SolvATE2024
7th meeting of the SolvATE network

November 25-26, 2024
L'Institut Agro Dijon

Book of abstracts

SolvATE2024

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Institut Agro Dijon-Site Déméter
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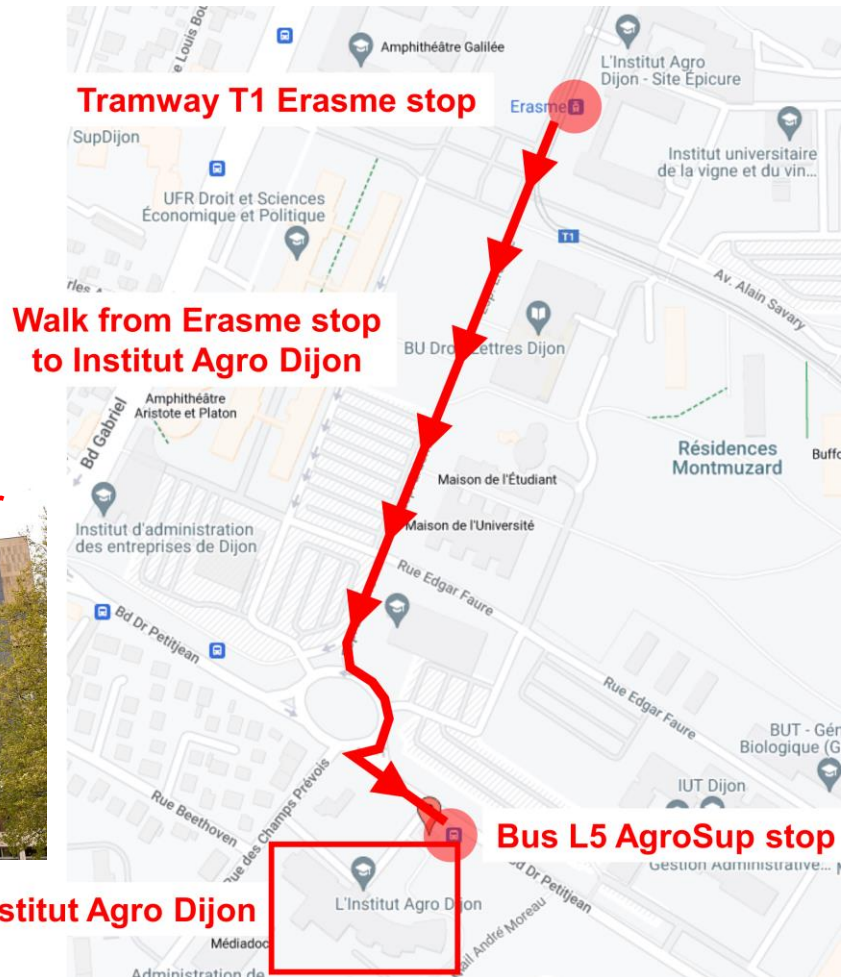
Program

Monday, November 25, 2024

08:30-10:00   Welcome

10:00-11:00   Olga Russina (Chemistry Dept., University of Rome Sapienza)
"Structural solvation features in novel solvent media"

11:00-11:30   Coffee break

11:30-12:00   Mohammad Nadim Kamar (IPR, University of Rennes)
"Deep eutectic solvents: properties induced by nanometric confinement"

12:00-12:30   Stella Christodoulou (LPCNO, University of Toulouse)
"Efficient machine learning-based new tools to design eutectic mixtures and predict their viscosity"

12:30-14:00   Lunch

14:00-15:00   Judith Peters (LiPhy, Université Grenoble Alpes)
"The many ways of biosystems for coping with extreme conditions"

15:00-15:30   Jean-Baptiste Chagnoleau (ICN, Université Côte d'Azur)
"Extraction of natural compounds using sustainable solvents"

15:30-16:00   Mélissa Justin (PAM, L'Institut Agro Dijon)
"Impact of $scCO_2$ on C-phycocyanin stability in presence of polyethylene glycol"

16:00-16:30   Coffee break

16:30-17:00   Nacer Idrissi (LASIRe, University of Lille)
"Local structure of supercritical fluids near the Widom line"

17:00-17:30   Antoine Carof (LPCT, Université de Lorraine)
"Fast calculation of solvation structure and thermodynamics in supercritical CO_2"

17:30-18:00   Artem Shagurin (LASIRe-UMET, University of Lille)
"Molecular dynamics analysis of interfacial properties of curcumin and supercritical fluids"

18:00-18:30   Rodolphe Pollet (NIMBE, Université Paris-Saclay)
"Chemistry in aqueous solutions as described by ab initio molecular dynamics: case of a green catalyst under "in-water" and "on-water" conditions"

18:30-19:15   Posters

19:15-21:30   Dinner

Tuesday, November 26, 2024

08:30-09:00 Welcome

09:00-10:00 Ellen Backus (IPC, University of Vienna)
"Structure and dynamics of water at photocatalytic interfaces"

10:00-10:30 Mohammed Bin Jassar (PASTEUR, ENS, PSL & Sorbonne Universities)
"On the chemistry at oxide/water interfaces: the role of interfacial water"

10:30-11:00 Stephan Steinmann (LCH, ENS de Lyon)
"Investigating organic molecules at the water-platinum interface: from single-crystal surfaces to nanoparticles via density functional tight binding"

11:00-11:30 Coffee break

11:30-12:00 Pierre Illien (PHENIX, Sorbonne University)
"Stochastic density functional theory for ions in a polar solvent"

12:00-12:30 Florent Calvo (LiPhy, Université Grenoble Alpes)
"Concurrent processes in the time-resolved solvation of alkali ions in helium nanodroplets"

12:30-14:00 Lunch

14:00-15:00 Alexander Lyubartsev (Dept. of Materials and Environmental Chemistry, Stockholm University)
"Multiscale modelling of biomolecules at inorganic surfaces"

15:00-15:30 Emeline Boyer (ICP, Université Paris-Saclay)
"Structure of flexible chiral molecules and unconventional solvents by vibrational circular dichroism spectroscopy"

15:30-16:00 Jean-Thomas Pouzens (ICMUB, University of Burgundy)
"SNAr reactivity of thiophene derivatives investigated using conceptual DFT"

16:00-16:15 Meeting closing

Invited lectures

Structural solvation features in novel solvent media.

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Solvation is a fundamental process characterizing a variety of technologically relevant processes. It represents an essential bridge between microscopic features of solvents and the overall thermodynamic, structural and dynamic macroscopic properties of solutions. Its exploration is of paramount importance, especially when considering the new generations of solvent media that have been proposed over the last couple of decades, including ionic liquids, (deep) eutectic solvents (DES) and low transition temperature mixtures (LLTM).

These novel media often represent breakthrough in terms of macroscopic performances, due to their specific and targeted solvation capabilities towards a variety of substances, including biomass, (bio) macromolecules, organic compounds and drugs.

In this contribution, I will report on our recent studies on a variety of solvents and on the detailed nature of their solvation capabilities, exploiting the synergy between experimental (X-ray or neutron scattering) and Molecular Dynamics simulations. This research approach looks quite relevant to explore solvation features, as both tools provide direct access to microscopic structural and dynamic scales (nm / nsec), thus accessing the very details of microscopic interactions that lead to efficient solvation.

I will cite recent results on the development of new, water based DES[1,2] and on their capability, similarly to reline, the prototype DES, to solvate complex carbohydrates, such as cyclodextrins (CD). Therein, the balance between hydrogen bonding and dispersive interactions turns out to be fundamental to stabilize CDs against flocculation. [3–5]

I will also report on recent results on newly developed, eco-sustainable LLTMs, which can efficiently dissolve polyethylene-terephthalate (PET) and illustrate the microscopic mechanism of solvation.

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The many ways of biosystems for coping with extreme conditions

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Life as we know it from our close environment corresponds to very narrow windows in external conditions, be it for temperature, pressure, pH, salinity or others. As they are suitable to the well-being of humans, we call them "normal". Nonetheless, a plethora of living systems cope with harsh conditions on Earth, in the oceans or the Earth crust and are well adapted to such conditions. Understanding their adaptation mechanisms gains more in more in importance to permit a better knowledge about the origin of life [1], modeling the impact of climate change on flora and fauna [2], establishing theoretical boundaries for life [3], and optimizing medical applications as thermal based treatments for cancer [4].

Neutron scattering is a well suited tool to disentangle various structural and dynamical elements allowing biosystems to withstand conditions hostile to life. Such studies can be combined with complementary laboratory methods and simulations for an in-depth picture. Based on research over the last years, we will present new insights into temperature [5, 6] and high hydrostatic pressure adaptation [7] (see figure below) and remind the impact of crowding and co-solutes [8] on biomolecular function especially under extreme conditions.
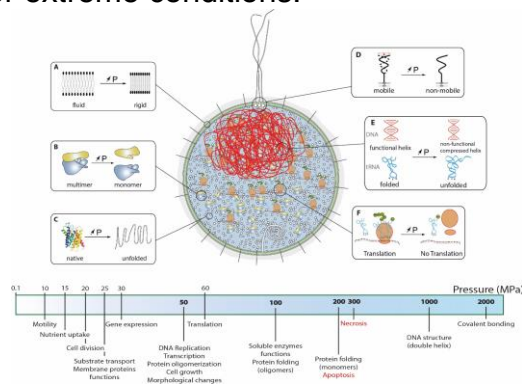

Figure : Impact of high pressure on cell components

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Structure and Dynamics of Water at Photocatalytic Interfaces

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Finding a clean and renewable energy source to replace fossil fuels has attracted much attention, the past few decades, as a step towards the sustainable development of societies. Direct hydrogen generation on TiO_2 by photocatalytic dissociation of water using sunlight was already proposed almost 50 years ago. However, despite extensive work in this area, the fundamentals of the process remain ill-understood, mainly due to the lack of a proper tool to specifically explore the interface between water and photocatalysts on ultrafast timescales. Sum frequency generation spectroscopy (SFG), is an inherently surface sensitive tool, allowing the study of the water-solid interface without monitoring the bulk water. From the intensity and frequency of the static SFG signal we extract information about the different water species binding to photocatalysts.

To obtain information on the mechanism of the water splitting process, in the first part of the talk we will look into the structure of water in contact with ironoxide, both hematite and magnetite [1]. In the second part, we will put our focus on a dynamical study at the water-TiO_2 interface after excitation with a short UV pulse mimicking sun light. Subsequently, the O-H stretch vibration of the interfacial species are monitored on a subpicosecond timescale with SFG spectroscopy. Our data show that the surface charge changes on ultrafast timescales upon excitation resulting in reorientation and partly dissociation of the water molecules on 10s of ps timescales. These UV-pump SFG-probe data illustrate the first steps towards following the photo-induced dissociation of water at the TiO_2 interface in real-time. [2]

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Multiscale Modelling of Biomolecules at Inorganic Surfaces

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Understanding of processes at hydrated surfaces of inorganic nanomaterials in biomolecular media is of crucial importance in many technological and biomedical applications, as well as in investigation of molecular mechanisms behind possible hazard effects of nanoparticles in living organisms. Experimentally it is very difficult to get information on details of the hydrated surface structure and biomolecular adsorption at nanosurfaces because of very small volume of the relevant region of space relative to the bulk. Physics-based computer modeling provides alternative route to characterize bio-nano interface. The challenge here lies in the range of scales that needs to be crossed from the detailed surface chemistry in atomistic representation to the relevant length scales covering typical nanoparticles and biomolecules (proteins and lipids). Here a systematic multiscale approach is presented that allows one to evaluate atomistic interactions at the bionano interface from the first principles simulations, and then proceed, without any empirical parameterization, to coarse-grain (CG) models enabling modeling of real-size nanoparticles with proteins and lipid membranes.

This approach is illustrated on modeling of biomolecular adsorption on TiO_2 nanoparticles. We start from ab-initio molecular dynamics (AIMD) simulations of TiO_2 surfaces in water from which information on detailed TiO_2 surface chemistry and hydroxylation pattern is obtained. Furthermore, AIMD simulations are used to parametrize atomistic force field for classical MD simulations, using DDCE6 partitioning of electron density and determination of partial atom charges and Lennard-Jones parameters from it. Next, *ab-initio* derived atomistic force field is used in classical molecular dynamics simulations of TiO_2 surfaces in water solution containing also lipid molecules. These simulations demonstrated that lipids bind to TiO_2 surface by their polar groups, and that strength of this binding depends on the lipid type and TiO_2 form (anatase vs rutile). Atomistic simulations were also used to determine interaction potentials for CG models by the Inverse Monte Carlo method, which provides for CG models the same structural properties as those observed in atomistic simulations. CG simulations of real size nanoparticles in presence of large amount of lipids showed deposition of lipids at the surface and formation of lipid bilayer attached to the nanoparticle surface. Implications of the obtained simulation results for toxicological in-vivo studies on inhalation of TiO_2 nanoparicles are also discussed.

Oral communications

Deep Eutectic Solvents: Properties Induced by Nanometric Confinement

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Over the past decade, Deep Eutectic Solvents (DESs) have garnered significant attention within the scientific community due to their remarkable functional properties, positioning them as promising alternatives to conventional solvents in green chemistry initiatives [1,2]. Notably, DESs exhibit unconventional behavior stemming from the formation of nanoscopic domains and dynamic heterogeneity across nanometers scale, attributed to the intricate interplay of ionic and hydrogen bonding interactions among their molecular constituents [3,4]. Consequently, unravelling the physicochemical intricacies of DESs at the mesoscopic level has emerged as a pivotal pursuit. The interrogation of DES behavior under mesoporous confinement stands as a particularly pertinent endeavour, given the pivotal role of interfaces and nanopores in numerous targeted applications of these solvents. Hence, a pressing question arises regarding the impact of mesoporous confinement on the structure and dynamic (diffusion, rotation and relaxation) heterogeneities inherent within DES systems [5,6].

The structural and dynamic behavior of Ethaline—a deep eutectic solvent (DES) consisting of choline chloride and ethylene glycol—was analyzed in both bulk and confined states within mesostructured porous silicas (SBA-15) using Neutron Diffraction and Incoherent Quasielastic Neutron Scattering (QENS) experiments. A broad dynamical range was achieved by combining of time-of-flight (IN5B) and backscattering (IN16B) QENS spectrometers, yielding complementary energy resolution capabilities. This study offers a detailed microscopic characterization of the confined Ethaline system, evaluating parameters including the elastic incoherent structure factor, diffusion coefficients, residence times, relaxation times, and their temperature-dependent behavior [7-9].
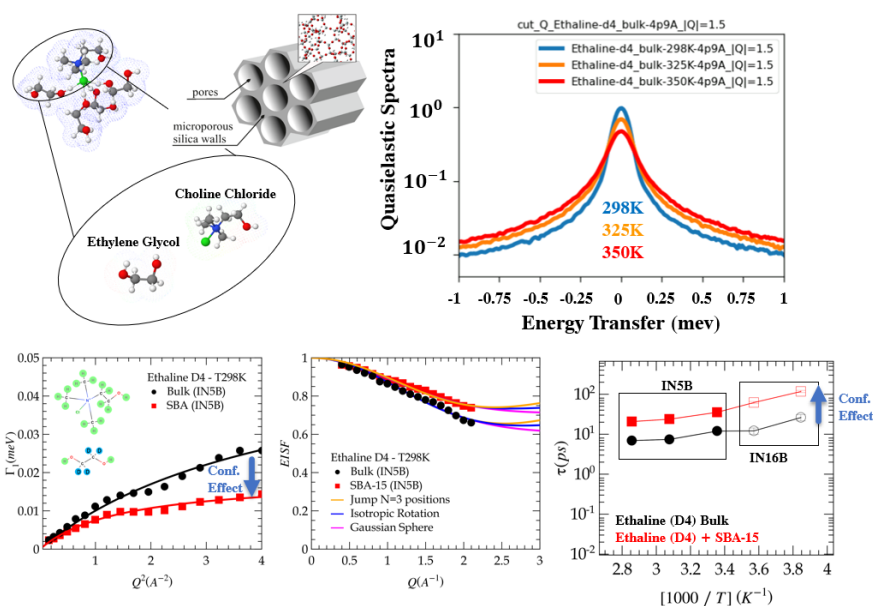

Figure: (upper panel) Sketch of studied systems and their dynamic structure factor. (lower panel) Confinement effect on the Quasielastic broadening of the slow (jump-diffusion) process, elastic incoherent structure factor (EISF), and temperature dependance of the residence time.

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Efficient machine learning-based new tools to design eutectic mixtures and predict their viscosity

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In response to the growing demand for sustainable solvents, DES (Deep Eutectic Solvents)[1] have emerged as green alternatives to conventional solvents. However, a major challenge limiting their industrial application lies in their often high viscosity, a property highly influenced by the temperature, the water content, the structure of the components and their ratio in the mixture. Given the vast landscape of possible mixtures, being able to predict the formation and the viscosity of DES has become essential.

To address this, we developed several machine learning models, including classification algorithms able to predict the formation of eutectic mixtures (EM) and regressors that predict their viscosity. The models have been trained on in-house experimental data with several structural descriptors and they have been further validated on sets of unseen data to ensure generalizability and fair extrapolation. In addition, eXplainable Artificial Intelligence (XAI) techniques were employed to quantify input feature contributions to the outputs of the top-performing models.

This talk will begin with a simple introduction to the algorithms and methods used in this study, placing them within the broader context of artificial intelligence (AI) and its applications in chemistry. The main results will then be presented, demonstrating how this study, among others, is a step forward enabling efficient screening of eutectic mixture compositions, tailored for specific applications.
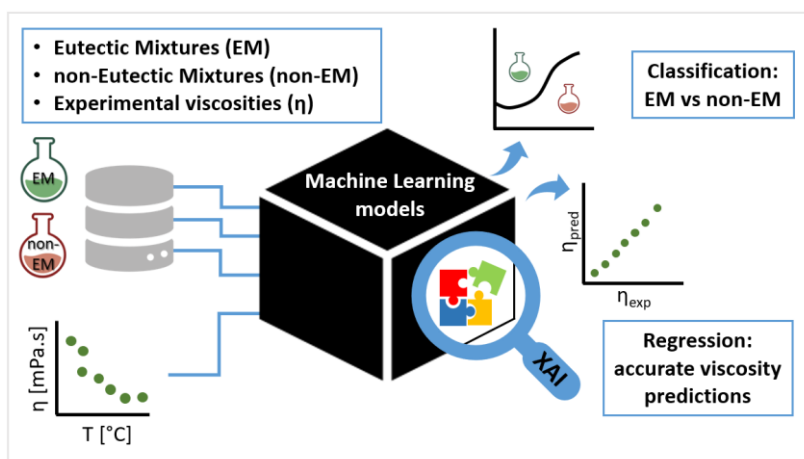

Figure 1: Schematic representation of our machine learning workflow

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Extraction of natural compounds using sustainable solvents

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Plant extracts are valuable ingredients for a wide range of applications including in cosmetics and perfumery. However, the majority of currently extraction processes involve volatile organic solvents (VOCs) and exhibit significant environmental impacts. In order to tackle these issues and be in line with the principles of sustainable chemistry and ecoextraction, sustainable alternative solvents have been developed as replacements to VOCs.[1] Among these solvents, biobased solvents (BioSol)[2], deep eutectic solvents (DES)[3] and ionic liquids (IL)[4] have been the subject of numerous studies. In addition, in the context of circular economy, by-products are now seen as an alternative source of natural compounds.

Therefore, this work presents results on the extraction of two different type of natural compounds: non-volatile bioactive compounds and volatile fragrance compounds, originating from an agriculture by-product and an emblematic perfumery plant, respectively.

In the case of non-volatile compounds, valorisation of discarded kiwis was proposed by extraction of bioactive compounds using DES. Results show that kiwi peels extracts obtained with DES exhibit improved antioxidant activity compared to conventional solvents.[5]

In the case of volatile compounds, extracts of *Rosa centifolia* petals were obtained by solid-liquid extraction in BioSol, DES and IL. Notably, BioSol improved extraction yields and extractions of 2-phenylethanol, the major volatile compound of *Rosa centifolia*. Additionally, perfumers' evaluations revealed that the extracts produced with Biosol, IL or DES had distinct olfactory characteristics compared to the reference *Rosa centifolia* absolute derived from hexane extract.

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Impact of scCO$_2$ on C-Phycocyanin stability in presence of polyethylene glycol

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Amid worldwide economic and environmental challenges, the urge to find sustainable processes and new sources of proteins has positioned supercritical CO$_2$ (scCO$_2$) as an interesting alternative solvent in chemical engineering and food science [1]. Its solvation properties may indeed be tuned by changes in thermodynamic parameters such as temperature (T > 31°C) and pressure (P > 74 bar) and/or by the addition of co-solvents such as water or ethanol. However, the use of scCO$_2$ as an extraction solvent in complex matrices remains essentially empirical, given the poor knowledge on its solvation properties at molecular scale in crowded environments. Molecular interactions and excluded volume effects in biological matrices induce macromolecular crowding, which may stabilize and protect the native structure of proteins under high-temperature and/or high-pressure conditions [2], [4].

However, much less is known on how such interactions evolve in scCO$_2$ solvent. For this purpose, we considered a simplified model composed of a globular protein, C-Phycocyanin (CPC) and a polymer, polyethylene glycol (PEG) that mimics the macromolecular crowding found in complex food matrices. Two PEG with different molecular weight (PEG 4000 Da and PEG 35 000 Da) have been chosen to modulate the hydration of the protein. Moreover, two conditions have been applied (T=50°C; p=400 bars) and (T=50°C; p=800 bars) at which the density of scCO2 increases from 0.92 g/cm^3 to 1.04 g/cm^3.

The viscosity and density of PEG solutions did not significantly change after exposure to scCO2 thereby suggesting no irreversible influence of scCO$_2$ on the specific volume or on the conformation of the polymer. Spectroscopic and differential scanning calorimetry (DSC) measurements showed strong structural and environmental alterations of CPC in presence of PEG. Even though no protein aggregation was observed, fluorescence spectroscopy showed favorable interactions between PEG and protein hydrophobic residues, increasing their exposure to solvent, meanwhile DSC highlighted alteration of the oligomeric equilibrium and denaturation temperatures. Exposure to scCO$_2$, regardless of PEG size or concentration, resulted in notable protein aggregation and structural destabilization.

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Local Structure of Supercritical Fluids Near the Widom Line

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Supercritical fluids (SCFs) are widely used [1] in many chemical industries, including pharmacy, materials science and more. Main advantages of SCFs include their environmental friendliness, unique combination of liquid density and gas diffusivity, as well as, perhaps most notably, their structural/dynamical fluctuations.

It has been long known, that within supercritical region exists a line, so-called Widom Line, that extends the vapor-liquid coexistence curve. Upon crossing this line, in either isobaric or isochoric conditions, many thermodynamical properties of the SCF have large fluctuations or even discontinuities. It is, therefore, possible, to optimize many of the processes utilizing SCFs by precisely picking the operating temperature and pressure. For this, a precise mapping of the Widom Line onto the phase-space is required. Traditional experimental methods may include [2] investigations of heat capacity, compressibility, thermal expansion coefficients and so on.

Previous theoretical investigations of the Widom Line also have focused on the changes in thermodynamically properties, such as isobaric/isochoric heat capacities. In contrast, we have proposed functions of local structural order as an indicator of Widom Line crossings. In this work, we have performed molecular dynamics (MD) simulations of TIP4P/2005 water from 175 bar to 375 bar between 300K and 1100K and Cygan et al. [3] carbon dioxide from 70 bar to 100 bar between 250K and 600K. We have analyzed the systems with such functionals as nearest-neighbor radial distribution functions, Voronoi space-tesselation analysis and DBSCAN. We show that certain extrema in the average values, fluctuations or rates of change of average values of respective local parameters can define purely local Widom Lines that are in decent agreement with experiments.

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Fast calculation of solvation structure and thermodynamics in supercritical CO_2

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Growing concern about the environmental impact of industrial activities is driving the chemists to develop more ecological processes. A major goal is to design new range of solvents, "greener" but as efficient as the widely used organic solvents. Supercritical CO_2 ($scCO_2$) is an interesting alternative.[1] It is non-toxic to humans and the environment, non-flammable and can be easily fine-tuned to precisely control the solvation power. The $scCO_2$ is used in several industrial processes: extraction of natural products, impregnation of polymer matrices, water purification or synthesis of nanoparticle A wider use of such ecological solvent would however require an accurate for predicting the solvation properties.

Different approaches exist to estimate the solvation properties in supercritical fluids. Industrial chemists rely on accurate parametric models, but many parameters must be fitted for each solute and each new solvent.[2] Molecular simulations (MD or DFT) are more flexible than the parametric models and can accurately calculate the solvation free energy and the other solvation properties: structure, enthalpy, molar volume. But despite enormous progress, MD is still too expensive to be considered as a predictive tool for large scale investigations (many solutes, different solvents and solvent mixtures and different thermodynamic conditions).[2]

We will present a powerful alternative strategy based on classical density functional theory (cDFT), a liquid-state theory. Such approaches provide the same solvation properties as MD, but at a computational cost that is 1000 times cheaper.[3] In our work, we built the excess free energy functional and compared the structure and the solvation free energy of several solutes in $scCO_2$ obtained with cDFT and MD.[4] We obain a very good agreement between MD and cDFT In this talk, we will detail the method, the implementation and the perspective for the development of this new accurate, flexible, and ultrafast prediction tool for solvation properties in $scCO_2$.

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Molecular Dynamics Analysis of Interfacial Properties of Curcumin and Supercritical Fluids

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Many of the so-called active pharmaceutical ingredients (API) have different polymorphic forms, which can radically affect crystallization dynamics, co-crystallization abilities, solubilities and dissolution rates of the final products. Recent experimental results [1] suggest that interfacial properties could play significant role in polymorphic control. Specifically, distribution of conformations on the solid-melt interface can be a good predictor of the ratio of specific polymorphs after the melt is cooled.

The main objective of the present study is to obtain a theoretical description of the correlation between the changes in the local structure of an interface and changes in the conformational distribution / polymorphism of active pharmaceutical compounds. To this end, we have performed molecular dynamics simulations of bulk Curcumin crystals and Curcumin-scCO$_2$ interfaces. Curcumin is both culturally important and medically interesting due to the recent reports [2] of its biochemical activity. Supercritical CO$_2$ is one of the most accessible, environmentally friendly and widely used supercritical fluid solvents, allowing us to contrast computational results against some experimental or previous theoretical trends.

Throughout this project we have selected and developed both Curcumin and CO$_2$ force field models, developed a method of monitoring conformational changes, selected methods of identifying interfacial molecules (ITIM) and integrated it with many methods of local-structure description (such as radial distribution functions, angular distribution functions, Voronoi analysis, etc.).

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Chemistry in aqueous solutions as described by ab initio molecular dynamics: case of a green catalyst under "in-water" and "on-water" conditions

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Ab initio molecular dynamics (AIMD) is a valuable tool for the investigation of chemical reactions involving the formation or breaking of covalent bonds as well as subtle interactions between solute and solvent molecules or ions. The computational cost that precluded the study of large systems or long-time properties has been recently reduced thanks to more efficient algorithms and new strategies of code parallelization [1].

We will focus on the theoretical study of an environmentally benign catalyst, namely choline hydroxide (ChOH), for the conversion from nitriles to amides [2], with water as a solvent, under two specific conditions: "in-water" (or bulk) conditions and "on-water" (at the air-water interface) conditions [3]. This investigation emphasizes some characteristics of aqueous solutions, namely the importance of the dynamics of hydrogen bonds, the possible occurrence of isomeric conversions, the structural diffusion of the hydroxide anion, and the influence of interfacial conditions.
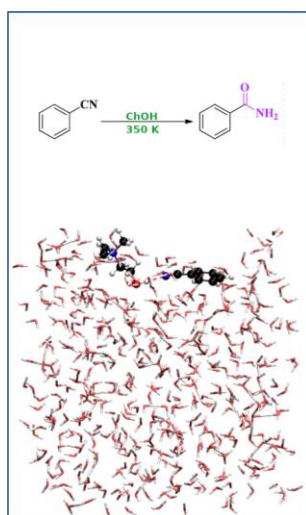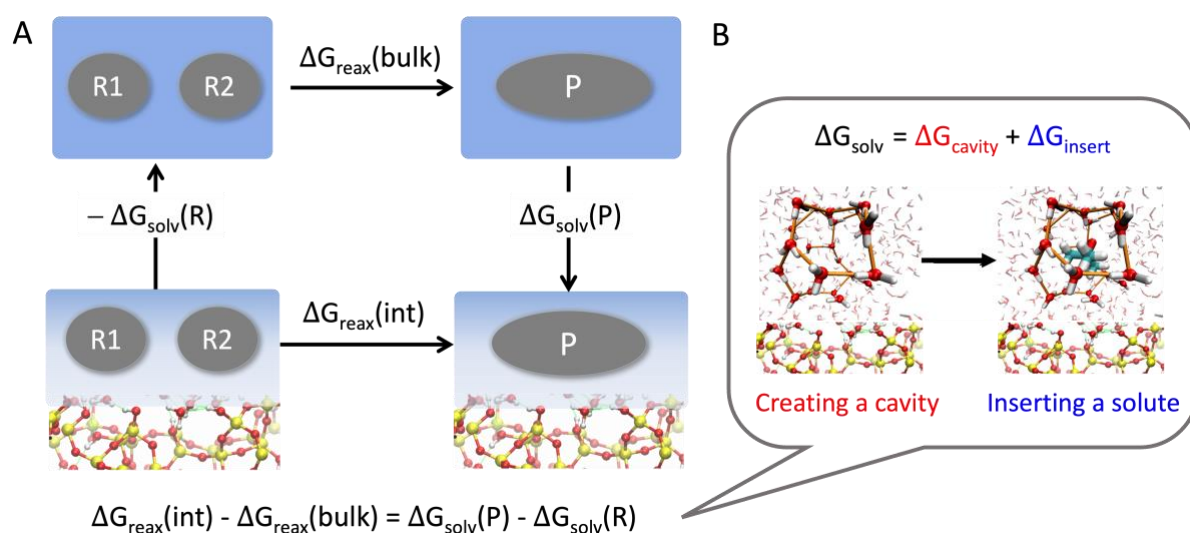
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On the Chemistry at Oxide/Water Interfaces: the Role of Interfacial Water

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Oxide-water interfaces host many chemical reactions in nature and industry. There, reaction free energies markedly differ from bulk. While we can experimentally and theoretically measure these changes, we are often unable to address the fundamental question: what catalyses these reactions? Recent studies suggest that surface and electrostatics contributions are insufficient to answer. The interface modulates chemistry in subtle ways. Revealing them is essential to understanding interfacial reactions, hence improving industrial processes. Here, we introduce a thermodynamic approach combined with cavitation free energy analysis to disentangle the driving forces at play. We find water dictates chemistry via large variations of cavitation free energies across the interface. The resulting driving forces are both large enough to determine reaction output and highly tunable by adjusting interface composition, as showcased for silica-water interfaces. These findings shift the focus from common interpretations based on surface and electrostatics, and open exciting perspectives for regulating interfacial chemistry.

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Investigating organic molecules at the water-platinum interface: From single-crystal surfaces to nanoparticles via density functional tight binding

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The platinum/water interface is a prototype to investigate the impact of transitioning from gas-phase petrochemistry to aqueous-phase biomass valorization. The aqueous environment is notoriously difficult to capture for computational methods:[1] implicit solvent models fail to capture near chemisorption on noble-metal surfaces, and DFT-based molecular dynamics are too costly in view of the slow diffusion constants at the solid/liquid interface. Even though QM/MM for the evaluation of the solvation free energy using dedicated force fields such as GAL17 leads to qualitative agreement with experiment.[2] To go beyond additive force fields, we introduce a density functional tight binding (DFTB) parametrization for the Pt/C/H/O system. We quantify the accuracy describing the adsorption and reaction of polyols on Pt(111) as well as the dynamic (morphological) changes of nanoparticles (Pt_{38}, Pt_{55} and Pt_{147}) to be around 10 kcal/mol. Our parametrization efforts show that DFTB requires a corrective three-body potential, introduced via ChIMES[3] to capture water adsorption on Pt(111) and for the structure and reactivity related to nanoparticles. We showcase the difference between DFTB and DFTB/ChIMES on the adsorption energy of phenol on Pt(111) in the gas-phase and in water, see Figure 1.

Figure 1 Comparison of DFTB and DFTB/ChIMES.
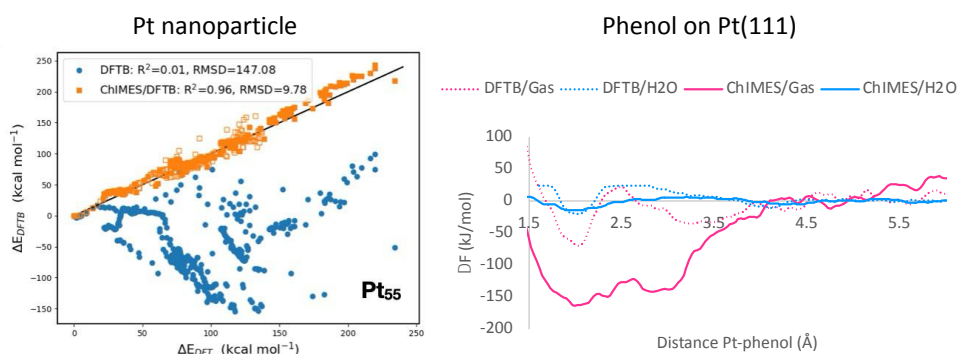
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Stochastic density functional theory for ions in a polar solvent

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In recent years, the theoretical description of electrical noise and fluctuation-induced effects in electrolytes has gained a renewed interest, enabled by stochastic field theories like stochastic density functional theory (SDFT). Such models, however, treat solvents implicitly, ignoring their generally polar nature. In the present study, starting from microscopic principles, we derive a fully explicit SDFT theory that applies to ions in a polar solvent. These equations are solved to compute observables like dynamic charge structure factors and dielectric susceptibilities. We unveil the relative importance of the different contributions (solvent, ions, cross terms) to the dynamics of electrolytes, which are key to understand the couplings between ions and the fluctuations of their microscopic environment.
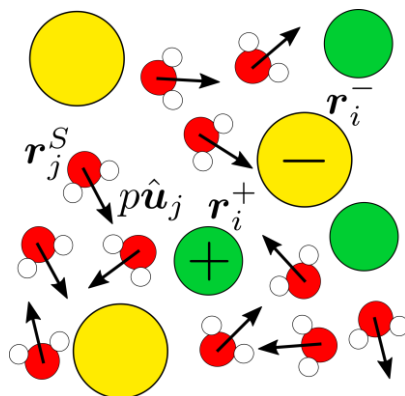
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Concurrent processes in the time-resolved solvation of alkali ions in helium nanodroplets

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Recent pump-probe experiments [Albrechtsen *et al.*, Nature **623**, 319 (2023)] have explored the gradual solvation of sodium cations in contact with helium nanodroplets, using a fully solvated xenon atom as a probe exerting a repulsive interaction after its own ionization. In this contribution, we computationally examine by means of atomistic ring-polymer molecular dynamics the mechanisms of successive ionizations, shell formation, and Coulomb ejection that all take place within tens of picoseconds, and show that their interplay subtly depends on the time delay between the two ionizations but also on the droplet size. The possibility of forming solvated Na^+Xe non-covalent complexes under a few tens of picoseconds in such experiments is ruled out based on fragment distributions.

Besides accounting for the main phenomenology of the sodium-xenon experiment, we extend the investigation to the case of potassium, still with the xenon dopant, and predict significantly smaller, partially solvated K^+ cations, owing to the even weaker interaction in the neutral state.

Finally, our first results involving molecular dopants (benzene, cyclohexane, and their dimers) will be presented.
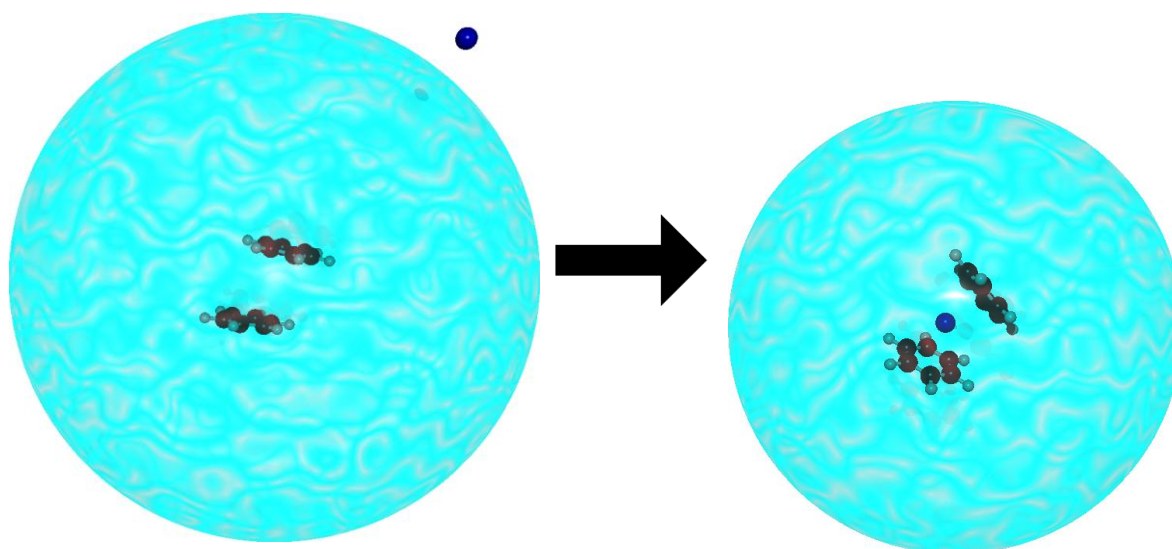
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Structure of Flexible Chiral Molecules and Unconventional Solvents by Vibrational Circular Dichroism Spectroscopy

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Vibrational circular dichroism (VCD) unveils molecular conformational nuances by discerning absorption differences in right- and left-circularly polarized light within the infrared range. This subtle technique elucidates molecular interactions, especially those that are sensitive to hydrogen bonding, thereby offering particular insight into the structure of unconventional solvents. Interpreting VCD signals necessitates meticulous comparison with theoretical models. However, incorporating environmental effects posed challenges, now mitigated by advancements in computational modeling. Recently, we proposed a new methodology based on classical molecular dynamics simulations associated with the AMOEBA polarizable force field to calculate VCD spectra of flexible molecules [1]. The crucial element in these VCD simulations is determining the magnetic dipole moment, an intrinsic dynamical quantity. Highly flexible molecules turn out to be particularly interesting to study using this method, like 1-phenyl-1,2-cyclohexanediol (PC), that was successfully studied in a dimethyl sulfoxide (DMSO) solvent, leading to the calculation of both infrared and VCD spectra. Modeling both the infrared and VCD spectra for these systems reveals useful insights into their properties and the complex interactions with their environment, with the intention to extend this work to ILs and DES, like spirocyclic pyrrolidinium with BF4- and menthol acid acetic, respectively.
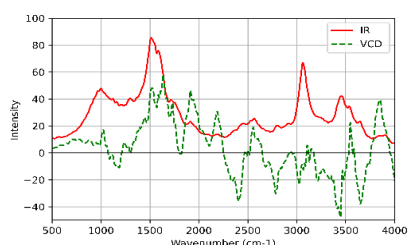

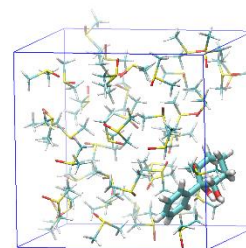*Figure 1. Infrared and VCD spectra of PC in a box of solvent (DMSO)*

Figure 2. Phenylcyclohexanediol in a box of DMSO

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S_NAr reactivity of thiophene derivatives investigated using conceptual DFT

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Thiophenes are heterocycles of industrial interest which have attracted considerable attention due to their versatility in different applications. For instance, substituted thiophenes are used to synthetize materials with photophysical properties and electrochemical systems and they are increasingly being employed in therapeutical applications.[1], [2] The formation of amino substituted thiophenes through aromatic nucleophilic substitution (S_NAr) have been extensively studied experimentally.[3], [4] To gain more insights on the substituent effects, the electrophilicities of numerous thiophenes derivatives have been provided using Mayr's electrophilicity scale.[5] However, further analysis of such properties and computational efforts to achieve a description of the reaction mechanism are rare.[6]

In this work, we performed quantum chemistry calculations to investigate the mechanism of the S_NAr reaction of pyrrolidine with seven substituted thiophenes.
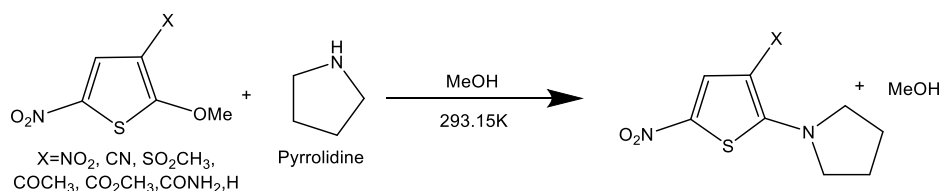
Scheme of the studied S_NAr reaction.

We then used conceptual DFT and Topological approaches [7] to rationalize the evolution of the computed activation energies by means of quantum descriptors, such as Parr's electrophilicity and the LUMO energy. We showed that, though the relative reactivity of different thiophene sites is hard to model, the reactivity of the thiophene derivatives nicely correlates with global descriptors.

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Posters

Unraveling the Release Mechanism of Sodium Alginate Network in Simulated Gastrointestinal Conditions

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Sodium alginate (SA), a natural polysaccharide extracted mainly from brown seaweed, consists of two types of monomers: mannuronic acid (M) and guluronic acid (G), arranged in block chains [1]. SA is extensively researched for bioencapsulation applications due to its safety and ionotropic gelation, wherein divalent cations such as calcium crosslink with the G blocks, resulting in a three-dimensional structure [2]. The forming network is considered for oral administration because it is stable and pH-dependent, suitable for encapsulating and delivering materials in both the gastric and intestinal phases [3]. In acidic pH conditions, such as in the stomach, the carboxylate groups of alginates can undergo protonation, resulting in decreased hydrophilicity, which impacts the gel network's water retention capacity and leads to a denser structure. Conversely, the alginate network can be loosened and completely dissolved under intestinal conditions. However, unlike the gelation process, the release mechanisms of encapsulated materials from the alginate matrix under gastrointestinal conditions remain poorly understood.

Recent studies indicate that the release behaviour of SA in simulated gastrointestinal fluids may be affected by interactions with environmental factors, particularly bile salts, resulting in ion exchange and the dissolution of the gel network. This study investigates how bile extracts affect the ion exchange and release behaviour of the alginate gel in gastrointestinal conditions. Comprehending these interactions may enhance the advancement of controlled release systems, especially for colonic drug delivery applications. This study seeks to address the knowledge gap in release mechanisms and improve the application of SA in encapsulation technologies.

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Asymptotic underscreening in highly concentrated electrolyte

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Recently, we developed a new optical type of measurement allowing the study of water/electrolytes organization [1-2]. The technique is based on the nonlinear optical process of second harmonic scattering (SHS), a nonlinear optical phenomenon involving the conversion of two photons at the fundamental frequency into one photon at the harmonic frequency nto water, this incoherent second order process is due to orientational fluctuations of the non-centrosymmetric H_2O molecules. However, when molecules are correlated in orientation, the scattered photons emitted by each individual molecule interfere and the scattering pattern is modified. Though tiny, this modification can be detected and attributed to orientational correlations and can be connected to rotational invariant of the g-orientational pair correlation function derived with integral equation. With this method, we explore the water organization in the highly concentrated regime of LiCl and NaCl solution. First, we show that the water organization reports the salt correlation function. Then, the SHS intensity, resolved in polarization, allows us to measure the screening length (or Debye Length) in the highly concentrated regime. We show that the decrease of the screening length depends on the inverse of the Debye length to the power one, instead of the power three, as previously reports by other measurements. So, we show that SHS could be a powerful technic, fully optical, to investigate correlations length in bulky systems.

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Glycine solvation study

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Understanding solvation dynamics is crucial in various scientific fields, ranging from biochemistry to materials science. Solvation involves the interaction of solute molecules with a solvent, which significantly influences the properties and behavior of the solute. This is particularly relevant in aqueous solutions.

Glycine is the simplest amino acid, that can exist in zwitterionic and neutral form. Studying glycine's solvation dynamics, especially in its zwitterionic form, provides insights into the behavior of more complex amino acids and peptides in aqueous environments. We studied behavior of glycine in the range of temperatures, starting from supercooled water at 238 K and up to 298 K. The effect of the concentration of zwitterion molecules was also taken into account, in the range from 5 to 30%.

Solvation is inherently complex, traditional experimental methods often provide limited insights into the molecular details of solvation shells. Kirkwood-Buff Integrals help to overcome these limitations. The data for KBIs was taken from molecular dynamics simulations, performed using NPT ensemble. The values of KBIs were obtained using 2 methods: integration over the radial distribution function (RDF) and calculation of fluctuations in the particle number[1]. Using values of KBIs for 2 component systems we derived such characteristics as partial molar volume of water and glycine, isothermal compressibility, and thermodynamic correction factor (Figure 1.)[2]. The structural analysis of water was performed using Q4 structure order parameter and Chill+ algorithm.
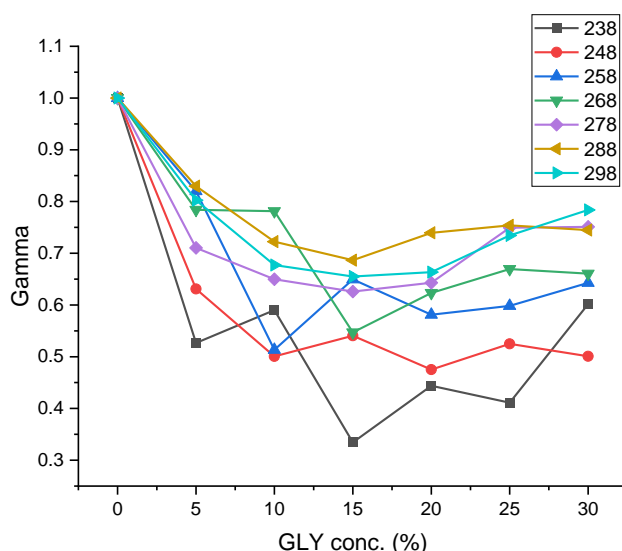
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The hydrophobic hydration of TBA ions at the gold/water interfaces

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In recent years, we have gradually recognized the critical role of hydrophobicity in electrochemical interfaces, as it significantly influences the rate and selectivity of electrochemical reactions. The strong interaction between metal electrodes and water at the electrochemical interface creates distinct hydrophilic/hydrophobic layer structures, thereby offering opportunities to modulate reactions involving hydrophobic or amphiphilic molecules such as CO_2 and N_2 reduction, water splitting, and alcohol oxidation. This unique isotropic environment can be tailored through metal-water interactions and the composition of interfacial water and electrolytes.

This study focuses on developing a novel approach to regulate hydrophobic solvation free energies by adjusting interface hydrophobicity and modifying the composition of hydrophobic reactive species. The tetrabutylammonium ion (TBA^+), a large hydrophobic molecule, can adsorb onto the interface, creating a significant hydrophobic environment and altering reactivity. We employed classical molecular dynamics methods and collaborated with an experimental group using THz spectroscopy, both revealing substantial structural changes upon the addition of TBA^+ cations to aqueous electrolyte solutions under varying applied potentials. These changes are characterized using computational tools such as the MetalWalls code, custom Python scripts, and Fortran programs. These tools calculate density profiles of each species, TBA^+/Cl^- and TBA^+/water coordination, and dynamics of hydrogen bonding as functions of potential to elucidate hydrophobic solvation properties at the interface.

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