Journées du GdR Solvate, Février 2019

4-5 Feb 2019
Lyon

Organized by
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The Lipid Membrane Chemistry: A hydration and surface potential perspective

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Lipid membranes are highly dynamic and complex structures that determine the fate of a cell. Although recognized as an essential building block, water is usually treated as a passive background in membrane studies. In contrast, water and ions play a key role, determine the electrostatic environment of the membrane and actively influence the surface biochemical reactions. In this talk, the main focus will be on what second harmonic scattering can tell us about the hydration and surface potential of lipid membranes.

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*Speaker

Water at electrochemical interfaces: interfacial pH and acid-base properties

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The interface between a model Pt(111) electrode and an electrolyte in absence of specific adsorption will be discussed. By using non-traditional strategies, the potentials of zero total and free charge can be determined. The dependence of these magnitudes with pH suggest that the pzfc is always constant and suggest a neutral interfacial equilibrium at significantly more acidic solutions. In a similar way, the surface pK of weak acids is lower than that measured in bulk solution, indicating a higher dissociation ability.

[*]Speaker

Chemically active domains of liquids

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Choosing the right solvent is important for the successful outcome of many reactions, therefore, an understanding on the molecular level behavior of the given liquid itself is mandatory if the full potential of the solvent should be reached. This is particularly the case if the liquid is actively participating in the reaction, not only as a solvent, but also as a catalyst. In this talk, we discuss liquids that are examples of such complex processes and we show how we analyze their behavior[1]. The catalytically active mixtures of 1,1,1,3,3,3- hexafluoro-2-propanol (HFIP) - which is one of the more stabilizing solvents for spin centers serves as such an example.[2] In another example, we elaborate on the structure of alcohols in ionic liquid (ILs).[3]
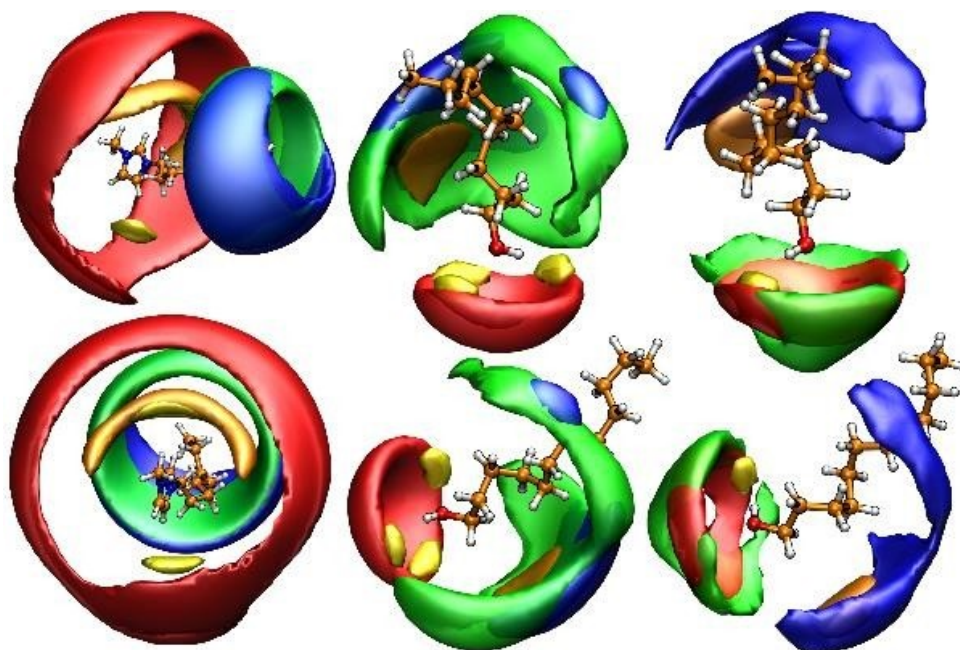
Figure 1: From Ref. 3: Spatial distribution functions of cation (left), alcohol (long side chain cation: middle; short side chain: right). Cation: red; anion: orange; side chain: green; OH: yellow; side chain alcohol: blue.

Structure-directing or template effects have been invoked several times for ILs to explain the different outcome in material synthesis. The successful imprinting of the ILs' order in the alignment of the alcohol molecules in these simple model systems (Fig. 1) shows that the microheterogeneous structure of ILs can indeed be applied to arrange reaction substrates in a predetermined fashion, opening new possibilities for explaining or enhancing the selectivity in chemical

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reactions in ILs. In electrolyte systems, the association of the ions to form ion pairs or other, low charge aggregates is a long discussed issue, since it can affect the manner and the extent of conduction by changing the number of charged species in the solution. Thus, we will cover ion pairing in ionic liquids[4] considering the bulk but also the interface gas-liquid. The charge of the ions is often assumed to ±1. Although this seems trivial, but due to a combination of polarization and charge transfer effects between the ions these charges are decreased in their absolute values.[5] The derivation and application of a polarizable force field in order to describe the TiO2-IL interface[6] playing a role in solar cell applications can account for those effects. Connected to this is structural diffusion.[7] We will also elaborate on voids in liquids to deepen our understanding of complicated liquids.[1]

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Phase separation and nucleation: from frustration to control

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Ever since it was suggested that the anomalous properties of liquid water could explained by an amorphous to amorphous liquid-liquid transition, the hunt has been on for other examples of such transitions.[1] Surprisingly, only two other examples of liquid-liquid transitions were found in molecular liquids and even these are highly controversial. I will show that one of these (in n-butanol) is, in fact, a liquid crystal transition but one in which the liquid crystal is not "in between" the liquid and the crystal but instead frustrates the formation of the crystal.[2] However, we are not content to passively observe phase transitions but desire to gain control over the nucleation of new phases. Although there are now numerous examples of control using laser-induced nucleation, a physical understanding is absent and preventing progress. I will show that concentration fluctuations in the neighbourhood of a liquid-liquid critical point can be harnessed by a laser-tweezing potential to induce concentration gradients.[3] A simple theoretical model shows that the stored electromagnetic energy of the laser beam produces a free-energy potential that forces phase separation or triggers the nucleation of a new phase. Experiments in a liquid mixture using a low-power laser diode confirm the effect. Phase separation and nucleation through a laser-tweezing potential explains the physics behind non-photochemical laser-induced nucleation and suggests new ways of manipulating matter.

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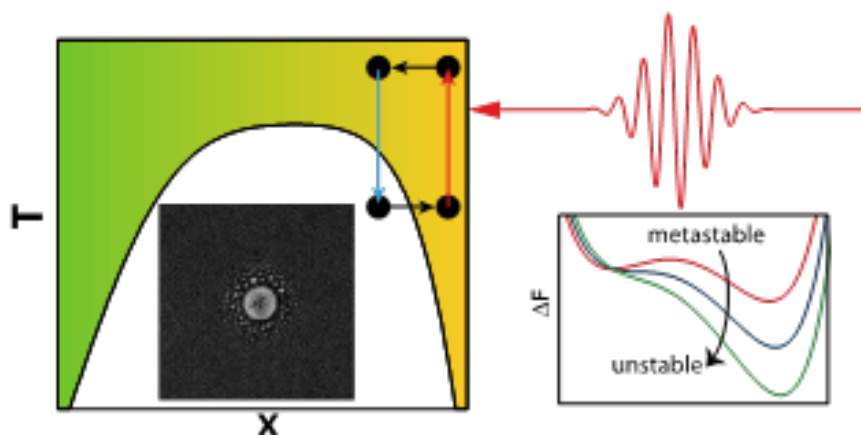
[*]Speaker

A New Method to Compute 3D (Number, Charge and Polarisation) Densities from Molecular Simulations & Application to Solvation

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The exceptional efforts both computational and human which go into to the production of trajectories in molecular dynamics simulations creates an impetus towards making the most of the data obtained. While obtaining some properties requires relatively low data density (such as radial distribution functions), to obtain an accurate three-dimensional density an exceptional amount of data is required. Given the huge applicability of 3D interfacial densities to the study of interfacial solvation, any method which could reduce the variance of their extraction would be highly advantageous. A previous study by Borgis et. al. provided a new method for the calculation of these densities by computing them from the 3 dimensional force density (1). This method allowed for a substantial improvement in the noise level of the data from the same number of recorded configurations.

Here we present an extension of this work. The reduced variance method has been adapted to calculate a general set of densities such as: number density (as in the previous case), polarisation density and charge density. This method will be validated by application to a simple model system: the structure of water around a single constrained water molecule. Further to this, the application of these methods to a more complex system, a lysozyme protein, will be presented. This new methodology provides access to a new way to understand solvation of nanomaterials, macromolecules, and protein molecules.

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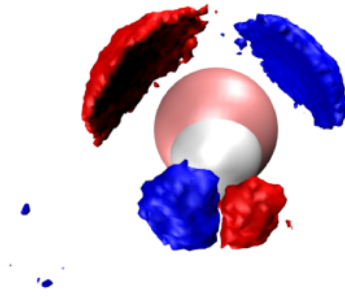
Fig. 1 *An image of the solvation shell of a single water molecule. Areas of high positive (red) and negative (blue) polarization density in the z direction (left-right within the image). This image could not be obtained using the conventional methodology.*

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Confronting Experimental Enthalpies to Theoretical Estimates

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Isotherm titration calorimetry is a powerfull means to determine the enthalpy of reactions occuring in the homogeneous phase. In the case of irreversible reactions, the measured raw heat flow gives a direct access to the reaction enthalpy. In the case of equilibria, application of appropriate algorithms describing the studied system may give access to Gibbs energy and entropy variation, and in fine to an estimate of the equilibrium constant. Our recent work has concentrated on providing experimental reference values of thermochemical parameters of simple irreversible and equilibrated organic and organometallic reactions for the purpose of benchmarking newly developed theoretical methods capable of accounting for the effects of Dispersion. It was indeed found that the theoretical reproduction of experimental trends of a number of chemical reactions depended not only on the inclusion of dispersion in the DFT method but also on accounting for solvation.1 Even though a number of systems could readily be modeled using DFT-D and regular implicit solvation models with good agreement with ITC and dynamic NMR analyses,2 a small number of reactions produced discrepancies that we assign to a significant role of explicit solvation. This communication will present consisely disclose our most recent results on the matter.

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Keywords: Organometallics, organics, ITC, DFT, D, COSMO

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DFT-MD and Cl-MD of oxide-water interfaces reveal interfacial structures, and show the need to go beyond simplified Gouy-Chapman type 1D-models.

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Water interfaces play a central role in a large variety of disciplines including e.g. atmospheric chemistry, electrochemistry, photo- & electro-catalysis, geochemistry, biophysics, material design, nanofluidics. Knowledge of the molecular structure and dynamics of water and dissolved ions at aqueous interfaces is essential not only for a fundamental understanding of this ubiquitous liquid, but also for a large number of technological applications, including new energies.

Structure and dynamics are intimately linked. Yet, common phenomenological models of ions at aqueous interfaces, like the Gouy-Chapman framework and continuum hydrodynamics models, all share the same 1D-representation, i.e. only the vertical dimension (above the surface) taken into account, while the couplings between structure, hydrodynamics and diffusion are not included. Real surfaces are however rough and heterogeneous, so that 3D-models should be more appropriate to capture the microscopic essence of interfacial phenomena. Moreover, water arrangement close to another medium is dictated by specific water-substrate interactions (or lack of), not included in continuum models, leading to unique anisotropic HB-networks formed by water in the first interfacial layer, denoted Binding Interfacial Layer (BIL).

We will illustrate these points with DFT-based MD simulations of oxide-water isoelectric and charged interfaces as well as with classical MD simulations. To provide a comprehensive characterization of the solid-water interfaces, MD simulations are systematically coupled with theoretical SFG spectroscopy, one of the very few experimental tools that reveal interfacial structures. We will show how to define the only two SFG active water layers at any charged interface, i.e. BIL (Binding Interfacial Layer) and DL (Diffuse Layer), and how to calculate BIL-SFG and DL-SFG spectra, and what the spectroscopic features reveal on the interfacial structure. See our recent refs below. With classical MD simulations, one can play more systematically with the surface charge and its spatial distribution (homogeneous *vs* inhomogeneous), and hence the following results will be presented and discussed: (1) from low to high ionic concentrations at interfaces and associated DL thicknesses for DL-SFG; (2) water orientations in the BIL and DL provided by homogeneous and heterogeneous surface charge distributions, and associated BIL-SFG and DL-SFG signatures; (3) structural organization of the water in the BIL first interfacial layer predominantly dictated by the hydrophilic/hydrophobic nature of the solid surface, and not following the electrostatic driving force below a certain threshold.

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- J.D. Cyran, M.A. Donovan, D. Vollmer, F. Siro-Brigiano, S. Pezzotti, D.R. Galimberti, M.-P. Gaigeot, M. Bonn, E.H.G. Backus, *Molecular Hydrophobicity at a Hydrophilic Surface.* Just

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*Speaker

accepted, PNAS (Dec 2018)

- F. Creazzo, D.R. Galimberti, S. Pezzotti, M.-P. Gaigeot *DFT-MD of the (110)-Co3O4 cobalt oxide semiconductor in contact with liquid water, preliminary chemical and physical insights into the electrochemical environment.* J. Chem. Phys. 150:041721-18 (2019)

- S. Pezzotti, D. R. Galimberti, Y. R. Shen, M.-P. Gaigeot *What the Diffuse Layer (DL) reveals in non-linear SFG spectroscopy.* Minerals, 8:305-321 (2018)

- S. Pezzotti, A. Serva, M.-P. Gaigeot *2D-HB-Network at the air-water interface: a structural and dynamical characterization by means of ab-initio and classical molecular dynamics simulations.* J. Chem. Phys., 148:174701-10 (2018)

- S. Pezzotti, D. Galimberti, , Y.R. Shen, M.-P. Gaigeot *Structural definition of BIL and DL: a new universal methodology to rationalize non-linear $\chi(2)(\omega)$ SFG signals at charged interfaces, including $\chi(3)(\omega)$ contributions.* Phys. Chem. Chem. Phys., 20:5190-5199 (2018)

- S. Pezzotti, D.R. Galimberti, M.-P. Gaigeot *2D H-Bond network as topmost skin to the air-water interface* J. Phys. Chem. Letters, 8:3133 (2017)

Keywords: DFT, MD, Cl, MD, solid, liquid interfaces, SFG spectroscopy, BIL, DL layers, 1D, continuum models

Des corrélations à très longue portée entre les molécules d'eau

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Nous décrivons des expériences d'optique non linéaire résolue en polarisation en phase liquide mettant en évidence des corrélations en orientation des molécules d'eau. Ces expériences montrent que les molécules s'organisent sur des distances beaucoup plus grandes que ce qui était habituellement admis jusqu'à présent. Nous démontrons ainsi que celles-ci s'arrangent sur des distances de plusieurs dizaines de nanomètres selon une distribution azimuthale. Ces travaux montrent aussi que lorsque l'on ajoute du sel, une transition apparaît, les molécules d'eau adoptant brutalement une distribution radiale à courte distance centrée sur les ions du sel

Keywords: water, correlation, second harmonic generation

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*Speaker

How to apply the Kirkwood–Buff theory to individual species in salt solutions ?

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It is generally assumed that the Kirkwood–Buff (KB) theory cannot be applied to anions and cations individually in a solution, as one cannot simulate this system in an open ensemble due to the electroneutrality constraint. By applying our recently derived KB theory for closed systems, we show that one does have access to single-ion properties in Molecular Dynamics (1). Our findings are supported by simulations for a model of a salt solution in which particles interact with WCA potentials, as well as for the NaCl/water system using the Particle Mesh Ewald technique for electrostatics.

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Keywords: Kirkwood Buff Theory, Molecular dynamics, salt solution

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*Speaker

Hydration of inorganic anions in the interlayer domain of layered double hydroxides

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Layered Double Hydroxides (LDH) is a family of layered materials in which hydroxides of cations with different oxidation states (II and III) gather to form layers of M(OH)2 octahedra. The presence of trivalent cations in the layers generates positive charges that are compensated by the intercalation of anions in the interlayer domain.

Due to their similarity with clays these compounds are sometimes described as "anionic clays", and like their cationic analogues, their structure is dependent on hydration. Indeed, the dimensions of the interlayer domain and the configuration of both anions and water molecules can be controlled by monitoring the relative humidity of the material.

In order to study interactions between layers, anions and water molecules, one has to intersect information from different characterization technics (XRD, vibrational spectroscopies) operating in controlled conditions. The experimental information is supplemented by numerical simulations (classical molecular dynamics, DFT calculations) in order to understand these interactions at a molecular level.

Here we will present the hydration of MgAl LDH intercalated with small inorganic anions (Cl^-, CO_3^{2-} and ClO_4^-), in order to show the role of water in the structuration of the interlayer domain.

Keywords: Vibration, DFT, Raman, Infrared, Layered Double Hydroxides, intercalation

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Hydrogen bonding interactions in ionic liquids

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The analysis of the hydrogen bond interactions becomes more complicated when the IL is mixed with a molecular solvent. Indeed, to overcome the high viscosity of the ILs, they are mixed with molecular solvents that induce a modulation of its overall physical chemical properties (viscosity, density, conductivity, melting temperature, surface tension ...) with a large changes occurring at low IL mole fraction xIL below 0.2. Then the understanding of the interactions, and in particular the hydrogen bonding ones, that exist between the component ions of IL and the molecular solvent is essential for the proper use these mixture in industrial application. For this purpose, in a first stage, we investigated, using molecular dynamics simulation, the hydrogen bonding interactions in the 32 types of imidazolium based ionic liquids combined with various type of anions.[1,2] In a second stage we investigated, the change of the hydrogen bond distances characteristics in four 1-butyl-3-methylimidazolium cation based ionic liquid combined with four perfluorinated anions in a mixture with three molecular solvents. In order to assess the changes of the hydrogen bonding interactions as a function of the anion type as well as to evaluate the effect of the IL mole fraction in a mixture, xIL, charge distribution model on these interactions, we introduce here a double distance characteristic of the hydrogen bonding arrangement, D-H$\cdots$A, of the donor moiety, D, the bonding H atom, and the acceptor atom, A. In the case of a linear hydrogen bond, which is qualified as strong one, the d2 distance is equal to the sum of the intramolecular D-H and intermolecular d1 distances. On the other hand, in the case of a bent, weaker hydrogen bond, the d2 distance is noticeably shorter than the sum of the D-H and d1 distances, and the hydrogen bond angle, q, can be estimated from the law of cosines. These distances are associated with the average distances calculated from the nearest neighbor distributions of the A atom around the H and D atoms.[3]

The results show that the cation-anions interactions are correlated with the hydrogen bonding strength as analyzed from the distance and angle characteristics and are dependent on the size of the anion and its collective interaction with various hydrogen atoms of the cation (including those of the methyl and butyl chains), while in the mixture the rate of weakening of the cation-anions interactions with dilution is associated with the rate of strengthening of the anion-solvent interactions.

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Keywords: Ionic liquids, hydtrogen bonding interactions

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[*]Speaker

Ion-specificity and surface water dynamics in protein solutions

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Ion-specific effects at the protein surface are investigated here in light of the changes they infer to surface water dynamics, as observed by 1H NMR relaxation (at 20 MHz). Two well-known proteins, hen egg-white lysozyme (LZM) and bovine serum albumin (BSA), show qualitatively opposite trends in the transverse relaxation rate, R2 (1H), along a series of different monovalent salt anions in the solution. Presence of salt ions <u>increases</u> R2 (1H) in the case of lysozyme and <u>diminishes</u> it in the case of BSA. The effect magnifies for larger and more polarizable ions. The same contrasting effect between the two proteins is observed for protein-solvent proton exchange. This hints at subtle effects ion-binding might have on the accessibility of water surface sites on the protein. We suggest that the combination of the density of surface charge residues and surface roughness, at the atomic scale, dictates the response to the presence of salt ions and is proper to each protein. Further, a dramatic increase in R2 (1H) is found to correlate closely with the formation of protein aggregates. The same ordering of salts in their ability to aggregate lysozyme, as seen previously by cloud point measurements, is reproduced here by R2 (1H). 1H NMR relaxation data is supplemented by 35Cl and 14N NMR relaxation for selected salt ions to probe the ion-binding itself.

Keywords: ion, specific effects, proteins, surface water diffusion, NMR relaxometry

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*Speaker

Modelling dynamic and environemental effects on the steady-state and transient optical properties of a prototypycal Ru(II)-polypyridyl dye sensitizer

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Charge transfer (CT) processes induced by light absorption are crucial in a variety of physico-chemical phenomena in different fields, ranging from the natural and artificial photosynthesis (1) to photovoltaic applications(2). When dealing with charge transfer excited states, which characterize the UV-Vis absorption of transition metal polypyridyl complexes, the response of the solvent molecules to the sudden solute's charge redistribution, directly affects the excited state energetic and dynamic. From a theoretical point of view, an accurate treatment of the environment and of its response, requires to explicitly include the solvent molecules into the simulated system and perform sufficiently long (ns) Molecular Dynamic (MD) simulations; this is clearly only affordable by resorting to classical MD approaches, whose routinely application to metal-organic compounds has been, however, hampered by the scarce availability of standard forces fields (FFs) able to correctly preserve the octahedral coordination structure and by the lack of FFs capable to describe the molecule in an excited electronic state. Here we present the development of an integrated multilevel approach, by combining classical MD simulations, extensive excited state calculations (TD-DFT) and solvation dynamics linear response analysis, to investigate the steady-state and transient optical properties and solvation structure of a prototypical heteroleptic Ru(II)-polypyridyl complex, widely employed in dye sensitized solar cells. (3) A polar protic (ethanol) and a strong nucleophilic aprotic (dimethyl sulfoxyde) solvent are chosen in virtue of their different hydrogen-bonding formation capabilities and of their different response to the electronic charge transfer excitations.

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*Speaker

Molecular dynamics simulations on the aggregation of Keggin-type polyoxometalate ions in aqueous solutio

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Aqueous solutions of polyoxometallate (a-PW12O403-) Keggin anions have been simulated by molecular dynamics, comparing between solutions with different neutralizing Mn+ counterions (Cs+, NBu4+, UO22+, Eu3+, H3O+and H5O2+). They reveal marked counterion effects. While the hydrophobic NBu4+ cations tend to surround a-PW12O403- anions via loose contacts, leading to "phase separation" between water and an overall neutral humid salty domain, the other studied cations are more hydrophilic and generally separated from the a-PW12O403- anions. The most important finding concerns the aggregation of a-PW12O403- anions, mostly as dimers with short contacts but also as higher (a-PW12O403-)noligomers (n = 3 to 5) with the proportion of the aggregates ranging from ca. 9 to 46%, depending on the counterion. While Eu3+and UO22+are fully hydrated and interact at short distances with a-PW12O403-as solvent-separated ion pairs, Cs+can form contact ion pairs, as well as solvent-separated ions.

Free energy profiles, obtained via potential of mean force "PMF" calculations, as a function of the P ... P distance show a flat profile with a tiny minimum at ca. 11 Å as the anions approach each other, showing that the anions can form "contact ion pairs" in the presence of either H3O+, UO22+ or Eu3+counterions.

The role of water is demonstrated by comparing PMFs in water and in methanol solution where there is no contact ion pair, but a free energy minimum at ca. 17 Å, corresponding to an ion separated pair a-PW12O403-...Eu(MeOH)93+...a-PW12O403-.

Keywords: Molecular Dynamics, Polyoxometalates, Ion Aggregation, Liquid, Liquid Interface

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*Speaker

Molecular origin of water dynamics acceleration or slowdown in aqueous ionic solutions

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Water in our environment is never found as the pure substance but always contains dissolved salts that affect its molecular properties and play a key role in a wide range of contexts. The perturbation of water structure, dynamics and of other properties such as viscosity depends on the nature of the ions and on their concentration. A key challenge for molecular dynamics simulations is to correctly account for the great variety of effects that is observed in the experiments, ranging e.g. from strong acceleration to slowdown depending on the nature of the ions. While many non-polarizable classical approaches fail to reproduce experimental results, we will show that a computationally-effective approach based on charge rescaling is much more successful. In particular, it allows us to explain why some ions accelerate water dynamics while others slow it down in the dilute regime, and why all salts lead to a slowdown of water dynamics at high concentration.

Keywords: water dynamics, ionic aqueous solutions, molecular dynamics simulations

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Solvation in porous ionic liquids

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Different ionic liquids have been incorporated into the pores of metal organic frameworks to form composites that show interesting performances in terms of gas absorption, catalysis or electrochemical properties.

In this work, we have stabilized a suspension of a well characterized metal organic framework in a phosphonium-based ionic liquid to produce a porous liquid capable of reversibly and selectively absorbing large quantities of gas.(1) The absorption carbon dioxide, methane and nitrogen was measured as a function of temperature and pressure in suspensions (2-5% w/w) of a zeolitic imidazolate framework (ZIF-8) in trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide. The amount of gas absorbed points towards an increase of the free volume of the suspension compared to that of the ionic liquid alone.

The variation of the gas absorption with temperature allows the calculation of the thermodynamic properties of solvation thus assessing the relative importance of the solute-solvent interactions and of the free volume of the solvent for the dissolution process. Molecular dynamics simulations showed that the ionic liquid is too large to penetrate the pores of the solid and allowed the study of the liquid structure near the pores.

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Keywords: ionic liquids, porous liquids, thermodynamics of solvation

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Solvation of noble metals surfaces in water by a local-surface/water forcefield

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Among the diverse chemically relevant systems, metal/liquid interfaces stand out by their difficulty to be simulated and their spreading presence in a lot of actual research topics. One key tool that is needed to properly simulate those systems is an accurate metal/water force-field. For example, this would allow to compute free energies of solvation of adsorbates sitting at the metal/liquid interface with a QM/MM approach (1). Interesting advances have been made for those surface/water force-fields in the '90s by the inclusion of many-body terms (2) (3), but their limited accuracy didn't allow a wide usage of them. Recently, the GAL17 force-field has shown some promising results on Pt (111)/water interfaces thanks to the insertion of the concept of plane in the force-field instead of single atoms as it is classically done (4). However, it uses the full surface as a 2D object with a pre-determined crystallographic structure, which is not compatible with more complex surfaces like kinks or nanoparticles. In this work, we have modified the way that the surface is considered to introduce a local plane and a way to detect is crystallographic nature with the help of generalized coordination numbers (5). This new description should allow the computation of these complicated surfaces and therefore to enhance the applicability of the force-field. Several changes have also been brought to the functional form and the force-field has been tested on diverse metals and crystallographic planes like Au, Ag, Cu, and Pd metals, respectively on (111) and (100) planes. With this new form, an already more accurate evaluation of single-water-molecule/Pt (111) interaction is achieved compared to the GAL17 force-field and in respect to DFT. For example, on a Pt(111) plane, the bottom of the attractive well is still reproduced at less than 1 kcal/mol on top sites compared to DFT calculations but the well on hollow sites is now approached at less than 0,1 kcal.mol from DFT, while it was respectively at 1 kcal/mol for and 4 kcal/mol for top and hollow sites with the GAL17 force-field. These promising results are already quite attractive on a single crystallographic plane because they would allow a reasonable simulation of several metal planes but the wider applicability to complex surfaces is even more exciting. We hope that in the future, this force-field becomes a reference for all metal/water applications.
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Solvent stability in Mg/Ion Batteries: an ab initio study

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Solvent electrochemical stability is one of the most important parameter in many electrochemical systems and in particular for Mg/Ion batteries that could be the next generation system for energy storage. The particular problem with Mg/Ion batteries is that the classical carbonates solvents developed for Li/Ion battery are not appropriate as they lead to the inactivation of the electrodes. Other solvents can be used such as DME or glymes and lead to far better results but with room for improvment.

With an ab initio electrochemical approach, we investigate the stability of free solvent or solvent in the first solvation shell of Mg2+ cations. We see that Mg2+ cations are activating the electrophilic reactivity of the solvents in the first solvation shell reducing the potential windows where the solvent can be used. We can then predict from this approach the products coming from the reduction of the solvent and the electrochemical mechanisms associated by means of Fukui functions. We then propose an extension to the thermodynamic stability of solvent to an extented passivation domain where the solvent is still metastable but not activated by electron transfer from the surface.

We also inverstigate ways to protect the solvent from the Mg2+ activation to improve the electrolyte stability.

Keywords: electrochemistry, Mg, Ion batteries, solvent stability

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Structural characterization of iron(II) in an iron(II)-pectin hydrogel by combining EXAFS and MD simulations

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The association of alginate or pectin chains induced by some biologically relevant divalent cations leads to the formation of hydrogels. It is usually described by the so-called " egg-box model ", but such coordination geometry has not been directly observed in hydrogels and thus proved. In this study, we determined the coordination geometry of Fe2+ in a polygalacturonate (polyGal) hydrogel by coupling X-ray absorption spectroscopy (XAS) measurements and molecular dynamics (MD) simulations. The XAS results reveal an octahedral coordination geometry of Fe2+ both in aqueous solution and in the hydrogel, with similar Fe-O distances (2.09 +/- 0.01 Å in hydrogel and 2.11 +/- 0.02 Å in water solution).The MD simulations evidence that standard empirical force fields are unable to accurately reproduce the Extended X-ray Absorption Fine Structure (EXAFS) spectra of Fe2+ in both systems. Interestingly, the best agreement between experimental and simulated EXAFS spectra was found when Fe2+ is monodentately coordinated to two carboxylate and two hydroxyl oxygens from a pair of polyGalA chains as well as to two water oxygens in an octahedral coordination geometry compatible with the " egg-box model ". It seems that mondodentate coordination induces a tighter association of polyGal chains that may prevent the oxidation of iron and also limit the reorganization of polyGal chains upon gelation. Therefore, the 3D network formed in the presence of iron(II) is expected to be more heterogeneous than the one formed in the presence of alkaline earth metals (Ca2+, Ba2+, ...) which bind to the carboxylate groups of polyGal in a bidentate mode.

Keywords: iron hydrogel polysaccharide binding

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Study of water distribution in real food products: molecular scale heterogeneities highlight by glass transitions.

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The physical state and mechanical properties of extruded cereal based products were studied as a function of sucrose content and relative humidity (RH) to evaluate how the presence of sucrose affects glass transition temperature (Tg) and sorption isotherm. Extrudates were prepared with different sucrose content (0 – 20% wt). Sorption isotherm showed the water content of extrudates decreased when product contains high sucrose at low water activity range and the inverse effect was observed at high water activity. This presentation shows some evidence of heterogeneities for water distribution because two glass transitions were detected using differential scanning calorimetry (DSC). Detail information will be presented to show how the heat flow first derivative curve can be analyzed to determine the present of heterogeneities. We gratefully acknowledge Agrosup Dijon (CS 171-CS 117) for financial support and the plateform RMB (rheology and structure of biological materials) sponsored by Bourgogne Franche Comté region.

Keywords: Extrudate cereal based, products, thermal properties, heterogeneity, sorption isotherm

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Toluene/Butanol Binary Solvents Confined in Periodic Organosilicates: New Insight From Neutron Diffraction Studies

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The confinement of liquid mixtures in porous channels provides new insight into fluid ordering at the nanoscale. In this presentation, we address a phenomenon of microphase separation, which appears as a novel fascinating confinement effect for fully miscible binary liquids. This phenomenon was firstly investigated for tert-butanol-toluene mixtures confined in the straight and mono-dispersed cylindrical nanochannels of MCM-41 and SBA-15 mesoporous silicates (D = 3.6 nm and 8.3 nm) [1,2]. The present study aims at extending this approach to different fluid-wall interactions. It shows that novel types of nanostructures can be generated using functionalized porous organosilicates with periodic alternating surface chemistry along the pore channel.

Keywords: Confinement, microphase separation, nanochannels, organosilicates, binary solvents

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The nanoparticle/water interface: a major actor of radicals production ?

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In 2004 Hainfeld et al. highlighted the important role gold nanoparticles (GNP) could play for therapy (1). They demonstrated in mice that the adjunction of GNP to X-ray treatment could lead to complete tumor regression. Surprisingly, this promising effect is not yet transposed to clinical phases. One main reason could be the absence of consensus about the benefit obtained by coupling GNP and irradiation. Not only the adding value of GNP can be quite different from a publication to another, but the GNP efficiency highly varies from a cell type to another (2).

With this in mind, we decided to study the GNP-radiation interaction in order to get a good knowledge of the mechanisms involved and developed a protocol to quantify the electrons and hydroxyl radicals emitted by irradiated nanoparticles (3). For uncoated GNP, massive quantities of both species were quantified and unexpectedly, gamma rays induce more radicals than X-rays. Energetic consideration from these results and additional experiments in the presence of low concentrations of salt or heavy water lead us to propose a key role of interfacial water around nanoparticles we would like to discuss with the GDR.

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Keywords: nanoparticle, hydroxyl radical, water radiolysis, radiosensitization

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Theoretical Study of Hydrated Gold Nanoparticles for Radiotherapy Applications

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The use of gold nanoparticles (Au NPs) for enchancing radiotherapy performance is very promising. This success has been demonstrated by highly active in vivo and in vitro experimental studies (1). High Z Au NPs contribute to radiosensitization effect, thus making tumor cells more responsive to ionizing radiation. Upon water radiolysis, Au NPs generate electrons and reactive species such as oxygenated compounds (ROS). Those species favor radiotherapy by amplifying the damages caused by radiations and by concomitantlly improving the radiation dose. In principle, Au NPs are synthesized in a PEGylated (encapsulated in a complex assembly of polyethylene glycol ligands) and aqueous environment. To date, little is known regarding the morphology, the structure, and energetics of those nanoparticle systems, especially at the atomic scale.

In this work, we use theoretical approaches to model the immersion of Au NPs in a biological environment (interface with liquid water) explicitly at the atomic level. In particular, we aim to rationalize the interaction between water molecules and Au NPs as a function of the nanoparticle morphology and size. Density Functional Theory (DFT) calculations including dispersion forces have been performed to explore the adsorption structures and energetics of water molecules on Au NPs, from single adsorption to saturation. Several morphologies of gold clusters have been modeled in the fluxional regime (0.9-1.8 nm). For a singly adsorbed water molecule, the most stable adsorption forms are similar (corners and edges) whatever the nanoparticle shape and size, although the adsorption strength differs significantly (0.15 eV). When a complete and explicit water solvation shell interacts with gold nanoclusters, metastable in vacuum and presenting a predominance of (100) square facets (ino-decahedra Au55 and Au147), these nanoparticles are found unstable and transform into closest morphologies exhibiting mainly (111) triangular facets and symmetries. The corresponding adsorption strength per water molecule becomes independent from shape and size and is enhanced by the formation of two hydrogen-bonds in average. For applications in radiotherapy, this study suggests that the shapes of small gold nanoparticles should be homogenized by interacting with the biological environment. All the calculations were performed using the resources of the Pole Scientifique de Modélisation Numérique (PSMN).This project is funded by Labex PRIMES (ANR 11-LABX-0063, PhD fellowship awarded to C-H.Chan).

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Keywords: gold nanoparticles, water solvation, DFT, radiotherapy

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Using Molecular Density Functional Theory to study electron transfer reaction in water

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The Marcus theory of charge transfer reactions in solution has provided a very simple two-chemical state picture, based on two intersecting parabola (1). It has been widely used in the electrochemical community because it made possible to understand the experimental data, to interpret them quantitatively but also to make predictions. Originally, the theory modeled the solvent by a dielectric continuum. The response of the solvent to the charged solute is linear which implies that the free energy curves of the reactant and product are quadratic, with the same curvature. The validity of this assumption can be tested by computer simulations, either using force field molecular dynamics (MD) or ab-initio MD (2). However, this is rather costly since it requires to run several several simulations on intermediate fictitious solutes to study one electron transfer reaction. Most of the computational times being spent to compute solvent-solvent interaction, it seems promising to have an implicit description of the solvent.

I will present here an alternative method based on liquid-state theory, namely molecular density functional theory, which is numerically much more efficient than simulations while still retaining the molecular nature of the solvent (3). By reformulating molecular ET theory in a density functional language it allows to compute the various observables characterizing ET reactions from an ensemble of density functional minimizations. In particular, a relevant order parameter for the reaction can be defined within that formulation and the Marcus free energy curves of both reactant and product states along that coordinate can be computed. The validity of the approach is demonstrated by studying the ET reaction of a spherical solute in bulk water and close to a solid/liquid interface.

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High-throughput solvation free energies by molecular density functional theory and machine learning

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The hydration or binding free energy of a drug-like molecule are key data for computer aided early stage drug discovery. Hundreds of thousands of evaluations are necessary to find few potential lead. This rules out the exhaustive use of atomistic simulations and free energy methods. Instead, the docking and screening processes are today relying on numerically efficient scoring functions that lose much, if not all, of the atomic scale information and hence remain error-prone. We show how our probabilistic description of molecular liquids as implemented in the molecular density functional theory (MDFT) predicts hydration free energies of a state-of-the-art benchmark of small drug-like molecules within 0.4 kcal/mol of atomistic simulations, along with water maps, for a computation time reduced by 3-5 orders of magnitude. Furthermore, these results can be improved to 0.6 kcal/mol of experimental results by coupling MDFT with machine learning approaches, without increasing the calculation time.

Keywords: solvation free energy, molecular density functional theory, machine learning, drug design

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