains connected by an intrinsically disordered region (IDR), making them an ideal model system for systematically investigating the interplay of folded and disordered regions in protein assembly.

Here, we present a methodology advancement based on using protein-protein docking combined with molecular dynamics simulations to study interactions between the folded domains. We demonstrate the approach for a well-characterized ubiquitin system after which we map the response of four different folded domains matching our experimentally realized systems [4,5]. The simulations results show a difference in the type and anisotropicity of the interactions that regulate coacervate propensity and the physical properties of the coacervates. A mesoscale coarse-grained model was constructed to better understand the protein assembly process. The results highlight a complex interplay of folded and IDR domain interactions.

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A computational take on designing self-assembling block copolymer films

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Interfacial coatings by, e.g., polymers, are often used to modify surface interactions of materials or to protect the underlying substrate. Self-assembling polymer coatings find use e.g., as protective layers in biomedical applications, as anti-corrosion coats protecting metallic surfaces, but also as preservative layers conserving stone materials in architectural monuments. Advanced uses require control of the assembling structure and coating spreading. Computational modelling provides an effective means to reveal guidelines for these e.g., in terms of polymer component choices, their miscibilities, or degree of polymerization.

Here, we employ coarse-grained, dissipative particle dynamics (DPD) simulations to study self-assembling polymeric coatings. We focus on a model system composed of a hydrophilic surface coated via self-assembly by linear amphiphilic di-block copolymers and hydrophobic polymers. The base model matches cellulose as the substrate while the hydrophilic segments represent starch and the hydrophobic material a random co-polymer of styrene and n-butyl acrylate (at equal weight ratio). Our results show that copolymers with equal block lengths form stable, well-ordered lamellar surface coatings while asymmetry leads to advanced patterning in the coating. We examine the effect of concentration, extracting coating spreading and optimal concentration trends for uniform, complete coatings, and map the sensitivity of the assembly to chemical composition by varying the DPD interaction parameters. The work provides guidelines to tune and control the self-assembly of polymeric coatings and their internal structures for surface modifying applications.

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Polymer coatings for drug delivery nanoparticles: Molecular dynamics simulation as design tool.

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From our first work performing all atom molecular dynamics (MD) simulation of the surface of a poly(ethylene-glycol) (PEG) coated, PEGylated liposome [1] to then considering alternate polymers to PEG[2] and ultimately poly(2-oxazoline) and poly(2-oxazine) based ABA triblock co-polymer micelles[3], developing MD simulation as a design tool for polymer coatings for drug delivery liposomes has been a journey of more than a decade of research. While I will discuss the entire journey, I will mainly focus on our most recent work concerning polymeric micelles. All-atom resolution MD simulations were performed of models of entire ABA triblock copolymer micelles, using structures characterized in previous experimental work [4] loaded with first curcumin [3] (fig. 1), then paclitaxel. Polymer drug interactions were analyzed; we studied the effect of altering polymer blocks. A correlation was found between the formulation with the highest drug loading capacity, as determined in prior experimental work [4], and the micelles that we observed in our simulation with the highest number of drug molecules encapsulated within the hydrophobic core. Also, systems with inferior drug loading showed more entanglement between the hydrophilic A blocks and the hydrophobic B blocks. Replacing poly(2-methyl-2-oxazoline) with poly(2-ethyl-2-oxazoline) as A block increased drug-shell interactions and reduced corona hydration; this possibly indicated impairment of the solubility and stability of the polymer micelle. Complementing experimental analysis, MD simulation allows for the rational design of drug delivery nanoparticles. Our work on ABA triblock copolymer micelles can be seen as a case study of this. Development of alternatives to PEG in drug delivery is an active field of research; MD simulation is a valuable tool that can be used to help achieve this.

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Tuning the properties of Janus van der Waals hetero structures by varying interface terminations

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The ever-growing energy needs demand technological development related to photo catalysis. Conventional photo-catalytic materials suffer from low quantum efficiency, charge-recombination, and chemical back-reactions. Janus van der Waals hetero structures are 2D materials where a metal atomic layer M is sandwiched between layers X and Y of two different chalcogen, halogen, or pnictogen atoms owing to finite out-of-plane dipole moments and possess enhanced photocatalytic properties due to their intrinsic Rashba effect, strongly bound excitons, and strong interaction with light [1]. In this study, two dimensional (2D) GaAs/MoSSe Janus interfaces were investigated using first principles calculations. The effect of different atomic terminations on the interface stability, electronic properties and charge transfer at the interfaces were analyzed and found that conducting properties are altered with respect to different terminations. Metallic states are formed at the stable MoSSe/GaAs interface due to the presence of 2D occupied antibonding states in MoSSe and the band alignment at the interface. We demonstrate that the non-symmetric structure of MoSSe Janus material plays a key role in controlling the electronic properties of the stable Janus interface, which will be crucial deciding factor for practical applications [2].

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Accelerating conformational transitions in molecular simulations

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Molecular dynamics simulations are a powerful tool for understanding the function of (bio)molecules. However, the time scales that can be reached are often orders of magnitude shorter than the timescales of transitions of interest. Enhanced sampling methods can enable sampling of such transitions. Here we will discuss several important aspects of enhanced sampling in the context of the accelerated weight histogram method. In particular the need for a metric and the choice of reaction coordinate(s).

Atomistic machine learning for materials modeling

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In atomistic modeling, there has traditionally been a gap between the description of large systems over long time scales, afforded by classical force fields, and small systems, afforded by quantum chemical methods. This gap is two faced. On the one hand, force fields are computationally cheap whereas quantum chemistry calculations are notoriously slow. On the other hand, chemical reactions cannot be described by classical force fields, which also need to be parametrized for a specific modeling problem; by contrast, quantum chemical calculations are "hands off", and one can expect good accuracy out of a typical calculation for a given input of atomic positions and chemical composition. Therefore, there is an inescapable tradeoff between accuracy and speed which has frustrated atomistic modelers essentially since the inception of the field.

Fortunately, we currently live in the middle of a data-driven revolution, which has led to the emergence of the *atomistic machine learning* subfield. Using different regression models, such as kernel-based regression [1] or artificial neural networks [2], we can now "learn" the quantum mechanical potential energy surface afforded by our method of choice (usually, but not exclusively, density functional theory [DFT]) and make predictions at force field cost. These so-called machine learning potentials (MLPs) have narrowed the gap between accuracy and size, allowing us to model large systems with quasi-DFT accuracy [3]. While the field is still under extremely rapid development, we are starting to witness some remarkable progress in the modeling of materials for problems that necessitate large scales or high-throughput screening. Furthermore, the flexibility of these new simulation frameworks is opening the door for imaginative approaches to augment atomistic simulation, e.g., by incorporating experimental observables directly into the structure optimization of materials [4].

In this talk, after giving a brief introduction to the field of atomistic machine learning, I will show different examples of how our group has used MLPs to study amorphous and nanostructured materials [4-6], achieving a degree of realism in materials modeling that was unimaginable less than a decade ago.

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Efficient Many-Body Representation of Atomic Environments for Machine Learning based models and beyond

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Mathematical descriptions of atomic environments play a central role in force field methods for atomistic simulations, especially in machine learning (ML) based interatomic potentials. These representations influence the accuracy and computational performance of many atomistic ML models, motivating the design of more efficient algorithms to expand the sizes and timescales of simulations.

A well-established many-body representation is the smooth overlap of atomic positions (SOAP) descriptor [1], introduced to ease the construction of similarity kernels within the Gaussian Approximation Potential (GAP) framework [2]. However, descriptor evaluation is still one of the main bottlenecks in GAP ML force fields, despite its further optimization [3]. Here, we will briefly introduce the SOAP formalism and the main limitations of the state-of-the-art soap_turbo descriptors [4]. We will also discuss different ongoing approaches to alleviate them, such as potential speedups and descriptor compression strategies.

Moreover, these representations provide a general characterization of atomic-scale properties, being a suitable input not only for ML modelling but also for data analysis and visualization. We will show a few examples of their application beyond ML force fields, combining soap_turbo descriptors with a cluster-based multidimensional scaling (cl-MDS) tool for data visualization [5,6].

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Incorporating explicit electrostatic interactions in machine learning atomistic simulations

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Long-range interactions such as electrostatics have long been a concern in developing accurate, efficient machine learning potential energy surfaces (ML-PES). Many approaches for incorporating such interactions into the structure of an ML-PES have been proposed over the past decade; however, no approach has yet exhibited the combination of accuracy, generality, and conceptual simplicity necessary to find wide acceptance. In this work, we revisit one of the earliest and simplest approaches, namely, machine learning local parameters (charges) that are incorporated into a simple functional form [1], which has recently found success in the context of van der Waals interactions [2]. We test this approach on lithium-intercalated graphite, a model system for battery electrodes [3], where experimental data is widely available, and explore the impact of electrostatic interactions on both the dimensional changes and the Li filling pattern. Finally, we discuss wider implications for incorporating long-range interactions in future machine learning models, including different approaches for incorporating polarization and charge transfer phenomena as well as coupling with external electric fields.

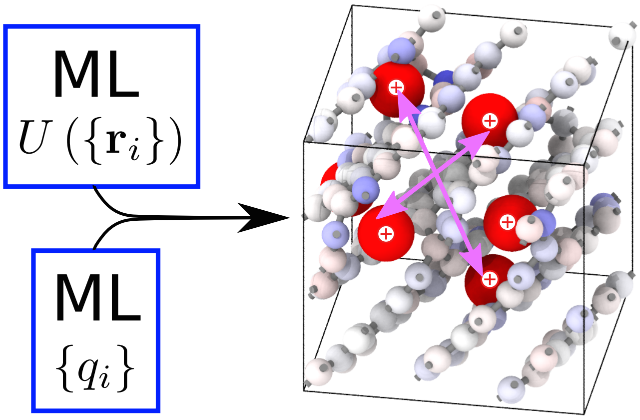

Figure 1: Combining two machine learning models – one for the local energy and one for partial charges – to build an accurate potential for lithium-intercalated graphite.

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Modelling the Growth of Zincone ALD/MLD Hybrid Thin Films using Density Functional Theory

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Purely inorganic, or organic thin films can be fabricated using either atomic or molecular layer deposition (ALD and MLD). By combining these two methods, one can fabricate hybrid thin films, which contain both organic and inorganic layers, and thus will drastically improve the applicability of the thin film technology. The reaction paths occurring during the hybrid thin film deposition process are still widely unknown. To tackle this problem, we studied the growth mechanisms of hybrid thin films on an atomic-level accuracy using DFT. Hybrid thin films under investigation utilize diethyl zinc and 4-aminophenol as precursors, and were studied using both gas-phase and surface reaction models, of which examples are presented in Figure 1.

4-Aminophenol reacts faster and more strongly with its hydroxyl than its amino group, which will dictate the alignment of 4-Aminophenol in the film structure. 4-Aminophenol adsorbed to the surface through physisorption, and after that, the hydrogen will migrate to an ethyl ligand utilizing primarily a ligand exchange but also a dissociation reaction. The amount of ethyl ligands partaking in the growth reaction of the hybrid thin film was approximately 20 to 25 percent. Different macrostructures of these hybrid thin films were compared and the effect of oxygen on the growth reaction mechanisms was discovered.

In addition, the gas-phase models were utilized in the screening of over a dozen compounds to discover the relative reactivity of diethyl zinc with different functional groups present in aliphatic and aromatic organic precursors. Our results on both the reactivity and bond strength between different functional groups agree qualitatively with experimental results. Thus, this rapid screening process enables the feasibility prediction of the potential organic precursors, and it can be expanded to hundreds of precursors.

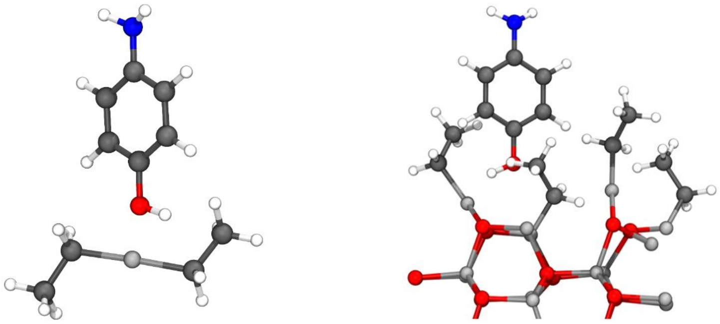

Figure 1: A hybrid thin film growth reaction between 4-aminophenol and diethyl zinc was studied using both gas-phase (left) and surface (right) models.

Modeling Porous Liquids with Machine-Learning-Assisted Molecular Dynamics

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Diverse applications benefit from porous materials, such as molecular separations and catalysis [1], enabling the efficient capture of greenhouse gases (CO_2 and CH_4) and valuable noble gases (Xe, Ar, and Kr). Xenon, widely used in optics, medicine, and nuclear processes, poses extraction challenges due to its low atmospheric abundance and inert nature, driving high commercial costs. Efficient xenon isolation requires materials with precise selectivity and high adsorption capacity. Porous liquids (PLs) incorporating cavities formed by porous organic cages (POCs) show promise in addressing these challenges [2]. Understanding the binding mechanisms, occupancies, dynamics, and equilibrium between host (PL/POC) and guest (Xe) is pivotal for the design of novel POCs tailored to specific functionalities. Molecular dynamics (MD) simulations have proven essential for understanding and exploring the physicochemical processes governing these systems. In MD simulations, atom movements are described by the potential energy surface (PES) of the system. Typically, the PES is accurately obtained by calculating the electronic structure using methods such as density functional theory (DFT). However, the combination of MD with DFT, although provides precise interatomic forces, is constrained by computational scalability, limiting simulations to tens of picoseconds and a few hundred atoms, thereby falling short of capturing realistic timescales and size of these porous systems. In recent years, machine learning, particularly neural networks (NNs), has emerged as a promising avenue to address these limitations [3], by learning accurate interatomic potentials from a set of high-fidelity reference calculations while maintaining computational efficiency.

In this work, we present accurate and data-efficient machine learning interatomic potential (MLIP) models built using Allegro [4], a local equivariant deep NN architecture. These models were trained, validated, and tested on DFT level data, covering energies, forces, and virials in structures with 600 to 1170 atoms (H, C, N, O, F, Cl, Xe). The structures include varying numbers of xenon atoms in different PLs and POCs, totaling 1.7 million atoms with around 12 million data points. The MLIP models enable simulating large-scale porous liquids at realistic physicochemical conditions and applied to provide microscopic interpretation of experimental ^{129}Xe NMR — a local probe critical for understanding the condition-dependent dynamic processes present in these systems — data both at the static and dynamic levels.

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Atomically thin metallenes are nanoscale amoebae

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Due to their delocalized electronic wave functions, metals inherently display isotropic bonding which makes their existence as two-dimensional (2D) nanostructures scarce [1]. Despite this property, there have been successful experimental realizations of atomically thin segments of certain elemental metals within a 2D covalent framework [2]. Yet, this progress has not been systematically reported for all metals, implying that the intrinsic nature of metals concerning the underlying mechanisms that can confer stability in two dimensions remains elusive. The precise mechanisms responsible for stabilizing metals in 2D configurations continue to be a subject of intrigue. A profound understanding at the atomistic level is imperative, and this can be effectively achieved through advanced computational methodologies [3-5].

To complement the *2D metals stability* research, we delve deep into the inherent stability criteria of 45 metals, in six distinct lattices—hexagonal, square, honeycomb, and their buckled analogs. Using density-functional theory, we assessed the dynamical stability of these free-standing metallic monolayers. Our findings indicate that the stability of these structures is more influenced by the available area per atom than merely the minimum energy. Among our observations, 129 stable lattices have been identified, frequently at densities not corresponding to the energy minimum or zero stress. Contrary to conventional energy minimum, we introduce a novel perspective on the stability of 2D metals. We suggest that 2D metals are more akin to nanoscale amoebas—adapting their conformation to the size and shape of the stabilizing pore—rather than being intrinsic structures with fixed lattice constants at zero stress. We anticipate that this approach will pave the way for experimental methodologies aiming to synthesize larger and more robust 2D metal samples, with potential applications in electronics, plasmonics, optics, and catalysis.

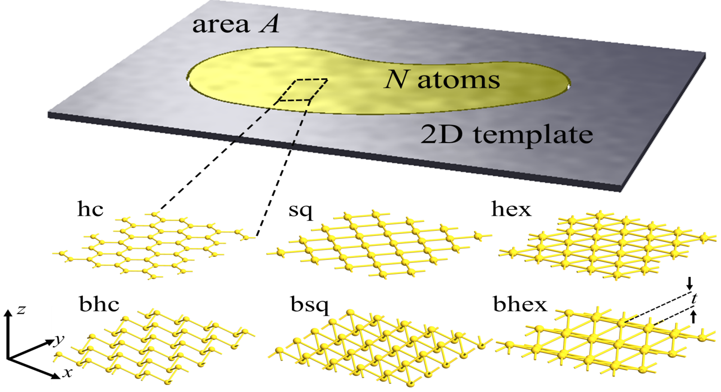

Figure 1: 2D metals' stability framework: A metal patch with N atoms stabilizes on a 2D template pore of area A. Lattice structures like honeycomb (hc), square (sq), and hexagonal (hex), with their buckled variants (bhc, bsq, bhex) are explored. Buckled layer thickness is t

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Posters

P-1

Understanding Selective Hydrogenation of Phenylacetylene on PdAg Single Atom Alloy

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Single atom alloys (SAAs) have proven to be effective catalysts, offering customizable properties for diverse chemical processes.[1] Various metal combinations are used in SAAs and Pd dispersed materials are frequently employed in catalyzing hydrogenation reactions.[1,2] In this work, we explore the hydrogenation of phenylacetylene to styrene and ethylbenzene on PdAg SAA using density functional theory calculations. Our results show that while PdAg SAA does improve the activity of the host Ag towards hydrogenation, a dilute PdAg SAA surface with isolated Pd-atoms is not selective towards partial hydrogenation of phenylacetylene.
Additionally, we investigate how the size of the reactant molecule, the size of the metal alloy ensemble, and a ligand effect impact the hydrogenation process. The SAA enhances the binding strengths of various organic adsorbates, although this effect diminishes as the adsorbate size increases. Our findings indicate the dilute PdAg exhibits selectivity towards hydrogenation of smaller molecules such acetylene due to its distinct adsorption geometry. The selective hydrogenation of phenylacetylene necessitates a surface Pd dimer ensemble. Our research highlights the importance of both reactant molecule size and surface configurations in SAA catalysts. This is particularly crucial when dealing with the adsorption of sizable organic molecules where the functional group can adopt different adsorption modes.

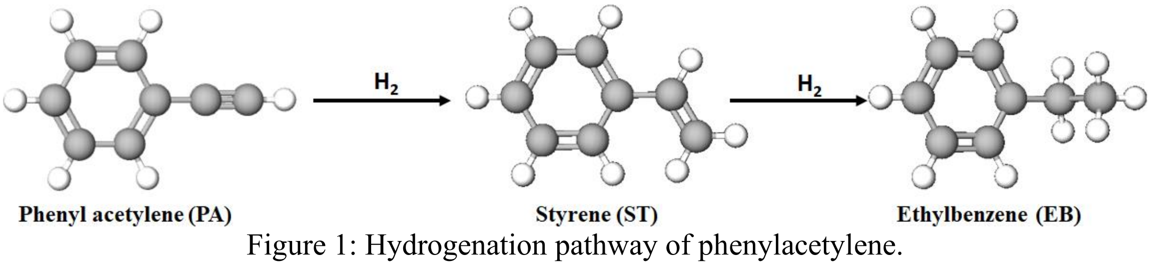

Figure 1: Hydrogenation pathway of phenylacetylene.

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P-2

DFT Mechanistic Investigation of Ni(II)-Catalyzed Hydroxylation of Benzene by H_2O_2

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Phenol and its derivatives represent a significant class of chemical compounds with diverse applications [1]. Therefore, the development of cost-effective and efficient methods for incorporating oxygen into aromatic C-H bonds holds paramount significance in synthetic chemistry. Itoh et al. [2] introduced a remarkable catalytic system in 2015, wherein nickel(II) complexes catalyze the hydroxylation of benzene and alkylbenzenes using H_2O_2 as the oxidant (Figure 1a). They proposed a dinickel(III) bis(μ-oxo) species (Figure 1b) as the key intermediate responsible for the benzene hydroxylation reaction, although their subsequent publication [3] indicates that such a species is inactive toward arene hydroxylation, leaving this issue as an open question.

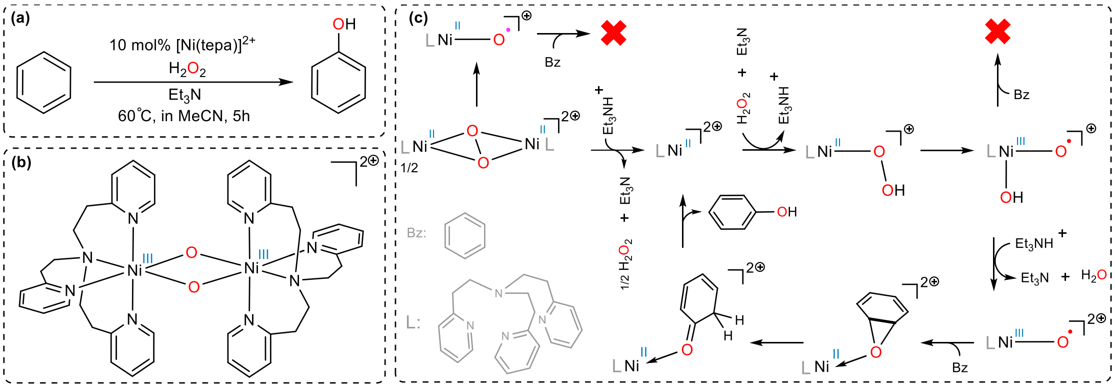

Figure 1: (a) Nickel-catalyzed hydroxylation of benzene using H_2O_2 developed by Itoh et al. (b) dinickel(III) bis(μ-oxo) complex (c) DFT-proposed mechanism.

Here, we present our recent study [4], which explores the mechanism of benzene hydroxylation with H_2O_2 catalyzed by by $[Ni^{II}(tepa)]^{2+}$ (tepa = tris[2-(pyridin-2-yl)ethyl]amine) using density functional theory (DFT) calculations (Figure 1c). It was revealed that the deprotonation of coordinated H_2O_2 renders it more susceptible to oxidative addition at the nickel center. This study introduces Ni-oxyl species as critical intermediates in such a transformation, highlighting how the spin density value on oxygen and positive charge on the Ni-O$^{\bullet}$ complex affect the activation barrier for the addition of benzene to oxygen, which serves as the rate-determining step. The knowledge supplied in this research can provide important information to guide experimentalists when interpreting previously reported reaction mechanisms of the intermolecular hydroxylation of aromatic compounds using H_2O_2 catalyzed by 3d metal complexes and may aid scientists in developing novel catalytic reactions.

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P-3

Tetragonal zirconia in isosynthesis

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Isosynthesis is a selective catalytic process to convert syngas, a mixture of CO and H_2, directly into isobutene. [1] This process is catalyzed by zirconia (ZrO_2), but it turns out that the product distribution in isosynthesis is highly polymorph-sensitive. While monoclinic zirconia ($m-ZrO_2$) exhibits relatively good selectivity towards isobutene production, tetragonal zirconia (t-ZrO_2) converts syngas to mainly methane and other C_1 compounds. [2,3]

This poster presentation tells about the ongoing computational study on syngas chemistry on t-ZrO_2 (101) and (134) surfaces, with emphasis on the methane production. The goal of the study is to use DFT + U calculations to better understand the reaction mechanism of methanation by tetragonal zirconia, and hopefully shed light onto the mechanistic details that lead to the experimentally observed polymorph-sensitivity in isosynthesis.

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P-4

The importance of CO Attack on the Formation of C2+ Products over Single Atom Catalysts

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Electroreduction of CO2 into value-added products with two or more carbon atoms (C2+) represents a promising approach for direct synthesis. Traditionally, CO2 reduction reaction (CO2RR) to C2+ products has predominantly employed solid-state heterogeneous electrocatalysts, such as copper (Cu) [1]. In contrast, single-atom catalysts (SACs) have typically been used to convert CO2 into C1 products like carbon monoxide, formate, methanol, and methane [2-3]. However, some experimental data suggest that iron phthalocyanine (FePc) as a SAC can produce small amounts of C2+ compounds, including ethylene (C2H4), ethane (C2H6), propane (C3H6), and propane (C3H8) [4-5]. Despite these findings, the mechanisms explaining this achievement are still lacking. Exploring these mechanisms could lead to the development of SACs based on transition metal-doped graphene. Our research aims to investigate various reaction mechanisms that could enable the formation of C2+ products over FePc using density functional theory (DFT) calculations. Our computational studies show that at a negative potential, CO binds more strongly to the Fe-CO intermediate, increasing the kinetic challenge of its release. This promotes the formation of post-CO intermediates through proton attacks on Fe-CO. After this stage, the reaction proceeds to form a Fe=CH2 through hydrogenation steps. Although methanol formation is thermodynamically possible, it faces a high activation barrier. Subsequently, C2+ products are formed through direct CO attacks on the carbon atom in Fe=CH2, encountering feasible thermodynamic and kinetic barriers in the process.

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P-5

Higher alcohols from syngas on a CuFe alloy catalyst: DFT and microkinetics

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Higher alcohols (HAs) from ethanol to fatty alcohols are vital in the chemical and energy sectors, with applications ranging from polymers to gasoline additives.[1] Currently, HAs are produced by the fermentation of sugars and the hydration of alkenes. To avoid the use of food- and petroleum-based feedstocks and increase efficiency, a one-stage process from syngas to HAs has been proposed. Cu-modified Fe can catalyze the reaction, with Fe activating CO and growing hydrocarbon chains, and Cu promoting CO insertion and hydrogenation.[2]

The 68 most significant HA synthesis reactions from syngas up to ethane and ethanol were studied on a periodic, perfectly mixed 1:1 CuFe(211) alloy catalyst model. The reaction and activation energies were calculated using vdW-corrected GGA-DFT and the climbing image NEB method. Based on the results, a microkinetic model was built to simulate the kinetics of the process and identify the key elementary steps determining the activity and HA selectivity.

The presence of Cu hinders the Fe-catalyzed C–O cleavage responsible for producing the CH_n chain-growth monomers, and this is the main overall rate-determining step. The relatively slow C–O cleavage is, however, beneficial for HA selectivity, as it allows for a sufficient coverage of molecular CO to form higher oxygenates by CO insertion. On the other hand, the presence of Fe, while crucial for CO activation and chain growth, severely hinders the formation of O–H bonds, making Cu-rich hydrogenation sites necessary for HA production. The results therefore highlight the importance of a proper Cu–Fe balance in HA synthesis.

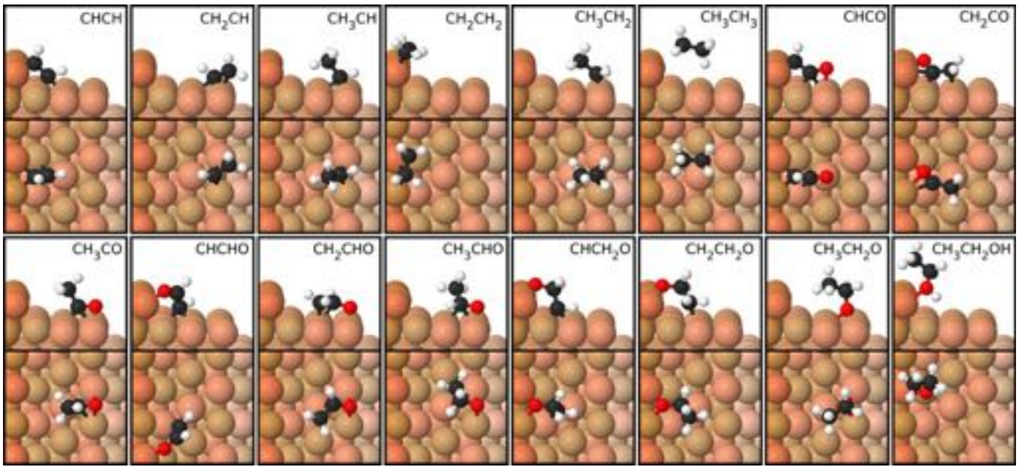

Figure 1: Adsorption geometries of the C_2 intermediates on CuFe(211).

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P-6

A DFT study on the reactions of methylamine, ethylamine and dimethylamine on Pt(111)

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During hydroprocessing of renewable feedstocks into renewable fuel, the removal of nitrogen-containing molecules such as amines and amides is required [1,2]. Noble metal-based heterogeneous catalysts have been studied for this purpose [3,4], but the reaction mechanism for C-N scission is not fully understood. In this work, we used density functional theory (DFT) to study the mechanism of C-N bond scission on a 3x3 Pt(111) surface for the aliphatic amines methylamine, ethylamine and dimethylamine. Calculations were performed using the BEEF-vdw functional in the GPAW software, the climbing image nudged elastic band (Cl-NEB) method was used to locate the transition states. The results show that for methylamine, ethylamine, and trimethylamine, initially C-H and N-H bond scission is favored over C-N scission. A variety of hydrogen-deficient species can thus form on the Pt surface. These species can undergo condensation reaction with each other, thus forming heavier amine products. However, loss of hydrogen from the carbon involved in the C-N bond also weakens this bond, so that C-N bond scission becomes significantly easier. These results are generally well in agreement with experimental results [3, 4]. A parallel can also be drawn to ethane hydrogenolysis, which occurs through hydrogen-deficient intermediates [5].

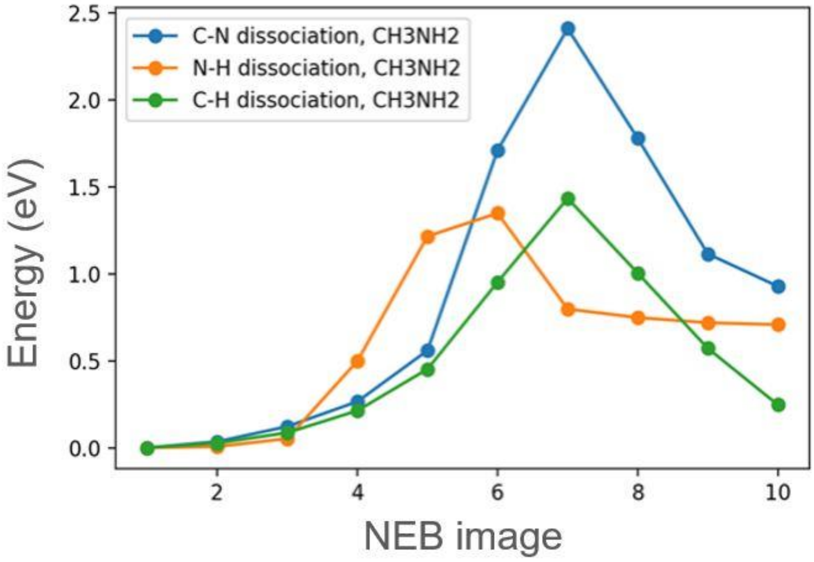

Figure 1. Reaction barriers for the initial C-H, N-H and C-N bond dissociation of methylamine on Pt(111), based on the Cl-NEB calculations.

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P-7

Comparative study of CO_2 reduction of metal porphyrins

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CO_2 reduction reaction (CO_2RR) converts the carbon dioxide into value-added chemicals. The CO_2RR in aqueous solution has the disadvantage of being always in competition with the hydrogen evolution reaction (HER). Also the low reactivity of CO_2 complicates the reaction.

Electro- and photocatalytic reduction using metal porphyrins (MP) as molecular catalysts is an active field of study, both experimentally and computationally. One crucial question in CO_2 reduction is the selectivity between CO and formate pathways. The formate pathway starts with the protonation of the porphyrin, either at the metal site or on the porphyrin ring, while the first step in the CO pathway is the formation of an $MP-CO_2$ adduct.

In this work, a comparative study of CO_2 reduction on metal porphyrins in aqueous environment for the first row transition metal from Fe to Zn using density functional theory is presented. We explore the key reaction steps, including the formation of a CO_2–porphyrin adduct, protonation of the adduct and the porphyrin, electron transfer to the porphyrin and the adduct. We also compute the relative stabilities of the intermediates in the aqueous environment. In addition, we explore the role explicit solvent molecules in the energetics of the pathways.

We find that the binding of CO_2 onto the active site is weak for all metals. We do not find any significant barrier for CO_2 binding onto the metal center. The protonation of CO_2 on the active site is barrierless, while the latter protonation step from $MP-COOH$ to CO and H_2O has a low barrier.

To compare the CO and formate pathways across the metal, the relative stabilities of the to intermediate species, $MP-H$ and $MP-COOH$, are compared by computing the pK_a values at different reduction states. We find that a singly reduced Co porphyrin may be protonated at low pH, but in general, all the metal porphyrins need to be doubly reduced for protonation to occur. Based on the pK_a values, the formate pathway is favoured for Cu porphyrin over the CO pathway.

P-8

Mechanistic investigations of the formal reduction of CO_2 to CO by a Rh-hydride complex

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Design by Wilkinson in 1966, $RhCl(PPh_3)_3$, has been the paradigm of homogeneous catalysts in, among other processes, hydrogenation reactions[1]. It is well known its ability to oxidatively add H_2 in these type of reactions, being the textbook example of a two-electron catalytic redox cycle[2].

Previous works by Timo Repo's group[3] have studied the formation of the parent $Rh(H)(PPh_3)_3$ aided by Barton's base (**2**), that has a direct application in the reverse water-gas shift reaction (*r*WGS), which is the formal reduction of CO_2 to yield CO.

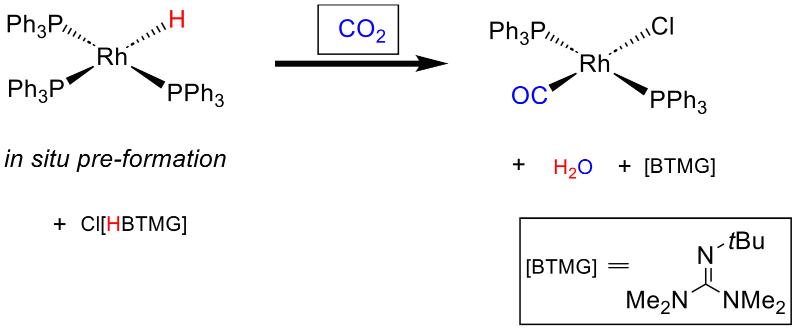

Figure 1: Formal reduction of CO_2 to give a *masked "Rh-CO"*.

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P-9

Pyroelectric Effect in Ferroelectric Perovskites Studied with Density Functional Theory

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Ferroelectric perovskites such as $BaTiO_3$, $KNbO_3$, and $PbTiO_3$ and various solid solutions based on them, such as $Pb(Ti_xZr_{1-x})O_3$ (PZT), are important functional materials in electrical engineering and related applications. In the pyroelectric effect, exhibited by all ferroelectrics, the spontaneous polarization of the polar material changes upon temperature fluctuation. This electric polarization is extractable as a current. Pyroelectrics are used in various sensor applications and other electronics, but the promise of turning heat fluctuation to electrical energy also shows potential for waste heat harvesting applications. Measurement of the pyroelectric effect is rather complicated experimentally, and computational tools could aid in the design of novel pyroelectrics by providing an accurate route to modelling and screening of the pyroelectric properties.

Study of the finite-temperature phonon properties and finite-temperature atomic displacements is enabled by the self-consistent phonon calculation (SCPH) formalism implemented in the ALAMODE package developed by Tadano *et. al.* [1,2]. We have developed a computational methodology, based on density functional theory (DFT), SCPH, and Berry phase theory of polarization, to evaluate the primary pyroelectric coefficient of tetragonal-structured perovskite ferroelectrics at finite temperatures [3]. The total pyroelectric coefficient consists of two parts, primary and secondary, where the secondary effect is a piezoelectric contribution. The secondary part can be evaluated with quasi-harmonic approximation (QHA) combined with the calculation of elastic and piezoelectric constants. Results obtained for $BaTiO_3$ show reasonable agreement with experimental values, indicating that the supercell-based methodology can further be used for known and hypothetical perovskite solid solutions.

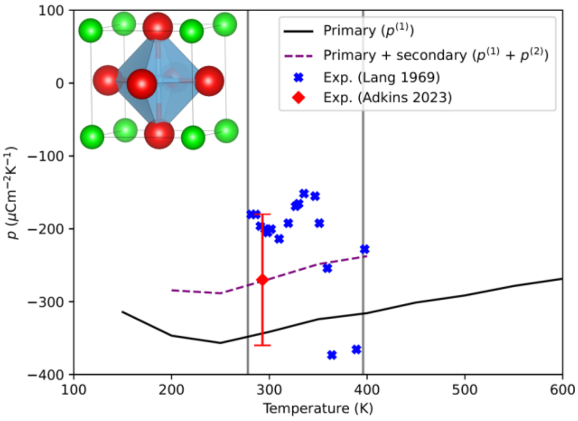

Figure 1: Pyroelectric coefficient of $BaTiO_3$ at finite temperatures calculated with DFT [3].

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P-10

Dynamic polarizabilities of photonic materials through Path Integral Monte Carlo analysis of Homogeneous Electron Gas model

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Increasing use and development of metamaterials in photonic technologies necessitates aquate characterization, which in itself calls for a deeper understanding of the most basic interactions of components of these materials. For this, *ab initio* methods provide exact results to the many-body problem of the electrons that determine the optical properties of these materials. In particular, the Path Integral Monte Carlo (PIMC) approach has proven to be a remarkable technique that has continuously shed light on the nature of matter, with applications ranging from the electron gas [1] to artificial graphene [2].

Of all electronic properties, polarizability is of special interest to photonics, for being the optical response of a material. However, even for simple systems, it is not extensively documented at finite temperatures. Remarkably, imaginary time data obtained from PIMC has been used to obtain static and dynamic polarizabilities at finite temperatures of simple atoms and molecules, while also allowing for individual observation of dipole, quadrupole and octopole contributions [3, 4].

We intend to extend the reach of PIMC to dynamic polarizabilities of notable photonic materials at finite temperature. To do this, we have chosen the Homogeneous Electron Gas (HEG) or jellium as a the precursor to more complex systems. The HEG can be seen as model of simple metals, highly used for analyzing effects that occur because of electrons and their interactions [5]. Since Ceperley's use of quantum Monte Carlo methods to determine the energy of the electron gas at different degrees of spin polarizability [6], Quantum Monte Carlo (QMC) methods such as PIMC have been tightly related to the study of this model.

We present the dynamic polarizabilities of the dipole and quadrupole components of the HEG with densities of $r_s = 2\text{–}5$, which are common for most metals. To compare to the classical Drude model, we first omit the exchange interaction between electrons, to be introduced later on. This novel use of PIMC has the potential tolead to a better characterization of the dynamic polarizabilities of more complex materials.

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Effect of Hindered Rotation in Gas Phase Compounds: Computational Study Focusing on Entropy

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Entropy and Gibbs free energy are fundamental thermodynamic properties that define the natural direction of chemical reactions. Computational values of these properties are particularly valuable in cases where the experimental values cannot be easily determined due to challenging conditions, including e.g. the fields of catalysis, combustion, atmospheric chemistry and astrochemistry [1,2]. The computational approach is based on the calculation of molecular energy levels, of which the vibrational ones have proved to be the greatest difficulty [3]. Usually, the vibrational contribution to the thermodynamic properties is obtained using the harmonic approximation (HA), which describes particularly poorly the low-frequency torsional vibrations. HA overestimates considerably the torsional potential energy barriers, preventing internal rotation from occurring [2]. These barriers are, however, easily overcome even at room temperature by quantum tunneling, resulting also in different conformations [4]. Therefore, torsional vibration is in most cases better described by hindered internal rotation [2-4].

In the present study, we reviewed the effect of hindered rotation and conformations in the entropy of gas phase compounds at MP2/def2-TZVPP level of theory. With HA, a fivefold increase in the mean absolute deviation of entropy was observed upon transition from rigid molecules (0.45 J/Kmol) to molecules with torsional degrees of freedom (2.24 J/Kmol). Addition of conformations resulted in a 25-fold increase (11.27 J/Kmol) compared to the rigid molecules. We tested both one and multidimensional approaches for hindered rotation, MFG (The Approximation of McClurg, Flagan and Goddard) and MS-T (The Multistructural Method with Torsional Anharmonicity), respectively [3,5-7]. MFG performed well for molecules with only one rotating bond (0.51 J/Kmol), as expected, but was found to overestimate the entropy for molecules with several rotating bonds (3.78 J/Kmol). For these molecules, more accurate results were obtained with MS-T (0.84 J/Kmol). Boltzmann weighted average was found necessary for molecules with conformations, as the inaccuracy of HA was cut in half by MS-LH (The Multistructural Local Harmonic Approximation) (5.22 J/Kmol) [3,7]. However, a further significant improvement was observed when hindered rotation was treated with MS-T (2.18 J/Kmol). Based on the results of this study, hindered rotation and conformations cannot be overlooked when aiming for high thermodynamic accuracy.

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P-12

Accurate Calculation of Binding Entropies for Bimolecular Complexes

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The clustering of strongly bound acid and base molecules is crucial for the aerosol particle nucleation and early growth. Rigorous physical modelling of this process requires knowledge of component-wise thermodynamic equilibrium constants of molecular clustering into complexes. These properties are challenging to determine experimentally due to difficulties in separating individual component-wise clustering events. [1] Thus computational chemistry is typically employed to determine the free energy of clustering, ΔG:

$$\Delta G = \Delta H - T\Delta S = \Delta E_0 + kT\left[\Delta N - \ln\left(\frac{Q_{\text{Cluster}}}{\prod_i^N Q_i}\right)\right]$$

Where on the right E_0 is the zero-point corrected electronic energy of clustering, N is the number of clustering molecules, and Q is the thermodynamic partition function. Previous computational studies have primarily focused on computing ΔE_0 accurately and relying on simple perturbational corrections to Harmonic Oscillator for the ln Q component. [2] This approach has been shown to fare poorly when it comes to the 6(N-1) *intermolecular* vibrational modes present in all molecular complexes. [3]

In the presented work we aim to calculale accurate ln Q contributions to ΔG for two model bimolecular complexes, by calculating the energy levels using a Hamiltonian (simplified presentation below) specifically tailed to model the intermolecular vibrations of bimolecular complexes. [4] Once this is done, we aim to find simple cost-effective approaches that can approximate these ln Q contributions, but this is future work at the time of writing. The two model bimolecular complexes used are $NH_3 + H_2SO_4$ representing a strongly bound bimolecular complex and triplet state $(CH_3O)_2$ representing a weakly-bound bimolecular complex. Systems of the latter kind are important for determining product branching ratios in atmospheric peroxyl radical recombination ($RO_2 + RO_2$) reactions, so the information gained from this study is crucial for multiple problems in computational atmospheric chemistry.

$$\hat{H}_{\text{AB}} = -\frac{\hbar^2}{2m_{\text{red.}}}\nabla^2 + \hat{H}_{\text{Rot,A}} + \hat{H}_{\text{Rot,B}} + \sum^{\text{Rot. States}} V_{L_A,L_A,J_A,J_B,\Omega}(r)$$

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P-13

Orbital contributions to magnetically induced ring currents

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An algorithm based on the GIMIC method [1] for calculating orbital contributions to the ring currents induced in molecules by a magnetic field has been derived and implemented in GIMIC. By employing the modified GIMIC program, we calculate the diatropic and paratropic contributions to the current density of molecular orbitals for a number of molecules characterized by different types of aromaticity. The calculated orbital contributions allow us to estimate the role of the HOMO, σ, and π orbitals in the formation of ring current. In particular, we show that for the studied antiaromatic molecules the HOMO gives the largest contribution to the ring current strength, which is not obtained for aromatic molecules that we investigated. We also show that the contribution from the σ orbitals increases when the molecular structure deviates from planarity.

Additionally, the approach allows visualization of orbital current densities. Figure 1 shows the current densities of the π orbitals of benzene.

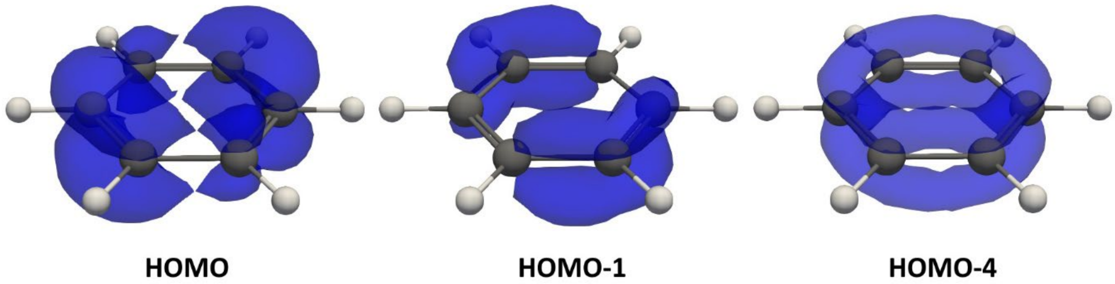

Figure 1: The diatropic current densities for three π orbitals of benzene.

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P-14

Induced current densities in porphyrin nanostructures

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Magnetically induced current densities (MICD) of Zn-porphyrinoid nanostructures have been studied at the density functional theory (DFT) level using the B3LYP functional. The studied Zn-porphyrinoid naostructures consist of balls (two crossing porphyrinoid belts), tubes, rings and clam-shell like molecule. The Zn-porphyrin units are connected to each other via butadiyne linkers as in rings and a recently synthesized porphyrinoid cross-belt structure.**[1-3]** The studied nanotubes are constructed by connecting the neighbors via ethyne bridges at their meso carbon atoms.**[4,5]** A clam-like molecule has porphyrin units connected on one side via butadiyne linkers and on the other side they are fused. The MICDs are calculated using the gauge-including magnetically induced currents (GIMIC) method.**[6,7]** Current-density pathways and their strengths were determined by numerically integrating the MICD passing through selected planes that cut chemical bonds or molecular rings. The current-density calculations of the nanoballs and rings show that they are globally non-aromatic but locally the individual porphyrin rings are aromatic but are 20% weaker than in a single Zn porphyrin, whereas oxidation leads to globally aromatic cations sustaining ring currents that are somewhat stronger than observed for a Zn porphyrin. Calculations of the current densities show that there is a paratropic ring current around the nanotubes. Fusing porphyrinoids as in the fully fused cross-belts and clam-shell molecules results in complicated current-density pathways that differ from the ones usually appearing in porphyrinoids. The neutral fused cross-belts molecule is antiaromatic, whereas its dication is non-aromatic.

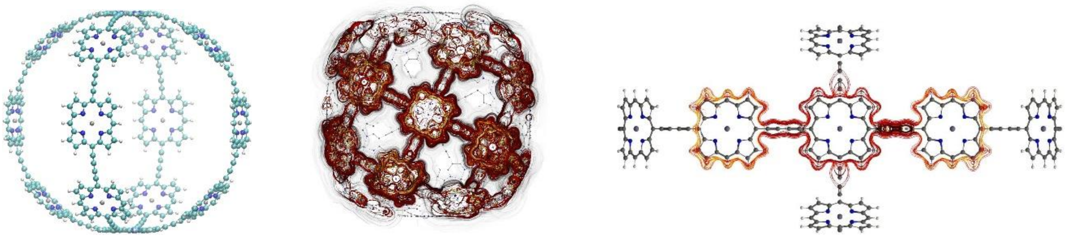

Figure 1: The magnetically induced current density in the nanoball and in a cross-belt porphyrinoid structure.

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P-15

Theoretical study on the nature of bonding in M-L complexes and clusters for coinage metals (M= Cu, Ag, Au) with L= thiolate, phosphine, and N-heterocyclic carbenes

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Exploring the novel material synthesis demands a thorough understanding of the first material interactions, their stable reaction products, and the binding motifs that define the final nanostructure. This exploration faces the unique challenge of developing materials where their properties and formation information are largely undiscovered. This study delves into systematically studying the binding properties of several ligands to group-11 metals (Au, Ag, Cu), providing insight into the development and features of ligand-protected metal clusters. Our findings, in particular, bring into question the dominance of gold (Au) in the formation of stable complexes and clusters, introducing copper (Cu) as a potential choice for improving surface motifs or the overall architecture of these structures. All calculations in this work have been done by using DFT as implemented in the real-space code-package GPAW (Grid-based projector-augmented wave method) [1]. This work has revealed the importance of charge transfer, metal characteristics, and the influence of d-bands in binding. Notably, our findings provide light on the preference for phosphines to bind predominantly to Au in mixed metal clusters, as well as the selective positioning of Cu at the metal-thiolate interface to improve structural stability. Furthermore, despite having the weakest bond compared to others, silver (Ag) prominently appears in preserving the structural and molecular composition of the end products, offering a novel perspective on ligand selection to maximize stability. Our theoretical models, validated against experimental data, demonstrate the high electronic stability of these clusters, with notable variations in binding energy that underscore the superior efficacy of NHCs over traditional stabilizers. This work not only broadens our understanding of the chemical formation of nanoclusters but also advances the potential applications of these insights in the rational design and synthesis of new materials.

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P-16

Effect of Water on the Electronic Structure and Otical Property of Inosine Mutant DNA Stabilized Silver Cluster

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DNA-stabilized silver nanoclusters (DNA-AgNCs) are comprised with small aggregate of silver atoms and cations wrapped in one or multiple DNA strands. Herein, we are interested to reveal the electronic structure of Inosine double mutant I7–I9 (5′-CACCTAICIA-3′), where both guanosines were substituted at the position 7 and 9 of Ag16NC embedded with two 10-base oligomers (5′-CACCTAGCGA-3′) containing two guanosines.[1] The starting structure was prepared from the crystal structure and KS-states are generated with PBE, TPSS, PW91, and GLLB-SC functionals. Next, optical absorption spectra was calculated with the PBE kernel (LRTDDFT) in presenc of implicit solvent model to check performance of functionals to reproduce the optical absorption spectra. None of the functionals were able to reproduce the pattern of the experimental absorption spectra with prominent single peak in the lower energy range. Then, we have implemented exclusive water molecules in the system at GLLB-SC functional to generate KS-states and obtained obtained nearly accurate optical spectra with the refernce of experimental data. The optical spectra splited in the lower energy range in absence of exclusive water molecules. These water molecules exhibit hydrogen bonding with the bases of AgNC, which inhibit to split the lower energy absorption peak. After that, we analyze the origin of the low-energy optical absorption peaks and the electron orbitals and make a evaluation on chirality.

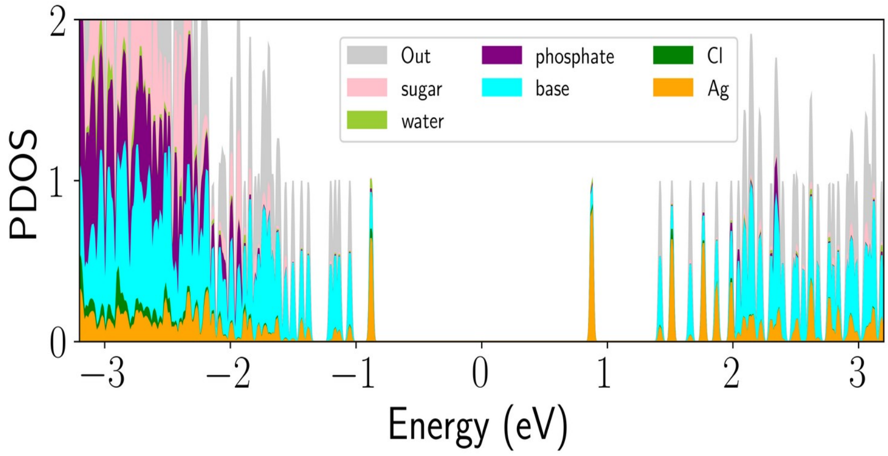

Figure 1: Projected density of electronic states (PDOS) to atom orbitals of Ag, Cl, base, phosphate, water and sugar groups of Inosine mutant AgNC.

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P-17

Inclusion complexes of selected anti-asthmatic drugs with β-cyclodextrin. Molecular modeling studies

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Inclusion complexes with cyclodextrins are widely used in pharmaceuticals, drug delivery systems, cosmetics, and the food industries. In the case of biologically active molecules, encapsulation may result in improved chemical or pharmacological properties compared to the host molecule alone. Such inclusion may improve aqueous solubility, modify the drug delivery site or the time profile [1,2]. In the present study, host-guest complexes between β-cyclodelrin (β-CD) and selected anti-asthmatic drugs salbutamol (SAL) and tulobuterol (TUL) were investigated. Structural aspects of the complexation were investigated using standard B3LYP with the basis set 6-31+G(d,p) Density Functional Theory (DFT) calculations in both gas phase and water environment, for which the Polarizable Continuum Model (PCM) model was used. Two orientations of the incoming host molecules inside β-CD were considered to determine the lowest energy complex, namely the head (ring first) and tail (chain first) orientations. The calculations confirm that the head orientation is more favorable than the tail one by about 8 kcal/mol for SAL and about 1 kcal/mol for TUL. The relative energies and geometric parameters of intermolecular hydrogen bonds for selected low-energy β-CD/SAL and β-CD/TUL complexes, in which non-covalent interactions have a key role, are presented. In addition, the calculated complexes allow estimating the interaction energy between the carrier molecule and the drug in question, as well as the geometrical parameters of the preferred complexes. In order to obtain workable results, it is additionally necessary to take into account the dispersion correction. Therefore, the relative energies and interaction energies were calculated with two different empirical Grimme corrections – D3 (B3LYP-D3) and D3BJ (B3LYP-D3BJ).

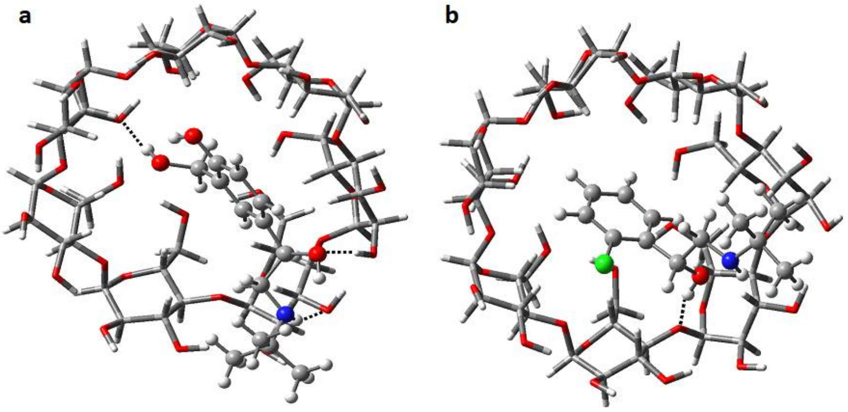

Figure.1 Low-energy β-CD/SAL (a) and β-CD/TUL (b) complexes calculated by the B3LYP-D3 method with the basis set 6-31+G(d,p) in the gas phase

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P-18

Statistical analysis of X-ray spectra of aqueous triglycine

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The folding of proteins is a complex and complicated question [1], affected by both intramolecular and intermolecular interactions. The process is ultimately dependent on the primary order of the amino acids and the surrounding solvent. While diffraction allows for atomistic structure determination of proteins, it requires a crystalline sample. Instead, owing to its localized mechanism, X-ray spectroscopy maintains its sensitivity to atomistic structure also in the liquid phase.

A liquid system allows for the movement of relatively strongly interacting molecules, which leads to a broad distribution of possible configurations. These individual configurations have been computationally observed to have significantly different X-ray spectra, only their ensemble mean predicting the experimentally observed spectrum. Although X-ray spectroscopy does not permit full structural reconstruction, its principles allow for discovery of structural information, especially when combined with statistical analysis [2-4] of computational results.

In this contribution, we present our ongoing statistical analysis of computational X-ray spectra of aqueous triglycine. Classical molecular dynamics was used to obtain the configuration distribution of the system. Then, X-ray absorption spectra were calculated with density functional theory.

The main goal of our study [4] is to determine if X-ray spectroscopy could be used to gain new structural information of aqueous tripeptides. As the systems are complex, simple tools like linear correlations between the internal coordinates of the system and its X-ray absorption spectrum do not deliver satisfying results. We approach this problem by applying neural networks and a specialized dimensionality reduction method, as already done with a different system [3]. The results are compared to X-ray Raman scattering spectra of liquid triglycine at the nitrogen K edge.

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P-19

Moving Lipid Nanoparticles Beyond PEGylation: Simulation Studies on Alternative Polymeric Coatings

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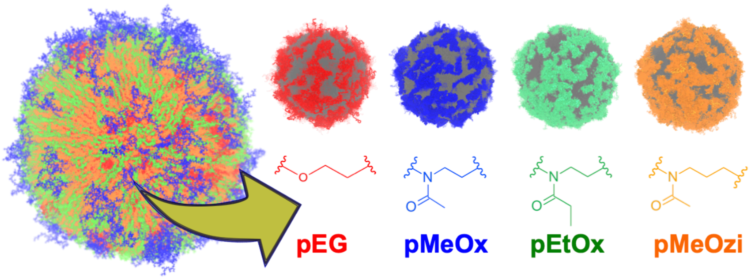
Ever since the great success of COVID-19 mRNA vaccines, formulation scientists are actively developing optimized nucleic acid-carrying lipid nanoparticles (LNPs) to be used for a broad range of anticancer, protein replacement and vaccine therapies [1]. Exchanging poly(ethylene glycol) (pEG) with alternative hydrophilic polymers functioning as stabilizing, stealth-inducing coating materials represents one possibility to influence both immunogenicity and biodistribution *in vivo* [2, 3].

In the present work, we performed all-atom molecular dynamics simulations on full-sized, mRNA-unloaded LNP variants that are covered with pEG, poly(2-methyl-2-oxazoline) (pMeOx), poly(2-ethyl-2-oxazoline) (pEtOx) or poly(2-methyl-2-oxazine) (pMeOzi). These polymers are used for various other biomedical applications [4]. We systematically compared interactions with different constituents of the outer LNP lipid monolayer, as well as hydration patterns and conditions at low pH, relevant for mRNA loading and transfection events.

Results for pEG conform to a previous modeling study [5], demonstrating selective coverage of hydrophobic, neutral aminolipids on the surface. In contrast, this preference cannot be observed for pMeOx, pEtOx and pMeOzi, thus potentially altering the nanoparticle biointerface and ultimately eliciting a fundamentally different protein adsorption and biodistribution profile within the bloodstream.



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P-20

Two Sides of the Same Coin: Unified Theoretical Treatment of Polyelectrolyte Complexes in Solution and Layer-by-Layer Films

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Polyelectrolyte coacervates, obtained by mixing solutions of oppositely charged poly-ions, and layer-by-layer films, produced by sequential adsorption of polyelectrolytes onto a surface, are two closely related types of soft materials. Although both types of materials are produced by the formation of polyelectrolyte complexes, their theoretical description has so far followed divergent paths. This work reports a unified theoretical treatment of polyelectrolyte complexation in solution and self-assembled thin films layer by layer using a molecular theory that describes polyelectrolyte complexation through the use of a chemical equilibrium formalism. It is shown that the theory predicts both the phase diagrams of polyelectrolyte mixtures in solution and the formation of layer-by-layer thin films in good agreement with experimental evidence. In the latter case, the theory correctly captures the effects of solution pH and ionic strength on the mass of deposited films, as well as the possibility of layer-by-layer deposition without complete charge reversal at extreme pH. Then, the theory is used to revisit the "*universal curve*" for the effect of salt concentration on layer-by-layer deposition previously proposed experimentally by Salehi et al. [Macromolecules 2015, 48, 400–409]. This universal curve makes predictions about the growth rate of a layer-by-layer film for a given polyanion/polycation pair using only information obtained from a mixture of the same polyelectrolytes in solution, thus linking both phenomena. Our theoretical results confirm the validity of the curve. This achievement demonstrates the practical importance of describing polyelectrolyte coacervates and multilayer films within a unified theoretical framework.

References: Salehi et.al. Macromolecules 2015, 48, 400-409

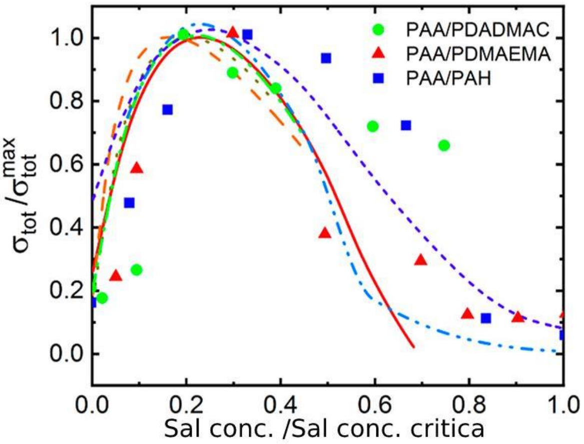

Figure 1: Effect of salt concentration LBL deposition (lines) with experimental comparison (dots). G. Debais et. al. Macromolecules. 2022, 55, 12, 5263-5275.

P-21

Computational Chemistry Days 2024

Quorum Sensing as a Target for Antibacterial Natural Products

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Introduction

Quorum sensing (QS) is a mechanism of intercellular communication among bacteria. To quorum sense, a bacterium produces a small molecule that is only sensed by that individual bacterium to signal population density and governs the pathogenesis of numerous organisms by modulating gene expression [1]. In addition, QS is a major controller of biofilm formation of pathogenic bacteria. Thus, QS systems present appealing targets for a new class of antibacterial drugs and agents that can induce chemical attenuation of pathogenicity [2]. Natural products serve as a source of antibacterial agents which could be applied as QS inhibitors, and the templates for the development of synthetic pharmaceuticals [3]. However, the precise mechanism of QS is still not well understood.

Aim

The objective of this study is to identify antibacterial agents from natural products using virtual screening. Additionally, the study seeks natural products from plants to disrupt QS-associated SdiA protein, thereby attenuating its virulence.

Method

Natural product database by MolPort was prepared with LigPrep. The binding site of SdiA protein was selected based on crystallized ligand. SdiA proteins, X-ray diffracted structures 4LFU (2.26 Å) and 4Y17 (2.84 Å), were applied in molecular docking using Glide in SP and XP precisions [4]. Antibacterial agents form hydrogen bonds (with Ser43, Trp67 and Asp80) and π-π-interactions (with Tyr71 and Phe59) in the binding site of SdiA. The antibacterial activity of compounds was tested *in vitro*.

Results

The docking analysis will be applied for the determination of the best binding modes of antibacterial compounds. The binding site is small, and it prefers small (≤ 0.3 kDa) non-rigid ligands. In Figure 1 is presented one natural compound in the binding pocket.

Conclusion

This study utilized computational tools to assess the antibacterial potential of established natural products against SdiA. Virtual screening is a rapid and economical tool for selecting ligands from large libraries of natural products. Natural products can bound SdiA's binding site and form critical interactions with the binding site's key residues. The possibility of these compounds to prevent QS will be studied further.

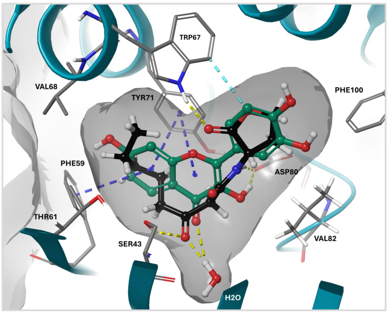

Figure 1: Natural compound (green) and crystallized ligand (black) bound in SdiA.

Acknowledgement

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P-22

Life-like patterns in electroferrofluids: An advective Swift-Hohenberg model for driven complex fluids

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Electroferrofluids are complex fluids that respond to stimuli from both electric and magnetic fields. Opposed to standard ferrofluids, that have recently been described by particle-based simulations [1], in which pattern formation and instabilities of the assembly patterns are controlled solely by a magnetic field, the additional responsivity to an electric field enables both advanced control of the fluids and their patterns but also, as recently demonstrated by us experimentally, a new type of patterning and active patterns [2,3]. Such novel patterning responses are fundamentally interesting but also open possibilities in functional colloids with life-like, active characteristics to create, e.g., optical, electrical, catalytic, and mechanical responses that are not possible in thermodynamic equilibrium.

We here examine an advective Swift-Hohenberg model for pattern formation and pattern dynamics in an electroferrofluid where the magnetically induced patterns form at a non-classical, diffuse interface. This diffuse interface is generated and controlled by the application of an electric field. The phenomenological model is matched against and demonstrated for our model experimental electroferrofluid. Our stochastically driven Swift-Hohenberg model captures both the pattern geometry, as well as its active dynamics. Notably, the phenomenological model shows striking similarities to the patterns observed in experiments. We analyse the patterns and their dynamics, and extract a scaling response of the data. The work charts the extent to which the simple stochastically driven model captures the active characteristics of the formed patterns and enables interpreting the electroferrofluid response in our experiments. Furthermore, the modeling unveils activity regimes beyond those observed in the experiments.

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P-23

Effect of Alcohol on Intrinsically Disordered Proteins: Molecular Dynamics Simulations

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Key to achieving biomolecule-based designer materials with advanced functionalities is controlling their assembly and interactions. One effective, scalable, environmentally friendly, and readily available processing means of protein materials is solvent processing, such as alcohol treatment. However, realizing the full potential of solvent processing requires a molecular-level understanding of the effects of alcohol as a solvent additive on the proteins and their interactions. We focus here on spidroins which are the main proteins of spider silk, an exceptional biomaterial with a unique set of properties.

By combining molecular dynamics simulations and experimental characterization, we chart here the effects of ethanol treatment on the aggregation state and secondary structure of a model spidroin system. We determine the role of amino acid sequence and generalize the findings to other intrinsically disordered proteins, revealing common features of the response. The results show that ethanol significantly enhances protein-protein interactions which increase secondary structure ordering. Glutamine residues provide the driving force for structure change while glycine provides the necessary protein segment flexibility for the changes [1]. The significance of the work is that we demonstrate that systematic molecular-level computational and experimental characterization can be used to derive bottom-up principles for biomaterial properties design via solution conditions, with ethanol treatment as an example.

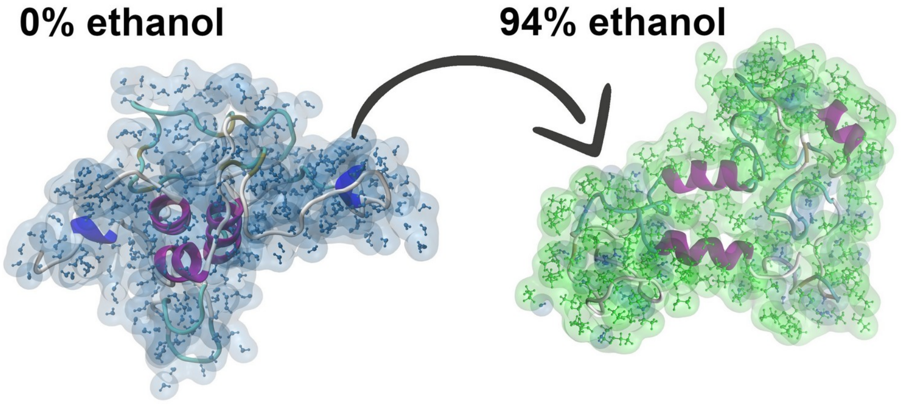

Figure 1: Molecular visualization of the effect of ethanol on a spidroin model.

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P-24

Salt Ions as a Control Means of Polyelectrolyte Interactions and Electrophoretic Mobility in Aqueous Environments

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Many charged macromolecules, including polyelectrolytes (PEs) such as DNA can be approximated by rigid charged rods. In aqueous solutions, rodlike charged macromolecules are surrounded by their counterions and often also by excess salt. Salt is a common means to control the effective charge of the molecules and their electrophoretic mobility (EM), as well as their interactions. This is important for controlling self-assembly and structural properties of PE assemblies. Experiments and theory have demonstrated that multivalent ions can induce correlations that result in an effective charge reversal of a PE, and consequently an attractive interaction between like-charged PEs. Similarly, reversal of the direction of EM motion under an external field has been observed for strongly charged macromolecules in the presence of multivalent counterions.

We consider here, by means of coarse-grained molecular dynamics simulations, the effects of ion size, shape, and charge on PE interactions. To gain a better understanding on the interactions between highly-charged PE rods in the presence of ions of different kinds, we have mapped the ion-size [1], aspect ratio [2], valency [2] and salt concentration [1, 3] dependence of the ion distributions and PE interactions at room temperature. Anisotropic ions induce an unexpected ion-valency and shape-anisotropy-dependent orientational ordering in the ion double layer. The response affects ion condensation on the PE, PE charge reversal, and PE-PE interactions. Our findings demonstrate that by considering the shape and steric effects alongside concentration and valency, one can systematically tune the type (attraction vs repulsion), range, and strength of the PE-PE interactions.

In addition, the effects of coion valency on EM reversal have not yet been systematically investigated. To this end, we address the effect of coion valency on the EM of a single rigid DNA-like PE [4]. We find that also the coion valency plays a crucially important role in determining the EM and its reversal. Previously it was assumed that the counterion valency is the key factor in EM. We find a non-monotonic dependence of the EM on salt and coion valency for PE solutions where the counterions are monovalent (no correlations induced by them). When salt with multivalent coions is added to such a system, the EM at low salt concentration is enhanced with increasing coion valency. However, for high salt concentration, close to 1 M, coions induce EM reversal which becomes more pronounced with increasing coion valency.

In summary, our work provides comprehensive guidelines for regulating PE self-assembly, as well as controlling polymer transport in aqueous solutions by salt and the nature of the salt ions.

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P-25

Analysis of protonation states in proteins from cryo electron microscopy and atomistic molecular dynamics simulations

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Cryo electron microscopy (cryo-EM) has revolutionized the field of protein structure determination [1]. High resolution cryo-EM structures of membrane proteins are routinely determined providing deep mechanistic insights fueling design of novel protein scaffolds and drug discovery. However, the resolution may not be high enough to resolve the position of hydrogen atoms in a protein structure, which puts restrictions on our understanding of the chemical nature of the environment and therefore the function of the protein [2]. Here, we will discuss how conventional atomistic molecular dynamics (MD) simulations of large membrane proteins with many titratable sites in different charged states can help in identifying the protonation states of amino acids [3,4]. Comparison of MD simulation data with cryo-EM structures and density maps can provide detailed insights on the charge states of amino acids in the cryo-EM sample. We show that an approach of combining pK_a prediction with cryo-EM density map analysis can help in improved atomic modeling of density data [4].

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Infrared Spectra From Molecular Dynamics Using Deep Learning

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Infrared spectra can routinely be modelled at the level of the harmonic approximation using standard Quantum Chemistry software. However, including the anharmonic effects is not straightforward. We have used the DeepMD package [1] to develop machine learning models that accurately predict the infrared spectrum of molecules based on molecular dynamics simulations. The method of calculating the infrared spectrum is based on the autocorrelation function of the time derivative of the dipole moment. An MD simulation is run at a semiempirical level to create starting molecular structures. To train our model, we performed single-point calculations at the MP2 level of for selected molecular structures. The calculated energies, forces and dipole moments are then used to train the neural network. The trained models are used in further molecular dynamics simulations to yield the time evolution of the dipole moment. The infrared spectrum is then modelled through a Fourier transformation of the autocorrelation function of the time derivative of the dipole moment [2].

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P-27

Explicit modeling of SnO_2 to Sn nanoparticle reduction process using machine-learned interatomic potential

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Post-transition metals are selective catalysts for electrochemical CO_2 conversion toward formate production [1-2]. Investigating how catalyst sites evolve under varying reaction conditions is crucial since it directly impacts catalyst stability. In this study, SnO_2 nanoparticles were computationally generated using a Machine Learning interatomic potential, specifically the Gaussian Approximation Potential (GAP) [3-6], adjusted with the experimental synthesis data. Additionally, we investigated the thermodynamic stability of various sizes under high-temperature annealing to model the reconstruction of the SnO_2 nanoparticles under the reduction process.

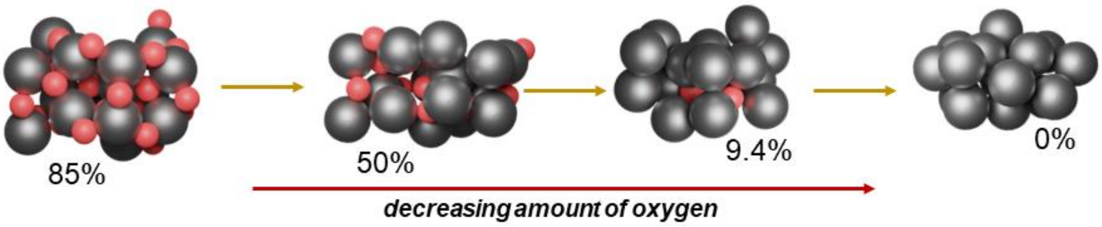

Figure 1: Scheme of explicit simulation of SnO_2 reconstruction under reduction process.

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P-28

Machine learning interatomic potentials for ion intercalations in nanoporous carbon-based materials

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Among the most abundant technologies today are lithium ion batteries in which the cathode is typically a complex oxide, whereas the anode is made of graphite or other carbon-based materials. However, lithium is a scarce resource on the Earth's crust and very difficult to recycle, which limits the future scalability of battery technologies. To overcome these limitations, we substitute Li by other ions (Na, K, Mg, Al, Zn). While Li ions intercalate in graphite, other ions don't. One possibilities to solve this issue is to use nanoporous carbon-based materials as electrodes. Gaining atomic-scale insight into these systems thus requires sophisticated atomistic modeling tools.

Trained from density functional theory (DFT) data, machine learning interatomic potentials reproduce ab initio accuracy and give access to systems much larger than DFT. We model ion intercalation in nanoporous carbon-based materials within the Gaussian approximation potential (GAP) [1] framework coupled to Monte Carlo simulations in the grand-canonical ensemble. Proof of concept is illustrated in Figure 1. Sodium and zinc ions don't intercalate in graphite whereas they do intercalate in nanoporous carbon (NPC) materials. Even more spectacular, dimensional change of Zn ions in NPC is smaller than Li ions in NPC.

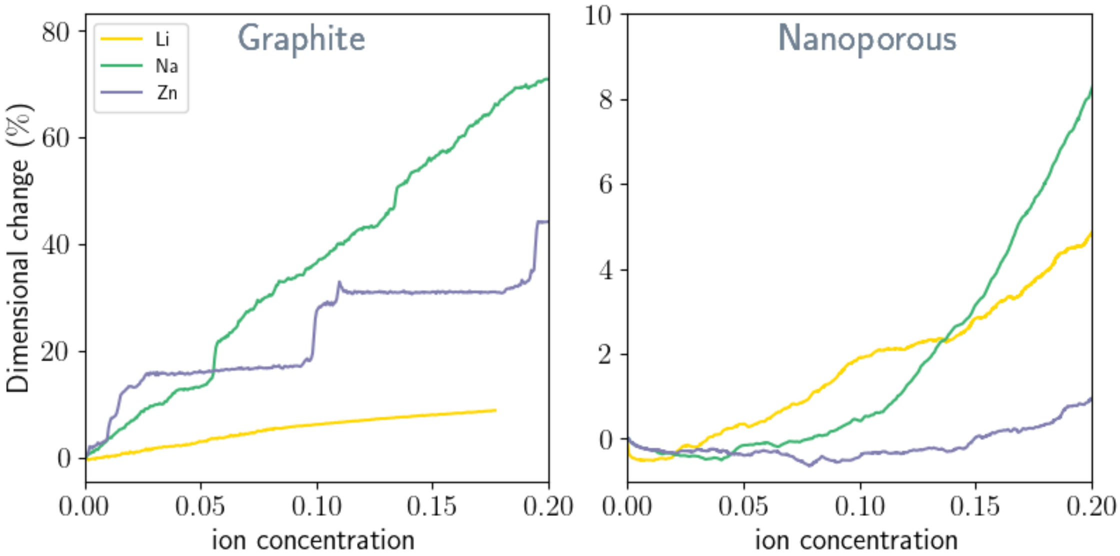

Figure 1: Ion intercalations in graphite (left) and in nanoporous carbon (right), lithium in yellow, sodium in green and zinc in grey.

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P-29

Bimetallic alloy catalysts for syngas conversion: a machine-learning survey

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Conversion of synthesis gas (CO+H_2) into higher value products generally benefits from the variety of structural detail supported by the catalytic interface. We use a DFT-based machine-learning method to discover bimetallic alloy compositions for a stepped, FCC(211) surface model with different Co, Ni, or Fe dilutions with Cu. Upon exposure to CO and H, a segregation of surface Co/Ni/Fe is found to be thermodynamically feasible, and the preferred surface structure depends heavily on the alloy metal and the strength of the metal–reagent bond. Surface Co exists as large domains separated from Cu, Ni becomes more evenly distributed in larger extent mixed with Cu, and Fe exists as singe-atom centres that form $Fe(CO)_3$-groups. Figure 1 shows a sample collection of 1:1 alloys for adsorption of 6 CO molecules and a 1:35 FeCu alloy for adsorption of 6 dissociated H_2 molecules.

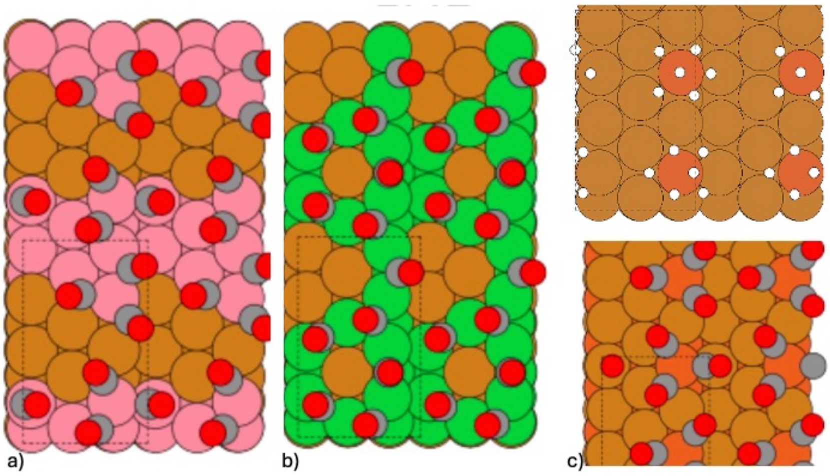

Figure 1: Alloy surface structures with adsorbed CO or H for a) CuCo, b) CuNi, and c) CuFe catalyst models as obtained by the machine-learning method ICEBEACON [1,2]. The simulation cell contains 12 on-top surface sites on the four-layer surface slab model. The DFT evaluations were made by the GPAW program.

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