

waterspain2017

July 6-7, 2017

Zaragoza

Organizers

Giancarlo Franzese (Universitat de Barcelona)

Elvira Guàrdia (Universitat Politècnica de Catalunya-Barcelona Tech)

Jordi Faraudo (Institut de Ciència de Materials de Barcelona, ICMAB-CSIC)

Jordi Martí (Universitat Politècnica de Catalunya-Barcelona Tech)

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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 beyond, as well as 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. This is the second meeting of the series. The first meeting was held in Zaragoza, on February 7-8, 2013.

PROGRAM

Thursday - July 6, 2017

14:45-15:00 **OPENING**

Session I: Chair Giancarlo Franzese

15:00-15:30 **Arieh Ben-Naim (invited speaker)**

Hydrophobic-Hydrophilic interactions in protein folding, protein-protein association and molecular recognition

15:30-15:50 **Valentino Bianco**

Modeling proteins in water to understand folding, stability and aggregation

15:50-16:10 **Klaas Wynne**

Slow and super-slow water translational dynamics around organic and biological solutes

16:10-16:30 **Carles Calero**

The role and properties of water in the interaction of phospholipid membranes with other phospholipid membranes and ions

16:30-17:10 **COFFEE BREAK AND POSTER SESSION**

Session II: Chair Jordi Martí

17:10-17:30 **Enrique Sánchez Marcos**

The identification of the coordination geometry of metal aquaions in water: a way to understand the rare-earth contraction of aquaions

17:30-17:50 **Rocío Semino**

Proton Solvation and Dynamics in Water Acetone Solutions and Mesoscopic Aggregates

17:50-18:10 **María M. Conde**

Spontaneous NaCl-Doped Ice: Focus on the Mechanisms of Ions Inclusion

18:10-18:30 **Luis G. McDowell**

Observation of a roughening transition on the surface of ice

18:30-18:50 **Jayant K. Singh**

Ice nucleation on nanotextured surfaces: Influence of surface fraction, pillar height and wetting states

18:50-19:10 **Chantal Valeriani**

Ice nucleation

21:30-23:00 **SOCIAL DINNER**

Friday - July 7, 2017

Session III: Chair TBA

9:00-9:20 **Albert Verdaguer**

Substrate-dependence of the freezing dynamics of supercooled water films: A high speed optical microscope study

9:20-9:40 **Francesco Alliota**

Kovacs effect and the relation between glasses and supercooled liquids

9:40-10:00 **Rossend Rey**

Ultrafast energy fluxes during solvation dynamics in liquid water

10:00-10:20 **Maria C. Morón**

Reproducing experimental data of relaxation phenomena in liquid water: ambient and low temperature

10:20-10:40 **Ioannis Skarmoutsos**

Local structural fluctuations, hydrogen bonding and structural transitions in supercritical water

10:40-10:55 **Oriol Vilanova**

Crystal polymorphism and hexatic phase in a many-body model for a water monolayer

10:55-11:30 **COFFEE BREAK AND POSTER SESSION**

Session IV: Chair Elvira Guàrdia

11:30-11:50 **Emilio Artacho**

Simulations of nanoconfined water between corrugated walls

11:50-12:10 **Luis Carlos Pardo**

Characterizing ordering in liquid water: An information theory approach

12:10-12:30 **Kazuhiro Fuchizaki**

SnI_4 —the substance that allows us to enter the no man's land

12:30-12:50 **Frédéric Caupin**

Viscosity of supercooled water under pressure and two-state interpretation of water anomalies

12:50-13:20 **Mikhail Anisimov (invited speaker)**

Do ordinary water and heavy water behave differently under supercooled and superstretched conditions?

13:20-13:30 **CLOSING**

Talks

Hydrophobic-Hydrophilic interactions in protein folding, protein-protein association and molecular recognition

Arieh Ben-Naim

Department of Physical Chemistry. The Hebrew University of Jerusalem, Jerusalem, 91904, Israel

Many biochemical processes such as protein folding or self assembly of proteins are highly specific. Proteins fold spontaneously into a very specific 3-dimensional structure. Proteins also associate spontaneously to form multi-subunit macromolecules. These processes occur in aqueous media. The question we pose is what is the role of water in these processes?

Until recently it was believed that the hydrophobic effect, i.e. the tendency of hydrophobic groups to “escape” from the aqueous environment is the dominant driving force for these processes.¹

Analysis of all the solvent induced contributions to the thermodynamic driving forces for protein folding and protein-protein association reveals that, contrary to the commonly accepted paradigm, hydrophilic interactions might be more important than hydrophobic interactions.²

This conclusion was reached after critically examining the data on the various contributions to the driving forces for protein folding, and protein-protein association. Examples on the role of hydrophilic interactions on solubility of proteins, protein folding, protein-protein association and molecular recognition will be presented. Thus, hydrophilic interactions not only helps in understanding the role of water in biochemical processes, but they can also be applies to design drugs that bind stronger to their targets.^{3,4}

[1] W. Kauzmann, *Advances Protein Chemistry* **14**, 1 (1959)

[2] A. Ben-Naim, *Biopolymers* **29**, 567 (1990)

[3] A. Ben-Naim, *Molecular Theory of Water and Aqueous Solutions*,
Part I: Understanding Water, World Scientific, Singapore (2009)

[4] A. Ben-Naim, *Molecular Theory of Water and Aqueous Solutions*,
Part II: The Role of Water in Biological Systems, World Scientific, Singapore (to be published 2011)

Modeling proteins in water to understand folding, stability and aggregation

Valentino Bianco

Computational Physics Department, Faculty of Physics, University of Vienna, Sensengasse 8/10,
1090 Vienna, Austria.

Proteins are molecules made of a sequence of amino acid that fold into the native structures. Such a structure is usually stable within a certain range of temperatures and pressures, beyond which a protein denaturate. Such a phenomenon is well known at higher temperatures, where the thermal fluctuations disrupt the native conformation. However, similar phenomena are observed by decreasing the temperature or by increasing the pressure, respectively known as cold- and pressure-denaturation. Moreover, in order to guarantee the correct biological functions, proteins have evolved to have a low enough propensity to aggregate within a range of protein expression required for their biological activity, but with no margin to respond to external factors increasing/decreasing their expression/solubility. Indeed, protein aggregation is mostly unavoidable when proteins are expressed at concentrations higher than the natural ones. Here, by means of a coarse-grain model which include explicitly the protein effect on the water dynamics, we investigate the folding, the stability and the aggregation of proteins.

- [1] Franzese G, Bianco V, Iskrov S, Food Biophys **6**, 186 (2011)
- [2] Bianco V, Iskrov S, Franzese G, J Biol Phys **38**, 27 (2012)
- [3] Bianco V, Franzese G, Food Biophys **8**, 153 (2013)
- [4] Bianco V, Franzese G, Scientific Reports **4**, 4440 (2014)
- [5] Bianco V, Franzese G, Phys. Rev. Lett. **115**, 108101 (2015)
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- [7] Bianco V, Pages Gelabert N, Coluzza I, Franzese G, <https://arxiv.org/abs/1704.03370>, submitted (2017)

Slow and super-slow water translational dynamics around organic and biological solutes

Gopakumar Ramakrishnan, Mario González-Jiménez, Adrian J. Lapthorn, and Klaas Wynne

School of Chemistry, WestCHEM, University of Glasgow, Glasgow G12 8QQ, United Kingdom

Solvation of molecules, in particular by water, is of great importance for the understanding of (bio)chemical reactivity, the determination of solubilities, and biological interactions vital to living organisms. For example, in the case of DNA and proteins, the hydration layer is essential in determining conformation and function.¹ The wide range in the relaxation times of water in the solvation shell predicted by theoretical modelling was only recently experimentally observed in DNA.² However, no experimental technique has yet allowed a detailed description of the distribution of relaxation timescales. The diffusive orientational and translational motions of liquid water as well as the hydrogen-bond bend and stretch modes are in the gigahertz to terahertz frequency range and have been widely studied. On adding solutes, the dynamics of water in the solvation shell are expected to change to a greater or lesser extent. However, diffusive and librational motions of the solute tend to mask these changes. We have applied the technique of optical Kerr-effect spectroscopy, which measures the depolarised Raman spectrum using a time-domain technique and is sensitive to reorientational molecular motions.³ Thus, this provides an opportunity to “switch-off” signals by using appropriately chosen solutes or solvents. Here we study the dynamics of solvation water in the solvation sphere of organic and biological solutes by using solutes that are “invisible” in the relevant frequency range. A slowdown factor of ~ 50 is observed even for relatively low concentrations of the solute.

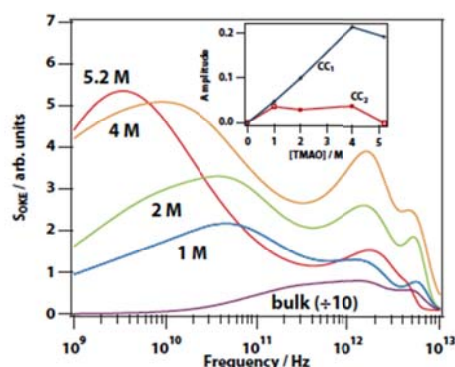


Fig. 1. Comparison of the modified solvation-water spectra for different concentrations of TMAO. Bulk-water spectrum and concentration-dependent solvation-water spectra in aqueous TMAO solutions determined by a fitting procedure and leaving out the bulk water contribution.

- [1] Duboué-Dijon, E.; Fogarty, A. C.; Hynes, J.; Laage, D. J. Am. Chem. Soc. **138**, 7610 (2016)
- [2] González Jiménez, M.; Ramakrishnan, G.; Harwood, T.; Lapthorn, A. J.; Kelly, S. M.; Ellis, E. M.; Wynne, K. Nat. Commun. **7**, 11799 (2016)
- [3] Turton, D. A.; Senn, H. M.; Harwood, T.; Lapthorn, A. J.; Ellis, E. M.; Wynne, K. Nat. Commun. **5**, 3999 (2014)

The role and properties of water in the interaction of phospholipid membranes with other phospholipid membranes and ions

Carles Calero^{a,b}

^aDepartament de Física de la Matèria Condensada, Universitat de Barcelona, Martí Franquès 1, 08028 Barcelona, Spain

^bInstitut de Nanociència i Nanotecnologia, Universitat de Barcelona, Av. Joan XXIII S/N, 08028 Barcelona, Spain

Biological membranes provide a limiting structure which separates the interior and exterior of cells and organelles. Being selectively permeable, they control the flow of substances in and out of the cell, which permits to regulate its composition and the communication between cells through signaling with ions. In the fulfillment of these functions, interfacial water plays a fundamental role, since it mediates in the interaction of the membrane with other biomolecules (such as proteins, sugars or other membranes), and it determines the electrostatic properties of the membrane.

In this contribution we discuss the properties and role of interfacial water in both membrane functions. First, we investigate using all-atom molecular dynamics simulations the properties of confined water in between interacting phospholipid membranes [1]. We show that both the translational and rotational dynamics of water molecules exhibit a monotonic dependence with the distance between the confining membranes. We interpret the results using a layering model of water molecules with the help of a local definition of distance to the membrane. Second, we study the effect of water in the interaction of phospholipid membranes with metallic ions. Using metadynamics simulations we quantify the free energy of adsorption of biologically relevant metallic ions and water to the membrane, providing a full characterization of ion adsorption [2]. Using the same technique we ascertain the effect of cholesterol in the adsorption of metallic ions to the membrane [3].

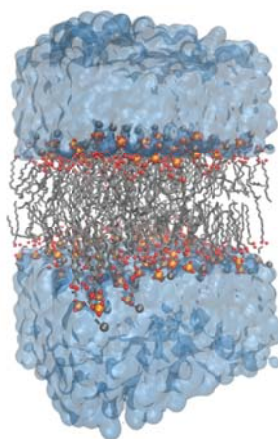


Figure: representation of model of hydrated membrane

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[2] Yang, J.; Calero, C.; Bonomi, M.; Martí, J. *J.Chem.Theor. and Comp.* **11**, 4495 (2015)

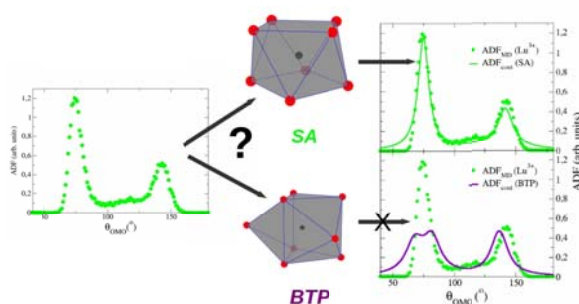
[3] Yang, J.; Bonomi, M.; Calero, C.; Martí, J. *Phys.Chem.Chem.Phys.* **18**, 9036 (2015)

The identification of the coordination geometry of metal aquaions in water: a way to understand the rare-earth contraction of aquaions

E.Sánchez Marcos[†], N. Morales , E. Galbis , J. M. Martínez and R. R. Pappalardo

[†]Departamento de Química Física.Universidad de Sevilla, 41012-Sevilla, Spain

The angular distribution function (ADF) associated to the oxygen-metal ion-oxygen (OMO) of several rare-earth aquaions has been used to identify the most probable coordination geometry of these aquaions in aqueous solutions. The ADFs extracted from the trajectories of Molecular Dynamics simulations have been compared with the discrete distributions corresponding to the coordination around a central ion following an ideal polyhedron pattern [1,2]. A procedure to convert the natural discrete distribution provided by the rigid structure of an ideal polyhedron in a continuous function incorporating specific quantum-mechanical information of the aquaion under study is proposed [3]. This procedure is applied to the analysis of four trivalent rare-earth metal ions in water, two of them representatives of the 8-fold hydration, $\text{Cf}[(\text{H}_2\text{O})_8]^{3+}$ and $\text{Lu}[(\text{H}_2\text{O})_8]^{3+}$, and the other two cations representatives of the 9-fold hydration, $\text{Ac}[(\text{H}_2\text{O})_9]^{3+}$ and $\text{La}[(\text{H}_2\text{O})_9]^{3+}$. Metal cation-water interaction potentials were built on the basis of a flexible and polarizable model developed from the Hydrated Ion approach [4,5]. For those 8-coordinated, the Square Antiprism (SA) coordination geometry is preferred. For the 9-fold coordination the simulation ADFs are more similar to that derived from a Gyro-elongated SA rather than to the usually proposed Trigonal Tricapped Prism. This finding leads to an alternative view of the evolution of the hydration number along the rare-earth series aquaion based on the dynamics properties of the capped water molecule of the Gyro-elongated SA aquaion rather than on the equilibrium between the octahydrated and enneahydrated aquaions. Applications of the methodology to other coordination numbers, such as 4, 6 and 7, have been explored to check the robustness of the proposed procedure.



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- [3]N. Morales, E. Galbis, J. M. Martínez, R.R. Pappalardo, E. Sánchez Marcos, J.Phys.Chem.Lett. **7**, 4275 (2016).
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Proton Solvation and Dynamics in Water Acetone Solutions and Mesoscopic Aggregates

Rocio Semino,^{†*} Jordi Martí,[‡] Elvira Guàrdia, María P. Longinotti[†] and Daniel Laria^{† §}

[†] Departamento de Química Inorgánica Analítica y Química-Física e INQUIMAE,
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria,
Pabellón II, 1428 Buenos Aires, Argentina

[‡] Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya-Barcelona Tech.
B4-B5 Campus Nord, 08034 Barcelona, Spain

[§] Departamento de Física de la Materia Condensada, Comisión Nacional de Energía Atómica,
Avenida Libertador 8250, 1429 Buenos Aires, Argentina

* Current address: Institut Charles Gerhardt Montpellier UMR 5253 CNRS, Université de
Montpellier, Place E. Bataillon, 34095 Montpellier Cedex 05, France

Aqueous proton transfer is controlled by the well-known Grotthuss mechanism, that takes place in the picoseconds timescale. Transferences involve translocations of the average position of the excess charge, which require successive spatial rearrangements along chains of hydrogen bonds. In this work, we analyze structural and dynamical characteristics of proton solvation in water-acetone bulk mixtures and mesoscopic nanoclusters. For this, we combined direct conductivity measurements with a reactive molecular dynamics simulation approach, based on a multistate empirical valence bond Hamiltonian model that incorporates a proton translocation mechanism.

Our conductivity measurements show that HCl and LiCl conductivities at infinite dilution are very similar for acetone-rich solutions, up to $x_w \sim 0.25$. From this composition onwards, the acid conductivity exceeds that for the salt, and the Grotthuss mechanism gradually activates as water content is increased. There is a qualitative change in HCl conductivity around $x_w \sim 0.8$. Accordingly, simulations show that at this composition, the concentration dependences of both the rate of proton transfer and its diffusivity change at a qualitative level. This transition can be traced back to modifications in the second solvation shell of the excess charge which, in acetone rich solutions, normally includes at least one acetone molecule. Our results suggest that one possible mechanism controlling proton transfer in the $0.25 < x_w < 0.8$ solutions, is the exchange of one of these tagged acetone molecules by nearby water ones. We further studied binary mesoscopic aggregates of the type $[\text{H}(\text{H}_2\text{O})_m((\text{CH}_3)_2\text{CO})_n]^+$, with $m = 50$ and $n = 6, 25$ and 100 . At low acetone contents, clusters consist of a water core partially coated by acetone. The excess proton is located at the surface of the water core, with at least three acetone molecules in its second solvation shell. The transfer dynamics is much slower than in bulk mixtures of equal composition, reaching the nanosecond timescale, and the transfer mechanism seems to involve a preliminary proton “immersion” into the underlying water core. In clusters with excess water, we found evidence of incipient water-acetone miscibility. The proton resides in aqueous domains of irregular shape, fully embedded within the acetone phase. Under these circumstances, we did not detect proton transfer events along ~ 30 ns trajectories.

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Spontaneous NaCl-Doped Ice: Focus on the Mechanisms of Ions Inclusion

M. M. Conde,[†] M. Rovere[†] and P. Gallo[†]

[†] Dipartimento di Matematica e Fisica, Università Roma Tre,
Via della Vasca Navale 84, 00146 Roma, Italy

Molecular dynamics simulations on microsecond time scale have been performed on an aqueous solution of TIP4P/2005 water and NaCl by using the direct coexistence technique to study the ice growth and the interface ice/liquid water. At ambient pressure, for temperatures above the eutectic point of the salt and at seawater concentration the brine rejection phenomenon and the spontaneous growth of a ice slab doped by the salt are obtained, as found in natural terrestrial and planetary environments. Experiments indicate that Cl^- goes substitutional to ice sites. In line with these evidences we find a new result: the Cl^- ion included in the lattice always substitutes not one but two water molecules leaving the ice structure around not distorted. The Na^+ ion shows lower probability to be included in the ice and it occupies an interstitial site, causing a local distortion of the lattice. No sign of significative ions diffusion is observed in the lattice [1].

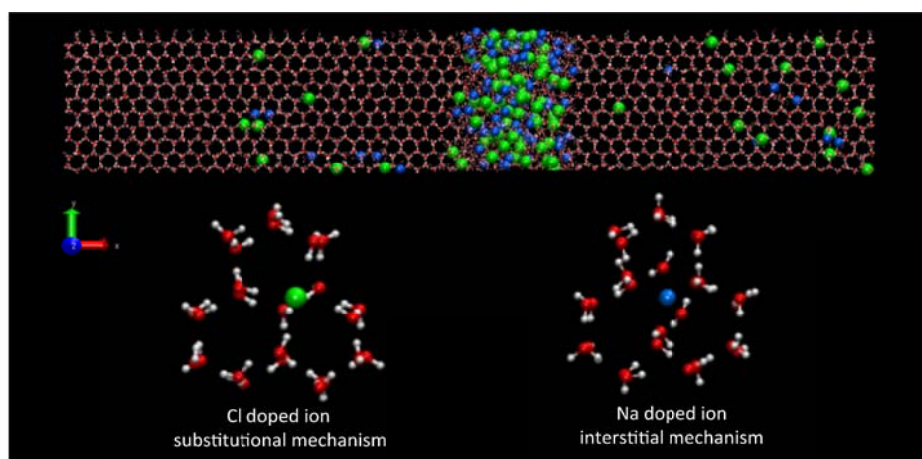


Fig. 1: Final snapshot for the ice/NaCl(aq) system after 2 μs at $\Delta T = -20\text{K}$ (top). Frontal view of a doped ice I_h lattice portion containing a Cl^- ion (bottom left) and a Na^+ ion (bottom right).

[1] M. M. Conde, M. Rovere, and P. Gallo. Phys. Chem. Chem. Phys. **19**, 9566 - 9574 (2017).

Observation of a roughening transition on the surface of ice

P. Llombart¹, J. Benet², E. Sanz¹ and Luis G. MacDowell¹

¹Departamento de Química Física, Universidad Complutense, Madrid, Spain

²Department of Physics, Durham University, United Kingdom

The habit of ice crystals in the atmosphere change from plates, to columns, to plates and yet back to columns as temperature is cooled down below the triple point [1]. Attempts to explain this puzzling sequence of events rely on the formation of a thin quasi-liquid layer of premelted ice [2]. Many efforts have been devoted to determine the onset of premelting and the thickness of the layer as the triple point is approached [3]. But precisely what is the influence of this film on the global behavior of the ice/vapor interface, and how could it impact on the mechanism of crystal growth is far from being understood [1]. In this paper, we argue that a thin premelting layer of ice hardly one nanometer thick is able to induce a structural transition of the Kosterlitz-Thoules type on the ice surface.[4] Our computer simulations reveal that the two distinct surfaces bounding the quasi-liquid layer behave at small wave-lengths as rough and independent ice/water and water/vapor interfaces. However, the finite thickness of the layer inhibits large scale fluctuations and drives the crystal surface smooth at long wave-lengths. Our results explain why ice crystal prisms retain a distinct hexagonal shape up to the triple point, and suggest the formation of a premelting film could slow down the growth rate of crystal facets. Understanding the structure and growth mechanisms of ice crystals also has important implications in atmospheric science, glaciology, and frost heaving [3]. In our study, we simulate the premelting layer of water a few Kelvin below the triple point. Using an adequate order parameter, it is possible to identify distinct ice/film and film/vapor, surfaces, which separate the premelting film from the bulk solid and vapor. The spectrum of surface fluctuations allow us to measure the wave-vector dependent components of the stiffness tensor, which are finite for a rough surface, but effectively diverge for smooth surfaces. At a temperature two Kelvin below the triple point, our results indicate that the stiffness coefficients for ice/film, film/vapor and coupled ice/film and film/vapor fluctuations converge to a finite value. Moreover, it is found that the fluctuations closely resemble those of independent ice/water and water/vapor interfaces at large wave-vectors, but eventually couple and produce an effective stiffness which is the sum of the stiffness coefficients of the independent interfaces. A few Kelvin below, however, the stiffness coefficients effectively diverge, and indicate the onset of a completely different regime with finite surface fluctuations that corresponds to a smooth surface. Accordingly, it is expected that the crystal growth rate of the prismatic facet will slow down below this temperature, and promote the growth of columnar crystals as observed in the atmosphere.

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Ice nucleation on nanotextured surfaces: Influence of surface fraction, pillar height and wetting states

Atanu K. Metya¹ and Jayant K. Singh^{1*}

¹Department of Chemical Engineering, Indian Institute of Technology Kanpur, India.

*Corresponding author e-mail: jayantks@iitk.ac.in

The formation of ice affects many industrial processes [1] such as transportation, power and agriculture [2]. Further, it can cause aircraft accidents due to icing on the wings and airframe. Thus, in order to minimize or control the ice formation on the various surfaces, scientists and engineers have put their efforts into designing ice-repellent materials for various practical applications. Recently, there has been significant interest in developing such material based on super-hydrophobic surfaces with a subsequent improvement in performance and stability [1,3]. However, the same super-hydrophobic surface need not be an anti-icing surface [4]. Thus, to design a suitable material for improving anti-icing efficiency in various industrial processes and applications, efforts are required to understand the principle underlying mechanism of ice nucleation.

In this work, we address the nucleation behavior of a supercooled cylindrical water droplet on nanoscale-textured surfaces using molecular dynamics simulations. Ice nucleation rate at 203 K on graphite based textured surfaces is evaluated using the mean fast-passage time method. The nucleation rate depends on surface fraction as well as wetting states. The nucleation rate is found to increase with increasing surface fraction for water in the Cassie-Baxter state, while contrary behavior is observed for the case of Wenzel state. Heterogeneous nucleation is observed at a high surface fraction. However, the probability of homogeneous ice nucleation events increases with decreasing surface fraction. We further investigate the role of nanopillar height on ice nucleation. The nucleation rate is found to enhance with increasing nanopillar height.

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Ice nucleation

Chantal Valeriani[†], J.Espinosa[‡], J.L.F.Abascal[‡], E.Sanz[‡], C.Vega[‡]

[†] Departamento de Física Aplicada I, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Avenida Complutense, 28040, Madrid, Spain

[‡] Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avenida Complutense, 28040, Madrid, Spain

Avoiding water freezing is the holy grail in cells cryopreservation and climate change modeling. Using a seeding approach [1], in which classical nucleation theory is combined with simulations of ice clusters embedded in supercooled water, we evaluate the nucleation rate at ambient pressure in a wide metastability range [2] and for several water models [3], and estimate the ice-liquid interfacial free energy up to coexistence conditions, in reasonable agreement with the reported experimental values. Experimental ice nucleation rates are closer to the ones obtained for TIP4P/ICE and mW water [4], water models with similar melting point and enthalpy but different freezing dynamics. Estimating the crystallisation time via the Avrami's expression, we conclude that the minimum crystallization time for TIP4P/ICE is about ten microseconds at 55K below melting, compatible with the minimum cooling rate required to avoid ice formation [4].

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Substrate-dependence of the freezing dynamics of supercooled water films: A high speed optical microscope study

E. Pach,[†] L. Rodriguez,[†] A. Verdaguer[§]

[†] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain

[§]Institut de Ciència de Materials de Barcelona ICMA-B-CSIC, Campus de la UAB, E-08193 Bellaterra, Spain

Icing in a cold atmospheric environment has a wide impact in various fields and it often represents a hazard for transportation systems such as aviation, shipping and road traffic. Although the mechanisms during freezing of supercooled droplets have been extensively studied for decades, the mechanisms during icing of surfaces it's still under debate [1,2]. Many icing theories focus only on the complex heat and mass transfer of water films, despite it's well known that surface can have a profound impact on water film structures [3] very little is known on the impact of that on the icing process. Here we report an optical microscope study, using a highspeed camera, of the icing process of supercooled water thin films (thickness <0.5 mm) on well defined relevant surfaces (mica, silicon, glass, gold, quartz..). Different stages of the freezing process were identified and its dependence on the substrate was studied. Of special interest was the study of dendrite formation and growth as a function of supercooled temperature and substrate used.

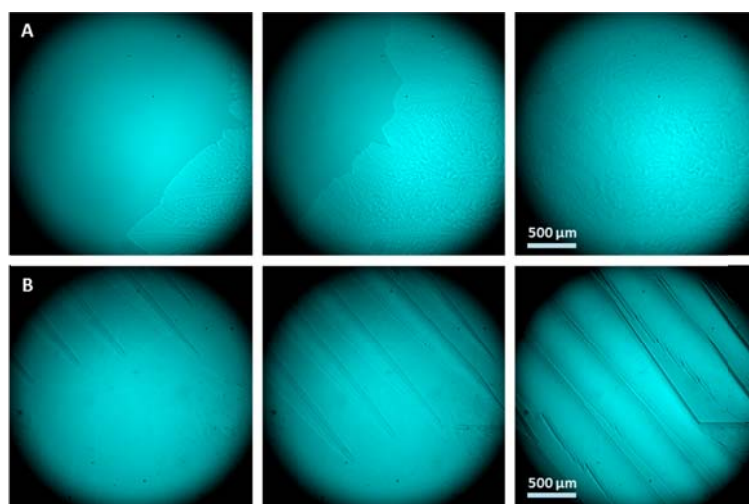


Figure: Freezing dynamics of a water film on silicon (A) and glass (B) at -1°C.

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Kovacs effect and the relation between glasses and supercooled liquids

¹F. Aliotta, ²P.V. Giaquinta, ¹R.C. Ponterio, ¹F. Saija

¹*CNR-IPCF, Messina, ITALY*

²*Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra,
Universit a degli Studi di Messina, Messina, ITALY*

We revisit Kovacs' effect, which concerns the way the volume of a glass-forming liquid, originally driven out of equilibrium, changes with time while the system evolves towards a metastable state. The theoretical explanation of this phenomenon has attracted a deep interest even in recent years, because of its relation with some subtle aspects of the still elusive nature of the glass transition. In fact, even if there is a rather general consensus on the fact that what is experimentally observed on cooling is the dramatic effect produced by the dynamical arrest of slower degrees of freedom over the experimental time scale, it is not at all obvious whether this phenomenology can be justified by an underlying (possibly, high order) phase transition at a lower temperature. We show how the phenomenon investigated by Kovacs can be explained in terms of the relaxation undergone by slow motions, on a time scale comparable with the experimental time windows. The results from a simple model system, namely o-terphenyl, are compared with indications from other glass formers, including water. The ability of a simple out-of-equilibrium approach in reproducing a wide class of phenomena related with the glass transition suggests the idea that the hypothesis of a thermodynamic phase transition should be reconsidered in favor of alternative scenarios.

Ultrafast energy fluxes during solvation dynamics in liquid water

R. Rey¹, J.T. Hynes^{2,3}

¹ Departament de Física, Universitat Politècnica de Catalunya, Barcelona, Spain

² Department of Chemistry and Biochemistry, University of Colorado, Boulder, USA

³ Chemistry Department, Ecole Normale Supérieure, Paris, France

We and several colleagues previously developed a work and power analysis scheme to unravel the ultrafast energy fluxes resulting from excitation of solute vibrations or rotations in neat liquid water. This revealed the identity and sequence of solvent modes/hydration shells absorbing the excess energy, and provided a qualitative and quantitative picture of the energy transfer pathway. More recently, we have applied the same energy flux approach to bring a previously absent molecular level perspective to the much-studied 'solvation dynamics' problem [1,2,3]. We focus on the classic, neutral monatomic solute immersed in water solvent, subjected to a sudden acquisition of a unit charge, here in a nonequilibrium perspective. The path and time scales of the subsequent energy flow to the water solvent's translations, rotations, and vibrations are analyzed via the energy flux scheme, as are the contributions from different hydration shells, and rotational axes. Other central issues, related to linear response theory, 'inverted' snowball effects, and inertial relaxation, are also analyzed.

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Reproducing experimental data of relaxation phenomena in liquid water: ambient and low temperature

María C. Morón,^{*†§} Diego Prada-Gracia[‡] and Fernando Falo^{§ &}

[†] Instituto de Ciencia de Materiales de Aragón, CSIC – Univ. Zaragoza, Campus San Francisco, E-50009 Zaragoza, Spain

[‡] Department of Pharmacological Sciences, Icahn School of Medicine at Mount Sinai, New York 10029, United States of America

[§] Departamento de Física de la Materia Condensada, Facultad de Ciencias, Univ. Zaragoza, E-50009 Zaragoza, Spain

[&] Instituto de Biocomputación y Física de Sistemas Complejos (BIFI), Campus Rio Ebro, 50018 Zaragoza, Spain

The relaxation dynamics of ambient and low temperature liquid water has been analyzed through all-atom molecular dynamics simulations, residence times, and time correlation functions from 300 K to 243 K. A nanodrop of neat water has been modelled as a sphere of nanometric dimensions. A stretched exponential function $\exp[-(t/\tau)^\beta]$ has been found to properly describe the decay of residence times calculated at different temperatures for the solvent molecules within that sphere. The relaxation time τ increases as the temperature decreases, exhibiting a divergence at $T_s = 227 \pm 3$ K. Since the stretched exponent amounts $\beta = 0.59 \pm 0.01$, and therefore $\beta \neq 1$, the presence of, not a unique decay time, but a distribution of relaxation times is indicated. The temperature independence of β suggests that such a distribution of decay times also holds at low temperature. An explanation for that heterogeneity can be found at the nanoscopic level (Fig. 1). Experimental data are quantitatively replicated by the above reported T_s and β values (previous numerical simulations in the bibliography do not do it).

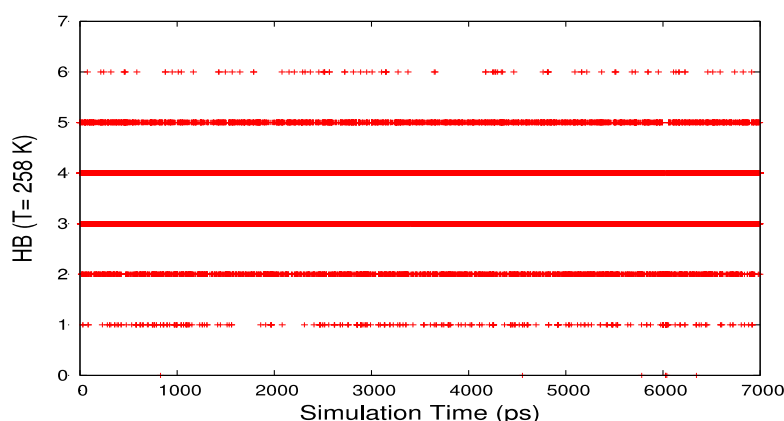


Fig. 1: Number of hydrogen bonds (HB) that, as a function of time, a water molecule can establish with their neighbours at 258 K.

Local structural fluctuations, hydrogen bonding and structural transitions in supercritical water

Ioannis Skarmoutsos,[†] Elvira Guàrdia[‡] and Jannis Samios[§]

[†] Institut Charles Gerhardt Montpellier, UMR 5253 CNRS, Université de Montpellier, Place E. Bataillon, 34095 Montpellier, Cedex 05, France

[‡] Departament de Física, Universitat Politècnica de Catalunya, Campus Nord UPC, 08034 Barcelona, Spain

[§] National & Kapodistrian University of Athens, Department of Chemistry, Laboratory of Physical Chemistry, Panepistimiopolis 15771, Athens, Greece

The contribution of hydrogen bonding interactions to the formation of local density inhomogeneities in supercritical water at near-critical conditions has been extensively studied by means of molecular dynamics simulations. Particular attention has been given to the effect of hydrogen bonding interactions on the bulk density dependence of the local density augmentation around the water molecules. The results obtained have revealed the strong effect of water molecules forming one and two hydrogen bonds on the determination of the local density augmentation in the fluid. The local structural order has also been studied in terms of the trigonal and tetrahedral order parameters, revealing the correlation between local orientational order and hydrogen bonding. The dynamics of the structural order parameters exhibit similarities with the local density ones. Interestingly, their corresponding relaxation times are maximized at the range of bulk densities where the local density augmentation also attains its maximum value. The local structural analysis performed in terms of nearest neighbors around the individual molecules provides additional significant evidence about the existence of a liquid-like to gas-like structural transition in supercritical water at the density range close to $0.2 \rho_c$, further supporting previous qualitative suggestions based on the interpretation of experimental thermodynamic data.

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Crystal polymorphism and hexatic phase in a many-body model for a water monolayer

Oriol Vilanova, Giancarlo Franzese

Departament de Física Fonamental, Universitat de Barcelona, Diagonal 645,
E-08028 Barcelona, Spain

We show that water confined in narrow hydrophobic slit pores, such as those formed by graphene-based membranes, is polymorphic when it crystallizes. We consider the case of a confined water monolayer and we find two crystals with different symmetry and density at low temperature T : a low-density crystal (LDc) at low pressure P , and a high-density crystal (HDc) at high P . By increasing T or decreasing P we find a pair of continuous phase transitions to a low density hexatic (LDh) phase and to a high density hexatic (HDh) phase at low T and a second pair of continuous phase transitions to a low density liquid (LDL) and to a high density liquid (HDL) at higher T , respectively. Furthermore, we find evidences of a LDL-HDL first-order phase transition ending in a liquid-liquid critical point. These results are presented within the framework of a many-body model of water where we consider explicitly the contribution of three-body interactions separated from the rest of many-body interactions. We discuss how our results depend on the choice of parameters of the model, opening the way for a systematic study of how the strength of three-body interactions in coarse-grained models of water affects the observability of the liquid-liquid phase transition.

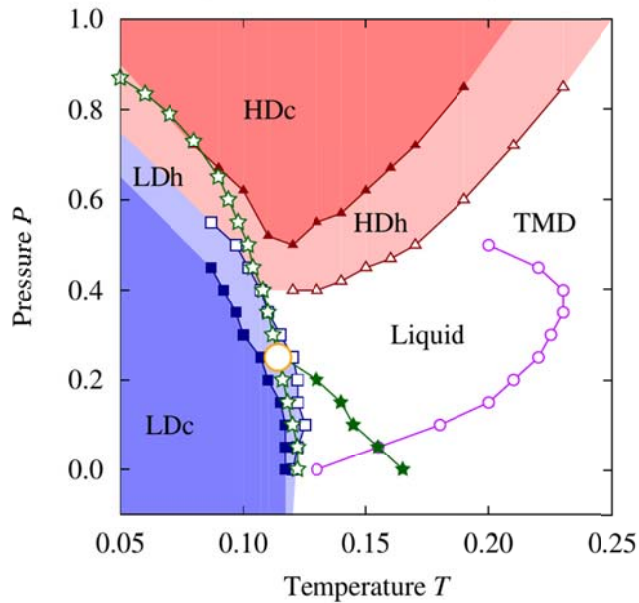


Fig. 1. P – T Phase diagram with parameters $\varepsilon = 1$, $J = 0.5$, $J_\sigma = 0.1$, $q = 6$ and $J_\theta = 0.10$. We identify various phases as: liquid (Liq), gas (Gas), low density hexatic with square symmetry (LDh), high density hexatic with triangular symmetry (HDh), low density crystal with square symmetry (LDc) and high density crystal with triangular symmetry (HDc). Other quantities such as the Temperature of maximum density (TMD), and the maxima in the specific heat CP are shown.

Simulations of nanoconfined water between corrugated walls

Jon Zubeltzu[†] and Emilio Artacho^{†‡§}

[†]CIC Nanogune and DIPC, Tolosa Hiribidea 76, 20018 San Sebastian, Spain

[‡]Basque Foundation for Science, Ikerbasque, 48011 Bilbao, Spain

[§]Theory of Condensed Matter, Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge, CB3 0HE, United Kingdom

Water confined to nanoscale widths in two dimensions between ideal planar walls has been the subject of ample study, aiming at understanding the intrinsic response of water to confinement, avoiding the consideration of the chemistry of actual confining materials. In this work [1], we study the response of such nanoconfined water to the imposition of a periodicity in the confinement by means of computer simulations, both using empirical potentials and from first-principles. For that we propose a periodic confining potential emulating the atomistic oscillation of the confining walls, which allows varying the lattice parameter and amplitude of the oscillation. We do it for a triangular lattice, with several values of the lattice parameter: one which is ideal for commensuration with layers of Ih ice, and other values that would correspond to more realistic substrates. For the former, the phase diagram shows an overall rise of the melting temperature. The liquid maintains a bi-layer triangular structure, however, despite the fact that it is not favoured by the external periodicity. The first-principles liquid is significantly affected by the modulation in its layering and stacking even at relatively small amplitudes of the confinement modulation. Beyond some critical modulation amplitude the hexatic phase present in flat confinement is replaced by a trilayer crystalline phase unlike any of the phases encountered for flat confinement. For more realistic lattice parameters, the liquid does not display higher tendency to freeze, but it clearly shows inhomogeneous behaviour as the strength of the rugosity increases. In spite of this expected inhomogeneity, the structural and dynamical response of the liquid is surprisingly insensitive to the external modulation. Although the first-principles calculations give a more triangular liquid than the one observed with empirical potentials (TIP4P/2005), both agree remarkably well for the main conclusions of the study.

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Characterizing ordering in liquid water: An information theory approach

L.C. Pardo,[†] A. Henao[†] and E. Guàrdia[§]

[†]Departament de Física, Universitat de Politècnica de Catalunya, C/ Eduard Maristany 10,
E-08019 Barcelona, Spain

[§]Departament de Física, Universitat de Politècnica de Catalunya, B4-B5 Campus Nord UPC,
E-08034 Barcelona, Spain

Information theory is a general method to quantify correlations and information content in N-dimensional Probability Distribution Functions. Since the structure of liquids is fully described by the six-fold Probability Distribution Function $g(r, \Omega)$ it is possible to apply the whole information theory formalism to the study of liquids in general and of liquid water in particular. To do that we have split the five angles Ω describing the ordering of two molecules in two sets: one describing the position in spherical coordinates $\Omega_{pos} = \{\theta_{pos}, \varphi_{pos}\}$ and another one that only has into account the relative orientation of the two molecules, characterized by the three Euler angles $\Omega_{ori} = \{\theta_{ori}, \varphi_{ori}, \psi_{ori}\}$. This partition allows us to characterize the ordering of liquids at a great level of detail [1]. More important, though, is that this separation in different contributions allows us to quantify how well ordered are liquids with respect to their relative position and orientation. Applying this method to liquid water has allowed us to determine that it is structured up to distances as long as 10 Å, where the effects of the tetrahedral structure of liquid water at short distances is still to be felt [2].

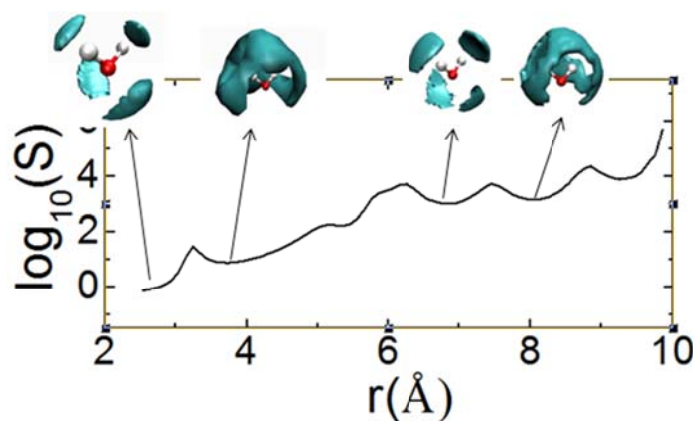


Fig. 1: Positional entropy in liquid water, together with the PDF associated to the angles describing the position of liquid water in spherical coordinates $\Omega_{pos} = \{\theta_{pos}, \varphi_{pos}\}$

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SnI₄— the substance that allows us to enter the no man’s land

Kazuhiro Fuchizaki,[†] Ayako Ohmura,[‡] Akio Suzuki,[§] Keisuke Nishida,[¶]

Hiroyuki Saitoh,[§] and Nozomu Hayama^{*}

[†]Department of Physics, Ehime University, Matsuyama 790-8577, Japan

[‡]Center for Transdisciplinary Research, Niigata University, Niigata 950-2181, Japan

[§]Department of Earth Science, Tohoku University, Sendai 980-8578, Japan

[¶]Department of Earth and Planetary Science, The University of Tokyo, Tokyo 113-0033, Japan

[§]National Institutes for Quantum and Radiological Science and Technology, Hyogo 679-5148, Japan

^{*}Graduate School of Humanities and Sciences, Ochanomizu University, Tokyo 112-8610, Japan

Tin tetraiodide has been shown to exhibit water-type polyamorphic nature; it has low-density amorphous (LDA) and high-density amorphous (HDA) states [1]. Unlike water, the corresponding thermodynamically stable liquid counterparts, low-density liquid (LDL) and high-density liquid (HDL) states, with different local structures and densities, could be identified in the bulk [2,3]. The pseudo-binary regular-solution model [4], a coarse-grained Potts model [5], and the Franzese—Stanley (FZ) model [6] could capture equally well the location of these states and phases on the pressure—temperature phase diagram [7]. All these models support the existence of the liquid—liquid critical point, whose location was predicted to be close to the breakpoint (at ~ 1.5 GPa and 950 K) of the melting curve of the crystalline phase [7]. This prediction has indeed been confirmed by our recent x-ray absorption measurement [8]. That is, the liquid—liquid critical region will never be “no-man’s land” for tin tetraiodide. Moreover, our recent x-ray absorption experiment revealed the existence of a temperature of maximum density in the region between 1100 K and 1400 K just below 1 GPa, which is quite consistent with the theoretical prediction [9]. In conclusion, SnI₄ is said to be polyamorphically similar to water, but SnI₄ allows us to enter the no man’s land of water [10].

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Viscosity of supercooled water under pressure and two-state interpretation of water anomalies

Lokendra P. Singh, Bruno Issenmann and Frédéric Caupin

Université Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622,
Lyon, France

Among the numerous anomalies of water, the effect of pressure on its transport coefficients is particularly striking. Around room temperature, an increase in pressure from ambient results in a decrease of viscosity and rotational correlation time, while the translational diffusion coefficient increases. At high enough pressure, around 200 MPa, the pressure dependence is reversed and water behaves as a normal liquid. The pressure anomalies for translational and rotational diffusion have been followed deep in the supercooled region. However, up to now, viscosity data for supercooled water under pressure was not available. We report for the first time such data [1], obtained with a Poiseuille flow experiment performed up to 300 MPa and down to 20°C below the melting line. Our data reveal a large intensification of the viscosity anomaly upon cooling: pressurization at 244 K reduces the viscosity of water by nearly a factor of 2. The location of the viscosity minimum follows that of the translational diffusion coefficient maximum.

We discuss experimental data on dynamic properties in the framework of two-state models for water. Combining a modified version of a previous dynamic model [2] with an existing, quantitative model for thermodynamics [3], we obtain an accurate description of dynamic properties of stable and supercooled water under pressure. We discuss the possible connection with a putative phase transition between two distinct liquid forms of supercooled water [4].

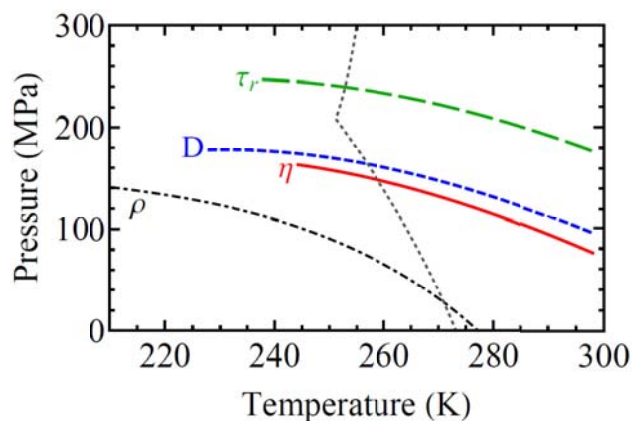


Fig. 1: Location in the pressure-temperature plane of the extrema along isotherms for viscosity η (full red curve), self-diffusion coefficient D (short-dashed blue curve), rotational correlation time τ_r (long-dashed green curve), and density ρ (dash-dotted black curve). The gray dotted curve shows the melting lines of ice Ih and ice III

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Do ordinary water and heavy water behave differently under supercooled and superstretched conditions?

Michal Duška^{1,2}, Jan Hrubý², Frédéric Caupin³, and Mikhail Anisimov^{1*}

¹Department of Chemical & Biomolecular Engineering and Institute for Physical Science & Technology, University of Maryland, College Park, U.S.A.

²Institute of Thermomechanics, Academy of Sciences of the Czech Republic, 182 00 Prague 8, Czech Republic

³Univ Lyon, Université Claude Bernard Lyon 1, CNRS and Institut Universitaire de France, Institut Lumière Matière, F-69622, Lyon, France

*Corresponding author: anisimov@umd.edu

Both ordinary water (H₂O) and heavy water (D₂O) exhibit similar thermodynamic anomalies in metastable, supercooled states. However, heavy water has even stronger hydrogen bonds, with a more distinct tetrahedral structure at higher temperatures, than expected. As a result, the anomalies are more pronounced in supercooled heavy water. We have revisited thermodynamic properties of heavy and ordinary water using a concept of two interconvertible structures, A and B, with a fraction of conversion controlled by thermodynamic equilibrium. We have developed a new version of the “two-structure” equation of state, in which structure A explicitly contains the information on the absolute-stability limit of the liquid state with respect to vapor. We have found a pronounced distinction between these two substances in supercooled conditions. In particular, the Widom line in heavy water is crossing homogeneous nucleation line at a positive pressure. We have also considered experimental consequences of this difference, especially for the detection of the anomalies in superstretched water (at negative pressures).

Posters

Ice sublimation in dry weather: Mars vs. Earth

Alexander Bittner

CIC nanoGUNE, Tolosa Hiribidea, 76 E-20018 Donostia - San Sebastian, Spain
a.bittner@nanogune.eu

Growth and sublimation of single and polycrystalline ice were followed in real time with an environmental electron microscope. Several well-known, and some new phenomena occur on the microscale, most notably in grain boundaries. In pure water ice, the findings do not require invoking the existence of liquid water [1].

[1] www.nanogune.eu/en/research/self-assembly/

Toward a coherent picture of the low density, high density and very-high density forms of bulk water

Luis E. Coronas,¹ Valentino Bianco,² Arne W. Zantop³ and Giancarlo Franzese^{1,4}

¹ Secció de Física Estadística i Interdisciplinària--Departament de Física de la Matèria Condensada, Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain

² Faculty of Physics, University of Vienna, Sensengasse 10/8, 1090, Vienna, Austria

³ Max Plank Institute for Dynamics and Self-Organization, Am Fassberg 17, 37077 Göttingen, Germany

⁴ Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain

We study, by Monte Carlo simulations, a coarse-grained model for bulk water that includes many-body interactions associated to water cooperativity. The model is efficient and allows us to equilibrate water at extreme low temperatures in a wide range of pressures. We calculate the specific heat (C_P), thermal expansivity (α_P) and isothermal compressibility (K_T), for which we find loci of strong and weak extrema. Our results show the presence of a low density liquid (LDL) and a high density liquid (HDL), separated by a liquid-liquid phase transition (LLPT) ending in a liquid-liquid critical point (LLCP) and a smooth structural change between HDL and very high density liquid (VHDL), recalling the structural transformation occurring among LD amorphous, HD amorphous and VHD amorphous. Our results clarify fundamental properties of bulk water that are consistent with the available experimental data.

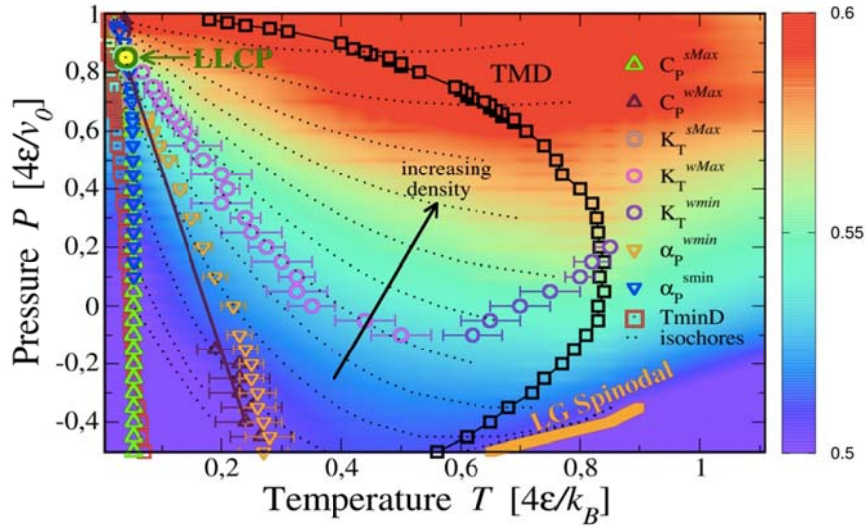


Fig. 1. Phase diagram of the bulk many-body model showing the temperature of maximum density (TMD) line, the liquid-gas (LG) spinodal, the liquid-liquid critical point (LLCP), color coded densities along isochores (dashed lines) and quantities described in the legend.

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Heterogeneous ice nucleation dependence on the crystallographic faces of K-Feldspar minerals

E.Pach[†], A.Verdaguer[§]

[†] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain

[§]Institut de Ciència de Materials de Barcelona ICMAB-CSIC, Campus de la UAB, E-08193 Bellaterra, Spain

Ice formation on aerosol particles is a process of crucial importance in Earth's climate, but it is still not understood at the molecular level. Heterogeneous nucleation of ice on solid particles in the aerosols is induced by active sites, local surface features where ice growth starts. What makes a local surface feature an active nucleation site is still unclear nowadays, however it is known that surfaces can induce ice-like structures on adsorbed water on their surfaces [1], even at room temperature [2]. Recently a publication reported electron-microscopic observations of aligned ice crystals on feldspar, an atmospherically important component of mineral dust [3]. These experiments were performed at low temperatures between -40 and -25 °C and they are thus related to deposition growth ice nucleation mechanism. Using environmental scanning electron microscopy (E-SEM), we found similar alignment for other feldspar species and faces, but at higher temperatures (from -20 to -10 °C after water condensation on the feldspar surface), indicating that this alignment is also induced for an immersion growth ice nucleation mechanism. Alignment of ice crystals was correlated with crystallographic directions on the feldspar structure for each face investigated.

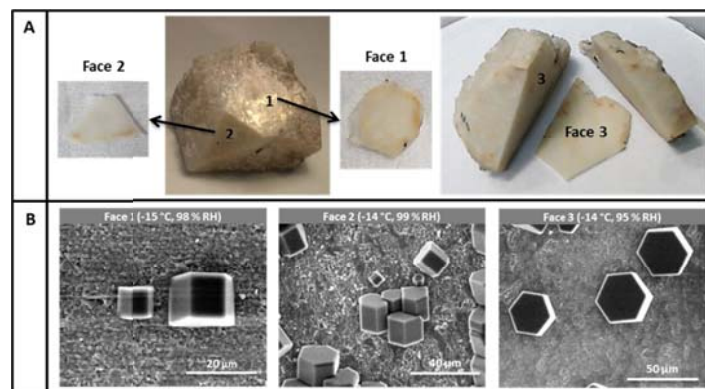


Fig. 1: **A:** Photographs of original Feldspar crystal and corresponding cuts parallel to known crystallographic faces. **B:** ESEM images of ice crystals alignment on different crystallographic faces of Feldspar.

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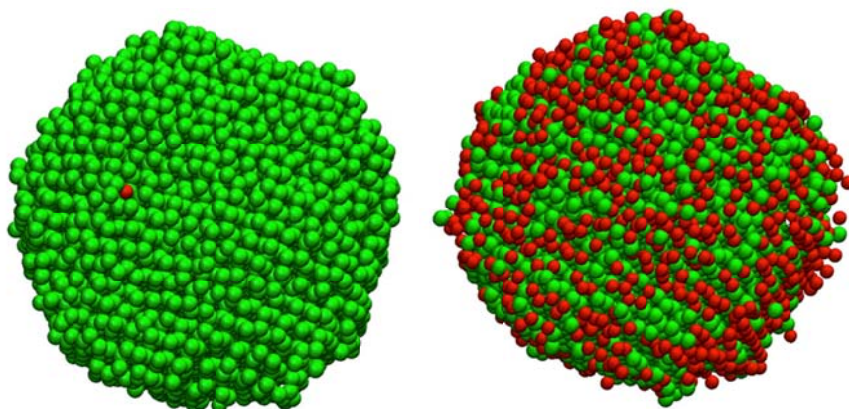
The Role of Ice 0 in Ice Nucleation

Jorge Reñe[†], Alberto Zaragoza[†], Pablo Rosales[†], Chantal Valeriani^{††}, Carlos Vega[†] and Eduardo Sanz[†]

[†] Departamento de Química-Física I, Universidad Complutense de Madrid, Spain

^{††} Departamento de Física Aplicada I, Universidad Complutense de Madrid, Spain

One of the fundamental questions regarding homogeneous ice nucleation is the structure of the critical cluster in terms of size, shape, and crystalline structure. By means of Molecular Dynamics we [1] study the role of the recently reported ice 0 [2] in ice nucleation in order to clarify whether this new polymorph participates in an early step of this process. Following the basis proposed in the seeding technique, we perform computer experiments consisting in embedding ice seeds in supercooled water and, with the aid of the Classical Nucleation Theory (CNT), we estimate the size of the critical cluster, the interfacial free energy and the nucleation rate which, in the end gives us an idea about whether a nucleation mechanism is more favorable than another. We found Ice 0 not to be the precursor of Ice Ih for its nucleation rate is 200 orders of magnitude below the same of Ice Ih. We have also found Ice 0 not to be part of the shell of Ice Ih, attributing the mislabeling to the order parameter; which should not be used to determine the crystalline structure of the molecules in the surface of any clusters, due to the irregular surroundings of the surface molecules.



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Genuine antiplasticizing effect of water on a glass-former drug

Guadalupe N. Ruiz^{1,2}, Michela Romanini^{1,2}, Astrid Hauptmann³, Thomas Loerting³, Evgenyi Shalaev⁴, Josep LL. Tamarit^{1,2}, Luis C. Pardo^{1,2} and Roberto Macovez^{1,2}

¹*Grup de Caracterització de Materials, Departament de Física, Universitat Politècnica de Catalunya, EEBE, Campus Diagonal-Besòs, Av. Eduard Maristany 10-14, E-08019 Barcelona, Spain.*

²*Barcelona Research Center in Multiscale Science and Engineering, Av. Eduard Maristany 10-14, E-08019 Barcelona, Spain.*

³*Institute of Physical Chemistry, University of Innsbruck, Innrain 52c, 6020 Innsbruck, Austria*

⁴*Allergan Inc. 92612 Irvine, USA*

E-mail: guadalupe.ruiz@upc.edu

Water is the most important plasticizer of organic and biological specimens [1-4], leading generally to enhanced molecular mobility and lowering of the glass transition temperature (T_g) of glass-forming samples upon hydration[5-8]. Such plasticizing effect of water in glass-forming solutions is so ubiquitous and consistent that a recent survey has suggested that aqueous solutions may display a universal dependence of T_g on water content, with a relatively steep decrease of the glass transition temperature upon addition of water [9]. In fact, it has even been suggested that the hydration water content can be quantitatively determined from the T_g value of the liquid mixtures [10]. Here we present the first-ever experimental evidence of an antiplasticizing effect of water on a molecular glass former, prilocaine. We study aqueous solutions of the prilocaine anesthetic by means of scanning calorimetry, vibrational spectroscopy, and ambient- and high-pressure dielectric spectroscopy. For a water molar fraction greater than approximately $x = 0.3$, the system separates in two stable liquid phases: a prilocaine-rich liquid with minority water content (liquid L₁), and a very dilute water-based solution of prilocaine (liquid L₂) [11]. For water molar fraction below 0.35, the homogeneous L1 liquid is formed. This phase displays an increase of T_g of up to 4 K and a concomitant slowing down of the cooperative molecular dynamics, an effect similar to that of applying an hydrostatic pressure on pure prilocaine. Vibrational characterization indicates that water molecules bridge together prilocaine pairs via water-donated hydrogen bonds. Our findings have important theoretical consequences as they shed a whole new perspective on the role of water as plasticizer, and are also of practical relevance as an increase in T_g implies a higher stability in the amorphous state, which is a crucial prerequisite to enhance the bioavailability of poorly water-soluble drugs.

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Water interacting with nanocarbons through IR, XPS and DFT calculations

Yuman Sayed-Ahmad-Baraza[†], Bernard Humbert[†], Wolfgang K. Maser⁺, Ana M. Benito⁺, Carla Bittencourt[‡], Dogan Erbahar[§], Toma Susi^{*} and Chris P. Ewels[†]

[†] Institute of Materials Jean Rouxel (IMN), CNRS / University of Nantes, UMR6502, 2 Rue de la Houssinière, BP32229, 44322 Nantes, France

⁺ Instituto de Carboquímica ICB-CSIC, C/Miguel Luesma Castán 4, E-50018 Zaragoza, Spain

[‡] Chemistry of Interaction Plasma-Surface (ChIPS), University of Mons, Mons, Belgium.

[§] Physics Department, Gebze Technical University, Gebze, Turkey.

^{*} Institute for Materials Chemistry, TU Vienna, A-1060 Vienna, Austria.

We have been studying the interaction between water and different carbon nanomaterials using a range of characterization techniques including notably near-IR, XPS and density functional calculations. Water interaction with C₆₀ crystals is of great interest for the interstellar chemistry community, with the recent proof of the existence of large quantities of C₆₀⁺ in space. In a range of XPS experiments we show that water-ice phase is present on C₆₀ crystal surfaces, even at room temperature under ultra-high vacuum conditions. Comparison with DFT calculations of oxygen-hydrogen-fullerene structures and associated calculated XPS-peak shifts identify the two peaks seen to correspond to an ice-like hydrogen-bonded water network, and hydroxyl groups. NEXAFS synchrotron measurements confirm that this layer is confined to the crystal surfaces. We speculate about the importance of this as a potential interstellar zone for UV-catalysed reactions [1].

In parallel we have been investigating the behavior of water and associated functional groups with graphene surfaces. The production of graphene oxide (GO) via the Hummers method results in a range of different surface functional groups [2]. In the current study we use near-IR measurements at different humidity to reveal the different functional group behavior and degree of hydrogen-bonding interaction with absorbed water [3]. This is compared to different density functional structural models. Understanding the behavior and changes in water-GO bonding will be critical for many future applications such as water filtration.

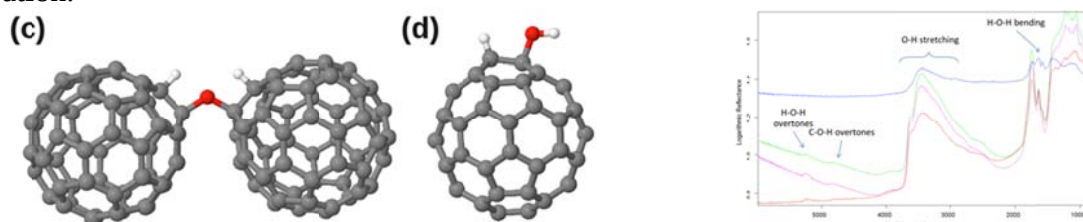


Fig. 1: (left) Two possible water-fullerene structures as modelled with DFT, (right) near-IR spectrum for humid graphene oxide samples.



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Atomic-Scale Sliding Friction on Graphene in Water

J. G. Vilhena,^{1,2} Carlos Pimentel,^{3,4} Patricia Pedraz,⁵ Feng Luo,⁵ Pedro A. Serena,²
Carlos Pina,^{3,4} Enrico Gnecco,^{5,6} and Rubén Pérez^{1,7*}

¹Departamento de Física Teórica de la Materia Condensada Universidad Autónoma de Madrid, Madrid, Spain

²Instituto de Ciencia de Materiales de Madrid (ICMM), Madrid, Spain

³Universidad Complutense de Madrid, Madrid, Spain

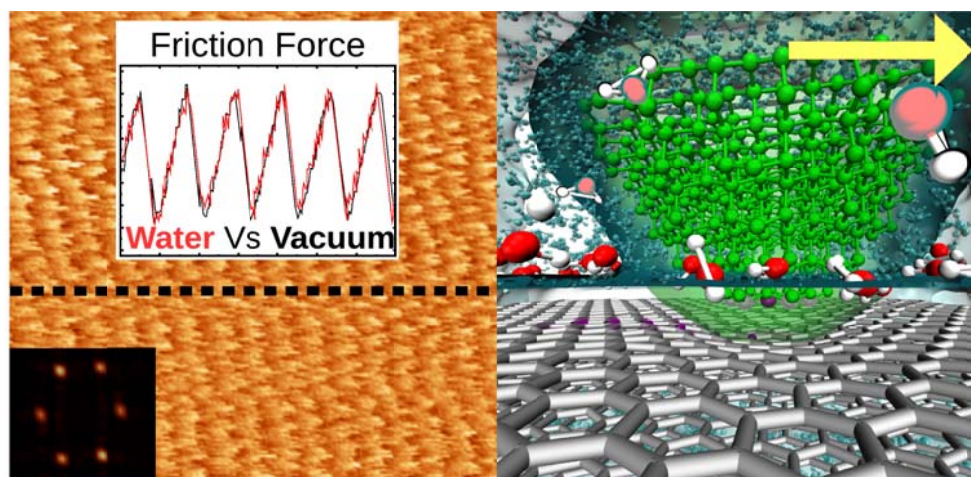
⁴Instituto de Geociencias (CSIC, UCM), E-28040 Madrid, Spain

⁵Instituto Madrileño de Estudios Avanzados (IMDEA), Madrid, Spain

⁶Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Jena, Germany

⁷Condensed Matter Physics Center (IFIMAC), Universidad Autonoma de Madrid, Madrid, Spain
E-mail: ruben.perez@uam.es

The sliding of a sharp nanotip on graphene completely immersed in water is investigated by molecular dynamics (MD) and atomic force microscopy. MD simulations predict that the atomic-scale stick-slip is almost identical to the one found in ultra- high vacuum. Furthermore, they show that water plays a purely stochastic role on sliding (solid-to-solid) friction. These observations are substantiated by friction measurements on graphene grown on Cu and Ni, where, oppositely to operation in air, lattice resolution is readily achieved. Our results not only promote friction force microscopy in water as a robust alternative to ultra-high vacuum measurements but also they suggest that friction measurements could unveil the subtle dynamical lateral order induced by a hydrophobic material like graphene on the water hydration layer.



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Effect of a DC Electric field on the melting temperature, nucleation and ice growth rate of TIP4P/Ice water

J. Ramirez[†], A. Zaragoza[§], J.R. Espinosa[‡], R. Ramos[†], J. A. Cobos[†], E. Sanz[‡], C. Valeriani[§],
C.Vega[‡]

[†]Departamento de Ingeniería Química Industrial y Medio Ambiente, Universidad Politécnica de Madrid, José Gutiérrez Abascal, 2, 28006 Madrid , Spain

[‡]Departamento de Química-Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Parque de las Ciencias, 28040, Madrid, Spain

[§]Departamento de Física Aplicada, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Parque de las Ciencias, 28040, Madrid, Spain

Ice nucleation is the most relevant phase transition on Earth. It has strong applications in many fields such as the food industry, cryopreservation, and environmental science. A lot of effort has been put in understanding the mechanism of ice formation, however, many questions still need to be answered. In this work, we study ice crystallization under static electric fields by means of computer simulations to find out how the field affects ice formation: whether it enhances or decreases it [1,2]. For that purpose we introduce ice Ih spherical seeds in polarised supercooled water in order to evaluate by Seeding+CNT [3-5] both interfacial free energies and nucleation rates. We also study crystal growth rate by means of direct coexistence simulations. Our conclusions are that the nucleation and growth rate are hampered for ice Ih under electric fields. However, when introducing a novel ferroelectric ice Ic polymorph (Icf), we have discovered that nucleation rates are similar (for the same supercooling) than the ones estimated for ices Ih/Ic without any electric field and the growth rates increased. In addition, for the Icf the melting temperature increases with the electric field (the contrary effect that happens for the ice Ih) which makes Icf nucleation much more favored. So for the first time, ice Ic presents significant differences respect to the ice Ih due to its ability for being completely polarised by the electric field.

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Participants

● Abascal, José Luis F.	Universidad Complutense de Madrid	<i>abascal@ucm.es</i>
● Abramczyk, Halina	Lodz University of Technology (Poland)	<i>abramczy@mitr.p.lodz.pl</i>
● Alliota, Francesco	IPCF-CNR, Messina (Italy)	<i>aliotta@ipcf.cnr.it</i>
● Anisimov, Michael	University of Maryland (USA)	<i>anisimov@umd.edu</i>
● Artacho, Emilio	Cavendish Laboratory, University of Cambridge (United Kingdom)	<i>ea245@cam.ac.uk</i>
● Ben-Naim, Arie	Hebrew University, Jerusalem (Israel)	<i>ariehbennaim@gmail.com</i>
● Bianco, Valentino	Universitat de Barcelona	<i>vbianco@ub.edu</i>
● Bittner, Alexander	CIC-NanoGUNE	<i>a.bittner@nanogune.eu</i>
● Calero, Carles	Universitat de Barcelona	<i>ccalero@ffn.ub.es</i>
● Caupin, Frédéric	Université de Lyon (France)	<i>frederic.caupin@univ-lyon1.fr</i>
● Conde, María M.	Università degli Studi-Roma Trè (Italy)	<i>mmconde@amaldi.fis.uniroma3.it</i>
● Faraudo, Jordi	Institut de Ciència de Materials de Barcelona ICMAB-CSIC	<i>jfaraudo@icmab.es</i>
● Franzese, Giancarlo	Universitat de Barcelona	<i>gfranzese@ub.edu</i>
● Fuchizaki, Kazuhiro	Ehime University, Matsuyama (Japan)	<i>fuchizak@phys.sci.ehime-u.ac.jp</i>
● Guàrdia, Elvira	Universitat Politècnica de Catalunya-Barcelona Tech	<i>elvira.guardia@upc.edu</i>
● López, M. Nieves	Instituto Ciencia Materiales- CSIC	<i>marianieves.lopez@csic.es</i>

● MacDowell, Luis G.	Universidad Complutense de Madrid	<i>lgmac@quim.ucm.es</i>
● Martí, Jordi	Universitat Politècnica de Catalunya-Barcelona Tech	<i>jordi.marti@upc.edu</i>
● Morón, M.Carmen	Instituto de Ciencia de Materiales de Aragón-CSIC	<i>nina@unizar.es</i>
● Pardo, Luis Carlos	Universitat Politècnica de Catalunya-Barcelona Tech	<i>luis.carlos.pardo@upc.edu</i>
● Pach, Elzbieta	Centre d'Investigació en Nanociència i Nanotecnologia, CIN2, (ICN-CSIC)	<i>Elzbieta.pach@icn2.cat</i>
● Rey, Rossend	Universitat Politècnica de Catalunya-Barcelona Tech	<i>rosendo.rey@upc.edu</i>
● Roldán, María Jesús	Instituto de Ciencia de Materiales-CSIC	<i>mariaj.rolan@csic.es</i>
● Rosales, Pablo	Universidad Complutense de Madrid	<i>pabros01@ucm.es</i>
● Sánchez-Marcos, Enrique	Universidad de Sevilla	<i>sanchez@us.es</i>
● Sayed-Ahmad, Yuman	Institut des Matériaux Jean Rouxel (CNRS)- Université de Nantes (France)	<i>Yuman.Sayed-Ahmad@cnrs-imn.fr</i>
● Semino, Rocío	Inst. Charles Gerhardt Montpellier (France)	<i>rocio.semino@gmail.com</i>
● Singh, Jayant	Indian Institute of Technology Kanpur (India)	<i>jayantks@iitk.ac.in</i>
● Skartmoussos, Ioannis	Inst. Charles Gerhardt Montpellier (France)	<i>iskarmoussos@hotmail.com</i>
● Valeriani, Chantal	Universidad Complutense de Madrid	<i>cvaleriani@quim.ucm.es</i>
● Verdaguer, Albert	Centre d'Investigació en Nanociència i Nanotecnologia, CIN2, (ICN-CSIC)	<i>albert.verdaguer@cin2.es</i>

• Vilanova, Oriol	Universitat de Barcelona	<i>oriol.vilanova@gmail.com</i>
• Vilhena, José Guilherme	Universidad Autónoma de Madrid	<i>guilhermevilhena@gmail.com</i>
• Wynne, Klaas	University of Glasgow, School of Chemistry (United Kingdom)	<i>klaas.wynne@glasgow.ac.uk</i>
• Zaragoza, Alberto	Universidad Complutense de Madrid	<i>azlorite@ucm.es</i>