waterspain2013

February 7-8, 2013

Zaragoza

Organizers

- **Giancarlo Franzese** (Universitat de Barcelona)
- **Elvira Guàrdia** (Universitat Politècnica de Catalunya)
- **Jordi Faraudo** (Institut de Ciència de Materials de Barcelona, ICMAB-CSIC)
- **Jordi Martí** (Universitat Politècnica de Catalunya)

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Scope

WaterSpain is the workshop that brings together those who do theoretical investigation about water in different contexts in Spain and those that are interested in getting in touch with this community. Its an initiative that aims to seed and foster new collaborations among researchers coming from different backgrounds and sharing the same multidisciplinary interests related to water and its uncommon properties.

PROGRAM

Thursday - February 7, 2013

14:45-15:00 *OPENING*

Session I: Chair J. Martí

15:00-15:20 **Fernando Bresme**
    Computer simulation studies of heat conduction in water: bulk and interfaces

15:20-15:40 **Jordi Faraudo**
    The missing link between the Hydration Force and interfacial water: Evidence from computer simulations

15:40-16:00 **Josep Bonet**
    Dynamics of encapsulated water inside Mo132 cavities, and other aspects of confined water

16:00-16:20 **Juan José Saenz**
    Capillary Adhesion Forces in Atomic Force Microscopy

16:20-16:40 **Giancarlo Franzese**
    Water at biological and inorganic interfaces

16:40-17:00 **Claudio Cerdeiriña**
    Compressible cell liquids for waterlike liquid-liquid criticality

17:00-17:40 *COFFEE BREAK AND POSTER SESSION*

Session II: Chair G. Franzese

17:40-18:00 **Enrique Lomba**
    Simple water-like models in one dimension

18:00-18:20 **Carlos Vega**
    Describing water using computer simulation

18:20-18:40 **José Luis F. Abascal**
    Propiedades del agua en condiciones extremas: región subenfriada y presiones negativas

18:40-19:00 **Chantal Valeriani**
    Cavitation of water at negative pressure

19:00-19:20 **Eduardo Sanz**
    The critical size of ice clusters in water freezing from simulations

21:30-23:00   *DINNER*

Friday - February 8, 2013

Session III: Chair J. Faraudo

9:00-9:20 **Enrique Sanchez-Marcos**
Computer simulations of metal ions in aqueous solutions

9:20-9:40 **Diego González-Salgado**
Molecular simulation of the {methanol+water} system: structure and thermodynamics

9:40-10:00 **Felix Llovell**
Insights into the behavior of organic compounds in water

10:00-10:20 **Carles Calero**
Simulation and theoretical study of the H^1-NMR relaxation times in bulk water and aqueous ionic solutions

10:20: 10:40 **Ronen Zangi**
The Induced Interactions of Water

10:40-11:20 ***COFFEE BREAK AND POSTER SESSION***

Session IV: Chair E. Guàrdia

11:20-11:40 **José M. Soler**
Efficient van der Waals density functional simulations

11:40-12:00 **Fabiano Corsetti**
The structure of water from first-principles simulations with van der Waals interactions

12:00-12:20 **Pepa Cabrera-Sanfelix**
Water on surfaces from first-principles: binding and reactivity

12:20-12:40 **Paolo Nicolini**
Force matching algorithm: towards classical force fields for water with ab initio accuracy

12:40:13:00 **Rossend Rey**
Energy pathways for rotational relaxation in liquid water

13:00-13:30 ***DISCUSSION***

Talks

"Computer simulation studies of heat conduction in water: bulk and interfaces"

Fernando Bresme

Chemical Physics Section, Department of Chemistry, Imperial College London, UK
and
Department of Chemistry, Norwegian University of Science and Tecnology, Trondheim

The investigation of water has attracted the interest of experimentalists and theoreticians. There are now well-established empirical water models that describe surprisingly well the thermodynamic and coexistence properties of water and ice in a wide range of thermodynamic conditions. Similarly, steady progress is being made in the *ab initio* simulation of water. Despite all these advances the investigation of heat transport in water has been largely neglected. This is surprising since water features the largest thermal conductivity of any molecular liquid. Also, the thermal conductivity of water features an anomalous dependence with temperature. The high thermal conductivity of water contributes towards the efficient thermal regulation of living organisms, e.g., by providing a medium to efficiently relax excess energy in biomolecules. Water is also widely used in heat management applications at industrial and nanomaterial levels. Hence, a microscopic knowledge of the mechanisms determining heat transport in bulk and at interfaces is desirable. In this talk, I will discuss our recent work on non-equilibrium molecular dynamics simulations of heat conduction in bulk water and in water-nanomaterial/biomolecule interfaces. Simulations provide a unique approach to quantify heat transport in a wide range of conditions, including extreme pressures and nanoscale interfaces which are difficult to tackle using current experimental approaches.

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"The missing link between the Hydration Force and interfacial water: Evidence from computer simulations"

Jordi Faraudo

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The continuous increase in computer power and the development of new algorithms for large-scale Molecular Dynamics Simulations (MD) has made possible its use as a kind of computational microscope to understand and predict the macroscopic/mesoscopic behaviour of matter from an atomistic and molecular view point.

In this presentation, I will review MD simulation studies relevant to the understanding of the physical origin of the hydration force. I'll focus on results from simulations of realistic models of systems of "real life" interest, skipping results coming from simplified models. The results presented here show a molecular perspective on how this repulsive, stabilizing force comes from interfacial water.

Summarizing, we can say that MD simulations show strong polarization and non-local dielectric response of interfacial water. This anomalous dielectric response of interfacial water has a deep impact on the electrostatic surface potential in hydrophilic charged or neutral surfaces. We propose that the hydration force is the electrostatic force arising from this strong polarization.
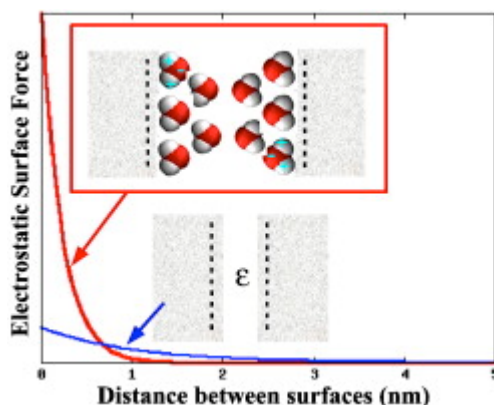

Fig. 1: Sketch of typical electrostatic force between two soft surfaces (for example, surfactant layers) calculated using MD simulations with explicit solvent or replacing water by a dielectric constant.

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"Dynamics of Encapsulated Water inside Mo132 Cavities, and other aspects of confined water"

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The structure and dynamics of water confined inside the almost rigid metal-oxide nanocapsule polyoxomolybdate $[\{(Mo)Mo_5O_{21}\ (H_2O)_6\}_{12}\{Mo_2O_4(L)\}_{30}]^{-72}$, where L stands for either the ligand $SO_4^=$ (sulphate), $HCOO^-$ (formiate), or benzoate have been studied by means of molecular dynamics simulations under ambient conditions [1,2]. We find that the characteristic three-dimensional hydrogen bond network present in bulk water is distorted inside the cavity where water organizes instead in concentric layered structures, in the case of the sulphate, or in three-dimensionally connected structures, in the case of the formiate. Hydrogen bonding, tetrahedral order, and orientational distribution analyses indicate that these layers are formed by water molecules hydrogen bonded with three other molecules of the same structure. The remaining hydrogen bond donor/acceptor site bridges different layers as well as the whole structure with the hydrophilic inner side of the cavity. In the case of the sulphate, the most stable configuration of the layers is thus that of a *buckyball* with 12 pentagons and a variable number of hexagons. In the case of the formiates, small variations in the properties of the inner side of the cavity cause strong modifications of the structure of water as compared with the sulphate. In both cases we find a very good agreement with the experimental X-ray data found in [3].

The main modes of motion at short times are correlated fluctuations of the entire system with a characteristic frequency. Switches of water molecules between layers in the case of the sulphate are rare events, due to the stability of the layers. However, the less stable structures for the case of the formiates permit a major transfer of water molecules across the nanocapsule. At long times, the system shows a power law decay in properties like the fluctuations in the number of molecules in the structures and the total dipole moment. Such behavior has been attributed to the complex relaxation of the hydrogen bond network, and the exponents found are close to those encountered in bulk water for the relaxation of the potential energy. The dynamic phenomenology observed has many points in common with the relaxation of glassy systems as, for instance, with the lack of universality of the exponents found.

Finally, when we use a rather larger ligand as the benzoate one can observe modifications in the catalytic effect of the nanocapsule [4].

Our results reveal the importance of the competition between the confinement and the long-range structure induced in this system by the hydrogen bond network. The results are compared with slightly different systems, as the reverse micelles, that however display a rather different behavior.

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[2] Garcia-Ratés, *Structure and dynamics of confined liquids: Giant polyoxometalates and CO2-brine mixtures*, Doctoral Thesis, Universitat Rovira i Virgili (Tarragona, 2011)

[3] Mitra, T.; *et al.*, *Gated and Differently Functionalized (New) Porous Capsules Direct Encapsulates' Structures: Higher and Lower Density Water*, CHEMISTRY-A EUROPEAN JOURNAL (2009), **15**, 1844-1852

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"Capillary Adhesion Forces in Atomic Force Microscopy"

Juan José Sáenz

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The sticking effect between hydrophilic surfaces occurring at increasing relative humidity (RH) is an everyday phenomenon with uncountable implications. Extensive study of the capillary forces acting at micro- and nanoasperity contacts has been performed over the last few years. In spite of the diversity of the experimentally obtained adhesion force versus RH curves, all the reported curves have one feature in common: starting from low RH values the adhesion force increases with humidity. Here we discuss on the inverse effect [1]: even in dry environments (at low humidity values) the adhesion force decreases with increasing RH. Starting from 0% RH we observe a monotonous decrease of the adhesion force for the entire RH range between two hydrophilic materials. It is shown that this unexpected result is related to the actual shape of the asperity at the nanometer scale: a model based on macroscopic thermodynamics predicts this decrease in the adhesion force for a sharp object ending in an almost flat nanometer-sized apex, in full agreement with experiments. This anomalous decrease is due to the fact that a significant growth of the liquid meniscus formed at the contact region with increasing humidity is hindered for this geometry. These results are relevant in the analysis of the dynamical behavior of nanomenisci [2]. They could also have an outstanding value in technological applications, since the undesirable sticking effect between surfaces occurring at increasing RH could be avoided by controlling the shape of the surface asperities at the nanometric scale.

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"*Water At Biological And Inorganic Interfaces*"

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We study, by simulations and analytic approach, the behavior of water in hydrophobic nanoconfinement or at the interface with proteins [1,2]. We analyze the metastability of supercooled liquid water with respect to ice formation [3]. For metastable liquid water between hydrophobic walls, at nanoscopic separation, we study how the diffusion constant parallel to the walls depends on the microscopic structure of water. We clarify how the interplay between breaking of hydrogen bonds and cooperative rearranging regions of 1-nm size gives rise to the diffusion extrema in nanoconfined water and offers a possible explanation for the ultrafast transport of water in nanochannels with size smaller than 1 nm [4,5]. For water confined in disordered nanochannels, we find a dramatic decrease of compressibility, thermal expansion coefficient, and specific heat at cryogenic temperature, relevant for the preservation of food and organic materials [6,7]. For water adsorbed on the protein surface, we calculate the temperature dependence of the relaxation time of the dynamics of the hydrogen bond network, predicting two dynamic crossovers in the supercooled regime, related to two specific heat maxima. The first is caused by fluctuations in the hydrogen bond formation, and the second, at a lower temperature, is due to the cooperative reordering of the hydrogen bond network. Experiments confirm our prediction [8,9].
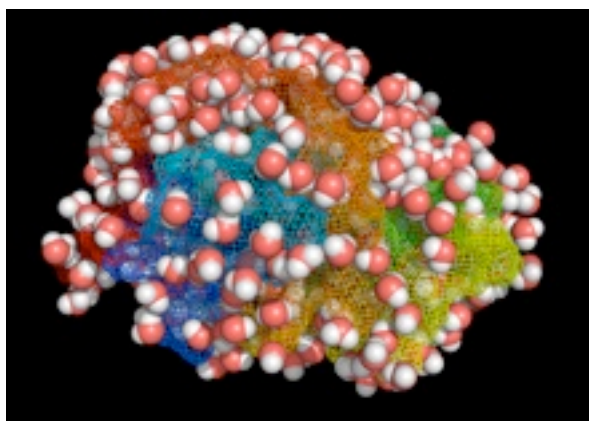
Water adsorbed on lysozyme protein.

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"Compressible Cell Liquids for Waterlike Liquid-Liquid Criticality"

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The study of phase transitions for pure substances in which two liquids of different density coexist in equilibrium acquired great interest in 1992 with water's second critical point hypothesis by Stanley and coworkers.[1] Such waterlike liquid-liquid phase transitions have been claimed from experiments for other fluids[2-5] and studied via simulations of water models and of fluids characterized by isotropic core-softened intermolecular potentials (see, e.g., Refs. 6 and 7). Despite recent work raising doubts on results from simulations,[8] it seems appropriate to investigate the nature of waterlike liquid-liquid criticality.

One may first inquire about the universality class of this sort of continuous phase transitions. This issue has an obvious intrinsic interest, but it is also relevant with a view to applying finite-size scaling techniques to simulation data.[9] Kurita and Tanaka[5] and Sciortino and coworkers[10] have asserted that, like for the liquid-gas case, waterlike liquid-liquid criticality should be of Ising character. On the other hand, Brovchenko et al.[11] have pointed out that it could belong to the universality class of the random-field Ising model. To the best of our knowledge, there is neither strong experimental evidence nor a detailed enough theoretical analysis on this particular question.

Here we tackle the problem by studying the properties of a simple cell model. Consider the space divided in cells which contain one particle and have two accessible volumes, say, v_+ and v_-. Particles in nearest-neighbor cells interact via a discretized energy $-\varepsilon_0$, which is supplemented by an additional energy $\delta\varepsilon$ whenever two adjacent cells are in the "+" state. Such compressible cell liquid (CCL) model can be mapped onto the Ising model, and is in certain respects related to a previously reported water model[12] and in others to the so-called compressible cell gases for asymmetric liquid-gas criticality.[13]

Application to water's hypothetical second critical point entails incorporating entropic effects ascribed to the geometric selectivity of hydrogen bonding. Such a task is accomplished by suitably imposing constraints on the free volume that a particle can explore in its cell. Specifically, when local low-density and low-entropy states are energetically favorable (that is, when low-temperature water's essential microscopic features are implemented), one finds that the slope of the coexistence line in the temperature-pressure plane dp_σ/dT is negative and that the isobaric thermal expansivity α_p diverges to $-\infty$ at criticality, in accord with available information. Correspondingly, "soft-core-like" behavior (viz., $dp_\sigma/dT > 0$ and $\alpha_p \to +\infty$) is obtained when low-density and high-entropy states are energetically favorable.

In summary, we will show that (Ising-like) CCL models provide theoretical support to the phenomenon of liquid-liquid transitions in pure substances. Some variants are consistent with what has been conjectured for water's liquid-liquid critical point, others with what has been learned from core-softened models. Implications of CCL's for isostructural solid-solid transitions in Cs, Ce, and certain rare earth metals[14] as well as for crystalline systems with short-range interactions[15,16] will be briefly outlined.

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"Simple water-like models in one dimension"

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We review the behaviour of a series of one-dimensional lattice models, mostly characterized by the presence of various repulsive ranges, that induce the typical anomalous behaviour present in water like fluids. We will see how the interplay between the attractive and repulsive ranges allows for a fine tuning of the phase diagram, that can reproduce qualitatively the behaviour of water and other singular liquids like bismuth. The simplicity of the model enables a clear understanding of the essential physics behind the much discussed singular behaviour of tetrahedrically coordinated liquids.

"Describing water using computer simulation"

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A important problem if one wishes to perform computer simulations of water is the description of the interaction energy between molecules, i.e the water potential.Such a potential can be obtained either from first principles or by using empirical potentials.
In our research group we have calculated the phase diagram of water using a number of different empirical potential models. Only the TIP4P model was able to provide a qualitatively correct description of the phase diagram of water. The parameters of this model were then fine-tuned in order to improve the melting point and overall phase diagram, leading to the TIP4P/2005 model. It will be shown that TIP4P/2005 provides a good description of the vapour-liquid equilibria,surface tension, global phase diagram, ice properties, maximum in density, structure, equation of state at high pressures, diffusion coefficient, and viscosity.The model is good enough to allow us to explore new physical phenomena for which the experimental results are limited or are unavailable, for instance: the existence of a quasi-liquid layer on the freesurface of ice, the existence of a liquid-liquid transition in super-cooled water,the possible appearance of plastic crystal phases in the phase diagram of water,and the impact on nuclear quantum effects on the properties of water. Results will be presented for these important problems. Nevertheless, the model does have some deficiencies andit should be improved by incorporating polarisation and quantum statistics in the description of water. All said and done, it is surprising to see how much understanding of water can by achieved by using simply 3 charges and 1 Lennard-Jones centre.

"Propiedades del agua en condiciones extremas: región subenfriada y presiones negativas"

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Trabajos experimentales recientes sobre la ecuación de estado del agua en la región subenfriada permiten por vez primera chequear capacidad predictiva de los modelos en la zona en que se presume la existencia de una transición líquido-líquido. La comparación de estos datos experimentales con las predicciones para el modelo TIP4P/2005 muestran una excelente concordancia. Debe esperarse por tanto que los resultados de simulación de este modelo se aproximen (incluso cuantitativamente) a los del agua real. Por ello hemosllevado a cabo exhaustivas simulaciones para localizar el punto crítico de la transición (LLCP). Hemos calculado también la línea de compresibilidad máxima(línea de Widom) que emana desde el punto crítico y se adentra en la región de presiones negativas. La línea de Widom acaba uniéndose con la línea de densidades máximas justo en el punto en que ésta cambia de pendiente(``retracing TMD"). Consideraciones termodinámicas han demostrado que, en el caso de TMD reentrante, la línea de Widom debe continuar con otra de compresibilidad mínima. Nuestros cálculos con el modelo TIP4P/2005 muestran la continuidad de ambas líneas y su contacto con la TMD a aproximadamente -1000 bar. También por consideraciones termodinámicas, el hecho de que la TMD sea reentrante permite descartar que la espinodal sea reentrante. Este hecho permitiría descartar uno de los escenarios alternativos a la existencia de un LLCP. Hemos calculado la espinodal líquido-vapor y hemos comprobado que (como se esperaba) es más o menos paralela a la TMD en la zona de muy bajas temperaturas.

"Cavitation of water at negative pressure"

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Liquid water is undoubtedly the most relevant molecule for living organisms both at a macroscopic scale (the human body consists of 65-70 % of water) and at a microscopic scale (a human cell consisting of 70-80 % of water). Thus, the study of physical and chemical properties of water is of fundamental interest from a biological and a medical point of view. Bubble nucleation is relevant in many diferent technologically relevant contexts, such as explosive boiling[1], cavitation erosion[2] and sono-chemistry[3]. In spite of the practical relevance of these phenomena, the mechanism by which the vapor phase nucleates from a homogeneous, metastable liquid is still under debate. In this work, we report numerical a study of cavitation of TIP4P/2005[4] water at negative pressures. To be able to capture the kinetics of bubble formation, we perform Molecular Dynamics simulations with the GROMACS 4.5 package[5,6].

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"The critical size of ice clusters in water freezing from simulations"

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Despite the extraordinary importance of water freezing, little is known yet of the mechanism by which this process takes place. Computer simulations offer the chance to get a molecular description of this phase transition. In fact, many simulation studies have been pursued with this motivation (see, e.g. J. Chem. Phys. 136, 054501 (2012) and references therein). However, the results are contradictory in terms of the size of the critical ice clusters and the rate of ice crystallization. We present a systematic study of the size of critical clusters as a function of temperature for some of the most widely used water models making use of state-of-the-art parallel computing. The size of the critical cluster sharply decreases as the supercooling is increased. We observe clusters with as many as 10^4 molecules for a supercooling of ca. 20 K below freezing. We compare our results with predictions from Classical Nucleation Theory.

"Computer simulations of metal ions in aqueous solutions"

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The main topic of the research team has been the theoretical modeling of metal-ion containing aqueous solutions. We have applied the hydrated ion concept to the semi-continuumquantum-mechanical (QM) approach as well as to statistical simulations. This strategy allowed us to handle in a convenient way the strong many-body interactions associated to the ionpolarizable solvent molecule interactions. The key point is to recognize that multi-valent cations are tightly joined to a discrete number of water molecules forming the hydrated ion. This entity or hydrolyzed forms of it, are the active species in solution rather than the bare ion. On this basis a hydrated ion-water (HIW) model was used to develop intermolecular interaction potentials to be used on classical molecular dynamics(MD) and Montecarlo (MC) simulations.[1] The potentials were built to reproduce QM interaction energies. The intrinsic dynamics of the hydrated ion is described by an additional ion-first shell water molecule (IW1).[2] This model has been applied along the last two decades to mutiply-charged metal cations of earthalkalines,d-transition metals, and radioactive species. Extensions of these potentials to deal with square-planar complexes (Pd^{2+}, Pt^{2+}, AnO_2^{2+}) has leaded to find a particular hydration structure of the axial region, which was called *meso-shell*.[3] Likewise, the hydration of counterions, such as the halide anions has also studied by coupling polarizable water model,[4] and more recently the hydrated ion concept has been adapted to the case of metal ion complexes, such as Cu^{2+} or Pt^{2+}.[5] X-ray absorption spectroscopies, EXAFS and XANES, have been used to provide experimental information of the closest ion environment. Simulations of EXAFS and XANES spectrum have been proposed to get insight into the interpretation of the spectra, and their sensitivity to characterize elusive hydration shells.[6] The synergy derived of the theoretical -experimentalcombination has allowed the elucidation of the hydration structure of the heaviest metal cation experimentally known, the Cf^{3+} cation. An extension of the HIW model allowing the exchange of water molecules between the first hydration shell and the bulk had to be developed to properly describe the Cf^{3+} hydration structure.[7] Some applications of the combined use of computer simulations ans XAS spectroscopy will be presented.

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"Molecular simulation of the {methanol+water} system: structure and thermodynamics"

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The {methanol + water} system has been extensively studied during the last several decades due at least for two reasons. On the one hand, it exhibits a strong anomalous behaviour reflected in high values of the excess thermodynamic properties. On the other hand, since methanol is the more simple molecule with an hydrophilic head and an hydrophobic tail, it is considered as the most simple system model for the description of biological macromolecules in water. During several decades, the theory proposed by Frank and Ives [1] was considered as the right description of the behaviour of this system at molecular scale. However, recent neutron diffraction experiments [2-4] have put in question theses ideas.

The molecular simulation is a useful tool for providing new light to this point. However, results are dependent on the intermolecular potential used for describing the system and up to now, a detailed analysis of the ability of the pairwise intermolecular potentials for the prediction of the structure and the thermodynamics is lack. Thus, in this work, extensive molecular simulations were carried out for this system using the most popular models for methanol and water. From these simulations, the excess properties and the radial distribution functions were computed and were compared criticality with the experimental data.

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"Insights into the behavior of organic compounds in water"

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The presence of organic compounds in water is a matter of concern from a toxicological point of view. Organic compounds include a massive family of molecules that appear in industrial streams and contaminate water resources. However, the toxicity of those compounds may vary considerably, going from low aquatic toxicity (non-halogenated hydrocarbons) to aromatic compounds (for example, benzene, naphthalene, benzo(a)pyrene) which are relatively toxic and potentially carcinogenic. In order to avoid the contamination of water, it is necessary to accurately know the thermodynamic behavior of aqueous solutions of these compounds. In particular, properties like the solubility of hydrocarbons in water is of crucial importance, in order to determine the amount of compounds present in an aqueous phase. Although a modeling approach would be highy desirable from a practical point of view, the microscopic nature of the associating interactions among water molecules results in some anomalous properties that are challenging to model: the solubility of the hydrocarbon in water is several orders of magnitude lower than the solubility of water in the hydrocarbon-rich liquid phase. Moreover, the solubility of the hydrocarbon exhibits a minimum at room temperature, while the solubility of water is a monotonic function that increases with temperature. Most of the available (software) thermodynamic models fail in estimating those solubilities and their particular behavior with temperature and pressure.

This contribution is intended to show a new class of equations of state, based on statistical mechanics, able to capture the main physical features of the molecules and, as a consequence, empowering its predictive ability to model those complex systems. We will present the capabilities of the soft-SAFT equation of state [1] as compared to simulation and experimental data. Soft-SAFT (Statistical Associating Fluid Theory) is a Statistical Mechanics-based equation that uses a Lennard-Jones as the interaction potential between the segments forming the molecules, while the association is taken into account through Wertheim's theory. An accurate molecular model for water within the soft-SAFT equation of state is presented and used to describe the solubility of organic compounds in water [2]. In addition, molecular dynamics simulations are used to provide some insights into the transport (diffusion) properties of some of these organic molecules in water as a function of temperature. The combination of soft-SAFT and molecular simulations allows a throughout characterization of the thermodynamic and kinetic behavior of water-hydrocarbon mixtures, as well as the calculation of the selectivities among different organic compounds in water.

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"Simulation and theoretical study of the H^1-NMR relaxation times in bulk water and aqueous ionic solutions"

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Understanding the relaxation of the nuclear spin in fluids is of fundamental interest and related to important applications such as nuclear magnetic resonance (NMR). The chemical shift spectra and the relaxation times (T_1 and T_2) obtained from NMR experiments are among the most reliable techniques to determine the molecular structure and chemical properties of a given substance. In fluid samples, the relaxation properties of the nuclear spin are different from those observed in solids due to the existence of rapid molecular motions of large amplitude and random character. In molecular fluids, the relaxation time for the nuclear spin is determined by its interaction with other spins through dipolar and quadrupolar coupling and also by the sudden changes of the chemical shift local field due to mechanical rotations [1]. To compute the NMR relaxation times T_1 and T_2 in a fluid it is necessary to faithfully describe the rapid random motions that particles undergo due to collisions with other particles. Traditionally, assumptions on the nature of the random molecular motions were made to simplify the problem. The most extended treatment, due to Debye, assumes that both the rotations of a molecule and the relative translations of two molecules could be described by a diffusion equation. In that picture, the angular Brownian motion of the water molecules are given by very small regular angular steps. In recent years, however, a combination of theoretical and experimental breakthroughs has provided consistent evidence suggesting a dominant reorientation of water via a mechanism involving large-amplitude sudden angular jumps [2]. Consequently, many of the interpretations of experiments and theoretical predictions based on Debye's picture, in particular those regarding the relaxation properties of nuclear spin of protons in water, need to be revised.In the present work we have devised a way to calculate the NMR relaxation times T_1 and T_2 for molecular fluids directly from the trajectories of MD simulations, with no assumptions made regarding the nature of the molecular motions. In particular, we have computed T_1 and T_2 for the nuclear spins of protons of bulk liquid water as described by different water models (SPC-E, TIP3P, TIP4P, and TIP4P/2005) for a wide range of temperatures and compared them with experiment. We have compared the results obtained from the analysis of MD simulations with different analytical models and quantitatively assessed the relative importance of the different contributions to the relaxation times. Furthermore, we have studied the dependence of the relaxation times T_1 and T_2 on the concentration of different salts containing either small (kosmotropic) or big (chaotropic) ions.

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"The Induced Interactions of Water"

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Solvent induced interactions can lead to few unexpected phenomena. In this talk I will present few examples of such interactions. In particular, the origin of hydrophobic forces, their modulations by salts (the Hofmeister Series) and urea, as well as, the attraction between like-charged ions.

"Efficient van der Waals density functional simulations"

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Van der Waals dispersion interactions are a non-local electron-electron correlation effect, that must be described by an appropriate electron density functional. Dion et al [1] have proposed such a true ab initio, universal and general-purpose vdW-DF functional, capable of describing quantitatively the week dispersion interactions, without compromising the accuracy of the best generalized gradient approximation (GGA) functionals for stronger ionic, covalent and metallic bonds. Subsequent vdW-DF versions [2-4] provide even more accurate energies and equilibrium distances. The direct evaluation of vdW-DF for large systems is very expensive, however, because it requires a double integral in real space. We have presented [5] an implementation that avoids this N^2 scaling by applying Fourier convolution techniques to an accurately interpolated kernel. The resulting method scales as $N\log N$ and it allows to perform vdW-DF simulations of essentially any system that can be simulated with GGA. This method provides a much improved description of liquid water [6] and clathrate hydrates [7] over that of GGA functionals.

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"The structure of water from first-principles simulations with van der Waals interactions"

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Ab initio molecular dynamics (AIMD) simulations of water using density functional theory (DFT) with semi-local (GGA) exchange-correlation functionals have been shown to be fairly inaccurate when comparing with experimental results for the structural and diffusive properties of the liquid. Using the SIESTA [1] DFT method we present an AIMD study of liquid water using several non-local functionals that aim to provide a description of van der Waals (vdW) interactions, missing in conventional GGA functionals. For our simulations we employ large system sizes of up to 200 molecules, allowing us to check for finite size errors. We discuss the effect of vdW interactions on the equilibrium density and compressibility of liquid water at ambient conditions, the structural information given by the radial distribution function for a range of densities, and the diffusivity, showing an overall improvement with respect to GGA [2]; in particular, the equilibrium density is noticeably improved, and the diffusivity is reproduced in good agreement with experiment without the need for temperature rescaling [3].

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"Water on Surfaces from first-principles: Binding and Reactivity"

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Most surfaces are covered by a thin layer of water under ambient conditions. In spite of its importance in biology, material sciences and chemistry, many of the properties and growth of this wetting are not fully understood yet. From the environmental point of view, the molecular level investigation of the water adsorption on ionic and carbonaceous substrates is fundamental to determine the microscopic behaviour of certain aerosols and to estimate their chemical response under different atmospheric gases. Density functional theory (DFT) calculations have been applied to study the most favourable water adsorption geometry at monolayer and at the submonolayer coverage on NaCl(100).[1, 2] The first steps of the deliquescence, occurring at the monolayer regime, are characterized by the spontaneous emergence of chlorine ions on top of the water layer.[3] Graphene represents a good surface science model to reproduce the water structure and interaction with carbonaceous particles. By DFT we show the enhanced water reactivity on defective graphene compared with pristine graphene.[4, 5]
Comprehending water wetting on metal substrates is basic to understand phenomena such as corrosion and surface reactivity. Self-organization of water on metallic surfaces occurs well by molecules clustering in a 3D-phase, by wetting the surface following a well-ordered 2D-adlayer or even, by undergoing partial dissociation within the water layer. A review of water wetting on different substrates such as Cu(110), Ru(0001) and O(2x1)/Ru(0001) will discuss the competition of self-assembled structures of different dimensionality, possible water dissociation, water induced surface reconstructions and substrate induced cooperative effects on water-water interactions.[6-9]

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"Force matching algorithm: towards classical force fields for water with ab initio accuracy"

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The simple functional forms of the interaction potential used in the classical force fields (FFs) could seem a rough approximation. On the other hand it has been shown that they can successfully reproduce some of the dynamical, thermodynamical and structural properties in certain temperature ranges[1]. In addition, classical FFs are the only ones that allow to perform long-time/bigsize simulations. Concerning this, the force matching algorithm[2] has been used in the last decade todevelop classical FFs for aqueous systems ([3] and references therein). The force matching algorithm isbased on a least-squares fitting of the differences among classical and reference (*ab initio*[4]) forces. In our contribution, this methodology is applied to parameterize new classical FFs for water in which polarization is taken into account explicitly, by using polarizable point dipoles method and damping functions[5]. Structural and dynamical properties is computed for the presented water models and they show a good agreement with the *ab initio* ones.
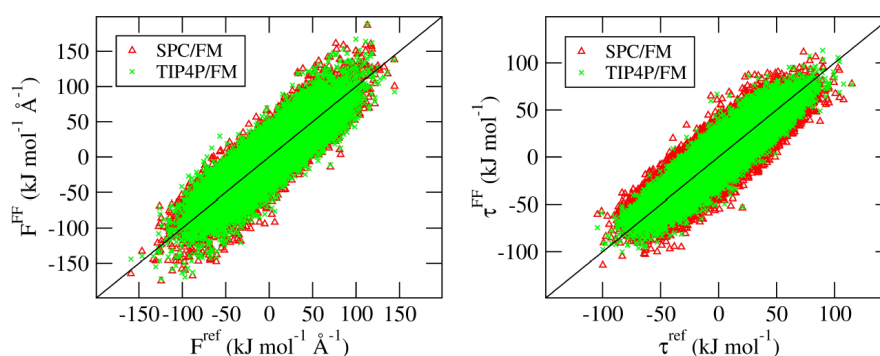
Scatter plots for simple point charges (SPC/FM) and four sites (TIP4P/FM) models obtained from the force matching algorithm. Classical forces (left panel) and torques (right panel) are plotted versus the reference ones.

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"Energy pathways for rotational relaxation in liquid water"

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The ultrafast relaxation of a rotationally excited $H2O$ molecule in pure liquid water is investigated by means of classical nonequilibrium Molecular Dynamics simulations and a power and work analysis. This analysis allows to follow in detail the mechanism of the energy transfer from the excited $H2O$ to its water neighbors, i.e. which water molecules receive the energy and in which degrees of freedom. It is found that the dominant energy flow is to the four hydrogen-bonded water partners in the first hydration shell, largely dominated by those partners' rotational motion. The variation of the energy flow characteristics with rotational axis, initial rotational energy excitation magnitude, method of excitation, and temperature has been adressed as well.

Posters

"Critical behavior of a water monolayer under hydrophobic confinement"

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We study by Monte Carlo simulations the low temperature phase diagram of a water monolayer confined between hydrophobic walls separated by $h \approx 0.5$ nm. By finite size scaling of the appropriate order parameter, we find a liquid-liquid critical point (LLCP) in the universality class of the two-dimensional (2D) Ising model in the limit of infinite walls. However, for wall sizes up to hundreds of times larger than the monolayer thickness h, the LLCP is better described by the 3D Ising model universality class, something unexpected based on studies for simple liquids. We ascribe this result to the strong cooperativity and the low coordination number of the hydrogen bond network.

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"Methane-graphene potential of mean force from DFT-based molecular dynamics simulations"

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A proper description of the interface of water with non-polar materials at the atomic level is a fundamental problem which has long been recognized to hold the key to the understanding of the hydrophobic interaction between apolar particles. Such water-mediated effective interaction plays an important role in phenomena as diverse as protein folding, lipid aggregation, forces between hydrophobic surfaces in water, or chemical self-assembly of macroscopic objects.

In this work, our goal is to establish a benchmark calculation for the potential of mean force of the interaction between a methane molecule and a graphene plane in water employing restrained ab-initio (DFT-based) molecular dynamics simulations. With such model system we intend to quantitatively characterize the generic interaction between a small hydrophobic solute (methane molecule) and an extense hydrophobic surface (graphene plane). In addition, we analyzed the dynamical and structural properties of water hydrating the methane molecule and at the interface with the graphene plane and relate such properties with the features of the calculated potential of mean force. The result could be used in coarse-grained models to take into account the effect of the hydrophobic interaction in realistic systems relevant to experiment.

Figure: Potential of mean force of the methane-graphene interaction in water as a function of their mutual distance. Circles: result obtained from restrained AIMD simulations.Rhombus: Potential of mean force calculated from classical ABF MD simulations.

# *"The hydrophobic effect as the driving force for Giant Charge Inversion and Ionic Specificity effects in Colloids"*

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Our simulation and experimental work identifies the hydrophobic effect as the driving force for both ion specific effects and charge inversion [1]. In the case of organic anions, our molecular dynamics (MD) simulations with full atomic detail show explicitly how the large adsorption free energies found for hydrophobic colloids are transformed into large repulsive barriers for hydrophilic colloids. Simulations confirm that solvation free energy (and hence the hydrophobic effect) is responsible for the build up of a Stern layer of adsorbed ions and charge inversion in hydrophobic colloids and it is also the mechanism preventing charge inversion in hydrophilic colloids. Overall, our experimental and simulation results suggest that the interaction of monovalent ions with interfaces is dominated by solvation thermodynamics, that is, the chaotropic/kosmotropic character of ions and the hydrophobic/hydrophilic character of surfaces. In the case of hydrophobic colloids, our experiments show that charge inversion is induced by chaotropic inorganic monovalent ions but it is not induced by kosmotropic inorganic anions. For organic anions, giant charge inversion is observed at very low electrolyte concentrations. In addition, charge inversion disappears for both organic and inorganic ions when turning to hydrophilic colloids.
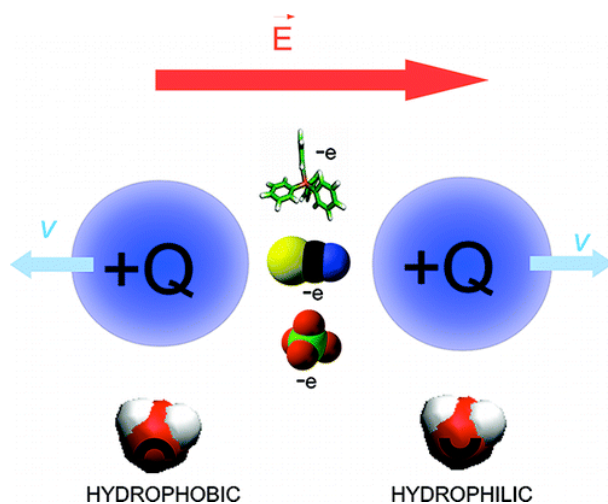
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"Water cavitation in carbon nanotubes at negative pressures"

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The aim of this work is to investigate the heterogeneous nucleation of water vapor inside carbon nanotubes in the unstable/metastable regions of the bulk water. The simulations were performed with the TIP4P/2005, which has been extensively tested during the last years showing it is the most accurate rigid empirical model developed to date. We have combined this water models with carbon potential from OPLS-AA to model the carbon nantubes. Unlike the TIP4P-2005, the force-fields to model carbon interactions are still subjected to certain level of uncertainty.

We have set up configurations of single wall carbon nanotubes (swcnt) in water. The final configurations were chosen to investigate the behaviour of bulk water and confined water. These configuration were used to investigate the heterogeneous nucleation of vapour in water. Vapour nucleation deforms the nanotube. Nucleation is observed outside the nanotube only, on its surface, and not in the confined region. The latter observation is most likely connected to the pressure imbalance across the curved surface. Additional simulations in the NVT ensemble were performed to investigate the cavitation inside the nanotube, by adding water inside the nanotube only with the same dimeter.

We have computed several cavitation trajectories in the phase diagram, above and below the spinodal line of the bulk water model. These trajectories were analyzed using different definition of the order parameter. The cavitation trajectories were further analyzed using the mean first-pasage time (MFPT), in order to quantify the nucleation rate, bubble critical volume and mucleation barrier.
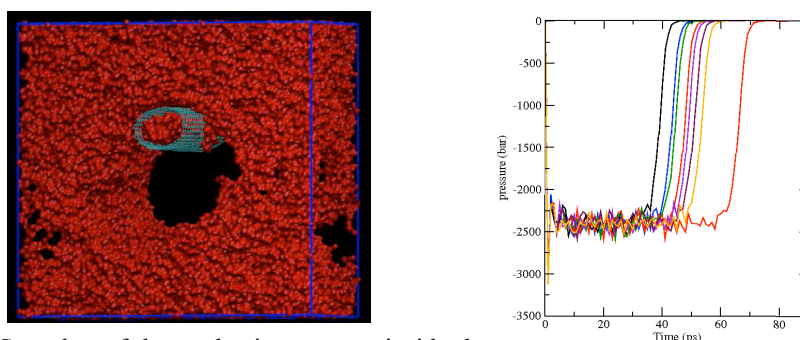

Figure 1: (Left) Snapshot of the nucleation process inside the spinodal region. The red spheres represent water, cyan carbon, The nanotube undergoes a strong deformation during the bubble growth. (Right) Pressure versus time eight random trajectories computed in the NpT ensemble.

"Influence of the nanostructure of prefunctionalized walls on the dynamics and the thermodynamics of a solution of globular proteins."

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Confinement can modify dynamic and thermodynamic properties of a liquid. We consider the case of soft sticky particles, modelling globular proteins, confined between walls prefunctionalized with proteins with different nanopatterns. Using molecular dynamics simulations, we find how different structures affect the coexistence among different phases, the crystal nucleation and the dynamics of the protein solution.

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"Dynamics of Biological Water: a Computational Approach"

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In this contribution it is shown how a better understanding of the dynamics of water surrounding proteins, in particular the inhibitor Barstar, may benefit from atomistic deeper approaches. Barstar is a protein of interest in cancer cell investigations, molecular recognition as well as amyloid fibrils research. Using all-atom molecular dynamics simulations, the dynamics of the first hydration shell surrounding that biomolecule (cutoff = 0.4nm) is analysed along 7ns through three different perspectives. Macroscopic view: time correlation functions show the existence of a broad distribution of relaxation times suggesting a complex landscape of the dynamics (averaged decay time = 84.0 ± 0.3 ps). Mesoscopic view: a power law distribution of residence times indicates that this hydration water exhibits a scale free dynamics with scaling exponent $\alpha = 0.57 \pm 0.04$. Microscopic view: evidence, at atomic level, of multiple time scales in the dynamics of such special solvent (10^{-1} to 10^{3} ps). That particular ultra-slow behaviour (nano second scale) has not been described for bulk water. These computational results are in agreement with recent experiments performed on native Barstar [1] and contribute to throw some light on solvation data collected by time-dependent dynamics Stokes shift (TDSS) measurements on some other proteins in solution [2].
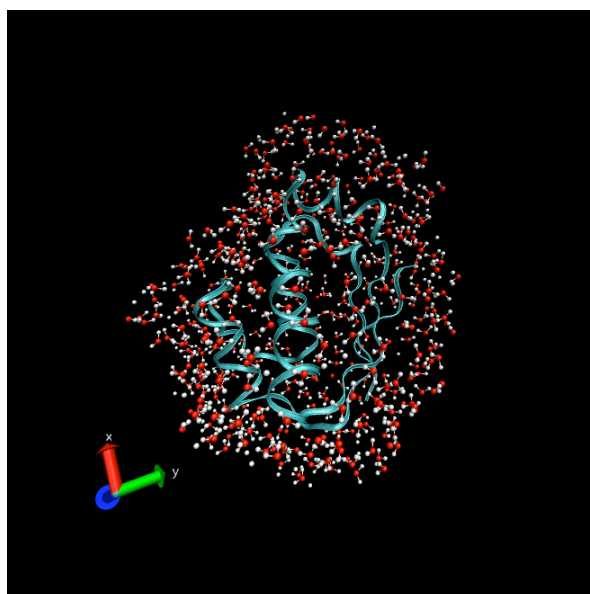

Fig. 1. First hydration layer around the protein Barstar (cutoff= 0.4nm).

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"Are the dispersion interactions essential in a SPC-like water model?"

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In recent years, the force matching (FM) algorithm[1] has proven to be a powerful and versatile instrument to parameterize effective force fields (FFs) from descriptions of higher level of theory; for example, empirical FFs from *ab initio* molecular dynamics or "coarse grained" FFs from atomistic ones. Taking advantage of this type of approach, many effective force fields for water have been presented in literature based on simple functional forms for the interaction potential. One of the drawbacks of the technique consists in the fact that the process of fiting could lead to parameter values to which it could be difficult to assign a physical meaning, as in the case of negative values for the C parameter[2,3] of the dispersive interaction in the Lennard-Jones potential. The central point of this contribution is summarized by the following question: is it possible to maintain the same level of accuracy of the force field in terms of ability to predict structural and dynamical properties, totally omitting the dispersive interactions? If the answer to this question is affermative, in one fell swoop we would have solved the problem of non-physical dispersive parameters and we got the simplest atomistic force fields for water. Starting from a force field presented by some of us[3], we have performed this type of study and compared the results obtained with the original force field and a derived force field in which is added a damping function on dispersive interactions (which can be considered the "correct" way to solve the problem of the negative C parameters).
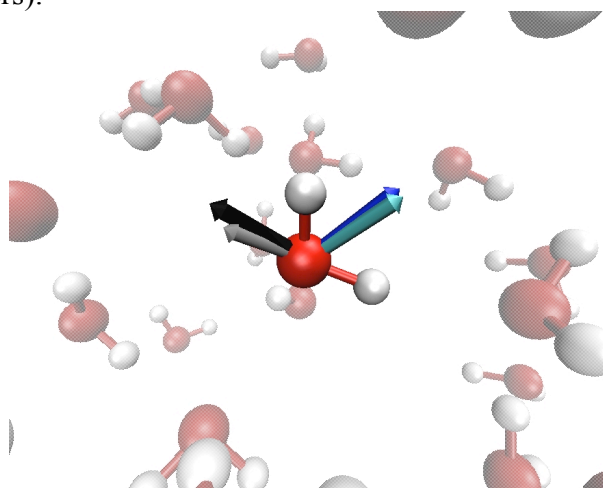
Representation of a typical FM snapshot. For a better visualization, we focus only on one molecule. The arrows represent the properties involved in the FM fit. Respectively blue and cyan arrows are the reference and effective net forces acting on the molecule and black and gray arrows are the reference and effective torques acting on the molecular center of mass.

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"Does water dissociates on the clean CeO₂(111) surface?: a study with van der Waals and hybrid density functionals"

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Water interacting with ceria surfaces is an essential step in many relevant catalytic processes. In spite of this, a detailed picture of the adsorption of H2O on the most stable facet of CeO2, the clean (111) surface, is still lacking. Previous experimental and theoretical works [1] have concluded that the molecule sits on top of a Ce ion. However, further structural information, e.g. if water adsorbs molecularly or as an ion pair (see Fig 1), is not yet clear. Currently, the only answer to this question comes from theoretical studies based on Density Functional Theory, and these have reached contradicting conclusions.

In this work [2], we study this issue employing higher levels of theory (van der Waals and hybrid density functionals) and also the same levels considered previously (GGA, GGA+U). We find that all methods point to the same answer: both structures are similarly stable, and they are thus expected to coexist. When van der Waals interactions are taken into account, the binding energy of water increases by ~0.18 eV, improving the agreement with the available experimental values. Our calculations also indicate that these two species can be distinguishable by their infrared spectra. Finally, we will also discuss the energy barriers connecting the molecular structure and the ion pair, and the equivalent adsorption positions, and provide an explanation for the contrast found in recent AFM studies on the water/ceria system.
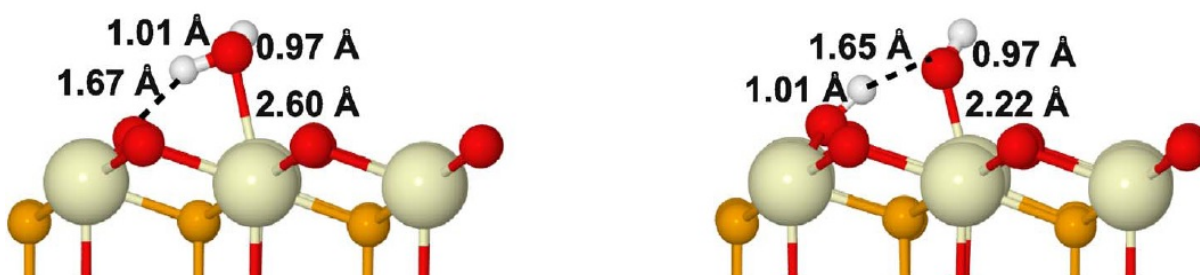

Fig. 1: Side view of the most stable structures for molecular and ion pair adsorption. Color code: oxygen atoms in the first surface layer are red and those in the third surface layer are orange, hydrogen atoms are white, and cerium atoms are pale yellow.

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"One-Dimensional Water Structures at Low Water Coverage on Cu(110)"

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The self-organization of water in metallic surfaces is determined by the competition between inter-molecular and metal-substrate interactions. An additional complication is given by the possibility that significant fraction of water molecules undergo partial dissociation.[1, 2]

The wetting of Cu(110) has been recently reported. At low temperature and coverage, water forms one-dimensional arrays that clear indicate the competition of different interactions mentioned above. Carrasco *et al.* identified this structure with a wire formed by side-sharing pentagonal rings formed by intact molecules.[3] We present here a combined experimental and theoretical study that challenges this interpretation. Our STM images show structures different that those reported by Carrasco *et al.* . We have compared our experimental STM images with a series of theoretical calculations of different linear structures based on pentagonal and hexagonal motifs. In this presentation we discuss different structures that produce simulated STM images in good correspondence with experiment. The most stable ones are based on hexagonal motifs with some dissociated molecules.
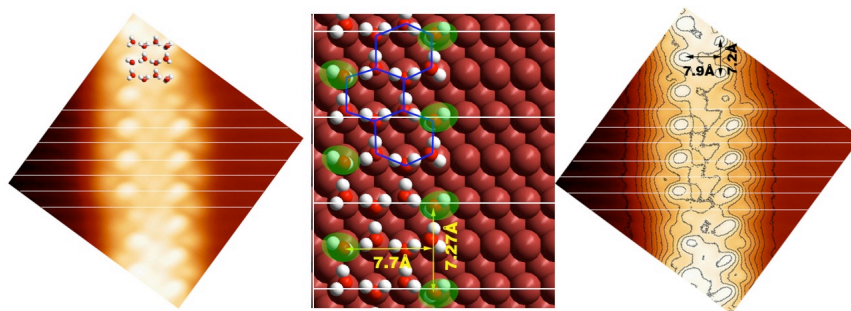
Figure 1. Left and right panels show experimental STM images of the structures formed by ~0.2ML water on Cu(110) after annealed at 78K. The panel in the middle shows a wire formed by hexagonal rings of intact molecules, as shown by the blue lines. The pointing down water molecules at the edges have been highlighted by green circles.

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"Water in hydrophobic nanoconfinement at low tempertaure: Crystal Polymorphism vs. Liquid-Liquid phase transition."

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Formation of ice in confined systems is relevant in nanoscience and biology, in areas like cryopreservation of biological material, such as food, human tissues or stem cells, where density fluctuations due to the ice formation can dramatically damage or destroy the cells.

Bulk water presents a large number of crystalline and amorphous ices. Nanoconfinement is known to affect the tendency of water to form ice. Here we develop a coarse-grained model for a water monolayer in hydrophobic nanoconfinement and study the formation of ice by Monte Carlo simulations. We find two ice phases: low-density-crystal ice at low pressure and high-density ice at high pressure with an intermidiate hexatic phase between liquid and ice [1].
Furthermore, we study the density fluctuations of the liquid approaching the crystal phase, finding that they can diverge due to the occurrence of a liquid-liquid critical point (LLCP) within the limit of stability of liquid water. We show how the accessibility of the LLCP depends on how strong is the three-body interaction in water with respect to the many-body interaction.

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"Water-hydroxyl phases on Cu(110): breaking the ice rules"

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Hydroxyl is a key reaction intermediate in many surface catalyzed redox reactions, yet establishing the phase diagram for water-hydroxyl adsorption on metal surfaces remains a considerable challenge for interfacial chemistry, in particular on reactive, open metal surfaces[1]. Based on scanning tunnelling microscopy and density functional theory calculations, we report the phase diagram for water-hydroxyl on Cu(110), providing a complete molecular description of the complex H-bonding structures formed [2]. Three distinct phases are observed as the temperature is decreased and the water-hydroxyl ratio increases: pure OH dimers, extended $1H_2O:1OH$ chains, aligned along the close-packed Cu rows, and finally a distorted 2D hexagonal c(2x2) $2H_2O:1OH$ network [3]. None of these phases obey the conventional "ice rules" [1], instead their structures can be understood based on weak H donation by hydroxyl, which favours H-bonding structures dominated by water donation to hydroxyl, and competition between hydroxyl adsorption sites. Hydroxyl binds in the Cu bridge site in the 1D chain structures, but is displaced to the atop site in the 2D network in order to accommodate water in its preferred atop binding geometry. The adsorption site and stability of hydroxyl can therefore be turned simply by changing the surface temperature and water content, giving a new insight as to how the open metal template influences the water-hydroxyl structures formed and the activity of hydroxyl.

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"MC simulations of a 3D coarse-grained model of water: phase diagram and dynamics."

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We show results of NPT Monte Carlo simulations for a coarse-grained model of water. The model is a natural 3D extension of a model previously proposed for a confined 2D monolayer [1]. The resulting phase diagram shows the line of temperature of maximun density (TMD) and other anomalies of water. Moreover, at lower temperatures, the model predicts a phase transition between a high-density and low-density liquid ending in a critical point, consisten with previous results in 2D. Concerning the dynamics, we study the diffusion of water molecules and we find, as temperature is decreased, maximum followed by a minimum of the diffusion coefficient D along isotherms. Therefore, our results show that the main features of the model are preserved going from the confined 2D case to the bulk 3D case. Nevertheless, we expect that the 3D model belongs to the 3D Ising universality class, while the 2D model belongs to the 2D Ising universality class [2].

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