



**EAU AUX INTERFACES:
NOUVEAUX DEVELOPPEMENTS EN
PHYSIQUE, CHIMIE ET BIOLOGIE**

**WATER AT INTERFACES:
NEW DEVELOPMENTS IN
PHYSICS, CHEMISTRY AND BIOLOGY**

(April 15-26, 2013)

Organizers

Marie-Claire Bellissent-Funel, Laboratoire Léon Brillouin, CEA-Saclay, FR
Giuseppe Zaccai, Institut de Biologie Structurale, Grenoble, FR

Scientific Committee

Marie-Claire Bellissent-Funel (LLB), Bertil Halle (Lund University, Sweden), Volker Kempter (Clausthal University, Germany), Marie-Christine Maurel (Paris University), Stanislas Pommeret (CEA-Saclay), Giuseppe Zaccai (ILL, Grenoble).

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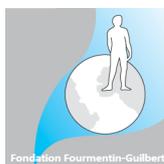
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INVITED LECTURERS (1 H 15 MINUTES+15 MINUTES QUESTIONS)

L1-M.-C. Maurel (Paris, France): Liquid water and the origins of life

L2- J. Teixeira (LLB, France): Bulk and confined water

L3- W. Kuhs (Gottingen University, Germany): Nanoscopic atmospheric pressure ice

L4- T. Loerting (Innsbruck University, Austria): Recent experimental developments in amorphous ices and their relation to deeply supercooled liquids

L5- A.K. Soper (ISIS, UK): The structure of water in bulk and in confinement by total neutron and x-ray scattering

L6- T. Yamaguchi (Fukuoka University, Japan): Thermal behaviour, structure and dynamics of low temperature water confined in mesoporous materials

L7- L. G. M. Pettersson (Stockholm University, Sweden): Fluctuations in ambient water

L8- P. Varilly (Cambridge, UK): Fluctuations in water and their relation to the hydrophobic effect near model surfaces and proteins

L9- T. Iiyama (Shinshu University, Japan): Structural Understanding of Water Confined in Hydrophobic Nanopores

L10- A. S. Pensado (Universität Leipzig, Germany): Ionic liquids and water in touch: A theoretical study

L11- Y. Ouchi (Nagoya University, Japan): Nonlinear Vibrational Spectroscopy and Molecular-Dynamics Simulations on Water/Ionic Liquid Interfaces

L12- P. Marquet (Lausanne, Switzerland): Exploring the water movements mediated by neuronal activity with digital holographic microscopy

L13-J.-M. Zanotti (LLB, France): Nanometric confinement of water: from interfacial interactions to one dimensional transport properties



L14- J. Swenson (Goteberg,Sweden): The Anomalous Properties of Water for the Dynamics and the Glass Transition of Proteins

L15- A.Oleinikova (Darmstadt University, Germany): Thermodynamic properties of hydration water: general regularities and effect of hydrogen bonding

L16- S. Meech (University of East Anglia, Norwich, UK): Time Domain Optical Kerr Effect Studies of Aqueous Solvation: Ions to Proteins

L17-T.Elsaesser (Max-Born-Institut, Berlin, Germany): Ultrafast Hydration Processes of DNA and Phospholipids

L18- M. Vogel (Darmstadt, Germany): Water Dynamics in Confinement: Insights from NMR experiments and MD simulations

L19- M. Weik (IBS, France): Proteins need it wet. Don't they?

L20- F. Sterpone (IBPC, Paris): The protein hydration layer: how different from the bulk? A mirror for protein conformations and stability ?

L21- A.Deriu (Università di Parma, Italy): Structural and Dynamic Properties of Organised Structures of Saccharide Systems in Aqueous Solution

L22- G. Zaccai (IBS, France): Neutrons reveal the ecology of protein and water dynamics

L23- M. Tarek (France): On the structure dynamics and electrical properties of membranes hydration water. Insights from Molecular Dynamics Simulations

L24- B. Bouvier (IBCP, Lyon, France) : Water in biomolecular recognition processes - the forgotten partner

L25- H. Abramczyk (Technical University of Lodz, Poland): Hydrogen bonds of interfacial water in human breast cancer tissue

L1

Liquid water and the origins of life

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Water is the universal solvent that supports all known forms of life. 90% of our life history took place in the ocean which occupies today more than 75% of the earth. Oceans host today simple forms of life (bacteria, viruses...) which constitutes the most important biomass of the planet. It is thus well-admitted that liquid water is mandatory for extant life as well as for the primitive one. Why and how does it work? According to the distribution of water in the Universe, how does liquid water came on the primitive earth? What are the main prebiotic steps which occurred in the primeval ocean leading to simple biology? What are the main physico-chemical properties of liquid water that permit the early evolution of the first biological processes. In this presentation we will consider that water, metals as well as simple organics, provide a window into the union of the inorganic/organic and biological worlds.

Hydration is considered to have a key role in biological processes ranging from membrane formation to protein and nucleic acids structure, dynamics and functions. Regarding the origins of the first functional macromolecules several hypothesis are at work. For instance the "RNA world" hypothesis proposes that early in the evolution of life, RNA was responsible both for the storage and transfer of genetic information and for the catalysis of biochemical reactions. Metals as well as water dependence activity of various natural hammerhead and hairpin ribozymes are explored showing how the catalysis depends on the surrounding biochemical conditions. On the other hand, the existence of contemporary life in extreme conditions such as diversified abyssal life, conditions which might have occurred during the evolution of life, encourage us to focus on the activity, persistence and dynamics of RNA at extreme temperatures, extreme pH and/or high pressure. Experimental data obtained under high pressure conditions, from nuclear magnetic resonance (NMR), neutron diffraction and spectroscopic measurements offer knowledges about the dependence of RNA dynamics under aqueous environmental conditions.

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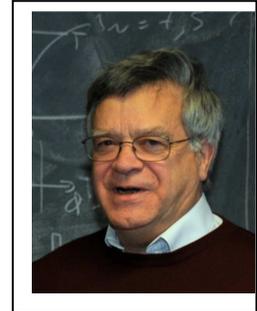
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L2

Bulk and confined water

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ABSTRACT

The complexity of liquid water is mostly due to the tetrahedral symmetry of the intermolecular potential and to the formation of bonds extremely dependent on local environment and thermodynamic conditions. The contradictory properties of strongly directional but shortly lived bonds generate exceptional properties of bulk water highly dependent on temperature and pressure.

The complexity is larger when bonds can be formed with other molecules, in particular at hydrophilic interfaces. The variety of situations can hardly be encompassed or described by general equations although a few current descriptions can be elaborated from detailed experiments completed by ad hoc molecular dynamic simulations. Hydrophobicity, super-hydrophobicity and wetting correspond also to a variety of situations that only recently have been studied in detail.

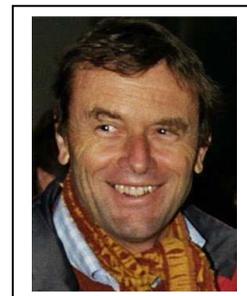
A short presentation will emphasize some aspects of the interaction of water molecules with interfaces showing that confined and bulk water share relatively few features. The large variety of situations observed in Biophysics implies detailed and specific studies prior to the establishment of general predictive models.

L3

Nanoscopic atmospheric pressure ice

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ABSTRACT

Crystalline ice has interfacial and surface properties different from the bulk which are important in a wide range of fields [1]. In this contribution I will try to shape a picture of the nanoscopic organization of water molecules exhibiting a number of microstructural bulk and surface defects which in turn also have considerable bearing on the reactivity of ice in various environments [e.g. 2, 3]. As an example recent work on a solid water phase known as "cubic ice", or "ice I_c" will be presented; it is frequently encountered in various transitions between the solid, liquid and gaseous phases of the water substance. It may form e.g. by water freezing or vapor deposition in the Earth's atmosphere or in extraterrestrial environments and plays a central role in various cryo-preservation techniques of biological material. There was multiple and compelling evidence in the past that this phase is not truly cubic but composed of disordered cubic and hexagonal stacking sequences [4,5,6]. The complexity of the stacking disorder, however, appears to have been largely overlooked in most of the literature. We show that correlations between next-nearest layers of water molecules are developed, leading to marked deviations from a simple random stacking in almost all investigated cases; this tells us something about the complexity of water-water interactions. The evolution of the stacking disorder is followed as a function of time and temperature at conditions relevant to atmospheric processes; a continuous transformation towards normal hexagonal ice, ice I_h, is observed [7]. A quantitative link between the crystallite sizes established by diffraction and from electron microscopic images is achieved; the crystallite size evolves from several nm into the μm-range with progressing annealing [7]. The crystallites are isometric [5,6] with markedly rough surfaces parallel to the stacking direction, which has important implications for atmospheric sciences [1,7].

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L4

Recent experimental developments in amorphous ices and their relation to deeply supercooled liquids

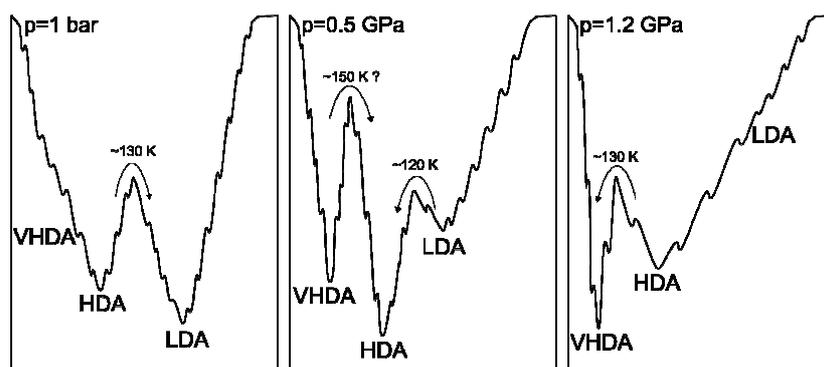
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ABSTRACT

There are many ways of preparing amorphous ice samples, which are categorized as low-density (LDA), high-density (HDA) or very high-density amorphous ice (VHDA)¹. Their relative order of stability is a function of external pressure (see Figure). The question whether these amorphous ices can be regarded as glassy, connected to deeply supercooled liquid water by a glass-to-liquid transition, is discussed controversially². For LDA-type amorphous ices (ASW, HGW, LDA) the glass transition onset temperature T_g was found by ambient pressure calorimetric studies to be at 136 ± 2 K. In case of HDA-type amorphous ices (uHDA, eHDA) other techniques, especially high-pressure techniques, have recently been developed in order to map T_g as a function of pressure³⁻⁵. In addition to introducing these studies I also discuss recent experiments aiming at answering the question whether the glass transition found in amorphous ices is indeed a transition to a deeply supercooled, ultraviscous liquid state or instead to another type of glassy solid state.



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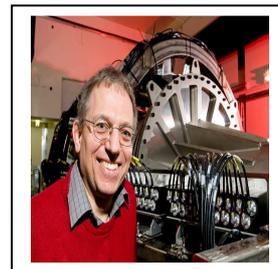
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L5

The structure of water in bulk and in confinement by total neutron and x-ray scattering

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ABSTRACT

In the past decade or so there has been a significant worldwide effort to try to obtain a consistent set of radial distribution functions for water. Exactly how those distribution functions should be interpreted in terms of the local order in water remains a somewhat open question – whether for instance they imply water has a degree of heterogeneity in its local structure or whether it is in fact a uniform fluid with normal statistical fluctuations in density and structure. However combining a number of different x-ray and neutron data sets together is now indicating a rather consistent view of the local distribution functions in water (see A K Soper, *ISRN Physical Chemistry*, submitted 2012). This consistency is achieved partly as a result of different researchers applying state-of-the-art data analysis methods to their data, both neutron and x-ray, but partly also by the application of computer simulation methods of structure refinement which help to eliminate some of the artifacts that can be introduced by uncertainties in that data analysis. The situation as regards confined water – indeed confined fluids in general – is much less clear, because the presence of the surface adds additional significant complications associated with the nature of the surface and the geometry of the confinement. It is possible to investigate water near a surface using radiation total scattering methods in the case where the pores which contain the water, whether sheet-like, cylindrical, or spherical, have a regular arrangement in the material. This is because the Bragg peaks arising from that regular arrangement are strongly affected in intensity depending on how the fluid is distributed within the pore. This talk will focus on the MCM41 silicas which have cylindrical pores on a hexagonal lattice, and on the layered clay materials which form a more or less regular array of silicate sheets. Combining the scattering data with computer structure refinement in the same way that is done for the bulk liquid is leading to unprecedented insight into how water is organized near the silicate surface. The talk will showcase these developments, with examples of recent results, particularly from the MCM41 system. This work is aimed at clarifying the underlying processes that may have lead to recent observations of fragile to strong transitions in these materials.

L6

Thermal behaviour, structure and dynamics of low-temperature water confined in mesoporous materials

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ABSTRACT

Water in confinement and at interface plays a vital role in various fields, such as separation science like chromatography, transport of minerals in soils, biological membranes of water and ion channels, nanotechnology, and drug delivery systems. Thus, the thermal behaviour, structure and dynamic properties of water in confinement at a molecular level are essential for understanding unique properties not available in bulk and underlying mechanisms of chemical processes in confined systems. The unique properties of confined water originate both from the water-wall interaction and from a confined geometry. This lecture gives the structure and dynamic properties of low-temperature water in porous materials with varying pore size and hydrophilic-hydrophobic nature of wall. Techniques employed were FTIR, X-ray and neutron diffraction with empirical potential structure refinement modeling and inelastic neutron scattering (quasi-elastic and spin echo methods). The adsorption/desorption, heat capacity and differential scanning calorimetry measurements were also made to characterize the pores and thermal behaviors of confined water, respectively. Various porous materials were used to change the characteristics of pore wall from hydrophilic to hydrophobic nature: MCM-41 with hydrophilic surface, periodic mesoporous organosilica PMO with hydrophilic and hydrophobic hybrid surface composed of inorganic silica framework embedded by organic groups like a phenyl group, and ordered mesoporous carbon OMC with hydrophobic nature. We discuss the relationship between confining conditions and the resulting thermal behaviour, structure and dynamics of water.

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Fluctuations in Ambient Water

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ABSTRACT

We emphasize the importance in simulations of water of reproducing the isothermal compressibility, dependent on density fluctuations in the liquid, for a correct description of structural fluctuations in simulated water [1]. I will introduce x-ray spectroscopy and scattering techniques as applied to water, ice and solutions. From these techniques a strict bimodality in terms of fluctuations between high- (HDL) and low-density (LDL) forms of the liquid has been reported [2-5]. The inherent structure in simulations, *i.e.* the structure quenched to 0 K, is found to be bimodal in terms of HDL and LDL in close correspondence to x-ray spectroscopy [6]. This bimodality is, however, smeared out in the real structure where temperature is included. We suggest that the local minima for the HDL and LDL local structures in the simulation need to be deeper and propose that many-body electronic structure effects and non-local van der Waals interactions will be important in this respect [7]. Much larger simulations than hitherto considered are likely necessary to catch the effects of both thermal and structural fluctuations in the simulated liquid. Since structural fluctuations can be expected to significantly affect the dynamics in the liquid it is important that these are taken properly into account when discussing hydrogen-bond breaking and reformation. Here it is essential that the model used correctly reproduces the temperature and pressure dependence in thermodynamic response functions.

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L8

Fluctuations in water and their relation to the hydrophobic effect near model surfaces and proteins

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ABSTRACT

The hydrophobic effect can be usefully understood in terms of an interplay of small-scale and large-scale density fluctuations in water, as in Lum-Chandler-Weeks theory. This view, which we discuss in detail, rationalizes many otherwise puzzling phenomena. In this talk, we focus on two such phenomena. First, we look at dewetting between assembling biomolecules (melittin and BphC), and show how small differences in fluctuation statistics lead to dewetting in some cases but not in others. We propose that hydrophobically driven assembly may, in some cases, be controlled by biomolecules sitting at the edge of a dewetting transition. Second, we look at how a large hydrophobic surface affects the thermodynamics of binding of nearby small solutes, and how the changes can be rationalized. Our findings suggest that hydrophobic surfaces can generically catalyze unfolding. Finally, we speculate on whether hydrophobic effects may rationalize certain aspects of amyloid fibril self-assembly.

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L9

Structural Understanding of Water Confined in Hydrophobic Nanopores

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ABSTRACT

The interaction of water with solid surfaces is one of importance research issues from fundamental science and technology, although it has been studied for a long time. It is well-known that water vapor begins to be adsorbed suddenly on hydrophobic nanoporous carbons and hydrophobic zeolites such as $\text{AlPO}_4\text{-5}$. This unusual behavior was studied by in situ X-ray diffraction, showing that water adsorbed in the hydrophobic carbon nanopores is not liquid, but solid-like at 303 K^1 . The formation of solid-like water can be partially understood from the growth of water molecular clusters in hydrophobic nanopores^{2,3}. The unusual water behavior should also be associated with the intensive confinement effect of the carbon nanopores; recent studies have shown the superhigh pressure confinement effect that the KI of high pressure phase which occurs above 1.9 GPa in the bulk phase is produced in the cylindrical carbon pores below ambient pressure^{4,5}. Comparison of confined water with confined organic molecular systems should give an useful information on the uniqueness of confined water in the hydrophobic carbon nanopores. Also the water adsorption on hydrophobic nanoporous carbons can be phenomenologically described by hydrophobicity-hydrophilicity transformation. Then, water confined in hydrophobic carbon nanopores has gathered a general concern.

This talk will cover how to extract important information on confined water and organic molecular assemblies with X-ray diffraction, the temperature dependence of confined water structure from 20 K^6 , the comparative studies on confined water and $\text{C}_2\text{H}_5\text{OH}^7$, CCl_4^8 , and structure of organic electrolytic solution^{9,10} and ionic liquids. Also recent hybrid study using X-ray and neutron scattering will be introduced.

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L10

Ionic liquids and water in touch: A theoretical study

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ABSTRACT

Ab initio molecular dynamics (AIMD) simulation methods allow modeling the microscopic behavior of chemical processes in condensed phases, resembling laboratory conditions and natural processes as closely as possible¹. These methods combine an explicit electronic structure calculation using a DFT method with the sampling of a molecular dynamics. The know-how of our research group involves the use of AIMD techniques to study different (mainly) solvated systems e. g. pure ionic liquids and ionic liquids with impurities like water. Water on ionic liquids is not just an impurity; water can be used as a co-solvent in order to improve some of the physicochemical properties of the IL, mainly related to the mass transfer. One major goal is to gain a deeper understanding on the microscopic structure², the kind and magnitude of the specific interactions, the presence of specific solvent or template effects, as well as the (short-time) dynamics. I.e. we want to understand how the ionic liquids are in touch with themselves, each other and with other substances, in particular with water. This aspect is particularly interesting to understand the dissolution of strong H-bond materials like cellulose in ionic liquids, and the further process of precipitation when water is added to the system.

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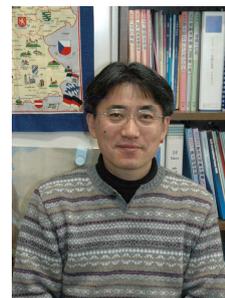
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L11

Nonlinear Vibrational Spectroscopy and Molecular-Dynamics Simulations on Water/Ionic Liquid Interfaces

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Infrared-visible sum-frequency generation (IV-SFG) vibrational spectroscopy has been demonstrated as a powerful tool for investigating surfaces and interfaces of various media. So far, structural and environmental information of room temperature ionic liquids (RTILs) obtained by IV-SFG has been limited to mostly those of free-surfaces or substrate/RTIL interfaces. In this study, IV-SFG and molecular dynamic simulations are successfully applied to sketch the structures of liquid/liquid buried-interfaces of RTILs ($[C_n\text{mim}]X$ ($X=\text{PF}_6, \text{TFSA}$, $n=4\sim 8$) with water(D_2O) and other polar and nonpolar solvents such as CCl_4 , alkanes and alcohols. SF signals from the interface in C-H, C-D, O-D, S-O, and C-F stretching regions are clearly observed depending upon the nature of solvents. The changes in the position and the width of SF resonance peaks indicate the local environments of the interfaces of RTILs are much different from those of bulk RTIL and/or air/RTIL interfaces. For example, RTIL/alcohol interface forms preferentially oriented alkyl-chain bilayer-structure due to the fact that the OH group of the alcohol strongly and preferentially interacts with PF_6 anions. RTIL/ H_2O interface also induces polar orientations of anions and specific hydrogen bonding network in H_2O phase. Figure 1 shows SFG spectra of SO_2 sym. str. of $[C_n\text{mim}][\text{TFSA}]/\text{water}$ interfaces. Maximum SF intensity is obtained at $n=8$, where polar orientations of $[\text{TFSA}]$ anions are strongly induced by hydrogen bonding of water.

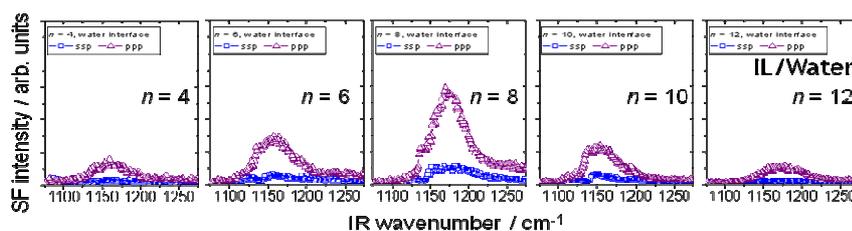


Figure 1 IV-SFG spectra(ssp, ppp) of $[C_n\text{mim}]\text{TFSA}$ ($n=4\sim 12$)/water interfaces.

References

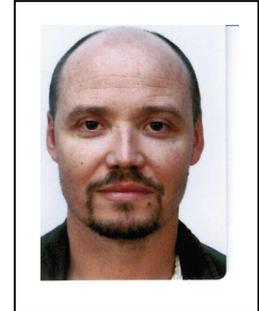
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L12

Exploring the water movements mediated by neuronal activity with digital holographic microscopy

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ABSTRACT

Water is the most abundant element of the brain. Practically, it is distributed between blood, cerebrospinal fluid, interstitial and intracellular compartments and moves across these compartments. At constant hydrostatic pressure gradients, water movement depends largely on the osmotic gradients, which are created by the osmolyte concentration at the extracellular and intracellular compartments. Principal osmolytes in brain cells, are the electrolytes present in high levels in the cytosol and extracellular fluids, i.e. Na^+ , K^+ and Cl^- , and small organic molecules including amino acids and derivatives (glutamate, glycine, GABA etc.)¹. At the microscopic level, water transport is involved in cell volume regulation and in controlling the dimensions of the extracellular space. Consequently, neuronal activity involving ion movements resulting from the opening of conductances as well as neurotransmitter release including glutamate, glycine, GABA are accompanied by transport of water across the plasma membrane. This implies that the transport of water across the plasma membrane, the regulation of the extracellular space as well as cell volume will depend on the level of neural activity. Hence, water transport in the brain is tightly regulated as it is critical to maintain neuronal excitability and to prevent damage derived from brain swelling or shrinkage².

Practically, water crosses cell membranes by several routes whose mechanism are far from being well identified including in particular mere diffusion through the lipid bilayer, specialized water channels (the aquaporins, AQP) and proteins usually associated with other functions such as uniports and cotransporters. It is important to note that astrocytes also significantly contribute to the transport of water through these different routes³.

Recently, we have developed a quantitative phase microscopy technique derived from digital holographic microscopy (DHM), allowing to visualize, with a few milliseconds temporal resolution and with a nanometric axial sensitivity, cell structure and dynamics^{4,5}.

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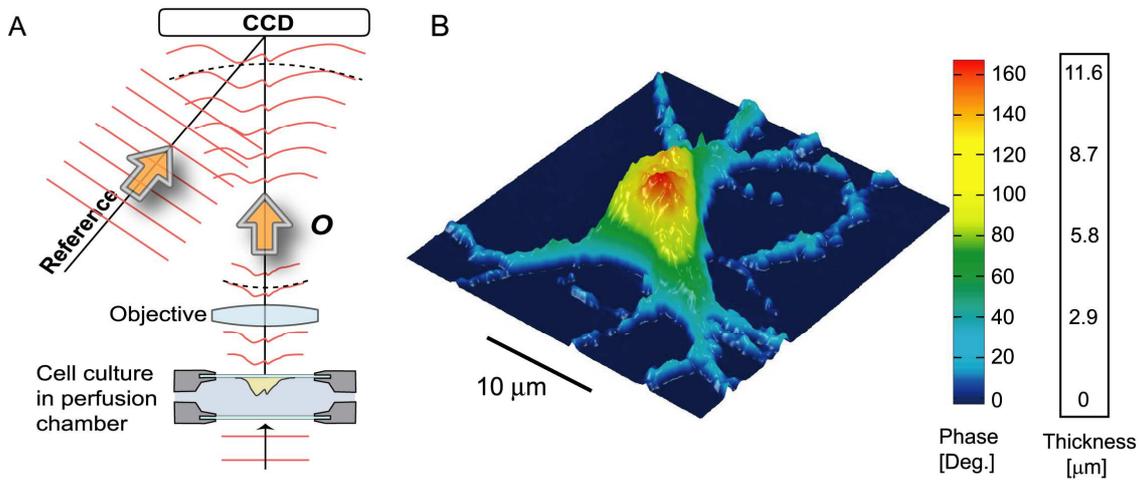


Figure 1: DHM of living mouse cortical neurons in culture. (A) Schematic representation of cultured cells mounted in a closed perfusion chamber and trans-illuminated (B) 3D perspective image in false colors of a living neuron in culture. Each pixel represents a quantitative measurement of the phase retardation or cellular optical path length (OPL) induced by the cell, with a sensitivity corresponding to a few tens of nanometers. By using the measured mean value of the neuronal cell body refractive index, resulting from the decoupling procedure, scales (at right), which relate OPL (Deg) to morphology in the z-axis (μm), can be constructed

Concretely, the quantitative DHM phase signal is highly sensitive to intracellular refractive index a parameter closely related to transmembrane water movements. Consequently, experiments combining electrophysiology and DHM, have allowed us to accurately study the neuronal and astrocytic transmembrane movements of water associated with neuronal electrical activity⁶. The main results obtained with this approach, highlighting that significant transmembrane water movements are tightly related to neuronal activity, will be presented. Consequently a better understanding of this close link between transmembrane water movements and neuronal activity could allow the development of diffusion functional magnetic resonance imaging (fMRI), through its water diffusion component, as an efficient approach to monitor neuronal activity with a high spatial and temporal resolution in comparison to the hemodynamic response detected by blood oxygenation level dependent fMRI which is indirectly related to the underlying neuronal activity through complex neurovascular coupling mechanisms. In addition, taking into account that the transmembrane water movements mediated by the neuronal activity could induce transient cell volume and structure changes, a non-synaptic modulation of the neuronal activity by these water-dependent transient morphological changes has been proposed⁷.

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L13

Nanometric confinement of water: from interfacial interactions to one dimensional transport properties

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ABSTRACT

Nanometric confinement of molecular fluids is often used to target three dimensional (3D) *pure volume* effects: it is a classical route to stabilize meta-stable states by achieving frustrations of the bulk *natural* fluctuations and/or phase transitions. Very significant melting point temperature depression of the confined material can for example be obtained. This property has recently been intensively used in the quest for experimental evidences of the existence of a Low Temperature Critical Point (LTCP) in bulk liquid water [1], at $T_s \approx 228$ K and $P_s \approx 100$ MPa.

Here, we will highlight that in confinement situation, *surface effects* (2D) cannot be neglected and can even become predominant. We will in particular detail the surprisingly rich low temperature (from 100 to 300 K) dynamical behavior of interfacial water [2]. We will propose a percolation model to account for the dynamical/thermodynamical transitions observed and reach a global and coherent view of this 2D water. The relevance of interfacial water will be discussed in particular in the field of Biophysics.

In a last part, we will introduce a physical system [3,4], where macroscopic orientation meets nanometric confinement with no *surface effects*, to induce strong 1D *pure volume effects* over macroscopic distances [5].

Neutron scattering techniques (SANS, diffraction, inelastic scattering) have made significant contributions to the fields addressed in this talk. These will be briefly introduced and a special attention will be paid to bridge them to other spectroscopic or calorimetric techniques.

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L14

The Anomalous Properties of Water for the Dynamics and the Glass Transition of Proteins

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ABSTRACT

Myoglobin with hydration water, or solvated in water-glycerol mixtures, has been studied by broadband dielectric spectroscopy, quasielastic neutron scattering and differential scanning calorimetry. The aim has been to understand the role of solvent in general and hydration water in particular for the dynamics and glass transition of proteins. For hydration water we observe a change in the physical nature of the water dynamics at roughly 170-180 K, and this dynamic crossover seems to be responsible for the glass transition of hydrated proteins [1,2]. Furthermore, we show that several protein relaxations are involved in the calorimetric glass transition, and that the broadness of the transition depends on the water content in the solvent, i.e. the slowest protein relaxations become even slower and thereby more separated from the faster protein relaxations with less hydration water [1,2]. However, despite the fact that the onset of long-range cooperative water motions are responsible for the protein glass transition the hydration water is not giving any direct contribution to the calorimetric glass transition of the hydrated protein [1,2]. This finding is in stark contrast to myoglobin in water-glycerol mixtures, where the calorimetric glass transition is dominated by the solvent contribution [1,2]. The unique behaviour of protein hydration water seems to be universal for all types of confined or interfacial water. Finally, we discuss the unique role of hydration water for protein dynamics and related biological functions. Myoglobin is working surprisingly well in a basically water free environment of glycerol, where CO can escape from the heme cavity to the solvent by large-scale conformational fluctuations of the protein [3]. Thus, water is not needed for such biologically important protein dynamics. Nevertheless, the specific properties of the hydration water are responsible for less global internal protein motions, which, for instance, in the case of myoglobin make it possible for CO to move between different cavities in the protein [3].

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L15

Thermodynamic properties of hydration water: general regularities and effect of hydrogen bonding

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ABSTRACT

Thermodynamic properties of fluids near surfaces are generally different from those in the bulk. Since the hydration water makes an important contribution to the properties of various aqueous systems (confined water, aqueous solutions, hydrated biosystems etc), it is important to know the thermodynamic properties of hydration water and their dependence on the surface properties, such as water-surface interaction and surface curvature (solute size). Density depletion and increasing thermal expansivity are the main effects of various surfaces on liquid water [1]. These effects gain more importance upon cooling, upon weakening water-solute interaction and upon increasing solute size. The obtained regularities are general for fluids and agree with the theoretical expectations, but they are especially strong for water, as directional H-bonding strongly suffers from the presence of a surface. Increasing thermal expansivity of liquid water near surfaces causes increase of its constant pressure heat capacity C_p and this effect is especially strong near hydrophobic surfaces. This conclusion is supported by the insensitivity of the constant volume heat capacity C_v of water near surfaces to the strength of water-surface interaction.

Hydrogen bonded network of hydration water transforms into an ensemble of small clusters upon heating. Near various polypeptides, this transition occurs at biologically relevant temperatures (from 310 to 330 K) and may be related to the unfolding transitions of proteins [2]. A rapid change in thermodynamics of hydration water is observed at this transition: contribution of water-water interaction within hydration shell to C_p of hydration water sharply decreases, whereas the contribution of interactions between hydration and bulk water to C_p sharply increases [3]. The improving of the connectivity between hydration and bulk water upon heating makes the surface of polypeptides effectively more hydrophobic that may cause their conformational changes and eventually their aggregation. Such effect is not seen near non-biological surfaces and can be attributed to the cooperative hydration of the peptide backbone, whose chemical structure is identical for all peptides.

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L16

Time Domain Optical Kerr Effect Studies of Aqueous Solvation: Ions to Proteins

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ABSTRACT

Solvation is a key step in very many reactions in the condensed phase. As a consequence it has been studied in great detail. Experimental techniques which have been applied to study the solvent include dielectric relaxation, NMR, ultrafast optical Kerr effect/THz Raman and 2D-IR spectroscopy. Techniques which focus on the solute include time resolved fluorescence, transient absorption and photon echo spectroscopy. In the analysis of these experiments molecular dynamics simulations have proved crucial, and underpinning all is the theory which connects molecular dynamics to the observable experimental signals. It is fair to say that a great deal of progress has been made in understanding solvation dynamics in solution.[1] The task of understanding solvation at an interface is incomplete. Although almost the entire battery of experimental methods has been deployed many problems remain. The experiments in particular are challenging because of the relatively low population of interfacial molecules and the difficulty in characterizing the structure of the interface.

In this lecture the ultrafast Optical Kerr effect method will be described in detail. It will be shown that the method presents a reliable means of characterizing the dynamics of a liquid.[2] This method will be compared with the time resolved fluorescence technique, which views the same dynamics through the solute response.[3] This background will be used to highlight the special problems associated with observing solvation dynamics in liquid water. Once the characterization of bulk liquid water has been addressed the OKE measurements will be extended to probe water in the presence of an ion,[4] then a peptide,[5] and finally at the interface between a biological macromolecule and aqueous solution.[6]

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L17

Ultrafast Hydration Processes of DNA and Phospholipids

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ABSTRACT

The structure and function of biomolecules are strongly influenced by interactions with their aqueous environment. The DNA double helix is held together by intermolecular hydrogen bonds in nucleic acid base pairs and stabilized by its hydration shell. Similar interactions are present in phospholipid systems. The elementary structural fluctuations of the water shell and dynamics of vibrational excitations of DNA and water occur in the time domain below 1 ps and can be mapped by femtosecond vibrational spectroscopy. This lecture gives an introduction into this research area and covers most recent results on hydration processes of biomolecules. After presenting the basic methods of ultrafast nonlinear infrared spectroscopy [1], ultrafast processes in neat water will be reviewed briefly [2]. This will be followed by a discussion of the vibrational dynamics of NH stretching excitations of DNA base pairs and phosphate vibrations in DNA and phospholipids [3-6]. The particular interactions of such biomolecules with their water shells and the water dynamics around biomolecules will be addressed in detail, using recent results from femtosecond two-dimensional infrared spectroscopy and molecular dynamics simulations. Such results demonstrate a moderate slowing down of hydration shell dynamics compared to bulk water and the function of water shells as primary heat sinks of excess energy in hydrated biomolecules. Hydration shells as small as 3 water molecules are shown to function as efficient acceptors in energy dissipation [7].

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L18

Water Dynamics in Confinement: Insights from NMR experiments and MD simulations

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ABSTRACT

NMR experiments [1] and MD simulations provide detailed insights into the dynamics of water in confinement. In particular, these methods yield valuable information about not only the time scale, but also the mechanism for the motion. Hence, the microscopic origins of macroscopic relaxations can be determined. We employ the capabilities of NMR and MD techniques to investigate the motion of water molecules in both protein and silica confinements, covering broad time and temperature ranges.

Using ^2H NMR to observe the rotational motion of $^2\text{H}_2\text{O}$ in the hydration shells of the proteins collagen, elastin, and myoglobin, we rule out the existence of a fragile-to-strong transition, postulated for supercooled bulk water as a consequence of a phase transition between high-density and low-density forms of liquid water [2,3]. Adding information about the translational motion of water from MD simulations [4] and field-gradient ^1H NMR [5], we find that, upon cooling, the mechanism for the observed water motion changes from isotropic reorientation associated with long-range transport, to anisotropic reorientation, which may be localized.

For water confined to nanoporous materials, ^2H NMR experiments reveal a kink in the temperature dependence of rotational correlation times. However, findings related to the mechanism for the reorientation imply that the effect is not due to a fragile-to-strong transition, but different relaxation processes are observed above and below the crossover, as was proposed by others [6]. Specifically, we suggest that, below the crossover, the above mentioned anisotropic and local process rather than the structural relaxation governs the experimental findings, in harmony with results from our MD simulations.

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L19

Proteins need it wet. Don't they ?

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ABSTRACT

As molecular workhorses, proteins fulfill a multitude of tasks that keep the complex machinery in biological cells alive. A protein's surface is either fully or partially covered with hydration water that is esteemed crucial for biological activity. Incoherent neutron scattering (INS) in combination with selective deuterium labelling puts the focus either on protein or on water motions on the ns-ps time scale and allows their dynamic coupling to be studied. This coupling proves to decrease in *tightness* from intrinsically disordered, *via* globular-folded to membrane proteins [1]. Thus, there exists a gradient of coupling with hydration-water motions across different protein classes. Specific labeling and INS has also been used to show that not only the surface of a soluble protein, but also its interior responds to changes in hydration water dynamics [2].

Do proteins really need it wet ? In order to answer this question, we investigated nano-hybrids of polymer-coated myoglobin that contain neither water nor any other solvent. Yet, these nano-hybrids surprisingly display biological activity. By examining deuterium labeled hybrids with neutron scattering, we revealed that the polymer coating exhibits similar flexibility than does hydration water, thus allowing the proteins they wrap to undergo motions necessary for biological activity [3]. These results highlight the potential for polymer-protein hybrids in that they show that the polymer coating can functionally and dynamically substitute for water or any other solvent and generate a new species that may be able to function in anhydrous environments, such as those frequently encountered in industry.

These pieces of research are the fruit of collaborations with colleagues whose names appear in references 1, 2 and 3. I am deeply indebted to them.

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L20

The protein hydration layer: how different from the bulk? A mirror for protein conformations and stability?

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Water is widely considered as necessary to life and to play a key role on protein stability and function.

In an effort to understand the molecular detail of such contributions, we have first investigated how water molecules surrounding a biomolecule get dynamically perturbed with respect to bulk. Through numerical simulations and analytic modeling, we have identified the key molecular factors which govern the dynamics of water next to proteins [1,2,3].

Next, we addressed the problem of how hydration contributes to the stability of proteins under temperature stress [3]. Namely we investigated how hydration responds to the change of protein chemical composition and conformations of homologues proteins of different thermal stabilities [4].

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L21

Structural and Dynamic Properties of Organised Structures of Saccharide Systems in Aqueous Solution

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ABSTRACT

The role of water and of its network of H-bond interactions in biological systems has been the subject of extensive studies with a large variety of techniques [1]. Many biomolecules have specific binding sites for water so that the first hydration shell around a biomolecule is made up from water molecules which are irrotationally bound (primary hydration water), and their dynamics closely follows that of the biomolecular skeleton [2,3]. Macromolecule-water interactions are short range, however their integrated effects may propagate to relatively large scale lengths so that the dynamic properties of interstitial water, even in low-concentration systems, are significantly different from those of pure water [4,5]

An important starting point for the analysis of complex H-bonded biomolecular systems is the availability of experimental data on well characterised model systems in which the thermodynamic parameters affecting the formation of the H-bond network (temperature, hydration, pressure, ...) can be varied in a wide range of values. In this respect saccharide-based macromolecular systems are, among others, excellent candidates. Saccharide systems, both in form of chains or polymeric networks (polysaccharides), and when they are conjugated to hydrophobic species (giving rise to amphiphilic molecules), or to peptides (in proteins or proteoglycans), show a large variety of structures stabilised by macromolecule-solvent interactions [6]. They range from ordered fibre packing at moderate hydration level, up to dilute gels (down to 1-2% biopolymer concentration). In these conditions the network of polysaccharide chains has typical pore sizes of hundreds of nanometers, and it is able to 'trap' large volumes of associated water modifying its microviscosity properties with respect to that of pure bulk water [5].

Besides a basic interest for the understanding of solvent-macromolecule interaction mechanisms, many polysaccharides are nowadays of interest for applications in modern 'food science' and in biomedicine. Modern approaches to food science give an increasing relevance to dynamic molecular properties, therefore concepts borrowed from synthetic polymer science as for instance that of dynamical glass-like transitions, are now currently applied. In biomedical areas recent advances in gene therapies and the availability of significant amount of biologically active proteins and peptides (owing to DNA recombinant techniques) require new advanced characteristics to matrices that are used

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both in the field of controlled drug delivery, and in tissue reconstruction and repair. Pharmacological research is therefore now oriented towards new classes of polymeric materials able to provide a medium favourable to cellular proliferation, while keeping the capability of hosting and releasing drugs. In this context several polysaccharide matrices are being tested [7].

The structural and dynamic properties, at the molecular level, of some important saccharide-based systems will be reviewed with special attention to the results obtained using advanced investigation techniques, as X-ray diffraction by synchrotron radiation, diffraction and inelastic scattering of neutrons, as well as from molecular dynamics simulations [8-11]. The comparison between experimental data and results of the simulations provides a guide for a deeper understanding of the molecular processes investigated.

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L22

Neutrons reveal the ecology of protein and water dynamics

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ABSTRACT

Biological macromolecules evolved over billions of years in their interactions with surrounding water to achieve dynamic structures adapted to their specific functions. Biological activity depends on appropriate structure and dynamics. Weak forces, which depend sensitively on the aqueous environment, not only define the active fold of the macromolecule but also its dynamics about the time-average structure. If its dynamics is inappropriate, a macromolecule will be inactive even in conditions in which its 'correct' structure is maintained and stable. Biology thrives on diversity. With respect to water in cells and water-protein interactions, although it is fundamental to understand the general *physical chemistry*, the biological questions are centred on *adaptation: i.e.* how are these interactions *different* for different proteins and different cell types, according to the respective function and environment. Neutron scattering experiments provided essential information that demonstrated the environmental dependence of dynamics-function relations in proteins and cell water.

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On the structure dynamics and electrical properties of membranes hydration water Insights from Molecular Dynamics Simulations

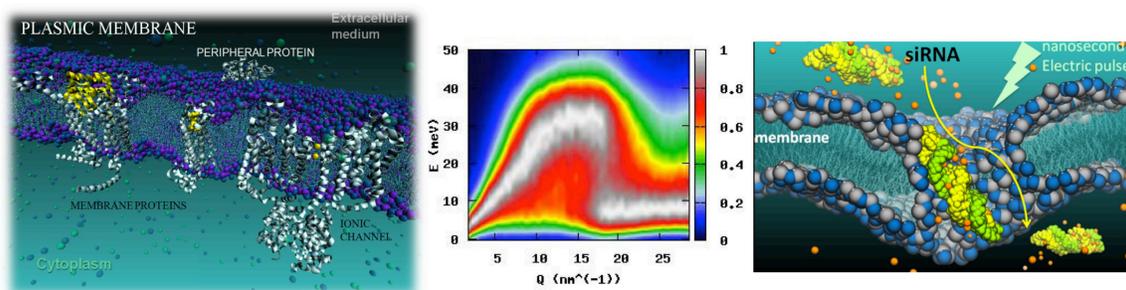


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Structure et Réactivité des Systèmes Moléculaires Complexes
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ABSTRACT

Biological membranes constitute the barrier that maintains a different chemical and biochemical environment in cells and outside of them. The main components of these membranes are phospholipid molecules that self organize into a bilayer, in which the polar head-groups are oriented towards of the aqueous solvent while the long non-polar hydrocarbon chains pack in the interior of the membrane to form a hydrophobic barrier. While the nature of the lipid component of membranes plays a key role in their properties and function, water located in their vicinity is also of major importance. The main aim of this lecture is to shed light on the fundamental role this water plays, *at the microscopic level*, in biophysical processes involving membranes using atomistic molecular dynamics simulations. Making connection with other lectures of this school we will first focus on the structural and dynamical properties of hydration water with a specific focus on collective dynamics. We then will discuss the electrical properties of membranes and how their stability may be breached upon application of an electric field, a process known as electroporation. We will demonstrate that this stems mainly from the properties of the membrane hydration water and its response to external electric perturbation.



[§]Research conducted in the scope of the EBAM European Associated Laboratory
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L24

Water in biomolecular recognition processes - the forgotten partner

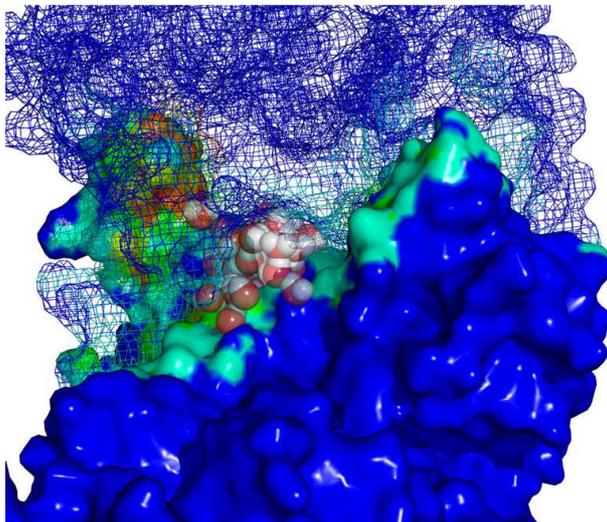
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ABSTRACT

Biomolecular recognition is a fundamental process of life. In the last few years, high-throughput sequencing methods have given us access to entire genomes, *i.e.* the complete catalogs of proteins produced by a growing number of living organisms. Each of these proteins accomplishes its biological function by specifically recognizing and interacting with nucleic acid (DNA, RNA) sequences or other proteins, forming very large and complex supramolecular machineries that implement the mechanisms of life. However, the cell is a crowded environment where random encounters between unrelated biomacromolecules are frequent, also resulting in a wide variety of nonspecific, transient complexes...



Water-filled cavity at the interface of a protein-protein complex, separating two "dry" patches.

Understanding the principles of macromolecular recognition is a very difficult task. Attempts to rationalize them through sets of simple general rules have failed to this day. Based on the study of individual cases, molecular recognition appears to be governed by a competition between the formation of favorable chemical contacts (*direct* recognition) and the energetical cost of deforming the macromolecules so that these contacts can form in the first place (*indirect* recognition).

Until very recently, the role of water in cellular processes in general, and biomolecular recognition in particular, has been thought to be limited to providing a suitable "passive" environment for the macromolecular partners. This view is now rapidly losing favor. Recent studies have shown that water plays an active part in both components of recognition, by mediating

L24

chemical interactions between macromolecules, and favoring structural rearrangements by slowing down the formation of biomolecular complexes (through desolvation).

In my lecture, I will discuss the characteristic hydration patterns of DNA and proteins and the role played by water in the formation of specific and nonspecific protein-DNA and protein-protein complexes. I will also present the methods employed to characterize the dynamics of water at bimolecular interfaces: explicit-solvent all-atom molecular dynamics and the geometrical characterization of hydrated interface topologies.

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L25

Hydrogen bonds of interfacial water in human breast cancer tissue

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ABSTRACT

Characterizing the solid–liquid interface is a key challenge in understanding the nano–bio interactions and dynamics. Although we often assume that the bulk properties of solutions can be translated to the solid phase, this approach must be considerably revised when considering the nano–bio interface. There are expanded efforts to find correlation between carcinogenesis and cell hydration, because there is growing evidence of links between carcinogenesis and cell hydration [1]. Although the role of water in mechanisms of carcinogenesis is still largely unknown, the properties of water at nano–bio interfaces have always been a central subject of investigation in cell biology. The biological function activity as well as stability, structure, and dynamics are largely dominated by interactions, energy transfer, and reorientation of water molecules in the restricted environments that differ drastically from those of bulk water properties. The confinement of water in biological structures does not represent a single pattern of behavior, but ranges from reverse micelles, hydrated membranes, DNA and protein interfaces. These hydrated interfaces play an important role in a variety of vital reactions involved in protein interactions, enzyme catalysis, molecular recognition, and various steps of proton and electron transfer pathways. Unraveling the role of interfacial water in biological systems has required the application of a number of different techniques. One of the most direct probes of the structure and dynamics of confined water are the infrared and Raman spectroscopies as well as Raman imaging. The stationary and time resolved vibrational spectra modified by interaction with biological interfaces can be used to extract microscopic information about the hydration layer. In this lecture we discuss properties of water confined in the cancerous breast tissue, particularly the spectral properties of the OH stretching mode and propose the mechanism of interaction responsible for the spectral features. According to our knowledge Raman vibrational properties of water confined in the normal and cancerous breast tissue have not been reported in literature yet. We have also obtained the first Raman ‘optical biopsy’ images of the non-cancerous and cancerous (infiltrating ductal cancer) of human breast tissues [2].

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EAU AUX INTERFACES: NOUVEAUX DEVELOPPEMENTS EN PHYSIQUE, CHIMIE ET BIOLOGIE
WATER AT INTERFACES: NEW DEVELOPMENTS IN PHYSICS, CHEMISTRY AND BIOLOGY (April 15-26, 2013)

SEMINAR SPEAKERS (35 MINUTES+10 MINUTES QUESTIONS)

S1-Ayotte Patrick (Sherbrooke University, Canada): ionization and enhanced photochemistry of nitric acid on ice

S2-Bove Livia (CNRS, Paris, France) : Exploring the phase diagram of salty water under high pressure: polyamorphism, crystallization and liquid-liquid transition

S3-Ladanyi Branka (Colorado State University, USA): Structure and dynamics of water in silica nanopores

S4-Brodie-Linder Nancy (LLB, France) : Confined Water in its role as a Ligand to Cu II in Hydrophilic and Hydrophobic Nanopores

S5-Judeinstein Patrick (CNRS, LLB, France): NMR : a reference tool to explore water in materials science

S6-Xantheas Sotiris (PNNL, USA): Accommodation of molecular species inside hydrate lattices

S7-Luzar Alenka (Virginia University, USA): Tunable hydration at the nanoscale

S8-Doster Wolfgang (Universität München): On Masters and Slaves: Does Water control Protein Motion and Function ?

S9-Russo Daniela (ILL, France): Hydration water collective density fluctuations in biological systems: from model peptides towards whole living cells

S10-Gustavsson Thomas (CEA-Saclay): The role of water in the (indirect) solvent effects governing the excited state dynamics of DNA bases

S11-Chazallon Bertrand (PhLAM, CNRS, Lille1 University) : Ice particle crystallization in the presence of ethanol: investigated by Raman scattering and X-ray diffraction

S1

IONIZATION AND ENHANCED PHOTOCHEMISTRY OF NITRIC ACID ON ICE



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ABSTRACT

Nitrates photolysis plays a key role in the chemistry of the polar boundary layer and of the lower troposphere over snow-covered areas (1). Using a combination of vibrational (2) and photoemission spectroscopies, we show that nitric acid is mostly dissociated upon its adsorption onto, and its dissolution in ice at temperatures as low as 45K. By irradiation in the environmentally relevant $n-\pi^*$ transition, we also observe that the photolysis rates are significantly higher for surface-bound nitrates compared to that of dissolved nitrates. Surface-enhanced photolysis rates on ice may contribute to the intense photochemical NO_x fluxes observed to emanate from the sunlit snowpack upon polar sunrise.

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S2

Exploring the phase diagram of salty water under high pressure: polyamorphism, crystallization and liquid-liquid transition

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It is widely accepted that ice, no matter what phase, is unable to incorporate large amount of salt into its structure. This conclusion is based on the observation that upon freezing of salt water, ice expels the salt almost entirely into brine. This is also the reason why little attention was paid, up to date, to the investigation of the phase diagram of salty water under high pressure, despite its potential relevance for the physics of icy bodies in the Universe [1].

We recently explored [2-4] the phase diagram of salty water ($\text{LiCl}:\text{RH}_2\text{O}$ solutions) under high pressure (GPa) by neutron scattering measurements and molecular dynamics simulations. The addition of salt to water promotes disordered and dense phases and allows, in the vicinity of the eutectic point ($R=6$), exploring the boundary between the deep undercooled state and the amorphous phases of water in solution.

In spite of the high amount of salt, $\text{LiCl}:\text{6H}_2\text{O}$ solution vitrifies at ambient pressure in a homogeneous, structurally compact form very similar to the high-density amorphous phase of pure water (e-HDA), and undergoes a polyamorphic transition, under annealing at high pressure, to a very-high-density amorphous phase (VHDA)[3], which is stable up to very high pressure. The transition is reversible and is linked to a net change of coordination around the Li ion (Figure 1a).

The deep undercooled liquid (180 K) shows, instead, a smooth transformation from a high-density to a very high-density liquid state. This observation questions the existence of a binomial relation between polyamorphism and liquid-liquid transition.

Under further temperature annealing of the salty-VHDA phase at high pressure the system crystallizes into the ice VII structure incorporating homogeneously the salt into the ice lattice [4] (Figure 1b). Such an 'alloyed' ice VII has significantly different structural properties compared to pure ice VII, such as 8% larger unit cell volume, absence of transition to the ordered ice VIII structure, plasticity, and most likely ionic conductivity. Our studies strongly suggest that there could be a whole new class of salty ices based on various kinds of solutes and high-pressure ice forms. If these exist in nature in significant quantity, their physical properties would be highly relevant for the understanding of icy bodies in the solar system.

S2

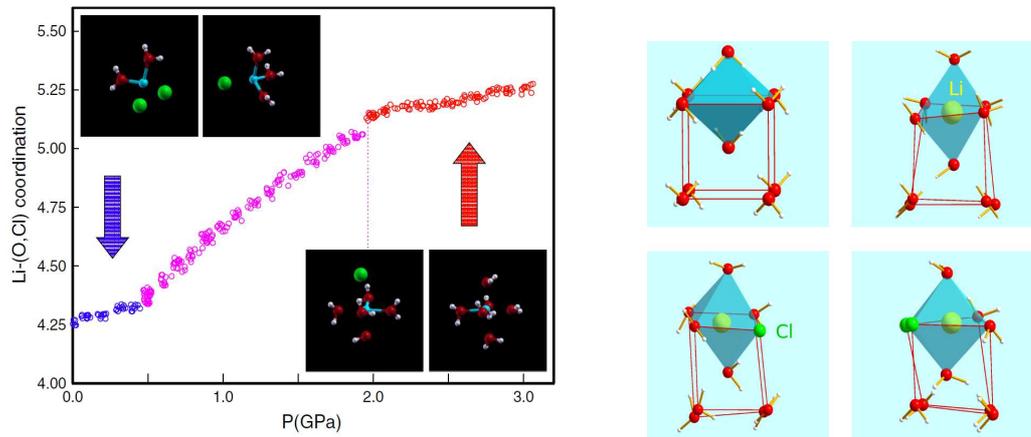


Figure :a) Li-coordination change during the polyamorphic transition under compression at 140 K. b) proposed structure for LiCl-ice VII.

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Structure and dynamics of water in silica nanopores

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ABSTRACT

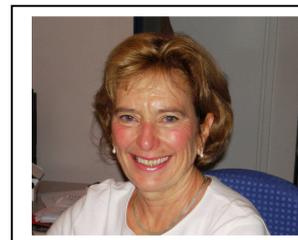
This presentation will focus on our molecular simulation results for the structure and dynamics of water confined in silica nanopores at full hydration and room temperature. The model systems are approximately cylindrical pores in amorphous silica, with diameters ranging from 20 to 40 Å. The filled pores are prepared using grand canonical Monte Carlo simulation and molecular dynamics simulation is used to calculate the water structure and dynamics.¹ We found that water forms two distinct molecular layers at the interface and exhibits uniform, but somewhat lower than bulk liquid, density in the core region. The hydrogen bond density profile follows similar trends, with lower than bulk density in the core and enhancements at the interface, due to hydrogen bonds between water and surface non-bridging oxygens and OH groups. Our initial characterization of water dynamics included translational mean squared displacements, orientational time correlations, survival probabilities in interfacial shells and hydrogen bond population relaxation. We found that the radial-axial anisotropy in translational motion largely follows the predictions of a model of free diffusion in a cylinder. However, both translational and rotational water mobilities are strongly dependent on the proximity to the interface, with pronounced slowdown in layers near the interface. Hydrogen bond population relaxation is nearly bulk-like in the core, but considerably slower in the interfacial region. In order to make contact with experiments on water dynamics within the pores, we have calculated and analyzed the self-intermediate scattering function (ISF), $F_s(\mathbf{Q}, t)$, of water hydrogens,² the observable in quasi-elastic neutron scattering (QENS) and the collective polarizability anisotropy time correlation $\Psi(t)$, measured in optical Kerr effect (OKE) experiments.³ In the case of $F_s(\mathbf{Q}, t)$, we investigated its dependence on the pore diameter, the direction and magnitude of the momentum transfer \mathbf{Q} , and the proximity of water molecules to the silica surface. We also studied the contributions to $F_s(\mathbf{Q}, t)$ from rotational and translational motions of water molecules and the extent of rotation-translation coupling present in $F_s(\mathbf{Q}, t)$. In the case of $\Psi(t)$, we investigated the relative contributions of molecular and interaction-induced polarizabilities and the effects of interlayer coupling on the relevant collective relaxation processes. Our findings on the dynamics of confined water detectable by QENS and OKE will be discussed.

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S4

Confined Water in its role as a Ligand to Cu II in Hydrophilic and Hydrophobic Nanopores



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ABSTRACT

The activity of confined copper II on silica surfaces has a wide variety of uses and has been shown to be particularly interesting in semi-conductor copper oxide compositions as well as in catalysis for organic synthesis, for trapping toxic gases like cyanide and for wet air oxidation of wastewater. It has also recently shown promising anti-bacterial activity.

Water is an important component in these systems as it serves as a ligand for copper. The number of water molecules bonded to Cu^{2+} confined in a silica pore and the strength of the water Cu^{2+} bond is not well-known but can play an important role in the availability of the copper II for reaction. Another complication can arise as the Cu^{2+} cation is bonded to the surface in a hydrophilic material but confined by weak interactions in a hydrophobic one.

We recently studied the complexation of the copper II cation in aqueous ammoniacal solution and its reactivity towards surface silanol groups of a mesoporous templated silicate material, SBA-15 [1].

We found that indeed surface bonded Cu II atoms readily formed bonds with water molecules, resulting in an increased amount of adsorbed water with respect to the original non-modified SBA-15. These water molecules seem to be strongly adhered to the Cu II atoms and are not easily released under thermal treatment. The particularity of this confined water bonded to surface Cu II atoms was illustrated recently during electron irradiation experiments with SBA-15 Cu materials. It was shown that the presence of Cu II on the surface reduced and inhibited the production of H_2 [2]. In order to study the interesting relationship between the confined Cu II cation and its aqua ligands, it was more convenient to create a hydrophobic environment for the confined Cu II cation so that any adsorbed water could be more easily controlled and observed. To create the condition of a confined “free” aquated Cu II cation, a novel method was developed involving MCM-41 mesoporous materials with hydrophobic surfaces. By using this method, we were able to create a unique situation where hydrophobic pores were capable

S4

of retaining adsorbed water but only when Cu II was present. The key to this situation is the presence of confined water in its role as an aqua ligand for Cu II.

An inside look into the behaviour of confined aqueous Cu II in both hydrophilic and hydrophobic nanopores will be discussed.

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NMR : a reference tool to explore water in materials science

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ABSTRACT

Nuclear magnetic resonance is a unique spectroscopy because it allows to investigate many aspects of the structure and the dynamics of chemical species on wide space and time domains. To this respect, it is a very efficient tool to explore the properties of water in all its state, because such a small molecule has three different observable nuclei (^1H , ^2H and ^{17}O), each of them providing specific NMR interactions.

In this talk we will present the power of NMR to study water at surface/interfaces in different systems relevant to material science, such as :

- hydration shells of ions in saline solution ;
- behavior of water mixed in ionic liquids ;
- structure and mobility of water layers in lyotropic systems ;
- mobility mechanisms in acid clathrate ;
- dynamic of water layer on silica interface ;
- swelling water in anisotropic polymers ...

We will show how the complementary NMR approaches (cryoporometry, quadrupolar interactions, pulsed field gradient) allows to get information on local structure and orientation, mechanisms of transport, interactions with surfaces

References

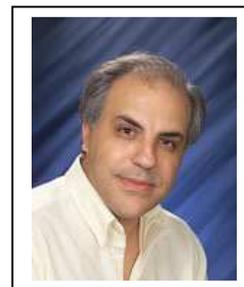
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Accommodation of molecular species inside hydrate lattices

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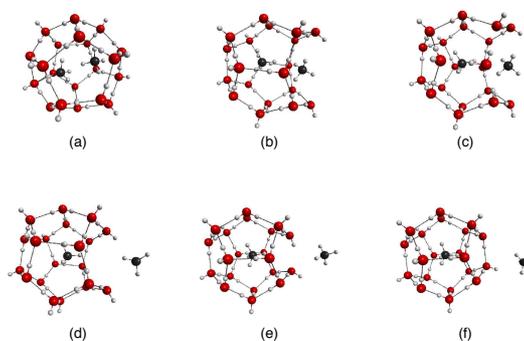
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ABSTRACT

Hydrate crystal structures are water scaffolds comprised of ‘host’ hollow cages that can accommodate ‘guest’ molecules such as Cl_2 , Br_2 , SO_2 , H_2S , H_2 and CH_4 via weak van der Waals interactions. These clathrate hydrate inclusion compounds – the combination of the host lattice and the guest molecules – have potential relevance in renewable energy (i.e. as molecular hydrogen storage devices). We will discuss the magnitude and nature of the molecular guest/host interactions for these and other prototype inclusion systems for a variety of molecular guests. We will further present first principles electronic structure simulations for the accommodation of hydrogen inside periodic structure I (sI) hydrate lattices aimed at probing processes related to the diffusion of molecules between cages. Our calculations suggest a mechanism involving the breaking and reforming of hydrogen bonds of the hollow cages that facilitates the diffusion of guest molecules between adjacent cages.



Snapshots of a gas phase D-cage with 2 CH_4 molecules: (a) initial (2 CH_4 molecules inside D-cage), (f) final (1 CH_4 molecule inside and one outside). Panels (b)-(e): intermediate steps for the extrusion of a CH_4 molecule via the breaking of a hydrogen bond of one of the pentagonal faces.

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S7

Tunable hydration at the nanoscale

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ABSTRACT

The lecture will review our recent theoretical and molecular simulation works that predict and elucidate changes in hydration and water-mediated interactions in response to surface texture, or to nanoelectrowetting. Examples will range from nanopatterning on synthetic and biological surfaces, to dynamics of the *Janus* interface, to ordering of nanoparticles in dispersion. These examples offer basic understanding in modulating local hydrophilicity/hydrophobicity of engineered and biological surfaces, and surface manipulation in nanofluidic devices. The notion can guide computer-assisted design of improved materials and help explain the solubility and function of biomolecules in aqueous solutions.

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S8

On Masters and Slaves: Does Water control Protein Motion and Function?

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ABSTRACT

The overall activity of most proteins vanishes in dehydrated environments. That bio-molecules operate only in the presence of water is one dogma of molecular biophysics. But in some cases, where function can be segregated into elementary steps, a more detailed picture emerges, which includes solvent-decoupled processes. It is a useful scheme, to classify molecular processes in proteins according to whether they require structural fluctuations of the solvent or not. Some workers call this solvent-slaved. Water in the vicinity of protein surfaces exhibits a modified chemical potential and behaves thus differently from bulk. In spite of this difference hydration water shares many structural and dynamical properties with the bulk phase. One interesting dividing feature is suppressed crystallization and the existence of a glass transition, which induces a protein dynamical transition. In this lecture we discuss solvent-dependent light-induced reactions in proteins together with neutron scattering experiments on fast structural fluctuations. The hydrogen bond dynamics of water and protein polar residues occur together on a femto- to pico-second time scale. Solvent effects on slower motions indicate the existence of a local viscosity of water near the protein surface. The question of local and collective processes in the context dynamics and function will be addressed. Beyond the conventional energy landscape picture, neutron scattering data reveal liquid-like interactions, which are more accurately described by a protein-water seascape.

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S9

Hydration water collective density fluctuations in biological systems: from model peptides towards whole living cells

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ABSTRACT

The role of water in the behaviour of biomolecules is well recognized. The coupling of motions between water and biomolecules has been studied in a wide time scale for the *self* part while *collective* dynamics is still quite unexplored. *Self* dynamics provide information about the diffusion processes of water molecules and relaxation processes of the protein structure. *Collective* density fluctuations might provide important insight on the transmission of information possibly correlated to biological functionality. The idea that hydration water layers surrounding a biological molecule show a *self* dynamical signature that differs appreciably from that of bulk water, in analogy with glass-former systems, is quite accepted. In the same picture Brillouin Terahertz spectroscopy has been used to directly probe *collective* dynamics of hydration water molecules around bio-systems, showing a weaker coupling and a more bulk-like behaviour. We will discuss results of collective modes hydration water, arising from neutron Brillouin spectroscopy, in the context of bio-molecules-solvent interaction.

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S10

The role of water in the (indirect) solvent effects governing the excited state dynamics of DNA bases

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ABSTRACT

The excited state dynamics of various DNA bases in protic water have been compared with those in aprotic solvents using femtosecond spectroscopy in combination with quantum chemistry calculations. The results are interpreted in terms of solvent tuned non-radiative relaxation channels, cf. dark $n\pi^*$ states, that indirectly govern the excited state evolution towards the $S_1 - S_0$ conical intersection, responsible for the ultrafast internal conversion to the ground state. It is shown that hydrogen bonds, in the ground and the excited states, play an important role in the energetic ordering and the dynamics of the electronic states involved.

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S11

Ice particle crystallization in the presence of ethanol: investigated by Raman scattering and X-ray diffraction

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ABSTRACT

The behavior of aqueous solutions at low temperature has been and is still widely examined because of its importance in many fields of research such as cryopreservation of living cells and organs,¹ cryoprotection and antifreeze protection of biological species² or atmospheric physico-chemical processes.³ In the atmosphere, aqueous solutions may exist at temperatures lower than 230 K in mixed clouds which both contain ice particles and supercooled droplets or in deep convective clouds.

During active deep convection, boundary layer air may be lifted to the upper troposphere (UT) within an hour resulting in the rapid vertical transport of volatile organic compounds (VOCs) and other reduced trace gases emitted from anthropogenic sources.⁴ Oxygenated VOCs such as light organic compounds (alcohols, ketones, aldehydes...) are widespread in the UT where they may influence the oxidizing capacity of the atmosphere providing substantial sources of free OH radicals that drive photochemical cycles and ozone budget.⁵⁻⁸ During vertical transport, these VOCs may be trapped in large amounts by supercooled droplets that subsequently freeze.

Whether the organic species are trapped in the bulk or rejected at the gas-ice interface is still unclear. In the latter case the ice particle reactivity is modified (in comparison to the pure ice case) and the species are also supposed to be easily released by rapid evaporation once in the UT.^{9,10}

The aim of this study is to examine the temperature behavior of supercooled droplets of ethanol aqueous solutions and identify their structures when the particle crystallizes during cooling on a wide temperature range (253 K – 188 K). We extend the temperature range down to 88 K to explore the phase diagram and the behavior below T_g in comparison to organic compounds of higher molecular weights¹¹. X-ray diffraction is carried out to corroborate the spectral changes observed in Raman experiments. Depending on the initial EtOH content, it is proposed that the particle results in a complex structure formed with a supercooled layer of relatively high ethanol content at the liquid/gas interface or with an ethanol hydrate and a supercooled layer of high ethanol content¹². Each case depends on temperature trajectories and may have the potential to impact several atmospheric processes.

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EAU AUX INTERFACES: NOUVEAUX DEVELOPPEMENTS EN PHYSIQUE, CHIMIE ET BIOLOGIE

WATER AT INTERFACES: NEW DEVELOPMENTS IN PHYSICS, CHEMISTRY AND BIOLOGY (April 15-26, 2013)

SHORT TALKS (15 MINUTES+10 MINUTES QUESTIONS)

ST1-Cassone Giuseppe (Messina-Paris University): *Ab initio* Molecular Dynamics study of proton conduction in ice under an electric field

ST2-Cipcigan Flaviu (Edinburgh): Effects of van der Waals forces and hydrogen bonds on the liquid-vapor interface

ST3-Szala-Bilnik Joanna (Lodz University) : Hydroxyl radical in high temperature water-mechanism of transport

ST4-Rebiscoul Diane (CEA Marcoule): Dynamics of water confined in gel formed during glass alteration at a picosecond scale

ST5-Drummond Carlos (CRPP): Ions-Induced Nanostructuring of Hydrophobic Polymer Surfaces

ST6-Bellavia Giuseppe (Lille): Raman scattering as a tool to investigate protein hydration shell

ST7-Achir Samira (Lille): Protein stability during lyophilization process and storage

ST8-Lerbret Adrien (Dijon) : Neutron scattering and molecular dynamics simulation study of lysozyme under high pressure

ST9-Orsi Davide (Parma University): Effects of antibiotic drugs on the mechanical properties of phospholipidic GUVs

ST1

***Ab initio* Molecular Dynamics study of proton conduction in ice under an electric field**

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ABSTRACT

Proton conduction in aqueous systems under an external or local electric field is a key phenomenon in many branches of science, from electrolysis to neurobiology. However, its microscopic description is difficult to achieve experimentally and only recently it has been studied for the first time with *ab initio* methods in bulk liquid water¹. Here we report on a detailed systematic first-principles study of the effect of an external electric field in ordinary hexagonal ice (phase Ih) and in its proton-ordered counterpart ice (phase XI). In particular, we have first identified the main reaction coordinates in the ordered case and calculated the corresponding static energy profiles as a function of the field intensity. Then, we performed *ab initio* Molecular Dynamics simulations of both phases and observed that fields beyond a threshold value of about 0.25 V/Å are able to induce an instantaneous molecular dissociations in both structures. We also found, quite unexpectedly, that in the case of proton-ordered ice XI field intensities above this threshold are also able to induce a series of correlated proton jumps that are necessary to sustain an ionic current. Instead, in proton-disordered ice Ih field intensities above \approx 0.35 V/Å are required to induce a permanent proton flow. Curiously, this latter threshold coincides with that observed in liquid water, suggesting, somehow counterintuitively, that crystalline order favors the autoprotolysis phenomenon which, instead, is hindered by static or dynamic disorder.

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ST2

Effects of van der Waals forces and hydrogen bonds on the liquid-vapor interface

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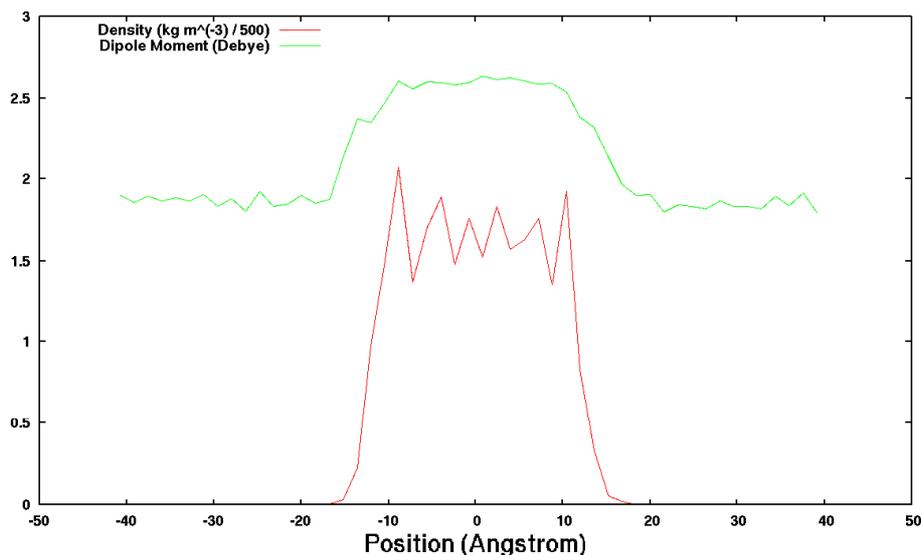


ABSTRACT

We have recently introduced [1] an electronically coarse grained model of water. The model closely reproduces all long-range interactions and many body responses via an embedded quantum oscillator, at a fraction of the cost of *ab initio* methods.

I will review this model and present and a study the properties of its liquid-vapor interface. Since the effects of polarization (giving rise to hydrogen bonds) and dispersion (giving rise to van der Waals forces) can be adjusted independently, the study will focus on the dependence of interfacial properties on the interplay between these forces.

The work is ongoing, and shows promising results. The properties of the liquid phase are reasonably reproduced and the surface tension ($70.5 \pm 1 \text{ mN m}^{-1}$) is within one error bar of the experimental estimate (71.73 mN m^{-1}). The dipole moment of the model also enhances smoothly moving from vapor to liquid (preliminary results shown below).



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ST3

Hydroxyl radical in high temperature water-mechanism of transport



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ABSTRACT

Knowledge of the $\bullet\text{OH}$ radical behavior in hot compressed water is required for mechanistic understanding of the radical reactions and transport in the systems of interest for nuclear power engineering and green chemistry technologies. In water cooled nuclear power reactors $\bullet\text{OH}$, generated as a transient product of water radiolysis, contributes to oxyhydrogen gas emission and corrosion, posing severe problems for nuclear power safety and integrity of materials.

The molecular dynamic simulation has been employed to examine the mechanism of transport of $\bullet\text{OH}$ radical in water for a wide range of thermodynamic conditions. The diffusion coefficient of $\bullet\text{OH}$ radical, D_{OH} , and the self-diffusion coefficient of water, $D_{\text{H}_2\text{O}}$, have been calculated using the mean square displacement, the Green-Kubo and the Stokes – Einstein relations.

Above the critical density D_{OH} and $D_{\text{H}_2\text{O}}$ are similar and both increase with the increasing temperature and decreasing density of water. Below the critical density, the self-diffusion coefficient noticeably increases, whereas D_{OH} varies slightly. We relate this behavior of D_{OH} with the hydration mechanism proposed in our previous study [1,2].

Acknowledgment

Research task No. 7 “ Study of hydrogen generation processes in nuclear reactors under regular operation conditions and in emergency cases, with suggested actions aimed at upgrade of nuclear safety” financed by the National Research and Development Centre in the framework of the strategic research project entitled “Technologies Supporting Development of Safe Nuclear Power Engineering” financial support is greatly acknowledged.

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ST4

Dynamics of water confined in gel formed during glass alteration at a picosecond scale

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ABSTRACT

The leaching of borosilicate glasses leads to the formation of a hydrated and porous silica layer named gel and filled of leachate (ionic species coming from glass alteration). This porous material is formed by hydrolysis and condensation of the silicate species and can display protective properties regarding the diffusion of elements coming from the glass (1). Rate laws and kinetics models generally take into account the properties of the gel and some thermodynamic data arising from measurements in diluted media (concentration of dissolved ions, thermodynamic constant) (2, 3). However, water within the gel is confined in pores smaller than 5 nm. Thus, probing confined water dynamics in porous gel can provide a better understanding of water transport mechanisms and chemical reactivity in such confined media. To better understand the water behaviour in these complex materials we have used model materials. Thus, we have tackled the first part of our scientific approach studying the impact of pore size and pore surface composition on the dynamics of water confined in porous silica-based materials having various pores sizes from 2 to 2.7 nm and Si-OH, Al-OH and Zr-OH pore surface 4. For time scale between 0.1 and 10 ps, we have shown by quasielastic neutron scattering (QENS) that one part of water molecules has the same mobility as bulk water ($2.9 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$) and the other part fixed at the pore surface is surface sensitive. Indeed, Al-OH pore surfaces lead to the highest proton immobilisation creating coordination bonds with water molecules 4. In the second part of our scientific approach, we have first

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investigated the effect of a leachate filling the model materials porosity on water dynamics since the presence of hydration shell around ions can hinder the water motions. We have shown that the presence of ions does not impact the water mobility in model materials whatever the pore surface composition. Second, we have characterized the water dynamics in gels formed during glass alteration. In the gel, water is two to three times slower than in the bulk and the fraction of fixed protons is similar to the one of the model material having Al-OH surface. Two hypotheses are proposed to explain these results: the ion concentrations in pores of the gel can be higher than in the leachate located outside the gel forming hydration shell around ions hindering the water motions and/or the pore wall composition of the gel consisting of elements such Al which can immobilize water molecules. In addition to Al effect, the presence of Ca can slow down the water diffusion due to the binding of H₂O molecules in strong complexes with Ca²⁺. The final goal is to relate the water dynamics in our model materials with the water dynamics in the gels formed during glass alteration.

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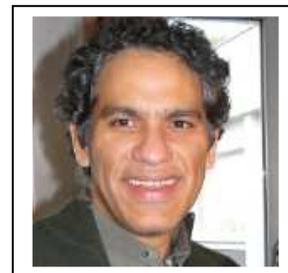
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ST5

Ions-Induced Nanostructuration of Hydrophobic Polymer Surfaces

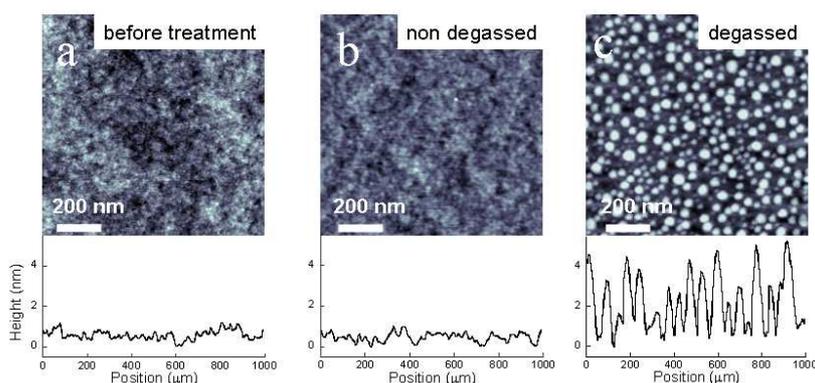
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ABSTRACT

When hydrophobic surfaces are in contact with water in ambient conditions a layer of reduced density is present at the interface, preventing the intimate contact between the two phases. Reducing the extent of this layer by degassing the water promote ionic adsorption on the hydrophobic. This process can induce long-lasting deformation of hydrophobic glassy polymer films, a process called ion-induced polymer nanostructuration, IPN. The self-assembled structure spontaneously relaxes back to the original flat morphology after few weeks at room temperature. This instability and the self-assembled structure are controlled by the hydrophobic surface charge, which is determined by the composition of the aqueous phase, and by the amount of gas dissolved. We have found that this process is ion-specific; larger surface modification is observed in the presence of water ions, hydrophobic and amphiphilic ions. Surface structuration is also observed in the presence of certain salts of lithium. This effect can be easily adjusted to modify different hydrophobic polymeric substrates at the submicrometer level, opening pathways for producing controlled patterns at the nanoscale in a single simple waterborne step.



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ST6

RAMAN SCATTERING AS A TOOL TO INVESTIGATE PROTEIN HYDRATION SHELL

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ABSTRACT

Introduction

Water has a fundamental role in protein stability and the solvent-accessible surface area (SASA) is a parameter intimately related to the native or denatured states of the protein. An experimental method to analyze the organization of bulk and hydration water, based on the detection of H/D isotopic exchange between the protein and hydration water by Raman spectroscopy is described for the model protein lysozyme.

Experimental

The Raman spectrum of lysozyme dissolved in D₂O (LWd) was taken in the 1500-3800 cm⁻¹ range and decomposed in two parts: (i) the Amide I region (1500-1800 cm⁻¹); (ii) the 2000-3800 cm⁻¹ spectrum plotted in Fig.1, dominated by the O-D stretching bands. Isotopic exchanges between the protein and hydration water are responsible for the weak band detected in region (3) and corresponding to the dilute DHO spectrum, and then to the uncoupled ν_{OH} spectrum [1] (Fig.1 inset). A shoulder is detected on the low-frequency side (see Fig.1 inset) of the LWd spectrum, not observed in the dilute DHO solution, and therefore corresponding to OH groups of lysozyme not exposed to the solvent.

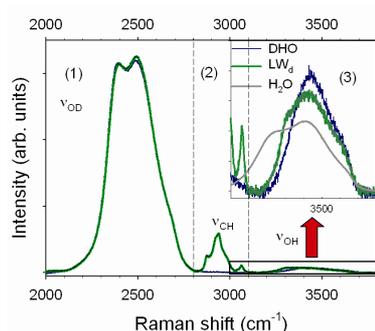


Fig.1. Description of the O-D(H) stretching hydrated lysozyme. The spectrum of LWd can be divided in 3 regions corresponding to the following intramolecular stretching vibrations: (1) O-D in bulk D₂O, (2) C-H in lysozyme and (3) O-H in HDO molecules resulting from isotopic exchange. The LWd spectrum is compared to DHO and H₂O in (3) in the inset.

Results and Discussion

The solution was heated from 20 up to 95°C. Fig.2 shows Amide I region vs. temperature, together with fitting results. A clear frequency downshift of Amide I band is observed, which was interpreted as reflecting enhanced NH/ND isotopic exchange, associated with the penetration of the solvent in the protein interior [2]. Above 70°C, a frequency upshift

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is observed, usually interpreted as α -helix unfolding process. If we adopt the consideration that the protons exchanges from lysozyme to D₂O quickly diffuse in bulk heavy water molecules, the intensity ratio between OH and OD stretching bands represents the proportion of water molecules involved in the isotopic exchange. Then the ratio $\rho_{\text{OH}}=I_{\text{OH}}/I_{\text{OD}}=0.0246\pm 0.0015$ is obtained at T_{room} . This indicates that a lysozyme molecule is surrounded by a bound layer of 198 ± 10 water molecules in the native state. ρ_{OH} can be then considered as directly representative parameter of the SASA and $\rho_{\text{OH}}(T)$ (see Fig.2c) was interpreted as reflecting the changes in the SASA. It is firstly observed that ρ_{OH} increases between 60 and 75°C, as the frequency of amide I band decreases. This confirms the solvent penetration within the tertiary structure. At $\sim 73^\circ\text{C}$, the number of water molecules bound to the protein in the molten globule state was estimated to 260 ± 13 , indicating the increase of the SASA by a factor 1.3. Secondly, upon further heating above 70°C, an additional increase of ρ_{OH} is observed, when the protein denatures and the SASA estimation is 1.75 times greater.

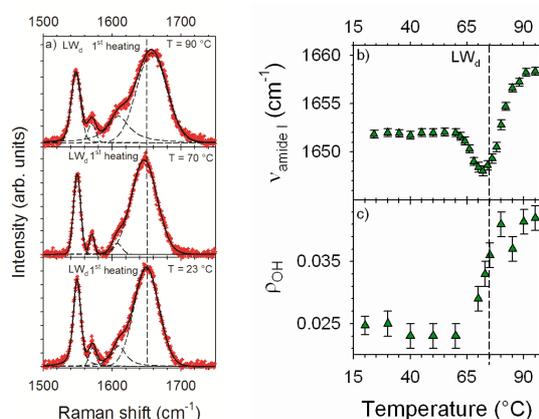


Fig.2. Temperature dependence of amide I band; a) Raman spectra b) $\nu(T)$ compared to c) $\rho_{\text{OH}}(T)$ curves.

Same experiments were performed in presence of trehalose (T). D₂O+T solution was previously freeze-dried, in order to substitute OH groups by OD. We obtain crucial information on the influence of trehalose on the bulk water, the hydration water and the SASA during the lysozyme denaturation, in relation with the unfolding process monitored by the temperature behavior of the amide I band.

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ST7

Protein stability during lyophilization process and storage

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ABSTRACT

Stabilization during storage of biological materials, in particular proteins, is the principal goal of the pharmaceutical industry. In solution, proteins are marginally stable over a limited temperature range which makes them very unstable over time. To improve their stability, proteins must be stored in solid form (powder). The most commonly used method for preparing solid protein is lyophilization (1) (2). This process consists to remove water from frozen sample by sublimation and desorption (3). The process of lyophilization can be visualized in terms of three steps: i) initial freezing, ii) Primary drying and iii) Secondary drying (4). Unfortunately, the process generates different stresses (the freezing stress; changed pH and drying stress) which affect the protein stability (5). To protect the protein structure during the process, excipients (PVP, Trehalose, and Sucrose) can be added to the protein solution (6). Even after successful lyophilization with a protein stabilizer, proteins in solid state may still have limited long-term storage stability (5).

Raman microspectroscopy is used to monitor structural changes of the protein and to analyze the physical mechanisms of bioprotection, during lyophilization and storage. The spectra of amide I and III bands between 800 and 1800 cm⁻¹, probe the α -helix and β -sheets structures of the protein and their transformation.

Water-replacement and vitrification models are often used to explain the protein stabilization of dried proteins.

The aim of the study is to determine the nature of stress responsible for protein denaturation and to give a better insight on bioprotective mechanisms, during lyophilization and long-term storage.

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ST8

Neutron scattering and molecular dynamics simulation study of lysozyme under high pressure

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ABSTRACT

The spontaneous unfolding of proteins at low temperature, known as cold denaturation [1], is one of the major causes of protein degradation during the freeze-drying process used to store foods and therapeutic materials [2]. Cold denaturation usually occurs at temperatures well below the equilibrium freezing point of water in room conditions, which has made it difficult to evidence experimentally. Applying high hydrostatic pressure is a well-known method to study cold denaturation [3]. As a first step towards this goal, we have performed inelastic neutron scattering experiments and molecular dynamics simulations to investigate the influence of pressure at room temperature on the vibrational dynamics of lysozyme and water at pressures up to 6 kbar [4]. The high-frequency shift of the low-frequency part (< 10 meV) of the protein vibrational density of states (VDOS) suggests a stiffening of internal motions upon pressurization, consistent with the decrease of the mean square displacement observed on lysozyme [5]. Furthermore, the nonlinear influence of pressure on the VDOS of lysozyme indicates a change of protein dynamics that reflects the nonlinear pressure dependence of the protein compressibility. An analogous dynamical change is observed for water and is ascribed to the distortion of its tetrahedral structure under pressure. Our study also reveals that the structural, dynamical and vibrational properties of water hydrating lysozyme are less sensitive to pressure than those of bulk water, thereby evidencing the strong influence of the protein surface on hydration water.

This work was supported by the ANR (Agence Nationale de la Recherche) through the BIOSTAB project (“Physique-Chimie du Vivant” program).

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ST9

Effects of antibiotic drugs on the mechanical properties of phospholipidic GUVs



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ABSTRACT

The study of biomimetic membrane systems and living cellular systems has taken advantage, in recent years, of several microrheological techniques. Among the others, the analysis of thermal fluctuations of giant unilamellar vesicles (GUV) is a recently developed technique based on micro imaging: it consists in investigating the properties of a spherical bilayer membrane, through the classic “flickering” analysis of the fluctuations of the contour of the 2D equatorial section of a GUV, observed by means of phase-contrast microscopy, which are tracked in time; the mechanical properties of the membrane are deduced by the analysis of the power spectrum of the membrane fluctuations [1].

Notably, bilayer vesicles represent a model system more adherent to real biological systems than flat monolayers, and more flexible experimentally than supported bilayers. This particular work took advantage of a new approach to the computational problem of contour tracking, consisting in fitting the grayscale digitalization of the contour while minimizing an energy term that accounts for the membrane curvature.

This approach was used to characterize the change of the bending modulus κ of DOPC phospholipidic GUVs in presence of several different antibiotic drugs, as a function of drug concentration, under controlled temperature, ionic strength and pH conditions. These changes seem to originate from perturbations in the membrane organization induced by the drug adsorption to the surface of the membrane [2]. This is interesting since it points to possible non-specific effects of these antibiotics.

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EAU AUX INTERFACES: NOUVEAUX DEVELOPPEMENTS EN PHYSIQUE, CHIMIE ET BIOLOGIE
WATER AT INTERFACES: NEW DEVELOPMENTS IN PHYSICS, CHEMISTRY AND BIOLOGY (April 15-26, 2013)

POSTERS

P1-Ayotte Patrick (Sherbrooke University, Canada): Spectroscopic Demonstration of Ortho-Water Enrichment using a novel Magnetic Focusing Methodology

P2-Cipcigan Flaviu (Edinburgh): Effects of van der Waals forces and hydrogen bonds on the liquid-vapor interface

P3-Dalla Bernardina Simona (Synchrotron Soleil): Connectivity of water molecules confined in Nafion

P4-Habartova Alena (Prague): Structural characterization of the interface between a fatty acid Langmuir monolayer and water using molecular dynamics simulations

P5-Ito Kanae (Fukuoka University): Thermal Behavior, Structure, Dynamic properties of Water Confined in Sephadex G15 Gel

P6-Kaieda Shuji (Lund University): Slow conformational dynamics of myoglobin as seen by internal water molecules

P7-Macron Jennifer (ESPCI) : Reservible adhesion of hydrogels in aqueous media

P8-Mohoric Tomaz (Ljubljana University): Monte Carlo study of the hydrophobic effect in a simple water model

P9-Persson Filip (Lund University): Intermittent Protein Dynamics Coupled to Internal-Water Exchange: Molecular Simulation versus NMR Experiments

P10-Orsi Davide (Parma University): Effects of antibiotic drugs on the mechanical properties of phospholipidic GUVs

P11-Russo Daniela (ILL, France); Nano-confinement tuning of biomolecules for biotechnological interest

P12-Schlesinger Daniel (Stockholm University): Structure of liquid water on a BaF₂(111) surface

P1

**SPECTROSCOPIC DEMONSTRATION OF
ORTHO-WATER ENRICHMENT
USING A NOVEL MAGNETIC FOCUSING
METHODOLOGY**



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ABSTRACT :

While methods for the separation of molecular hydrogen spin isomers are well established, allowing their physico-chemical properties to be investigated, a suitable separation method for the spin isomers of water remains elusive. A recent proposal involving a chromatographic method¹ sparked raging controversies both over its efficacy in separating water spin isomers² and the claims of their unexpected long lifetimes in the condensed phase³. These results prompted some of us to develop a physical separation method inspired by the Stern-Gerlach experiment.⁴ Using this novel methodology, which allows magnetic focussing of ortho-water in a molecular beam, we prepared highly enriched samples of ortho-water in the gas phase, which were then condensed in rare gas matrices where they were stored and investigated spectroscopically.⁵ The abundance of ortho-water and para-water was established using rovibrational spectroscopy, which also allowed to monitor their inter-conversion kinetics. These are the first steps in an ongoing effort to understand the mechanism(s) for their inter-conversion in the condensed phase with applications ranging from magnetic resonance imaging/spectroscopy to astrophysics.

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P2

Effects of van der Waals forces and hydrogen bonds on the liquid-vapor interface

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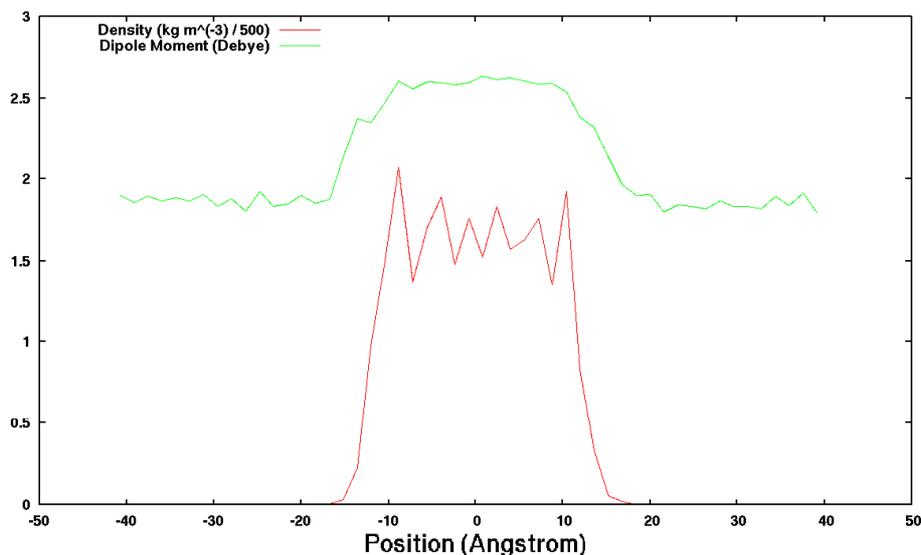


ABSTRACT

We have recently introduced [1] an electronically coarse grained model of water. The model closely reproduces all long-range interactions and many body responses via an embedded quantum oscillator, at a fraction of the cost of *ab initio* methods.

I will review this model and present and a study the properties of its liquid-vapor interface. Since the effects of polarization (giving rise to hydrogen bonds) and dispersion (giving rise to van der Waals forces) can be adjusted independently, the study will focus on the dependence of interfacial properties on the interplay between these forces.

The work is ongoing, and shows promising results. The properties of the liquid phase are reasonably reproduced and the surface tension ($70.5 \pm 1 \text{ mN m}^{-1}$) is within one error bar of the experimental estimate (71.73 mN m^{-1}). The dipole moment of the model also enhances smoothly moving from vapor to liquid (preliminary results shown below).



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P3

Connectivity of water molecules confined in Nafion

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ABSTRACT

The Nafion, a perfluorinated ionomer membrane, is the best electrolyte for fuel cells due to its unchallenged proton conductivity. Water plays a fundamental role in it: it is the pore former, the pore filler and the vehicle of protons through the membrane. Nafion is formed of a hydrophobic perfluorinated backbone with grafted perfluorinated chains sulfonic acid groups. One important feature in Nafion is that swells upon water uptake: a denser H-bond network is formed as hydration increase. With a controlled Relative Humidity (RH) device, we have measured at the AILES beamline of synchrotron SOLEIL [1] the far and mid infrared spectra at room temperature for the following hydration sequences: dry to 11, 11 to 22, 22 to 32, 32 to 52, 52 to 75, 75 to 85, 85 to 100%. We were able to measure simultaneously, with a high resolution, the water connectivity and libration (far IR) bands and the O-H bending/stretching bands (mid IR). Moreover infrared spectroscopy gives access to the vibrational modes of the Nafion (fluorinated backbone and polar head-groups) [2]. This allowed us to characterize the state of water molecules (bonded to the surface, bulk like or free) and also the macromolecular organization of the Nafion.

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P4

Structural characterization of the interface between a fatty acid Langmuir monolayer and water using molecular dynamics simulations

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ABSTRACT

Chemical processes occurring at aqueous-organic-air interfaces play an important role in many fields, from atmospheric chemistry to biology and medicine to nanotechnology. We focus on investigation of physical and chemical properties of one- and multiple-component organic surfactant monolayers at the air-water interface. Using molecular dynamics simulations (MD), we aim to gain detailed microscopic information about structure and dynamics of both the organic monolayer and the adjacent water interface.

In this contribution, we present results of an MD study of Langmuir monolayer comprised of palmitic acid, $C_{15}H_{31}COOH$ (PA). The model consisted of a liquid water slab (6770 SPC/E water molecules) with a palmitic acid monolayer (116 PA molecules) at each of the two slab surfaces (Fig.1). The system was placed into a rectangular cuboid simulation box with a square cross-section, and three-dimensional periodic boundary conditions were employed, yielding infinite, albeit periodic, fatty acid monolayers at both water-vapor interfaces.

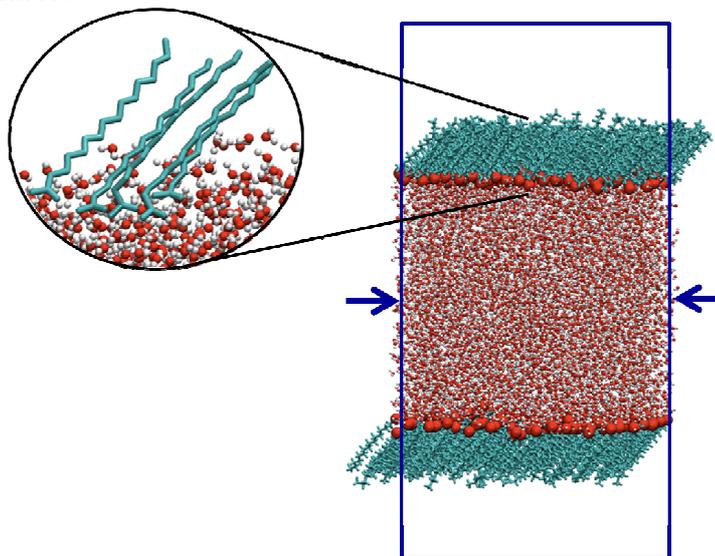


Fig.1 Simulated system consisting of a water slab with PA monolayers at both water-vapour interfaces (alkyl chains rendered in cyan, COOH head groups as red beads).

P4

We performed a set of isochoric-isothermal (NVT) simulations at 293 K and 310 K for different compression stages of the monolayer corresponding to the region of the experimental pressure – area isotherm between 0.19 and 0.38 nm² per PA molecule. This was achieved by varying the lateral box dimensions between 4.7 and 6.6 nm. The PA molecules were modeled using the OPLS-AA force field [1], which has been successfully used in MD studies of Langmuir monolayers of long chain alcohols [2]. Three different sets of atomic charges were tested: (A) standard OPLS-AA charges, (B) RESP charges based on *ab initio* HF/6-31G* calculation, and (C) modified OPLS-AA charges for the PA alkyl chain adopted from MD simulations of phospholipids [3] combined with the RESP charges for the COOH head groups.

Analysis of MD trajectories shows that charge set C fails to reproduce the correct structure of PA monolayer, yielding the alkyl chains too disordered, whereas the other two charge sets, A and B, both provide good description of the overall structural behaviour of the monolayer. In particular, we have found very good agreement of the PA chain tilt angle for different compression stages of the monolayer with available experimental work [4]. The charge parametrizations A and B, however, differ significantly as regards the conformations of the PA molecules in the COOH head group region of the monolayer. These differences in prevailing orientations of the COOH head groups are, in turn, likely to affect the structure and dynamics of the interfacial water molecules. Further simulations and experimental investigations of the fatty acid monolayer – water interface are therefore warranted.

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Acknowledgements

This work was supported by the Czech Science Foundation (grant 13-06181S).

P5

Thermal Behavior, Structure, Dynamic properties of Water Confined in Sephadex G15 Gel

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ABSTRACT

Water in confinement plays an important role in various fields, such as separation in chromatography, biological membrane proteins. The dynamical properties of confined water are essential for understanding physicochemical processes in the systems. So far, most of the porous materials studied were those of either hydrophilic pores, such as Develosil [1], Vycor[2], MCM-41[3], or hydrophobic ones such as activated carbon fiber (ACF) [4]. Recently, a new class of porous materials, periodic mesoporous organosilica (PMO), has been reported [5]. On the other hand, Sephadex G-type gel is made from cross-linked dextran polymer and has flexible interfaces as for biological systems. In this work, the thermal behavior and structure of water confined in Sephadex G15 gel were investigated over a temperature range of 298-173 K at hydration levels h (= mass of water / mass of dry G15 gel) of 0.24-1.38 by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) method, respectively. The ice-melting peaks on the DSC curves were deconvoluted to estimate the amounts of three states of water in G15 with h : free water, freezable bound water, and unfrozen water. The X-ray radial distribution functions of unfrozen water at $h = 0.24$ revealed that the hydrogen bonded structure of water is largely distorted, due to hydrogen bonding with the surface hydroxyl groups of gel substrates, compared with those of freezable bound water at $h = 0.47$ and bulk water. The quasi-elastic neutron scattering (QENS) measurements were performed over a temperature range of 290-245 K. Within the scattering vector range Q of 0.2-1.4 Å⁻¹, the QENS data showed the self-diffusion coefficient of confined water obtained at 290 K is larger by a factor of ~ 2 than that of bulk water. It suggests that the self-diffusion coefficient is influenced by the hydrophobic surface.

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P6

Slow conformational dynamics of myoglobin as seen by internal water molecules

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ABSTRACT

Ever since its atomic-resolution structure was determined in the 1950s, myoglobin (Mb) has served as a prototype for biophysical studies of protein dynamics. The main function of Mb is to transport oxygen in muscle tissues. The O₂ molecule, as well as other small gaseous ligands like CO and NO, interacts with the buried heme iron, but the pathway along which the ligand migrates to and from this binding site is not apparent from the static mean structure. Ligand entry and exit must therefore be controlled by conformational fluctuations, but the details of this "gating" process have not been firmly established. To shed new light on conformationally gated ligand migration in hemoprotein, we have used the water magnetic relaxation dispersion (MRD) method on freely tumbling and immobilized Mb. Since the exchange of internal water molecules is also conformationally gated, water MRD can be used to probe conformational dynamics. In particular, when the protein is rotationally immobilized by chemical cross-links, the MRD method can access the elusive nanosecond–microsecond time scale.¹ Previous crystallography and MD simulation studies indicate at least partial water occupancy in some of the internal cavities of Mb.^{2,3} Most of these cavities have been implicated in ligand migration.⁴ Our MRD results show that Mb contains five internal water molecules with exchange time of $\sim 6 \mu\text{s}$. The temperature dependence of the MRD data suggests that conformational gating of water exchange is rate-limited by entropy reduction rather than disruption of hydrogen bonds. The results suggest that the water molecules are distributed over the cavities in Mb and that they exchange with external solvent via the same microsecond gating mechanism that controls ligand access to the heme.

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Reservible adhesion of hydrogels in aqueous media

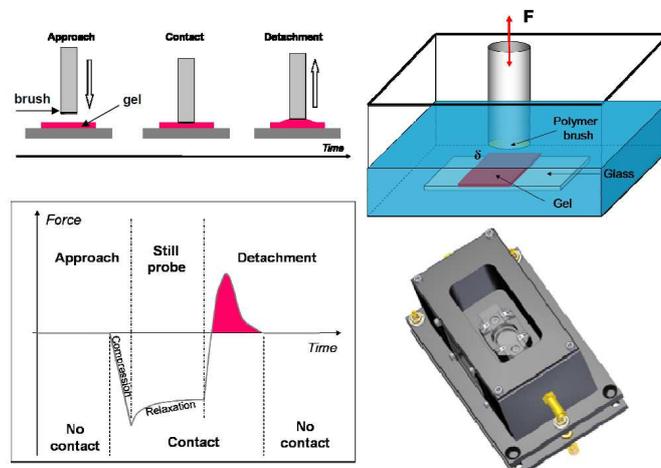
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ABSTRACT

The emergence of new materials showing tunable adhesive properties is a major stake in the biomaterial field. Hence, the quantifying of macromolecular adhesion between two surfaces in aqueous solution is essential to enlighten the understanding of specific interactions at molecular scale.

The experimental setup shown below was previously developed and validated to carry out the macroscopic study of interactions at interfaces^[1-3]. The aim of the present work is now to develop and control the adhesion properties between polymer surfaces by using various specific and reversible polymer-polymer interactions and by controlling the environmental parameters (pH, ionic strength, temperature).



The system under investigation is the adhesion between a hydrogel plate prepared by radical polymerization of N,N-dimethylacrylamide (PDMA), 2-hydroxyethylmethacrylate (PHEMA), acrylic acid (PAA) or acrylamide (PAM) and a Si wafer functionalized with a PAA brush obtained by a “grafting to” method. We will show the impact of the interpolymer complex formation under pH and temperature control on the macroscopic adhesion energy.

P7

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P8

Monte Carlo study of the hydrophobic effect in a simple water model

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ABSTRACT

I studied the hydrophobic effect within the simplified (Ben Naim's) model of water. The main question was whether this simplified model of water is capable of reproducing the thermodynamics of hydrophobic effect (i.e. characteristic temperature dependences of thermodynamic functions of transfer of hydrophobic particle from vacuum to water). Another important aspect of hydrophobic effect is its size dependence (i.e. characteristic thermodynamics changes with the size of the hydrophobic particle). I performed Monte Carlo simulations with hydrophobic particles of several different sizes and at different temperatures.

The results of computer simulations qualitatively agree with the experimentally determined characteristics of hydrophobic effect. The model correctly predicts the change in thermodynamics of hydration of small and large hydrophobic particles. The pair distribution functions and the number of hydrogen bonds in the first hydration shell also confirm the change in mechanism of hydration.

P9

Intermittent Protein Dynamics Coupled to Internal-Water Exchange:

Molecular Simulation versus NMR Experiments

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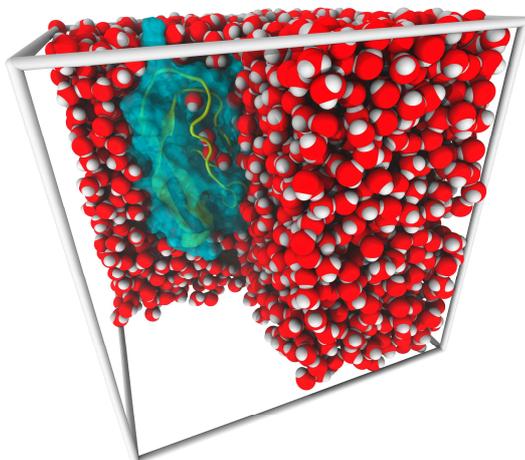


Most globular proteins contain internal water molecules that exchange with external solvent on time scales of 0.01 – 100 microseconds. Because the exchange involves intermittent large-scale conformational changes, internal water molecules can be used to probe slow protein dynamics. Internal water exchange rates can be determined by deuteron magnetic relaxation dispersion (MRD) measurements on fully hydrated but rotationally immobilized (by chemical cross-linking) proteins [1]. For example, the exchange rates of the 4 internal water molecules in the 58-residue bovine pancreatic trypsin inhibitor (BPTI) have been determined by MRD [1,2]. Until recently, the long time scales of internal water exchange were inaccessible by Molecular Dynamics simulation, but the recently reported [3] millisecond MD trajectory for BPTI enables, for the first time, a detailed comparison with experimental internal water exchange rates. Here we report the results of such a comparison, revealing details about the exchange mechanism, suggesting refinements of the MRD model, benchmarking the simulation force field and further show how a general computational approach can be used to study intermittent protein dynamics from molecular simulations.

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3D rendered snapshot from the 1 ms simulation [3] of BPTI (blue) highlighting the four internal water molecules.

P10

Effects of antibiotic drugs on the mechanical properties of phospholipidic GUVs



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ABSTRACT

The study of biomimetic membrane systems and living cellular systems has taken advantage, in recent years, of several microrheological techniques. Among the others, the analysis of thermal fluctuations of giant unilamellar vesicles (GUV) is a recently developed technique based on micro imaging: it consists in investigating the properties of a spherical bilayer membrane, through the classic “flickering” analysis of the fluctuations of the contour of the 2D equatorial section of a GUV, observed by means of phase-contrast microscopy, which are tracked in time; the mechanical properties of the membrane are deduced by the analysis of the power spectrum of the membrane fluctuations [1].

Notably, bilayer vesicles represent a model system more adherent to real biological systems than flat monolayers, and more flexible experimentally than supported bilayers. This particular work took advantage of a new approach to the computational problem of contour tracking, consisting in fitting the grayscale digitalization of the contour while minimizing an energy term that accounts for the membrane curvature.

This approach was used to characterize the change of the bending modulus κ of DOPC phospholipidic GUVs in presence of several different antibiotic drugs, as a function of drug concentration, under controlled temperature, ionic strength and pH conditions. These changes seem to originate from perturbations in the membrane organization induced by the drug adsorption to the surface of the membrane [2]. This is interesting since it points to possible non-specific effects of these antibiotics.

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P11

Nano-confinement tuning of biomolecules for biotechnological interest

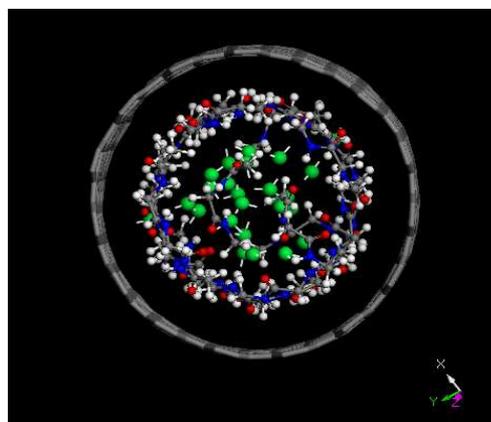


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ABSTRACT

Individual biomolecules can be encapsulated with the purpose of preventing self-aggregation, isolating some allosteric conformational states, protecting them from microbial degradation, and preservation and delivery of drugs. Confinement can be achieved either by the presence of other stable macromolecules or by the wall of a cage as silica matrix, pores or nanotubes. Molecular dynamics simulations have been used to study the confinement packing characteristics of small hydrophilic and hydrophobic bio-molecules [1] in carbon nanotubes (CNT). The self-diffusion coefficients and radial densities of confined peptides and water molecules were calculated. The results show that biomolecules can hardly penetrate in CNT with a diameter smaller than 15 Å, while for a diameter of 20 Å, hydrophilic peptides fill CNT quickly and easily, and organize themselves in geometrical configurations which remind the structural organization of confined water [2]. Hydrophilic peptides adopt a corona like structural organization with a thickness of 3 Å and a minimal distance from the CNT walls equal to 2 Å. In this geometry, all water molecules are segregated towards the central part of the nanotubes. Hydrophobic molecules converge slower into the CNT acquiring a different configuration, always accompanied by water segregation. New opportunities for interesting applications, such as intelligent drug delivery, can be envisaged.



Hydrophilic peptides and hydration water (green dots) as confined in 20 Å CNT

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P12

**Structure of liquid water
on a BaF₂(111) surface**

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ABSTRACT

In this study, we focus on the structure of liquid water on a BaF₂(111) surface under ambient and supercooled conditions. The crystal surface was thought to be a good host for substrate-induced ice formation due to its lattice constant being very close to the one of hexagonal ice Ih. This has been controversially discussed and investigated. Experimental results from x-ray absorption spectroscopy (XAS) studies indicate, however, that the structure of supercooled water on the BaF₂(111) surface still resembles a high density-like liquid.

We perform molecular dynamics (MD) simulations and calculate pair-correlation functions (PCFs) within layers parallel to the surface in order to investigate the structure of the liquid at the interface. Independently, the XAS experiments and the MD simulations show features of strongly compressed water.

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Highly compressed two-dimensional form of water at ambient conditions.
Sci. Rep., 3:1074, 2013

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