WaterX
exotic properties of water under extreme conditions

Book of Abstracts

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Venue

Circolo Ufficiali Della Marina, Lungomare Ammiraglio Mirabello, 6 - 07024 La Maddalena (OT)
Maddalena Island, 07024 La Maddalena, Province of Olbia-Tempio, Sardinia (Italy)

Web Site

https://www.water-x.eu

WaterX - Program May 25 - May 30 2024 - La Maddalena (Italy)

time	Saturday May 25
18:30	Welcome Cocktail
21:00	Opening Lecture: Pablo Debenedetti

time	Sunday May 26
8:30	Opening & Registration
9:00	Osamu Mishima
9:45	Valeria Molinero
10:15	Anders Nilsson
10:35	John Loveday
10:55	Claudia Goy
11:15	Coffee Break
11:40	Federica Coppari
12:10	Graeme Ackland
12:30	Qingyu Kong
12:50	Xijie Wang
13:10	Lunch
14:30	Gabriel Tobie
15:00	Simone Di Cataldo
15:20	Maria Rescigno
15:40	Robert Bauer
16:00	Shunsuke Nozaki
16:15	Excursion: Caprera Trail and beach or Caprera Memoriale Museum
19:30	Sunset at Baia Trinita

time	Monday May 27
6:00	Sunrise Trail to Tahiti #
9:00	Martina Havenith
9:45	Richard Saykally
10:15	Damian Laage
10:35	Simone Pezzotti
10:55	Wanlin Chen
11:10	Coffee Break
11:40	Heloisa Bordallo
12:10	Margarita Russina
12:30	Frederic Caupin
12:50	Jan Eichler
13:05	Lorenzo Rovigatti
13:20	Lunch
	Free Time Possibility of Scuba Diving **
16:00	Patrick Charbonneau
16:30	Letizia Tavagnacco
16:50	Maria Grazia Izzo
17:10	Paola Gallo
17:30	Sergey Buldyrev
17:50	Poster Shower
18:20	Poster & Drinks

time	Tuesday May 28
9:00	Katrin Amman-Winkler
9:45	Kazuki Komatsu
10:15	Leonardo Del Rosso
10.35	Bertrand Chazallon
10:55	Tomasz Poreba
11:10	Coffe Break
11:40	Stefan Klotz
12:10	Keishiro Yamashita
12:30	Andreas Hermann
12:50	Fabio Finocchi
13:10	Lunch
14:30	Nønne Prisle
15:00	Barbara Wyslouzil
15:30	Thorsten Bartels-Rausch
15:50	Ivan Saika-Voivod
16:10	Miguel De La Puente
16:25	Coffee Break
16:45	Nigel Wilding
17:15	Francesco Paesani
17:35	Eduardo Sanz
17:55	Carlos Vega
18:15	Francesco Guidarelli Mattioli
18:30	Walk to Punta Tegge for Sunset Apero *

time	Wednesday May 29
8:45	Patrick Ayotte
9:15	Kenji Mochizuki
9:35	Xavier Michaut
9:55	Lilli-Ruth Fidler
10:10	Boat trip to Maddalena Arcipelago ##
20:00	Social Dinner

time	Thursday May 30
9:00	Giuseppe Graziano
9:45	Lorna Dougan
10:15	Fatima Matroodi
10:30	Max Warburton
10:45	Carlo Andrea De Filippo
11:00	Coffe Break
11:30	Andreas Neophytou
12:00	Lars Patterson
12:20	Neta Ellert
12:40	Johannes Giebelmann
13:00	CLOSING

max 10 places available.
* An apero-dinner is available at Zi' Anto restaurant in Punta Tegge under request (its cost will be set soon).
** Scuba-diving will be operated by Best Shark Diving Center under request (price of Introductory lesson, or excursion will be set soon).
This activity is NOT included in the registration fee. Its cost (lunch included) will be set soon.

WaterX@2024 International Workshop May 25 – 30, 2024

A Computational Perspective on Supercooled Water

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The preponderance of experimental evidence is consistent with the existence of a metastable first-order transition between two liquid phases in supercooled water [e.g., 1-3]. Computer simulation has played a major role in defining the frontiers of knowledge in this area [4]. Results from a broad range of computational and theoretical approaches, including molecular dynamics [5], free energy calculations [6,7,8], the theory of critical phenomena [5], density functional theory [8,9] and machine learning [8,9], support the existence of a metastable critical point in supercooled water. This has important consequences for the observed behavior of ordinary, stable liquid water at ambient conditions.

[1] K.H. Kim et al., Science 2017, 358, 1589
[2] K.H. Kim et al., Science 2020, 370, 978
[3] J. Bachler et al., PNAS 2021, 118, e21081944118
[4] J.C. Palmer et al., Chem. Rev. 2018, 118, 9129
[5] P.G. Debenedetti et al., Science 2020, 369, 289
[6] J.C. Palmer et al. Nature 2014, 510, 385
[7] F. Sciortino et al., J. Chem. Phys. 2024, 160, 104501
[8] T.E. Gartner et al., Phys. Rev. Lett. 2022, 129, 255702
[9] T.E. Gartner et al., PNAS 2020, 117, 26040

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Temperature of maximum density of water at high pressure and a saddle point

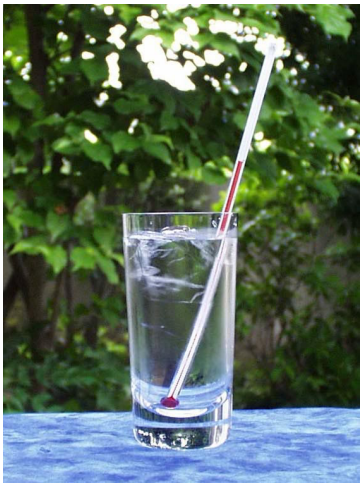
Osamu Mishima
NIMS Emeritus Fellow

The maximum density of liquid water at 4 degrees Celsius is a well-known phenomenon. We recently estimated the maximum density temperature (TMD) under pressure and proposed the location of the TMD line in the pressure-temperature diagram [1]. And since the hypothetical liquid-liquid critical point (LLCP) of water should be on the low-pressure and low-temperature side of the TMD line, the pressure at the critical point was suggested to be below about 150 MPa. Therefore, the critical pressure of about 170 MPa proposed in several recent papers is likely incorrect. In addition to this, we have introduced a "saddle point (SP)" on the water-volume surface, which was presumed to be in the "no man's land" [1]. I will discuss the relationship between SP, LLCP, and the TMD line, referring to previous papers [2, 3].

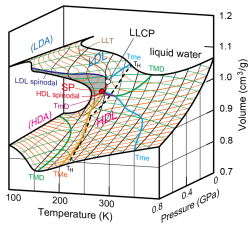
[1] O. Mishima and T. Sumita, J. Chem. Phys. B 2023, 127, 1414-1421.

[2] P. H. Poole et al., Phys. Rev. Lett. 1994, 73,1632-1635.

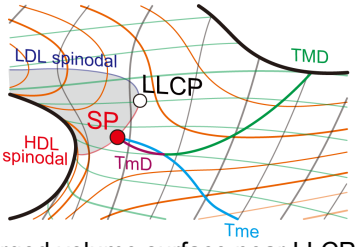
[3] F. Sciortino et al., Phys. Rev. Lett. 2003, 91, 155701.



Ice water in a glass and a red alcohol thermometer



An estimated volume surface of water.[1]



Enlarged volume surface near LLCP.

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Cold, Stressed, and Under Pressure

Valeria Molinero, Ingrid de Almeida Ribeiro, Debdas Dhabal, Rajat Kumar
The University of Utah, USA

Suvo Banik, Subramanian Sankaranarayanan,
University of Illinois Chicago, USA

Recent research has unveiled a new dimension of complexity to water polyamorphism with the discovery of medium density amorphous (MDA) ice (Rosu-Finsen et al., Science 2023, 379, 474-478), raising questions about its relationship with the long-known low density amorphous (LDA) and high density amorphous (HDA) phases, and its connection to the liquid state. In this study, we employ molecular dynamics simulations to investigate the formation and properties of MDA. Our analysis reveals that MDA is a distinct shear-driven non-equilibrium stationary phase of water, with properties that depend on the pressure, temperature and rate of shear rate but not the parent phase from which it is formed. We find that the density of the shear-driven amorphous phase spans all the range from that of LDA to HDA, and demonstrate that shearing provides access to amorphous states of water that cannot be reached by hyperquenching.

*VM, DD and IAR acknowledge support from Air Force Office of Scientific Research through MURI Award FA9550-20-1-0351. We thank the Center of High-Performance Computing at the University of Utah for technical support and a grant of computing time.

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Experimentally Visiting the Region of the Liquid-Liquid Critical Point in Supercooled Water

Seonju You[1], Marjorie Ladd Parada[2], Kyeongmin Nam[1], Aigerim Karina[2], Cheolhee Yang[1], Myeongsik Shin[1], Yeseul Han[1], Sangmin Jeong[1], Seoyoung Lee[1], Kichan Park[1], Kyeongwon Kim[1], Minjeong Ki[1], Robin Tuburski[2], Jae Hyuk Lee[3], Intae Eom[3], Minseok Kim[3], Rory Ma[3], Sangsoo Kim[3], Peter H. Poole[4], Katrin Amann-Winkel[2,5], Kyung Hwan Kim[1], and Anders Nilsson[2]

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One hypothesis to explain the apparent divergence of thermodynamic response and correlation functions [1,2] is that there exists a liquid-liquid transition (LLT) with a liquid-liquid critical point (LLCP) at rather high positive pressures [3]. The challenge is that the diverging temperature lies below the homogeneous ice nucleation temperature 232 K, a region of the phase diagram that has been denoted as “no-man’s land”, since ice crystallization occurs extremely fast compared to the experimentally accessible time scale in a typical laboratory setting. Changing the temperature or pressure quickly, followed by probing of the liquid on ultrafast fast time scales using x-ray lasers have opened-up the possibility of studying water within “no-man’s land” [4]. These experiments have demonstrated the existence of a LLT at positive pressure, one phase behavior at 1 bar at temperatures down to 228 K, and the presence of maxima in several thermodynamic response functions at 1 bar and 230 K [4] consistent with the LLCP hypothesis [3]. However, even after more than 3 decades, since the LLCP hypothesis was proposed, no experiment has yet directly visited the potential critical region of bulk supercooled water.

Here we used nano-second IR laser pulses to heat high-density amorphous ice (HDA) to temperatures higher than the previous LLT study [5] and then probe the liquid state at various densities during the decompression with x-ray scattering from the x-ray laser PAL. Here we see signatures of a transition from a two-phase to a one-phase region as the temperature is varied in the first peak of the structure factor simultaneous with high values of the low momentum transfer (q) region, a consistent behavior as expected with the presence of a LLCP.

[1] R. J. Speedy, C. A. Angell, J. Chem. Phys. 1976, 65, 851-858.
[2] C. Huang *et al.*, J. Chem. Phys. 2010, 133, 134504.
[3] P. H. Poole, F. Sciortino, U. Essmann, H. E. Stanley, Nature 1992, 360, 324-328.
[4] A. Nilsson, J. Non-Cryst. Solids X 2022, 14, 100095 and references therein.
[5] K. H. Kim et al., Science 2020, 370, 978-982.

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Have X-ray laser studies killed off studies of amorphous ices?

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One of the main drivers for studies of amorphous ices has been the two liquids model proposed by Poole *et al* [1]. This model proposes a second critical point at ~0.15 GPa and ~220 K in supercooled liquid water and that at temperatures below this point a line of first order transitions separates high density liquid water from low density liquid water. Because water could not be maintained as a bulk liquid in this region for long enough to be studied, amorphous ices have been used as assumed glassy analogues of the two liquids. The desire to obtain insight into the proposed two-liquids has been at least a partial motivation for the majority of the substantial body of theoretical and experimental studies of amorphous ices that have been undertaken in the past three decades.

Developments in short pulse x-ray and infra-red sources now make it possible to observe liquid water in the supercooled region before it is able to crystallise. Nilsson and co-workers in a series of experiments have exploited these possibilities and found substantial evidence that the model proposed by Poole *et al* is correct [1–3]. Although community acceptance of this conclusion is not complete, it appears that a consensus is building that the two-liquids model is correct. This then raises the question as to whether further studies of amorphous ices are needed since the two liquids can now be studied directly.

In my presentation, I will argue that there is still a place for further of studies of amorphous ices, and that their importance is enhanced because the status of the amorphous ices as glassy analogues has been established. I will also present some suggestions for such further studies.

[1] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, *Phase Behaviour of Metastable Water*, Nature **360**, 324 (1992).
[2] K. H. Kim et al., *Experimental Observation of the Liquid-Liquid Transition in Bulk Supercooled Water under Pressure*, Science **370**, 978 (2020).
[3] K. Amann-Winkel et al., *Liquid-Liquid Phase Separation in Supercooled Water from Ultrafast Heating of Low-Density Amorphous Ice*, Nat Commun **14**, 1 (2023).

WaterX@2024 International Workshop May 25 – 30, 2024

Probing Supercooled Water Through Combined X-ray Emission and Raman Spectroscopy

Claudia Goy[1], Robert Bauer[1,2], Yi-Ping Chang[3], Alexander Gierke[1], Manuel Harder[3], Felix Lehmkühler[1], Florian Trinter[4], Zhong Yin[5], and Robert Grisenti[6,7]

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Waters anomalies in the supercooled region and its specific properties and possible structural and dynamical origins have been extensively studied. X-ray emission spectroscopy (XES) is sensitive to the hydrogen bonds, and indeed the x-ray emission spectrum of liquid water under ambient conditions shows a splitting in the lone pair orbital ($1b_1$), an observation that has been debated to be either the result of contributions from two structural motifs [1] or the signature of the ultrafast dissociation on the time scale of the O 1s core hole [2]. Recent studies using molecular dynamics simulations indicate the importance of including the core-hole dynamics for reproducing a splitting of the $1b_1$ level [3,4] and an all x-ray attosecond transient absorption spectroscopy measurement found no splitting on the sub-fs timescale indicating to hydrogen dynamics as the main origin of the splitting [5]. Temperature-dependent studies can help to understand the connection to the response to different structures. However, previous measurements on supercooled heavy water did not reveal a clear trend of the two components of the $1b_1$ peak in the low-temperature range [6]. Here, we present experiments in which liquid water droplets cooled by evaporation in vacuum are studied simultaneously by XES [7] and Raman spectroscopy [8]. For the specific sample environments, the methods provide access to the temperature-dependent behavior of the inter- and intramolecular vibrational modes, the electronic structure, and also to optical properties such as the refractive index of the liquid.

[1] T. Tokushima, et al., *Chem. Phys. Lett.* **460**, 387 (2008).

[2] O. Fuchs et al. *Phys. Rev. Lett.* **100**, 027801 (2008).

[3] V. W. D. Cruzeiro et al. *J. Phys. Chem. Lett.* **12**, 3996 (2021).

[4] O. Takahashi et al. *Phys. Rev. Lett.* **128**, 086002 (2022).

[5] S. Li et al. *Science* **383**, 1118 (2024).

[6] J. A. Sellberg et al. *J. Chem. Phys.* **142**, 044505 (2015).

[7] Z. Yin et al. *Opt. Lett.* **43**, 4390 (2018).

[8] C. Goy et al. *Phys. Rev. Lett.*, **120**, 015501 (2018).

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Exploring the properties of water ices at extremes with nano-second X-ray diffraction experiments at large laser facilities

Federica Coppari

Lawrence Livermore National Laboratory, Livermore, CA

Multi kJ lasers, such as the NIF (National Ignition Facility, Livermore CA) and the Omega Laser (University of Rochester, NY), can launch shocks and compression sound waves capable of compressing materials to TPa pressures and heating them to thousands of K in a few nanoseconds. Combined with *in-situ* x-ray diffraction and ultra-fast optical diagnostics, these *dynamic* compression techniques become a powerful tool to investigate material properties at unprecedented extreme conditions, providing key insights into the occurrence of phase transitions and materials' equation of state.

Initially liquid water is compressed into the solid state by launching a series of weak shock waves and diffraction measurements document the nucleation of a crystalline lattice in nano-second timescale. In this talk, I discuss the results of these experiments and our understanding of the properties of water ices at extreme pressure and temperature conditions and the implications for high pressure material science and (exo)planetary science.

This work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract No. DE-AC52-07NA27344

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Supercritical Water at the Molecular level

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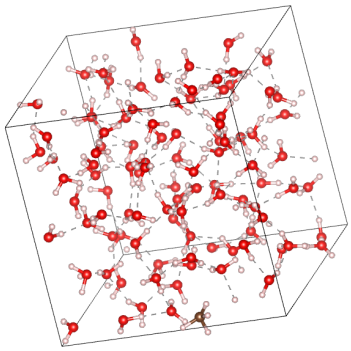
United Kingdom

Water has a critical point at 647K, 22MPa where the liquid and gas phases become indistinguishable. Water is referred to as supercritical above these conditions, but the concept of "above" a point is not physically motivated. Typically a phase diagram shows the region bounded by an isobar and an isotherm emanating from the critical point. The definitive IAWPS equation of state extends to 1273K and 1GPa, but makes no explicit mention of a supercritical state. Nevertheless, "supercritical water" exhibits distinctive properties such as the reversal of solubility such that non-polar molecules become soluble in water. Here, thermodynamic and ab-initio calculations are used to determine the boundaries of a region which can sensibly be defined as supercritical water. No liquid-liquid phase transformation is observed, but the "near-isobar" boundary can be characterized by the region of the Widom lines which naturally extend the liquid-gas phase line. Meanwhile, the "near-isotherm" region is associated with the breakdown of the hydrogen bonding network in the system. This boundary region intercepts the melt curve around the ice VII region, implying that above 10GPa all liquid water can be regarded as supercritical (or ultimately superionic). I will present a density functional theory study demonstrating the molecular level changes to the water structure and it becomes supercritical, which illuminate the reasons for the phenomenon of reversed solubility.



Snapshot from molecular dynamics simulation of methane in water, showing the disruption of the H-bond network (GJA, unpublished work)

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Ultrafast X-ray solution scattering reveals “breathing” dynamics of a broken tetrahedral cage

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Xiaoyi Zhang, Cunming Liu *X-ray Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60349, USA*

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Wenkai Zhang *Department of Physics and Applied Optics Beijing Area Major Laboratory, Center for Advanced Quantum Studies, Beijing Normal University, Beijing 100875, China*

Tsu-Chien Weng *School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China*

Alfredo Pasquarello *Institut de physique, Ecole polytechnique fédérale de Lausanne, CH-1015 Lausanne, switzerland*

Michel H. J. Koch *European Molecular Biology Laboratory, Hamburg Outstation,EMBL c/o DESY, Notkestrasse 85, 22603 Hamburg, Germany*

Michael Wulff *European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France.*

Peiyuan Su, Kai Zhang, Qingyu Kong *Synchrotron Soleil, L’Orme des Merisiers, 91190 Saint-Aubin, France*

The hydrogen bond breaking and structural dynamics of tetrahedral cage with an inserted interstitial H_2O molecule after IR laser excitation were followed by time-resolved X-ray solution scattering with a temporal resolution of tens of femtosecond thanks to the ultrashort and ultrahigh-intensity X-ray pulses from FXE EuXFEL (see left panel). Our results revealed a “breathing” dynamics: laser excitation enhances the OH stretching and bending motions, eventually leading to the breakage of one of the H-bonds in the tetrahedral cage, which frees up space for a H_2O molecule to enter (interstitial H_2O) and pushes the center H_2O molecule towards the nearby H_2O, leading to a contraction of the

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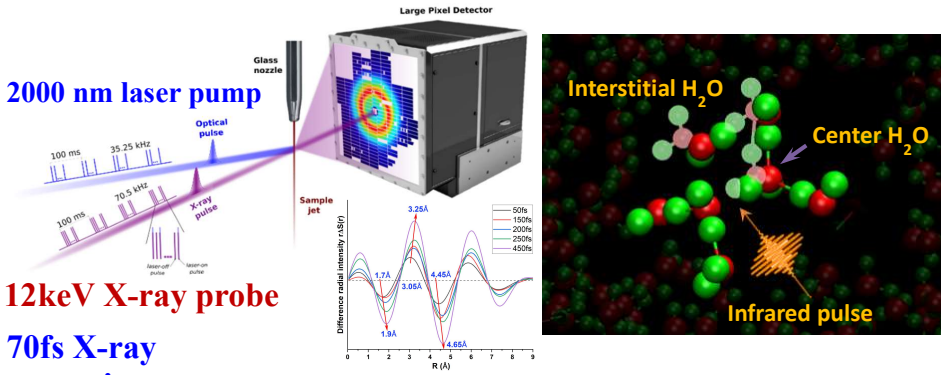
H-bonds and O-O distances at the onset of the reaction. The deformed tetrahedral cage then gradually relaxes and pushes the interstitial H_2O away, reaching equilibrium after 250fs. The fragmented tetrahedron inhales and exhales the interstitial H_2O during the first few hundred fs of the reaction. (In the right panel, the dark solids and light colors represent contracted tetrahedron at 70fs and the relaxed interstitial H_2O, the center H_2O and the top H_2O at 250 fs, respectively).



Ultrafast X-ray solution scattering with a time resolution of a few tens of femtosecond (left) revealed a breathing dynamics (right)

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Imaging hydrogen bond dynamics and proton transfer using MeV electrons

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Hydrogen-bond dynamics and proton-transfer play fundamental role not only to water's anomalous properties, but also in many chemical and biological processes. Direct imaging Hydrogen-bond dynamics and proton transfer required femto-seconds temporal and atomic spatial resolution. Neutron does not possess required time resolution while X-ray is insensitive to hydrogen-bond and proton, the only technique available to study those processes is spectroscopic methods. This limitation is lifted by the successful operation of the first liquid phase MeV-UED [1]. The liquid phase MeV-UED enabled the first direct imaging of hydrogen bond dynamics in liquid water, capturing short-lived hydroxyl-hydronium pair in ionized water, and first glimpse of proton transfer [4]. In this talk, I will first discuss water science enabled by the liquid phase MeV-UED, and present the plan for a new generation of liquid phase MeV-UED @ UA Ruhr of Germany. The new generation liquid phase MeV-UED will possesses the sensitivity and time resolution (< 50 fs) to image the three stages of water radiolysis for the first time.

[1] J.P. F. Nunes *et al*, Struct. Dyn. **7**, 024301 (2020).

[2] J. Yang *et al*, Nature **596**, 531–535 (2021).

[3] M.-F. Lin *et al* , *Science* **374**, 92 (2021).

[4] E. G. Champenois *et al*, Phys. Rev. Lett. **131**, (2023).

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Exploring Jupiter's ocean worlds with Juice and Europa Clipper: New challenge for water in exotic conditions

Gabriel TOBIE
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Magnetic data gathered by the Galileo mission [1,2] and telescopic observations with the Hubble space telescope [3] provide evidences for deep salty water oceans within Jupiter's moons, Europa, Ganymede and Callisto, under their cold icy surface. However, the composition, depth, and physical properties of these internal oceans remains very poorly constrained. Identifications of magnesium-bearing, sodium-bearing salts and volatile compounds, such as CO_2, at the surface of Europa [4], and to a lesser extent at the surface of Ganymede [5], indicates exchange with their subsurface ocean. However, the link with the oceanic composition still remains unclear, as the thickness of the ice shell and the efficiency of chemical transfer through it remains unconstrained. Based on thermal evolution predictions, Europa's ice shell thickness is estimated between 10 to 40 km, while Ganymede and Callisto may have an ice shell as thick as 100 km. Due to their large volume of H_2O compared to Europa, Ganymede and Callisto are expected to have an high-pressure ice mantle separating the ocean base from the rock core. However, the thickness of this high-pressure mantle and its physico-chemical properties remains unconstrained.

Future geophysical and compositional measurements by the ESA JUpiter ICy moon Explorer (JUICE) [6] and the NASA Europa Clipper mission [7] will provide crucial constraints on chemical exchange between the surface and the ocean, the hydrosphere structure, the ocean composition and the deep interior structure of these bodies. The interpretation of the data that will be collected by the two missions will require reference laboratory data on aqueous solutions and icy solids on a wide range of temperature (100-500 K) and pressure (a few Pa to a few GPas), for a variety of exotic composition representative of the moons surface and interior. In this presentation, I will review the scientific objectives and investigations to be performed by these two ambitious missions and highlight the laboratory data for which new acquisitions are necessary to achieve these objectives.

[1] Khurana, K. K. et al. Nature, 397, 777-780 (1998) ; [2] Kivelson, M. G. et al. Icarus, 157, 507-522, (2002) ; [3] Saur, J. et al. J. Geophys. Res., 120, 1715-1737 (2015) ; [4] Ligier, N. et al. Astrophys. J. 151:163 (2016) ; [5] Ligier, N. et al. Icarus, 333 :496-515 (2019); [6] Grasset, O. et al. Planet. Space Sci., 78, 1-21 (2013) ; [7] Howell, S. M., & Pappalardo, R. T. Nature Comm. 11(1), 1311 (2020).

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Observation of the most H_2-dense filled ice under high pressure

Umbertoluca Ranieri, Simone Di Cataldo, Maria Rescigno, Lorenzo Monacelli, Richard Gaal, Mario Santoro, Leon Andriambariarijaona, Paraskevas Parisiades, Cristiano De Michele, Livia Eleonora Bove

Sapienza University of Rome

Hydrogen hydrates exhibit a varied phase diagram as function of pressure. The various phases share a host-guest structure type, consisting of polyhedral cages formed by hydrogen-bonded water molecules, with hydrogen molecules trapped in the cages. In particular, above 3 GPa the so-called compound phase 2 (C_2) phase forms, characterized by water in the cubic ice I*c* structure, and a H_2 to H_2O molar ratio of 1:1 [1]. After few experiments with contradicting results, the phase diagram above 3 GPa remained unclear.

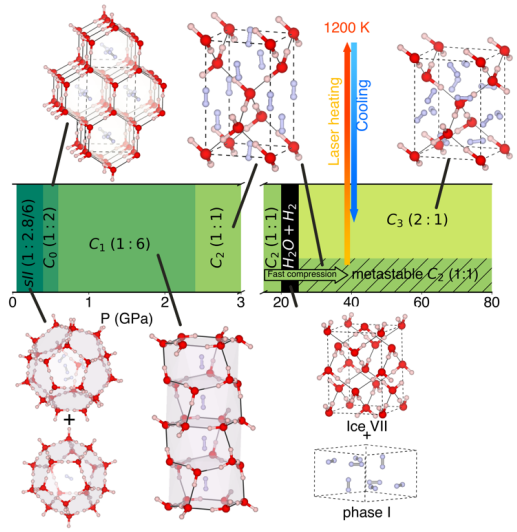

Figure 1: sketch of the phase diagram of hydrogen hydrates as a function of pressure. Arrows indicate thermodynamic pathways. Oxygen, hydrogen in water, and molecular hydrogen are shown as red, pink, and blue spheres, respectively. Hydrogen bonds are shown as solid lines.

In our work, we combined X-ray diffraction and Raman spectroscopy with *ab initio* calculations based on Density Functional Theory to study the hydrogen hydrate phase diagram. We found the most H_2-dense phase of hydrogen hydrate so far reported, namely the compound 3 (or C_3) [2], with a H_2 to H_2O molar ratio of 2:1. Its synthesis requires heating, else the C_2 phase survives as a metastable phase, in excellent agreement with our calculations.

The extreme (up to 90 GPa and likely beyond) pressure stability of this hydrate phase is a unique result of the close-packed geometry of the hydrogen molecules caged in the ice I*c* skeleton.

[1] W. L. Vos, L. W. Finger, R. J. Hemley, et al., Phys. Rev. Lett.71, 3150–3153 (1993)
[2] U. Ranieri, S. Di Cataldo, M. Rescigno, et al., PNAS 120, 52 (2023)

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To what extent does water exhibit plastic behaviors?

M. Rescigno[1,2], A. Toffano[3], U. Ranieri[4], H. Zhang[5], F. Alabarse[6], S. Klotz[7], F. Martelli[8,9], J. Russo[1], L.E. Bove[1,2,7]

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[8]IBM Research Europe, Keckwick Lane, Daresbury, WA4 4AD, United Kingdom.
[9]Department of Chemical Engineering, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom.

Molecular rotations play a pivotal role in shaping the behavior of water, impacting several dynamic and thermodynamic properties such as viscosity, heat capacity, thermal conductivity, and solvating capability [1]. In recent Quasi-Elastic Neutron Scattering (QENS) experiments, we have made intriguing observations indicating that solid water can exhibit plasticity [2]. This means that, structurally, it behaves as a solid, but it shows rapid reorientation dynamics akin to a liquid, with time scales ranging from picoseconds to nanoseconds. This hybrid behavior is characteristic of various states of water, including high-pressure crystalline [3-5] and amorphous [6] forms.

Our experiments have revealed this unique behavior in a variety of contexts, such as high-pressure crystalline ice VII along its melting line [3], water-ammonia solid solutions under extreme pressure and temperature conditions [4], salty ice VII [5], and even pure water under strong confinement at ambient pressure [6]. In this talk I will review some of our experimental results on plastic water, both under high pressure, in solutions and deeply undercooled in strong confinement. I will discuss how, depending on the thermodynamic conditions and on the environment, rotations can be isotropic, or can occur through reorientational jumps between preferential orientations.

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[3] M. Rescigno et al. Observation of Plastic Ice VII by High-Pressure Quasi Elastic Neutron Scattering, Nature, *submitted.*
[4] H. Zang et al J. Phys. Chem. Lett. 2023, 14, 2301−2307
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[6] M. Rescigno et al J. Phys. Chem. B 2023, 127, 4570−4576

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An experimental search for pre-clathrate cage formation

Robert Bauer[1,2], Claudia Goy[1], Alexander Gierke[1], John Tse[3], Felix Lehmkühler[1]

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[3] *University of Saskatchewan, 116 Science Place, Saskatoon, SK S7N 5B2, Canada*

Clathrate hydrates, a cage like structure of ice, are present throughout nature from the depths of the ocean to distant planets and comets [1]. First reported by Davy in 1810, the formation process of clathrates is not fully understood [2]. Simulations by Jacobson et al. suggest a preliminary clustering of the guest molecules induces cage formation, naming this stage of nucleation "blob" (Fig. 1) [3]. The work presented looks at nucleation from two perspectives, first from an amorphous solid mixture and second from a liquid jet. Both experiments were performed under vacuum with the amorphous solid mixture at 10^{-7} mbar and the liquid jet at 10^{-5} mbar. The amorphous mixtures were continually heated as the structure was probed with synchrotron X-rays between 25 and 32 keV, the heating continued until the sample sublimated in vacuum. Several known clathrate forming guests were used to investigate the clathrate nucleation process, and a few unexpected clathrates also formed. Using high atomic number guests, the guest arrangement can be inferred. Utilizing a liquid jet injected into vacuum enables to probe supercooled liquids, due to evaporative cooling. Using XFEL radiation the liquid jet was probed using 23 keV photons, to attain the pair distribution function of single femtosecond pulses. Near instantaneous snapshots of the interatomic distances were collected.

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[2] H. Davy. *Philos. Trans. R. Soc.* 100, 16-74 (1810)

[3] L.C. Jacobson, W. Hujo and V. Molinero. *J. Am. Chem. Soc.* 132.33, 11806-11811 (2010)

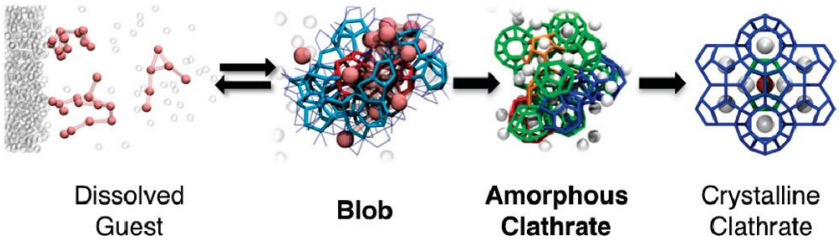

Figure 1: Simulated potential nucleation process for clathrate hydrates, noting a two-stage nucleation with initial "blob" guest clusters, adapted from Ref. [3].

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WaterX@2024 International Workshop May 25 – 30, 2024

Ammonia incorporation into methane clathrate hydrate in the subsurface ocean of Titan and Pluto

Shunsuke Nozaki[1,2], Yasuhito Sekine[2], Gabriel Tobie[3], Yunfeng Liang[4], Takeshi Tsuji[4], Hidenori Genda[2]

[1]*Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan*
[2]*Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan,*
[3]*Laboratory of Planetology and Geosciences, Nantes University, CNRS, Nantes, France*
[4]*Graduate School of Engineering, The University of Tokyo, Tokyo, Japan*

On early Titan and Pluto, methane (CH_4) clathrate would have generated at the interface between the icy crust and primordial subsurface ocean, affecting the thermal evolution and volatile inventory [1,2]. Together with CH_4, primordial ammonia (NH_3) would be present in the subsurface ocean; however, incorporation of NH_3 into CH_4 clathrate is still in debate [3,4]. Using molecular dynamics simulations, we investigate incorporation of NH_3 upon CH_4 clathrate formation from H_2O-NH_3-CH_4 fluids with various NH_3 concentrations (0–30%). The pressure-temperature condition (200 MPa and 270 K, respectively) of the simulations corresponds to those of the subsurface ocean of Titan and Pluto [2]. We find that a significant fraction of NH_3 is incorporated into clathrate cages (Fig. 1). The occupancy of NH_3 in cage increases with NH_3 concentration until 10% NH_3 in the initial liquids. The occupancy becomes 40% at the NH_3 concentration of ~10% and then reaches a plateau at 10–25% NH_3 concentrations. Given the NH_3 abundance in comets, NH_3 concentrations in the primordial subsurface ocean may have been 0.5–5 %. Our results suggest that NH_3 occupancy in clathrate formed on early Titan and Pluto would have been up to ~0.25. Incorporation of NH_3 would lead to destabilization of clathrate and release of CH_4 upon its advection near the surface [5], possibly replenishing CH_4 on the surface of Titan and Pluto.

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[5] Choukroun, M. et al. (2010) Icarus, 205(2), 581-593

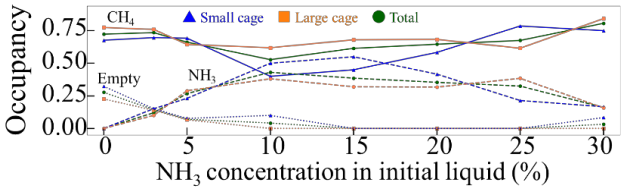

Fig.1. NH_3 concentration dependence of cage occupancy of CH_4 (solid) and NH_3 (dashed), and occupancy of empty cages (dotted) after several tens to hundreds ns simulation at 200 MPa and 270 K. Occupancy in small, large, and all cages is shown in blue, orange, and green, respectively. Values of the 54 and 37 new cages are used for 25% and 30% NH_3 cases due to slow clathrate growth, respectively. In comparison, values of 72 new cages are used for other concentrations.

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WaterX - Program May 25 - May 30 2024 - La Maddalena (Italy)

time	Saturday May 25
18:30	Welcome Cocktail
21:00	Opening Lecture: Pablo Debenedetti

time	Sunday May 26
8:30	Opening & Registration
9:00	Osamu Mishima
9:45	Valeria Molinero
10:15	Anders Nilsson
10:35	John Loveday
10:55	Claudia Goy
11:15	Coffee Break
11:40	Federica Coppari
12:10	Graeme Ackland
12:30	Qingyu Kong
12:50	Xijie Wang
13:10	Lunch
14:30	Gabriel Tobie
15:00	Simone Di Cataldo
15:20	Maria Rescigno
15:40	Robert Bauer
16:00	Shunsuke Nozaki
16:15	Excursion: Caprera Trail and beach + Caprera Memoriale Museum
19:30	Sunset at Baia Trinita

time	Monday May 27
6:00	Sunrise Trail to Tahiti #
9:00	Martina Havenith
9:45	Richard Saykally
10:15	Damian Laage
10:35	Simone Pezzotti
10:55	Wanlin Chen
11:10	Coffee Break
11:40	Heloisa Bordallo
12:10	Margarita Russina
12:30	Frederic Caupin
12:50	Jan Eichler
13:05	Lorenzo Rovigatti
13:20	Lunch
	Free Time Possibility of Scuba Diving **
16:00	Patrick Charbonneau
16:30	Letizia Tavagnacco
16:50	Maria Grazia Izzo
17:10	Paola Gallo
17:30	Sergey Buldyrev
17:50	Poster Shower
18:20	Poster & Drinks

time	Tuesday May 28
9:00	Katrin Amman-Winkler
9:45	Kazuki Komatsu
10:15	Leonardo Del Rosso
10:35	Bertrand Chazallon
10:55	Tomasz Poreba
11:10	Coffe Break
11:40	Stefan Klotz
12:10	Keishiro Yamashita
12:30	Andreas Hermann
12:50	Fabio Finocchi
13:10	Lunch
14:30	Nønne Prisle
15:00	Barbara Wyslouzil
15:30	Thorsten Bartels-Rausch
15:50	Ivan Saika-Voivod
16:10	Miguel De La Puente
16:25	Coffee Break
16:45	Nigel Wilding
17:15	Francesco Paesani
17:35	Eduardo Sanz
17:55	Carlos Vega
18:15	Francesco Guidarelli Mattioli
18:30	Walk to Punta Tegge for Sunset Apero *

time	Wednesday May 29
8:45	Patrick Ayotte
9:15	Kenji Mochizuki
9:35	Xavier Michaut
9:55	Lilli-Ruth Fidler
10:10	Boat trip to Maddalena Arcipelago ##
20:00	Social Dinner

time	Thursday May 30
9:00	Giuseppe Graziano
9:45	Lorna Dougan
10:15	Fatima Matroodi
10:30	Max Warburton
10:45	Carlo Andrea De Filippo
11:00	Coffe Break
11:30	Andreas Neophytou
12:00	Lars Patterson
12:20	Neta Ellert
12:40	Johannes Giebelmann
13:00	CLOSING

max 10 places available.
* An apero-dinner is available at Zi' Anto restaurant in Punta Tegge under request (its cost will be set soon).
** Scuba-diving will be operated by Best Shark Diving Center under request (price of Introductory lesson, or excursion will be set soon).
This activity is NOT included in the registration fee. Its cost (lunch included) will be set soon.

WaterX@2024 International Workshop May 25 – 30, 2024

THz-Calorimetry

Martina Havenith

Ruhr Universitat Bochum

Here, we lay out the concept of THz-calorimetry, a technique that allows to deduce and quantify changes in solvation entropy and enthalpy associated with biological processes in real-time, i.e., on time scales of seconds down to picoseconds. Fundamental biological processes are inherently non-equilibrium: A small imbalance in free energy can trigger protein condensation or folding. Strikingly, water being a generic solvent, the intermolecular protein-water interactions act as a strong competitor for intramolecular protein-protein interactions, leading to a delicate balance between functional structure formation and complete solvation. Characteristics for biological processes are large, but competing enthalpic (ΔH) versus entropic (ΔS) solvation contributions to the total Gibbs free energy with subtle energy differences of only a few kJ/mol, which dictate the biological function.
THz-calorimetry is a technique that puts a spotlight on these intermolecular coupled protein-water interactions.
With experimental advances in THz technology, a new frequency window was opened, which is ideally suited to probe these low frequency intermolecular interactions. THz-calorimetry is based exclusively on spectroscopic observables of protein hydration. Therefore, unlike traditional calorimetry, measurements can be carried out even in inhomogeneous mixtures (protein condensates) and under non-equilibrium conditions. The future impact of these studies is based on the belief that the observed changes in solvation entropy and enthalpy are not mere epiphenomena, but dictate biological function.

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WaterX@2024 International Workshop May 25 – 30, 2024

Reversed Fractionation of Aqueous Carbonate and Bicarbonate at the Air–Water Interface[1]

Richard J. Saykally

Department of Chemistry

University of California-Berkeley

Berkeley, CA. USA

In the course of our investigations of the adsorption of ions to the air-water interface, we previously reported the surprising result that doubly-charged carbonate anions exhibit a stronger surface affinity than do singly-charged bicarbonate anions. In contrast to monovalent, weakly hydrated anions, which generally show enhanced concentrations in the interfacial region, multivalent (and thus strongly hydrated) anions are expected to show much weaker surface propensity. Recently, we used resonantly enhanced deep-UV second harmonic generation spectroscopy to measure the Gibbs free energy of adsorption of both carbonate and bicarbonate anions to the air-water interface. Contrasting the predictions of classical electrostatic theory, and in support of our previous findings from X-ray photoelectron spectroscopy, we find that carbonate anions do indeed exhibit much stronger surface affinity than do the bicarbonate anions. Molecular dynamics simulation reveals that strong ion pairing of carbonate with sodium counter-cations in the interfacial region, resulting in formation of near-neutral “agglomerates”, is responsible for this counterintuitive behavior. These findings not only advance our fundamental understanding of ion adsorption chemistry, but will also impact important practical processes such as ocean acidification, atmospheric aerosol chemistry, and mammalian respiration physiology.

1. Devlin, S.W., Jamnuch, S., Xu, Q., Chen, A.A., Qian, J., Pascal, T.A., Saykally, R.J. "Agglomeration Drives The Reversed Fractionation of Aqueous Carbonate and Bicarbonate at the Air-Water Interface. " *J. Am. Chem. Soc.*, **2023**

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WaterX@2024 International Workshop May 25 – 30, 2024

On the mechanism of excess proton transport in water

Axel Gomez[a], Ward H. Thompson[b], Damien Laage[a]
[a] *PASTEUR, Dept of chemistry, Ecole Normale Supérieure, PSL University, Sorbonne University, CNRS, Paris, France*
[b] *Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA*

The transport of excess protons in water is central to acid-base chemistry, energy production, and biochemical processes. However, elucidating its molecular mechanism remains challenging due to the ultrafast proton dynamics. While pioneering molecular simulations [1-4] had proposed a mechanism, the latter was recently questioned by nonlinear vibrational spectroscopy measurements [5-7]. We performed neural-network potential-based ring-polymer molecular dynamics simulations and vibrational spectra calculations to characterize the molecular mechanism of proton transport and identify its rate-limiting step. We determined that excess proton transfer in water involves successive intermediates where the proton is localized and hydrated by distinct and stable Eigen-like and Zundel-like hydrogen- bond configurations, whose spectral properties are in agreement with the nonlinear vibrational spectroscopy observations [*5-7*]. The proposed mechanism [8] in Fig. 1, supported by simulations, thus provides a molecular picture consistent with the latest experimental characterizations of proton dynamics. Our results show that proton transport in water is controlled by sequential exchanges between stable hydrogen bonds around the proton-donating and accepting water molecules.

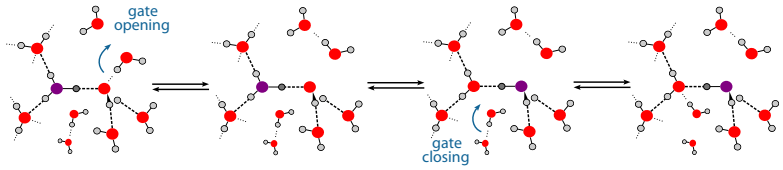

Fig. 1 Excess proton transfer mechanism in bulk water

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[2] D. Marx, M. Tuckerman, J. Hutter, M. Parrinello, *Nature* **397**, 601-604 (1999).
[3] O. Markovitch, H. Chen, S. Izvekov, F. Paesani, G.A. Voth, N. Agmon, *J Phys Chem B* **112**, 9456-9466 (2008).
[4] T.C. Berkelbach, M.E. Tuckerman, *Phys. Rev. Lett.* **103**, 238302 (2009).
[5] M. Thämer, L. De Marco, K. Ramasesha, A. Mandal, A. Tokmakoff, *Science* **350**, 78 (2015).
[6] F. Dahms, B. P. Fingerhut, E. T. J. Nibbering, E. Pines, T. Elsaesser, *Science* **357**, 491 (2017).
[7] J. A. Fournier, W. B. Carpenter, N. H. C. Lewis, A. Tokmakoff, *Nat Chem* **10**, 932 (2018).
[8] A. Gomez, W.H. Thompson, D. Laage, doi: 10.26434/chemrxiv-2024-tx5t7

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Hydrophobicity at electrified metal-water interfaces: implications for adsorption and reactivity

Simone Pezzotti

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Adsorption of ions and hydrophobic solutes are key processes in electrochemistry. The former regulates the Electric Double Layer and dictates important quantities, e.g. capacitance. The latter has major implications for heterogeneous catalysis, where small hydrophobic molecules are commonly involved as reactants and products. Despite solvation of charged and hydrophobic species are remarkably different, I will show in this presentation that the exotic way hydrophobicity arises at electrified metal-water interfaces influences both of them with a common underlying molecular mechanism.[1-3]

I will first show from classical molecular dynamics[1] that the peculiar molecular arrangement of electrified gold/water interfaces induces atypical fluctuations of the liquid water density, resulting in a hydrophobic water-water interface formed close to the metal. I will then illustrate how such hydrophobicity dictates solvation free energy and regulates the accumulation of hydrophobic solutes (e.g. CO)[1,3], as well as some ions (e.g. Cl^-)[2], at the interface. I will finally discuss some implication of these findings for electrochemical reactions involving hydrophobic molecules, with examples for CO_2 and N_2 reduction.[1,3]

[1] A. Serva, M. Salanne, M. Havenith, S. Pezzotti. PNAS 2021,118, e2023867118.

[2] S. R. Alfarano, S. Pezzotti, C. Stein, et al. PNAS 2021, 118, e2108568118.

[3] A. Serva, S. Pezzotti, J. Chem. Phys. 2024, 160, 9.

[4] A. Serva, M. Havenith, S. Pezzotti. J. Chem. Phys. 2021, 155, 204706.

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Tuning acid-base chemistry at an electrified gold/water interface

Steffen Murke[1], Wanlin Chen[1], Simone Pezzotti[1,2], and Martina Havenith[1]
[1]*Department of Physical Chemistry II, Ruhr University Bochum, D-44801 Bochum, Germany*
[2]*Current address: PASTEUR, Département de Chimie, Ecole Normale Supérieure, PSL University, Sorbonne University, CNRS, 75005 Paris, France*

Acid-base reactions are ubiquitous in both fundamental research and technological applications. In electrochemistry, acid-base equilibrium plays a pivotal role in electro-catalytical processes that often involve proton-coupled electron transfer reactions. However, macroscopic concepts derived in solutions, such as pKa and pH, differ significantly at electrified metal-aqueous interfaces, due to specific solvation and applied voltages. Understanding how acid-base reactions are modulated by electrochemical interfaces requires operando spectroscopic techniques, which can provide molecular information under the effect of applied voltages. Here, we measure pKa values of an amino acid, glycine, at a gold/water interface under varying applied voltage by means of spectroscopic titration using surface-enhanced Raman spectroscopy. Combined with state-of-the-art constant potential molecular dynamics simulations, we propose a model to understand potential-dependent pKa shifts in terms of local hydrophobicity and electric fields, which generally manifest at electrochemical interfaces. These parameters can be tuned by adjusting the metal surface and applied voltage, respectively, offering promising paths to regulate reactivity. Our results change the focus with respect to common interpretations based on e.g. local pH effects, and open interesting perspectives for electrochemical reactions steering.

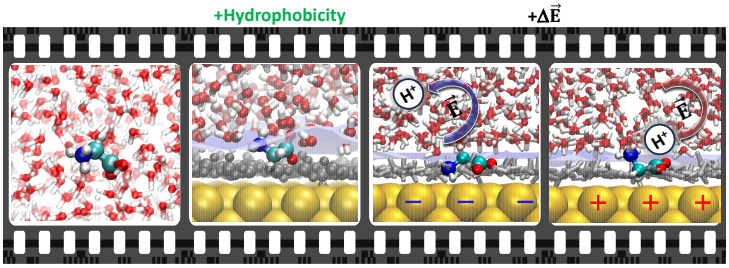

Figure. Proposed mechanism tuning acid-base chemistry at electrified metal-water interfaces. From left to right, the sketches illustrate that local hydrophobicity at the interface [1] destabilizes the zwitterionic form of glycine, i.e. the pH window where it exists is reduced with respect to bulk, already at low applied voltages. By further varying the applied voltage at fixed pH conditions, the additional local electric fields generated by both metal surface and interfacial water induce proton transfer that either deprotonates (at negative voltages) or protonates (at positive voltages) the glycine zwitterion.

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[1] A. Serva, M. Salanne, M. Havenith; S. Pezzotti. “Size dependence of hydrophobic hydration at electrified gold/water interfaces”. Proc. Natl. Acad. Sci. 118, e2023867118 (2021).

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What water does and how it arranges itself under confinement and around molecules?

Heloisa N. Bordallo
Niels Bohr Institute – University of Copenhagen, Copenhagen - Denmark

Water is fundamental in controlling many physical, chemical and biological processes. In the bulk, water exhibits amazing properties that arise mainly from the presence of a network of hydrogen bonds, which can drastically change under confinement. Therefore, the molecular mechanisms underlying interaction of water with materials that will lead to new structural, thermodynamic, and dynamic (both translational and orientational) properties have continuously attracted attention in the research community. Despite this, a large gap still exists in relating what is known to rationalize how the molecular organization of water on and within these materials impacts real life processes. In this perspective, I will outline the importance of water in biomaterials and clays science and give indications for future research directions towards a comprehensive picture of water, materials and daily life.

[1] A. Bouazza Geotextiles and Geomembranes. 2002, 20 3–17.]

[2] M. L. Martins, Medicine. 2022, 58, 654.

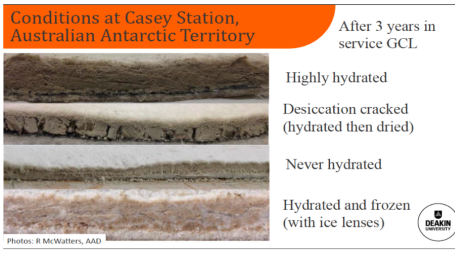

Fig 1: Geosynthetic clay liners (GCLs) are used as environmental protection barriers in transportation facilities (roads and railways) and geotechnical applications to minimize pollution [2].

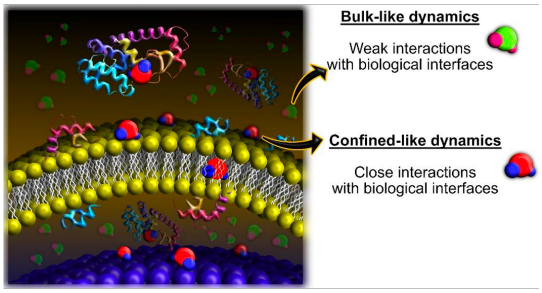

Fig. 2: Illustration of the complex chemical environment within living cells and the different water populations. This picture can be used under CC BY license [2].

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WaterX@2024 International Workshop May 25 – 30, 2024

Cooperative intermolecular correlations in bulk and confined water

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It is currently believed that molecular mechanisms behind the majority of water's anomalous features can be traced to the existence and properties of so-called hydrogen bonds, which results from electrostatic and van der Waals intermolecular interactions between hydrogen and oxygen from molecular neighbors. Hydrogen bonds lead to increased cooperativity in the molecular behavior. Even dynamic processes, which one usually associates with motion of one water molecule, such as self-diffusion and molecular rotational reorientation, still require active and highly cooperative interactions with neighbors including rearrangements of water network and evolutions of hydrogen bonds. While self-molecular dynamics has been sufficiently well studied, the exploration of cooperative aspects in water behavior remained extremely difficult due to the absence of long-range order and very often short lifetimes of the involved molecular correlations. We have investigated cooperative molecular motion in water using polarization analysis in neutron spectroscopy. This approach allowed us to unambiguously detect and successfully separate cooperative water dynamics from the stochastic self-molecular motion in H_2O and D_2O in the dynamic domain up to 1 ns [1]. Thus, we observe a clear coherent neutron scattering signal originating from cooperative molecular dynamics at the intermediate Q range (< 1 $Å^{-1}$) that corresponds to longer distances than the ones between two nearest neighbours. Secondly, in H_2O the signal is by an order of magnitude higher than the signal expected for rigid, non-interacting and randomly oriented molecules. This is clear evidence that the intermolecular correlations in water are spread to more distant molecules and involves more complex interactions than the simple hydrogen bonds [1]. Confinement can enhance cooperative interactions and resulting intermolecular correlations. Indeed, for water confined into subnanometer linear pores we see the formation of ordered water chains with distances between nearest neighbours of 3.4-4 Å, which are substantially longer than the regular hydrogen bonds in bulk water [2]. This ordered and less dense water shows a high degree of cooperativity in the molecular nanoscale dynamics and poses unusual combination of properties of solid and liquid states, which will be reviewed here [3].

References:

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WaterX@2024 International Workshop May 25 – 30, 2024

Shear and bulk viscosity of water under high pressure

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Water flows in Earth's deep crust at pressures in the gigapascal range. Despite its relevance for natural processes, measurements of the shear viscosity of water under these extreme conditions are scarce and in disagreement with each other [1-3]. We have performed such a measurement at ambient temperature and pressure up to 1.5 GPa, i.e. in the metastable liquid state above the melting pressure of ice VI. The method, which we previously used at low pressure in supercooled water [4-6], is based on the Brownian motion of polystyrene spheres (350 nm in diameter) in a diamond anvil cell. We compare our results to previous works and discuss possible origins for the observed discrepancies. We also report our preliminary measurements at higher temperature. Moreover, at room temperature, we measured sound attenuation with Brillouin spectroscopy, which gives access to the bulk viscosity of water. We performed molecular dynamics simulations of shear and bulk viscosities. They are in qualitative agreement with the experiment and give additional microscopic insight.

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[4] A. Dehaoui, B. Issenmann, and F. Caupin. Proc. Natl. Acad. Sci. USA, 2015, 112, 12020-12025.

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From structure-maker to structure-breaker: viscosity of supercooled NaCl solutions

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Electrolytes are traditionally classified based on their effect on the viscosity of aqueous solutions, which is phenomenologically measured through the viscosity B-coefficient in the Jones-Dole expression for viscosity [1]. When B is positive, electrolytes are called "structure-makers" or “kosmotropes”, whereas when B is negative, they are called "structure-breakers" or “chaotropes”. Although this simplistic view about the relation of B to the structure of water is much debated, the positive B coefficient conventionally places NaCl among the "structure-makers".

In recent years, we successfully measured the Brownian motion of colloids with Differential Dynamic Microscopy (DDM) to obtain the viscosity of H2O [2,3] and D2O [4] in the supercooled regime. The use of DDM in electrolyte solutions is challenged by the frequent aggregation of the colloids involved. Here we show how the choice of appropriate colloids and experimental procedure allowed us to measure the viscosity of NaCl solutions with molality 1, 2, and 3 mol kg^{-1}. The results (Figure 1) show a surprising behavior: the concentration dependence changes with temperature, leading to a crossing between the viscosity curves in the supercooled region. For all three studied concentrations, we observe such a crossing point, below which the NaCl solution becomes less viscous than pure H2O, i.e., where NaCl turns from "structure-maker" into "structure-breaker".

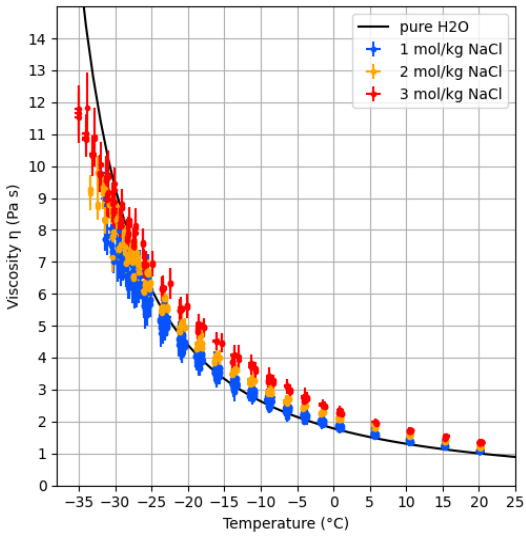

Figure 1: Viscosity of supercooled NaCl solution.

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WaterX@2024 International Workshop May 25 – 30, 2024

Diffusion, viscosity and linear rheology of network fluids

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We numerically investigate the dynamics and linear rheology of network-forming systems made of limited-valence particles. We focus on particles decorated with patches arranged on a tetrahedron, mimicking tetravalent molecular fluids such as water, and investigate the role that temperature and bonding mechanism have on the dynamics at the optimal network-forming density. We demonstrate that diffusion and viscosity are enslaved to bonding, and display an activated behaviour at low temperature. In addition, we confirm the validity of the Stokes-Einstein relation, with two caveats: (i) the diffusion constant requires a finite-size correction[1], and (ii) there is the onset of a breakdown that appears at the lowest temperatures considered, in qualitative agreement with data on supercooled liquids such as water[2].

We also extend our analysis to binary mixtures of particles with different valences, finding that, in some cases, the storage and loss moduli exhibit an apparent power-law dependence on frequency, hinting at the possibility of using the composition to finely tune the rheological response of these materials. The wealth of data we present will help to develop and test theoretical frameworks aimed at describing the dynamics of limited-valence particles that self-assemble into network fluids[3].

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[3] S. S. Gomez and L. Rovigatti, *in preparation*

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Sugar in Water, and the Origin of Grained Confections

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Candy-making entails finely controlling the phase transitions of sugar in water. Both kinetic and thermodynamic aspects of sugar crystallization from an aqueous solution are indeed at play in the art of confectionery (Fig. 1). As part of a course on the science of cooking taught at Duke University, I illustrate these undergraduate-level concepts by preparing and contrasting two traditional candy recipes (Fig. 2)—one glassy, the other microcrystalline (or grained)—that, remarkably, differ only in their tempering [1]. The experience provides students with an immediate appreciation for material microstructure. Physical chemistry insights have also been helpful in tracing back the unexpected origin of these materially complex preparations. Unlike many confectionery innovations, grained candies did not arise from the high-end shops in European capitals, but from rural traditions of sugar refining [2-4].

[1] I. Altan, P. Charbonneau, and J. De Valicourt, Sugars: Soft Caramel and Sucre à la crème — an Undergraduate Experiment about Sugar Crystallization, in *Handbook of Molecular Gastronomy*, R. M. Burke et al., eds. 2021, CRC Press: New York. p. 545-547.
[2] P. Charbonneau and J. M. Pilcher, From Panocha to Fudge: Mexican Roots of an American Candy. *Gastronomica*, 2023. **23**(1): p. 100-111.
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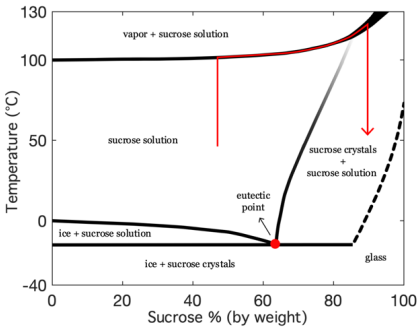

Figure 1: Phase diagram of sucrose in water (soli black lines), along with a traditional candy preparation scheme (red).

Figure 2: (left) Soft caramel has a smooth and shiny appearance; (right) *sucre à la crème* contains microcrystals that heavily scatter light, thus its matte appearance.

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Water slowing down drives the occurrence of the low temperature dynamical transition in microgels

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The protein dynamical transition marks an increase in atomic mobility and the onset of anharmonic motions at a critical temperature, which is considered relevant for protein functionality. This phenomenon is ubiquitous, regardless of protein composition, structure and biological function. Recently, a dynamical transition has also been reported in non-biological macromolecules, such as poly(N-isopropyl acrylamide) (PNIPAM) microgels, bearing many similarities to proteins [1,2]. Here, I will focus the microscopic origin of the dynamical transition in microgels. By comparing atomistic molecular dynamics simulations and elastic incoherent neutron scattering experiments with selective deuteration I will discuss water and PNIPAM roles. I will show that from room temperature down to about 180 K, polymers exhibit only modest changes of dynamics, while water, being mainly hydration water under the probed extreme confinement, significantly slows down and undergoes a mode-coupling transition from diffusive to activated. These findings therefore challenge the traditional view of the dynamical transition, demonstrating that it occurs in proximity of the water mode-coupling transition [3].

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The interplay between liquid-liquid and ferroelectric phase transition in deeply supercooled water

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A Liquid-Liquid (LL) phase transition in supercooled water has been hypothesized to explain its anomalies, so as the presence of solid polyamorphism. Recently, Molecular Dynamics (MD) simulations provided evidence for phase transition between a High Density Liquid (HDL) and a Low Density Liquid (LDL) in deeply supercooled water [1], though full experimental validation is still awaited. Speculations on possible ferroelectric phase transition in water and, more generally, in polar liquids are longstanding [2]. However, the two scenarios, namely LL and ferroelectric phase transitions, have never been correlated. We reanalyze the MD results of Ref. [1], discovering a clear correlation between density and total polarization in deeply supercooled water: while the HDL retains the characteristics of a paraelectric phase, LDL polarization's trend suggests a ferroelectric character, as shown in Fig. 1. In light of this result, starting from the microscopic interaction potential, we developed a classical density functional theory in a mean field approximation able to describe the concomitant occurrence in polar liquids of ferroelectric and LL phase transitions. Focusing on the LL Critical Point (CP) and encompassing both the Widom and the first-order LL phase transition lines, we compare the density and polarization phase diagram of water obtained from MD simulations and theory, finding notable agreement. As further confirmation of ferroelectric order existence in LDL, Goldstone modes, stemming from the spontaneous breaking of the continuous rotational symmetry group O(3), have been identified in MD results.

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[2] M. A. Pounds, and P. A. Madden, J. Chem. Phys. 126, 104506 (2007)

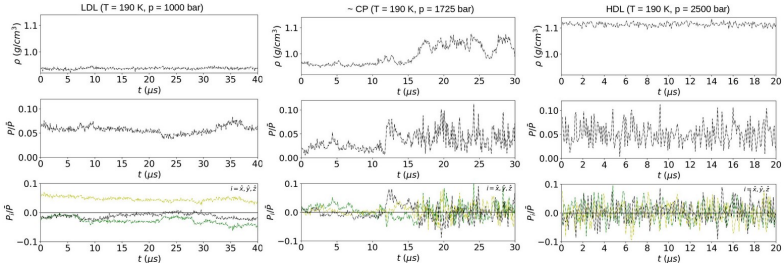

Fig. 1 Temporal evolution of density (ρ) total polarization magnitude (P) and components (P_i) of water MD simulations [1] in LDL, near CP and in HDL. $\bar{P} = N\,p$, where p is the water's molecule dipole moment and N the total particles number in the simulation box.

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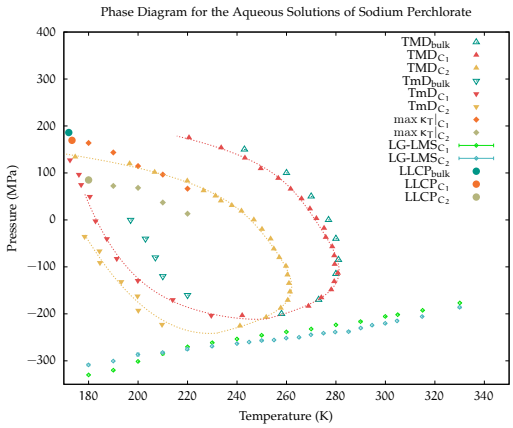
Molecular dynamics simulations study of supercooled aqueous solutions of sodium perchlorate: the effect of Martian solutes on thermodynamics and structure of water

Paola Gallo
Università degli studi Roma Tre

I will show recent results of molecular dynamics simulations on the influence of solutes on the phase diagram of water [1]. I will focus into the supercooled region where the anomalies that water shows with respect to other simple liquids, are enhanced. After reviewing previous results with alkali halides solutes, I will concentrate on the thermodynamic behavior of sodium perchlorate solutions in supercooled water. These solutions are of special interest because of the recent experimental results that led to hypothesize the presence of liquid water in perchlorate solutions beneath the Martian soil. Water is modeled using the TIP4P/2005 potential. The phase diagrams obtained for solutions with concentrations 1.63 and 15.4 wt% show the temperature of maximum and minimum density lines and a liquid–liquid phase transition where the liquid–liquid critical point shifts to slightly higher temperatures and lower pressures with respect to the bulk water value. The structure of the systems is also analyzed, and it is shown that even at the highest concentration considered, the solutions still retain water anomalous behavior. These anomalies might play an important role in the existence of Martian liquid water since they are controlled by the local structure of water that is also connected to ice nucleation.

[1] P. La Francesca e P. Gallo J. Chem. Phys. 159, 125401 (2023).



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WaterX@2024 International Workshop May 25 – 30, 2024

Minimal lattice model for a liquid-liquid transition in water: a Monte-Carlo study

Sergey V. Buldyrev[1,2], Frédéric Caupin[3], Thomas J. Longo[4], Mikhail A. Anisimov[4,5]

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The blinking-checkers model is a minimal lattice model [1] which in the mean-field approximation reproduces the phenomenon of fluid polyamorphism. This model is a binary lattice-gas, in which each site has three possible states: empty, occupied with particles of type 1 (blue, see Figure), and occupied with particles of type 2 (red). Additionally, particles may interconvert from one type to another. Equilibrium interconversion imposes a constraint that makes this model thermodynamically equivalent to a single-component system. In this work, Monte-Carlo simulations of the blinking-checkers model are performed, demonstrating the polyamorphic phase behavior of this system. The locations of the liquid-liquid and liquid-gas critical points are found to be different from the mean-field predictions for this model with the same interaction parameters, as the phase behavior is significantly affected by critical fluctuations. Based on the computed values of the critical exponents of the correlation length and the order parameter, we confirm that the blinking-checkers model, for both liquid-gas and liquid-liquid equilibria, belongs to the three-dimensional Ising class of critical-point universality. Additionally, we investigate the behavior of the interfacial tension and lines of extrema for the thermodynamic response functions in the vicinity of the liquid-liquid critical point. We find a set of parameters for which the phase diagram resembles that of water, which has a density anomaly, and increase of the isothermal compressibility upon cooling. In this case, particles of type 1 and 2 should be understood as two different structures of the local environment of water molecules. We investigate how small changes in the interaction parameter ω_{12} between particles of type 1 and 2 affect the phase diagram of the system.

[1] F. Caupin and M. A. Anisimov, Phys. Rev. Lett, 2021, 127,185701.

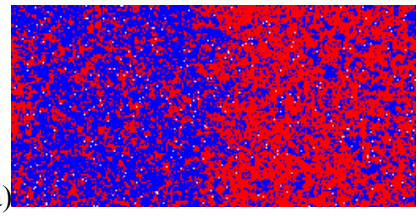
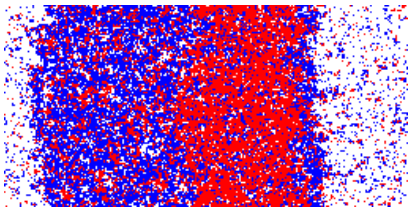
(a)  (b) 

Figure caption: Snapshots of slices of a three-dimensional box with size 128x128x256. Blue sites are particles of type 1, red sites are particles of type 2, white sites are empty. (a) Phase equilibrium near the liquid-liquid critical point for ω_{12}=1.4. (b) The system at the triple point for ω_{12}=1.3.

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WaterX - Program May 25 - May 30 2024 - La Maddalena (Italy)

time	Saturday May 25
18:30	Welcome Cocktail
21:00	Opening Lecture: Pablo Debenedetti

time	Sunday May 26
8:30	Opening & Registration
9:00	Osamu Mishima
9:45	Valeria Molinero
10:15	Anders Nilsson
10:35	John Loveday
10:55	Claudia Goy
11:15	Coffee Break
11:40	Federica Coppari
12:10	Graeme Ackland
12:30	Qingyu Kong
12:50	Xijie Wang
13:10	Lunch
14:30	Gabriel Tobie
15:00	Simone Di Cataldo
15:20	Maria Rescigno
15:40	Robert Bauer
16:00	Shunsuke Nozaki
16:15	Excursion: Caprera Trail and beach or Caprera Memoriale Museum
19:30	Sunset at Baia Trinita

time	Monday May 27
6:00	Sunrise Trail to Tahiti #
9:00	Martina Havenith
9:45	Richard Saykally
10:15	Damian Laage
10:35	Simone Pezzotti
10:55	Wanlin Chen
11:10	Coffee Break
11:40	Heloisa Bordallo
12:10	Margarita Russina
12:30	Frederic Caupin
12:50	Jan Eichler
13:05	Lorenzo Rovigatti
13:20	Lunch
	Free Time Possibility of Scuba Diving **
16:00	Patrick Charbonneau
16:30	Letizia Tavagnacco
16:50	Maria Grazia Izzo
17:10	Paola Gallo
17:30	Sergey Buldyrev
17:50	Poster Shower
18:20	Poster & Drinks

time	Tuesday May 28
9:00	Katrin Amman-Winkler
9:45	Kazuki Komatsu
10:15	Leonardo Del Rosso
10.35	Bertrand Chazallon
10:55	Tomasz Poreba
11:10	Coffe Break
11:40	Stefan Klotz
12:10	Keishiro Yamashita
12:30	Andreas Hermann
12:50	Fabio Finocchi
13:10	Lunch
14:30	Nønne Prisle
15:00	Barbara Wyslouzil
15:30	Thorsten Bartels-Rausch
15:50	Ivan Saika-Voivod
16:10	Miguel De La Puente
16:25	Coffee Break
16:45	Nigel Wilding
17:15	Francesco Paesani
17:35	Eduardo Sanz
17:55	Carlos Vega
18:15	Francesco Guidarelli Mattioli
18:30	Walk to Punta Tegge for Sunset Apero *

me	Wednesday May 29
:45	Patrick Ayotte
:15	Kenji Mochizuki
:35	Xavier Michaut
:55	Lilli-Ruth Fidler
0:10	Boat trip to Maddalena Arcipelago ##
0:00	Social Dinner

time	Thursday May 30
9:00	Giuseppe Graziano
9:45	Lorna Dougan
10:15	Fatima Matroodi
10:30	Max Warburton
10:45	Carlo Andrea De Filippo
11:00	Coffe Break
11:30	Andreas Neophytou
12:00	Lars Patterson
12:20	Neta Ellert
12:40	Johannes Giebelmann
13:00	CLOSING

max 10 places available.
* An apero-dinner is available at Zi' Anto restaurant in Punta Tegge under request (its cost will be set soon).
** Scuba-diving will be operated by Best Shark Diving Center under request (price of Introductory lesson, or excursion will be set soon).
This activity is NOT included in the registration fee. Its cost (lunch included) will be set soon.

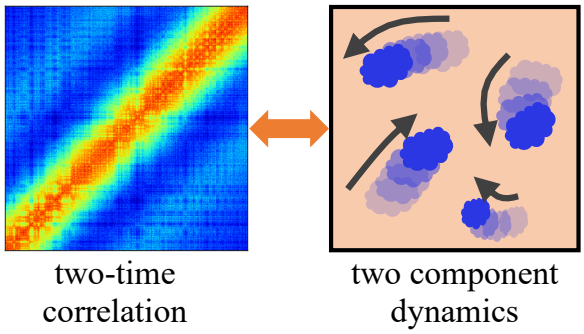
WaterX@2024 International Workshop May 25 – 30, 2024

Under pressure: dynamics in amorphous ice

Katrin Amann-Winkel
Max Planck Institute for Polymer research & Johannes Gutenberg University Mainz

Since the discovery of two distinct amorphous states of ice with different density (high- and low-density amorphous ice, HDA and LDA) it has been discussed whether and how this phenomenon of polyamorphism at high pressures is connected to the occurrence of two distinct liquid phases (HDL and LDL). The glass-to-liquid transition of the two states is still not fully understood. The almost opposite pressure dependence of the two glass transition temperatures leads to a crossing at elevated pressures. While experimental determination of the glass transition at elevated pressure and cold temperatures is technically difficult to implement, measurements on water and amorphous ices are even more challenging, as the glass transition is interrupted by crystallization. In my talk I will give an overview about recent X-ray photon correlation spectroscopy (XPCS) measurements on amorphous ice at ambient pressure [1,2], as well as new experiments at elevated pressure using a diamond anvil cell. We also applied the method to investigate other aqueous systems.

[1] M. Ladd-Parada, et al., Environ. Sci.: Atmos., 2, 1314 (2022)
[2] H. Li et al., JPCL 14, 49 (2023)



Two time correlation function derived from coherent X-ray diffraction, shows a heterodyne signal which originates from the interplay of a static and a dynamic component. [2]

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Neutron diffraction study for hydrogen bond symmetrisation in ice

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Hydrogen bond symmetrisation, the phenomenon where a hydrogen atom is located at the centre of a hydrogen bond, involves nontrivial phenomena such as the notable isotope effect on the symmetrisation pressure which may relate to the nuclear quantum effect. This has led to substantial attention and numerous experimental and theoretical research have been conducted. However, the precise determination of hydrogen atom positions and consequently the reported transition pressures have remained inconsistent [e.g., 1-4].

In this study, we present the direct observation of the atomic distribution of deuterium in D_2O ice, elucidated through neutron diffraction techniques at pressures exceeding 100 GPa [5]. Our investigation unveils a remarkable transition from a bimodal to a unimodal distribution of deuterium at approximately 80 GPa, marking the first observation of this phenomenon. Concurrently, at the transition pressure, considerable narrowing of the peak width is found, which would be attributed to structural relaxation induced by alterations in elastic properties in ice. I also discuss various intermediate states during the process of hydrogen bond symmtrisation and whichever can be regarded as thermodynamically distinct phases.

[1] Meier, T. et al., Nat. Commun. 9, 2766 (2018).
[2] Lei, J., et al., J. Phys. Chem. Lett. 12, 4707-4712 (2021).
[3] Méndez, A. S. J. et al., Phys. Rev. B103, 064104 (2021).
[4] Tsuchiya, J., et al., arXiv preprint arXiv:2307.14214 (2023).
[5] Komatsu, K. et al., under review

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WaterX@2024 International Workshop May 25 – 30, 2024

Porosity as a new perspective in the ice landscape

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Traditionally, the different crystalline phases that compose the rich ice polymorphism landscape can be characterized for their crystal structure, thermodynamic stability, and proton ordering. However, the discovery of the ice XVII, obtained by out-diffusion of H_2 from a C_0 hydrate [1], opened the route to study these compounds also for their gas absorption and desorption properties. Indeed, ice XVII has a low-density, is highly porous, and presents accessible spiraling channels where H_2 can be reversibly hosted in an essentially one-dimensional geometry [2]. Later, a similar property was also observed by dosing different types of gases on both ice XVI [3] and ice XVII [4], further enhancing the fundamental and applicative interest in these low-density materials. In this talk we will show our studies concerning the structure as well as the vibrational and diffusional dynamics of the gas-refilled ice XVII, mainly performed through Raman and neutron scattering experiments [5]. We will also discuss about the porosity of other pure ice (or emptied hydrate) forms obtained to date [5,6].

[1] L. del Rosso et al., Chem. Phys. 2021, 544, 111092.

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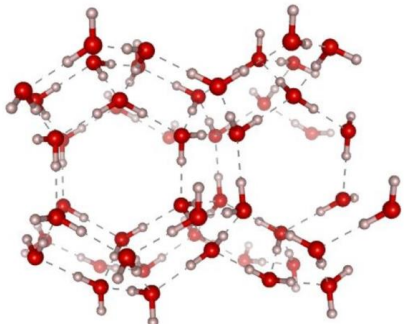

Crystalline structure of ice XVII

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WaterX@2024 International Workshop May 25 – 30, 2024

A characterization of the removal of salt and simultaneous capture of CO_2 by hydrate formation: investigation by optical microscopy and Raman spectroscopy

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The growing of economic and world's population pose a twin crisis syndrome related to the increasing concentration of CO_2 in the atmosphere and, at the same time, a serious crisis in available fresh water. Recently, it has been proposed that both ongoing challenges in the form of global warming and water scarcity (SDG 6 and 13 from UN) can be addressed by employing a single technic working with the hydrate methodology [1]. The working principle of this integrated approach at the molecular scale is based on the selective trapping of CO_2 molecules (guests) in clathrate hydrate cages and, at the same time, the exclusion of the salt from growing hydrate crystals.

In this work, we develop a set-up based on the synthesis of hydrates in high pressure capillaries to investigate growing process of hydrates, their distribution in the reactor, and the structure of hydrogen bonded water. The effect of salt (NaCl) concentration on hydrates formation at different subcooling temperatures is followed both optically and spectroscopically by Raman. A monitoring of the rise of the salt concentration in the remaining liquid phase during the hydrate formation is observed in-situ [2]. This reveals how water is primarily extracted from the saline solution to participate in the formation of the CO_2 hydrate lattice structure. Furthermore, as gas hydrates crystallization progresses, salinity increases in the remaining solution due to salting-out effect. Depending on the salt concentration, the affinity of water molecules towards solution ions and their participation in the hydrogen bonding network differs significantly. The analysis of water stretching vibration by micro-Raman reveals that a weakening of the structural network of water can occur. These results brought new insights into the molecular understanding of the salting-out effect by clathrate formation. They are of valuable help in the development of the hydrate-based-desalination process with CO_2 capture.

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NaCl Salty Ice VII: The Search for Planetary Relevant Salty Ice

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A number of years ago, salty ices were discovered [1-3]. These novel structures featured substantial quantities of LiCl and LiBr salts incorporated into the crystalline structure of ice VII under high pressure [4]. The presence of these salt ions within the ice VII lattice led to various changes in its properties. Notably, there was an expansion of the unit cell by 18–20% within the lattice [1], disorder in the orientation of water molecules [2], remarkably high ionic conductivity [1], and prevention of the transition to the ordered ice VIII phase [1,2] and the symmetric ice X phase [3,5] upon decreasing temperature or increasing pressure, respectively. To achieve ion inclusion, the eutectic solution (LiCl: 6.5 D_2O, LiBr: 7 D_2O) was rapidly cooled (>10^3 Ks^{-1}), resulting in the formation of a high-density amorphous structure lacking long-range order. Subsequently, re-crystallization occurred by thermally annealing this amorphous precursor at high temperatures. Under compression, the amorphous precursor adopted a higher coordination configuration around the salt ions, akin to the configuration observed in salty ice VII [6-8]. Consequently, upon raising the temperature, the ions retained their local configurations, but the amorphous structure underwent a transition into an ice VII structure, culminating in the formation of salty ice.

Here we explore the potential inclusion of salts, particularly NaCl, which holds significant importance for planetary modelling. Initial x-ray diffraction data and molecular dynamics (MD) simulations indicate that NaCl-ice VII may exist at pressures exceeding 6 GPa and temperatures above 273 K. The incorporation of NaCl brings about notable changes in lattice volume (5-7%) and thermal properties. Such changes could prove highly significant for modelling the deep interiors of icy moons like Enceladus or Ganymede, where subsurface salty oceans are known to exist [9,10], as well as for understanding the anomalous magnetic fields of "ice giants" Neptune and Uranus.

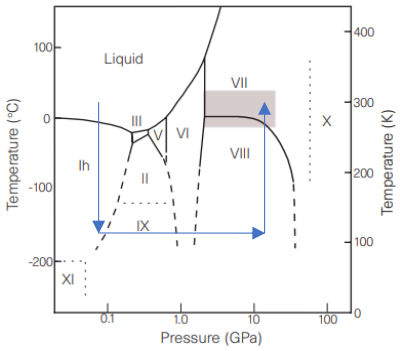

Fig. 1 – Shaded region T > 300K, P > 6GPa is where we are interested in, with the indicated thermodynamic path. Diagram taken from [4].

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Phonon dispersion and proton disorder in ice VII and VIII

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Among the ~ 20 ice phases presently known, two high-pressure phases, ice VII and ice VIII (Fig. 1) are remarkable in several aspects: (1) Their extreme stability under compression over more than 50 GPa, making them the two dominant forms of water's phase diagram, (2) their relatively simple structures, and (3) the fact that ice VII is the fully hydrogen-disordered form of ice VIII. Here we show an investigation of the phonon dispersion of ice VII and that of its proton-ordered analog ice VIII through a combination of inelastic x-ray scattering (IXS) measurements and first-principles calculations of the oxygen sublattice dynamic structure factor. The data show that, despite a full proton disorder, the acoustic phonon branches of ice VII clearly inherit the periodicity of its body-centered cubic oxygen sublattice. However, the calculations predict the presence of gap openings in the one-atom phonon dispersion. These predictions are supported by revisiting the analysis of previous single-crystal IXS measurements along the longitudinal [111] branch of ice VII.

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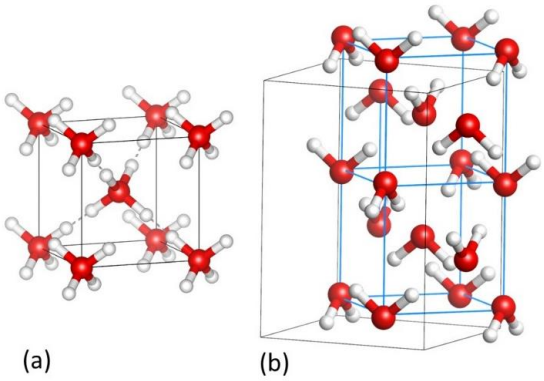

Figure: Structure of ice VII (a) and VIII (b) with O in red and H in white. In ice VII the orientation of the molecules is disordered which gives 4 hydrogen sites around each oxygen, each occupied at 50% on average. Ice VIII is the ordered version of phase VII

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Intermediate H-ordered state between ice V-XIII pair

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One uniqueness of water ice is its tremendous structural variety that originates from both sublattices of O- and H-atoms. The H-sublattice, corresponding to molecular orientations and dipoles, is the key ingredient enriching ice polymorphism. However, understanding the transitions between hydrogen order and disorder is often difficult, especially about the partially-ordered forms [1,2], because of the problem of kinetic freezing [3].

Ice V is a disordered high-pressure phase stable at 0.3-0.6 GPa below 270 K. This phase takes at least two pathways of hydrogen ordering at 105-120 K upon cooling [4], which are not fully understood. Its ordered form is known as ice XIII, but it is unclear where the second pathway leads to. Here, we re-examine the hydrogen-ordering process at ambient pressure using differential scanning calorimetry (DSC) [5]. Based on the time evolution of H-order under isothermal conditions, we simultaneously extract thermodynamic and kinetic information. These trends imply a different (but unknown) ordered state with boundaries at 112-113 K and 120 K, which may also differ from both ices V and XIII in an H-order manner. Further details will be discussed in the presentation with comprehensive observations.

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Anderson localization of harmonic phonons in isotopically disordered ice VII and VIII

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Ice VII covers a large area of P-T space in water's phase diagram, and consists of a body centered cubic array of oxygen atoms tetrahedrally linked by disordered hydrogens bonds. This forms two interpenetrating, but not interconnected, cubic diamond lattices. Many of the transitions from ice VII to adjacent phases only involve the hydrogen atoms and leave the oxygen lattice intact: upon cooling (to proton-ordered ice VIII), upon compression (to proton symmetrized ice X), and upon heating (to plastic and superionic phases) [1-3]. Isotopic substitution (deuteration) is an ideal tool to manipulate those transitions, while Raman spectroscopy is an ideal probe to study the hydrogen sublattice dynamics.

Raman spectra from molecular systems are typically regarded as comprising a set of sharp peaks, while their broadening is typically assigned to thermal, linewidth, and anharmonic effects. Here we present significant broadening in the Raman signal from partially deuterated water ices VII and VIII, which is absent in the pure systems. This isotopic broadening is much greater than any anharmonic effects. Lattice dynamics calculations show that it arises from mass disorder induced phonon localization. This localization leads to many overlapping modes with a range of frequencies dependent on local isotopic environment and Raman activity due to lack of distinct molecular or crystalline symmetry.

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Orientational disorder drives site disorder in plastic ammonia hemi-hydrate

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Ammonia hydrates are present in the interiors of Uranus and Neptune and are known to contribute substantially to their properties. Recent experiments in the 5-10 GPa pressure range have shown that this class of molecular solids undergo a phase transition with increasing temperatures, from ordered crystals to intermediate plastic phases before becoming liquids at higher temperatures. However, the microscopic description of such plastic phases is still an open question. Previous simulations were not able to solve this problem, probably because time lengths and system sizes were not sufficiently large. Here, by using large-scale (~10^5 atoms) molecular dynamics simulations on unprecedented long time scales (~10 nanoseconds) for this system, we characterize the atomic-scale structure of the plastic phase and describe the mechanisms and the dynamics of the phase transition.

Our results agree with the experimental measurements and provide the explanation of some previous conjectures on the basis of a consistent picture. In particular, we confirm that the plastic phase is characterized by dynamical orientational disorder, which triggers the diffusion of the molecules through the crystal sites, and eventually leads to the plastic site-disordered phase. The dynamics of the directional hydrogen bonds reveals that the weakening of the strongest OH...N hydrogen bonds causes the transition to the plastic phase and activates the molecular diffusion that yields site disorder. We will show that the correlation between those two kinds of disorder (rotational and configurational) – that we call Orientational-Disorder-Driven Site Disorder (ODDSD) – in plastic ammonia hemi-hydrate under pressure is likely at work in other hydrates at high pressures, including the recently studied case of the elemental ice-VII phase.

[N. Avallone et al. under review.]

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Water - the dark matter of the atmosphere

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Water vapor is the most abundant atmospheric trace gas, but concentrations show strong temporal and spatial variation. Furthermore, interactions of water with other atmospheric components often result in highly non-ideal mixtures, especially in the condensed aerosol and droplet phases (Prisle et al., 2010). Therefore, the influence of water on the physics and chemistry of atmospheric aerosols is often poorly constrained.

Many organic components of atmospheric aerosols are surface active in aqueous solution. In aqueous aerosols and droplets, surface adsorption lead to enhanced surface concentrations compared to the (interior) bulk, but can also strongly deplete the bulk phase due to the very high surface area (A) to bulk volume (V) ratio in sub-micron size ranges. This effect can be so strong that aerosol or droplet size and resulting A/V becomes the determining factor for surface tension (Bain et al., 2023). The surface tension may in turn impact a wide range of physical and chemical properties of aqueous aerosols and droplets (Prisle, 2024). Organic aerosols also include numerous species with Brønsted acidic or basic character. The concentrations of acidic or basic species affect aerosol pH, which in turn influences the protonation state of individual acidic or basic aerosol components. The contribution of organic aerosol acid-base dissociation on aerosol H^+ concentration is often overlooked in atmospheric models, but can significantly impact aqueous aerosol chemistry, sulfate mass formation, and predicted cloud radiative effect (Sengupta et al., 2024). When organic aerosols are simultaneously surface active and Brønsted acidic or basic, the effects of water interactions are complex and non-linear, in particular as the dissociation state of acids and bases at the aqueous surface may deviate strongly from that in the bulk (Prisle, 2024).

We have recently found that water can be taken up to aerosol surfaces at extremely low ambient humidities, much below the deliquescence point or any measurable hygroscopic growth (Lin et al., 2021). In these nano-confined surface layers, water can mobilize and lead to segregation of ions, and even catalyze chemical transformations. We have also found several examples of how non-ideal water interactions can lead to previously unrecognized perturbations in the composition and morphology of laboratory-generated aerosols, potentially biasing decades of aerosol process studies (Rissler et al., 2023).

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Freezing nanodroplets: Probing water's phase transitions under extreme conditions

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Nanometer sized particles, droplets or crystals, form both in the environment and in large scale industrial processes. Accurate predictions of the phase transition rates, and the phase or structure of the particles, are critical for developing reliable models of industrial processes, climate, and atmospheric chemistry. From a fundamental point of view, particles with radii < 10 nm are also important because they lie in the critical transition zone between large molecular clusters and bulk materials. For small enough particles, internal droplet pressure can easily reach ~30 MPa. This talk will summarize our recent work following freezing of highly super-cooled water. Studies [1,2] use a range of techniques including small angle x-ray scattering (SAXS), wide angle X-ray scattering (WAXS), infrared spectroscopy, and pressure measurements. For water, the small droplet size and the rapid cooling rate means that liquid water only begins to freeze below ~225 K – a temperature that is well below the homogeneous freezing limit for bulk water or even micron size water droplets. These experiments show the expected decrease in freezing temperature with decreasing droplet size, or alternatively, with increasing droplet internal pressure. The final phase of the ice is also highly cubic ice I rather than the more stable hexagonal ice I.

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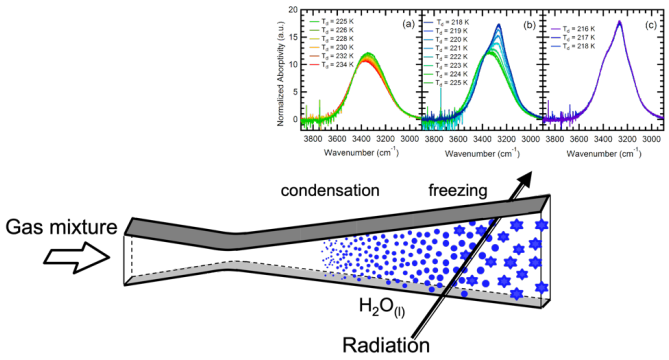

Schematic of supersonic nozzle and FTIR spectra as water freezes in 10 nm droplets.

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WaterX@2024 International Workshop May 25 – 30, 2024

Interfacial acid-base chemistry of hexylamine and nitric acid

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Multiphase chemistry at the air interface of atmospheric particles and ground surfaces impacts cloud formation, atmospheric chemistry, and human health [1]. Many of these chemical reactions are affected by acidity [2]. Using X-ray excited electron spectroscopy at near ambient pressure, we have suggested that the dissociation of acids adsorbed to ice is governed by the availability and mobility of water molecules to stabilize the dissociated ions and that the degree of dissociation at the air-ice interface differs from that predicted based on dissociation behavior in aqueous bulk solutions [3,4,5,6]. Ice and snow host chemistry relevant to the atmosphere and essential in cold regions of the Earth.

Here, we present new results of fundamental experimental work on the structure of the hydrogen bonding network of interfacial water and the dissociation of the acidic trace gas nitric acid and protonation of the basic trace gas hexylamine upon adsorption. We show results from a wide temperature range of the acid-base interfacial chemistry at -50°C and -20°C, addressing the impact of the increased liquid-like character of ice at the air-ice interface at temperatures approaching the melting point. This increased flexibility of water molecules at the air-ice interface has also been called the pre-melting or quasi-liquid layer [3]. Taken together, the data indicate a dominating role of the water availability on dissociation rather than the acidic strength or its temperature trend. We discuss how the limited availability of water may also be applied to other interfaces to explain the dissociation of acidic adsorbates there

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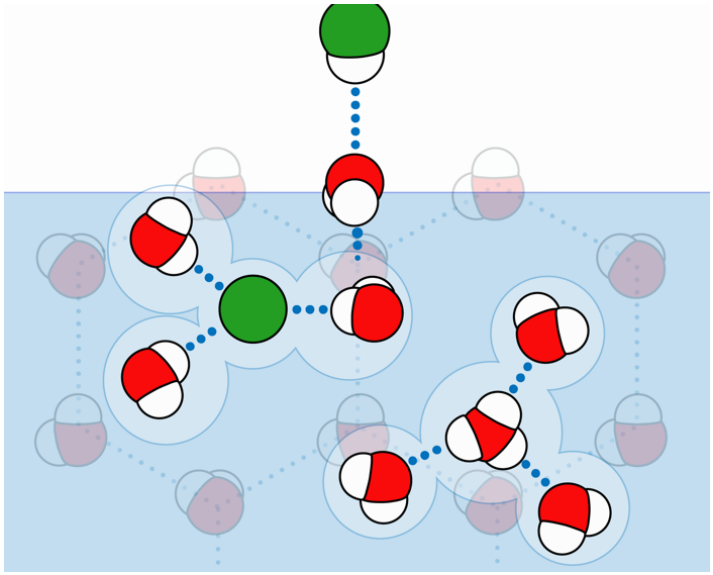

The emerging picture of acid-base chemistry at the air ice interface with HCl adsorbing at the surface and dissociating upon formation of solvation shells within the interfacial region.

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Characterization of Anomalies in Water Nanodroplets

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Liquid water nanodroplets are candidate systems for understanding supercooled water because they resist crystallization and because their interiors are expected to reach pressures on the scale of 100 MPa owing to the Laplace pressure. Varying size thus affords a way of probing the equation of state near the liquid-liquid critical point (LLCP) hypothesized to exist at low temperature and high pressure. For the TIP4P/2005 model of water, we have reported that for droplets over a range of sizes and temperatures, the interiors follow the bulk equation of state, deviating only on approach to the LLCP [1,2]. With a critical pressure P_c = 185 MPa, hallmark anomalies of the LLCP occur in TIP4P/2005 droplets containing only 100s of molecules (radius R~2 nm). By contrast, for the WAIL model of water, for which P_c = 50 MPa, we find that a transition between low- and high-density liquids is clearly observable for significantly larger droplets (N~10,000 and R~4-5 nm). A feature of nanodroplets on cooling, when the interior pressure is low enough, is that as the low-density network emerges in the interior, the subsurface remains disordered and at a high density. This heterogeneous environment influences the distribution of simple ions and other charged species within a nanodroplet [3,4]. We report on efforts to characterize the liquid-liquid transition and structural heterogeneity in terms of static (Fig. 1) and dynamical quantities of relevance to experiments.

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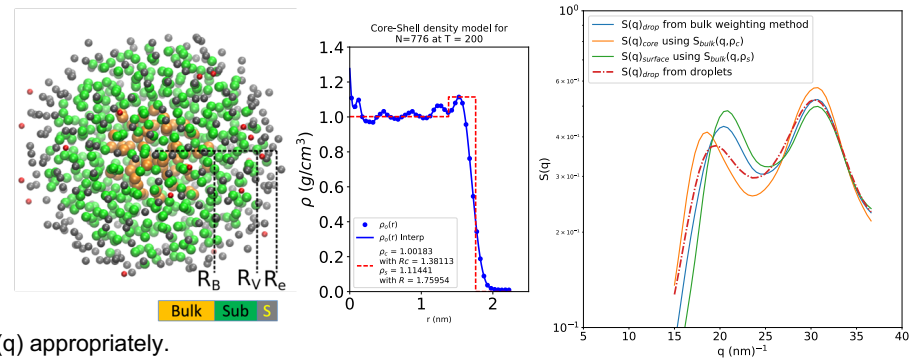

Fig. 1 Core and subsurface densities may be discernable by fitting low-q data with a core-shell form factor and then modelling S(q) appropriately.

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Neural-Network-based Simulations of Acidity at the Surface of Aqueous Aerosols

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Chemical reactivity at the air-water interface is remarkably different from that known in the bulk liquid. Since acidity is a key factor in many reactions, understanding the acidity of the air-water interface is key for rationalizing many atmospheric processes. However, whether the air-water interface is more or less acidic than bulk water is a long-standing debate. Most recent spectroscopic measurements have pointed to an increased presence of acidic hydronium cations [1], but the interpretation of such measurements is still highly debated. Indeed, determining the thickness of the interfacial region that is being probed in different experiments and to what extent the acid-base properties are modified with respect to the bulk are major difficulties in solving this disagreement [2]. Furthermore, a surface-induced change in acid-base properties implies a dependence of this key quantity on the system size, which can be critical for the smaller systems such as, e.g. nucleation aerosols.

We employed neural-network potentials to reproduce the behavior of pure and acidified water interfaces with air at a Density Functional Theory (DFT)-level of description to probe the acidity of the air-water interface with a molecular resolution. Our results unambiguously show that hydronium cations are favored at the air-water interface with respect to hydroxide anions. This has unexpected consequences both for the acid-base reactivity of any air-water interface and for the pH of the smaller interfacial systems [3]. We have also employed a new methodology to compute Sum-Frequency Generation spectra of pure and acidified water surfaces, as this technique provides one of the main experimental evidences of interfacial excess protons. Our simulations reproduce all the qualitative features of the experimental spectra, which both validates our results concerning the surface activity of hydronium cations and provides a molecular interpretation for their spectral signature [4].

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Understanding the Physics of Hydrophobic Solvation

Mary K. Coe, Francesco Turci, Robert Evans and Nigel B. Wilding

Simulations of water near extended hydrophobic spherical solutes have revealed the presence of a region of depleted density and accompanying enhanced density fluctuations. The physical origin of both phenomena has remained somewhat obscure. This talk describes investigations of these effects via the combined means of mesoscopic binding potential analysis, classical density functional theory (cDFT) calculations for a simple Lennard-Jones solvent, and Grand Canonical Monte Carlo (GCMC) simulations of a monatomic water model. We argue that the density depletion and enhanced fluctuations are near-critical phenomena. Specifically, we show that they can be viewed as remnants of the critical drying surface phase transition that occurs at bulk liquid-vapor coexistence in the macroscopic planar limit, i.e. as the solute radius $R_s \to \infty$. Focusing on the radial density profile $\rho(r)$ and a sensitive spatial measure of fluctuations, the local compressibility profile $\chi(r)$, our binding potential analysis provides explicit predictions for the manner in which the key features of $\rho(r)$ and $\chi(r)$ scale with R_s, the strength of solute-water attraction ε_{sf} and the deviation from liquid-vapor coexistence of the chemical potential, $\delta\mu$. These scaling predictions are confirmed by our cDFT calculations and GCMC simulations. As such our theory provides a firm basis for understanding the physics of hydrophobic solvation. The talk concludes with a brief description of recent methodological extensions that facilitate sensitive measurements of water density fluctuations on Angstrom length scales in MD simulations of complex solutes.

WaterX@2024 International Workshop May 25 – 30, 2024

Phase Behavior of Water

Francesco Paesani
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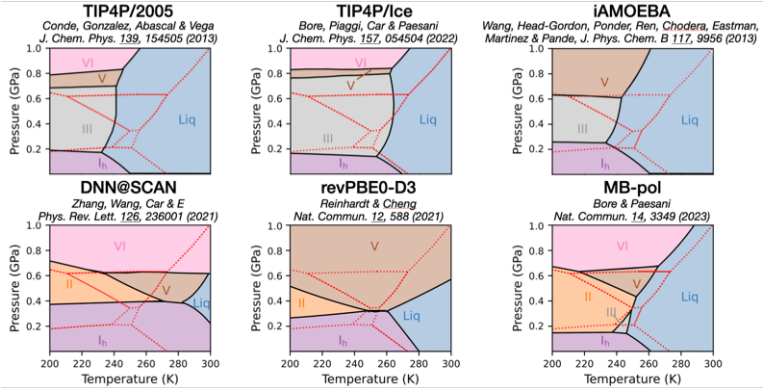
Despite almost 50 years having passed since the first computer simulations of liquid water, and with numerous computational studies reported since then, achieving a realistic molecular-level picture of water's properties across all phases has remained elusive. In the past decade, the development of efficient algorithms for correlated electronic structure calculations of small molecular complexes, accompanied by tremendous progress in machine-learned representations of multidimensional potential energy surfaces, has opened the doors to the design of highly accurate molecular models. These models are built upon a rigorous representation of the many-body expansion (MBE) of the interaction energies. Here, we provide a comprehensive overview of the performance of the MB-pol data-driven many-body potential that enables realistic simulations of water, ranging from gas-phase clusters to liquid water and ice.[1] This is due to its unique ability to quantitatively represent each individual term of the MBE, providing a physically correct description of both short-range and long-range many-body contributions. Comparisons with experimental data probing different regions of the water phase diagram demonstrate that MB-pol effectively represents the long-sought-after "universal model" of water, capable of correctly predicting the molecular properties of water under various conditions and in different environments.

[1] S.L. Bore and F. Paesani, Nat. Commun. 2023, 14, 3349.



Phase diagram of water calculated with TIP4P/2005 (a), TIP4P/Ice (b), iAMOEBA (c), DNN@SCAN (d), revPBE0-D3 (e), MB-pol (f). Figure adapted from S.L. Bore and F. Paesani, Nat. Commun. 14, 3349 (2023); licensed under a Creative Commons Attribution (CC BY) license.

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A simulation study of heterogeneous ice nucleation

M. Camarillo [1,2], J. Oller-Iscar[2], M. M. Conde[2], J. Ramírez[2], E. Sanz[1]
[1]*Dep. Química-física, Universidad Complutense de Madrid, Spain*
[2]*Dep. of chemical engineering, Universidad Politécnica de Madrid, Spain*

Heterogeneous nucleation is the main path to ice formation on Earth. The ice nucleating ability of a certain substrate is mainly determined by both molecular interactions and the structural mismatch between the ice and the substrate lattices. We focus on the latter factor using molecular simulations of the mW model. Quantifying the effect of structural mismatch alone is challenging due to its coupling with molecular interactions. To disentangle both factors, we use a substrate composed of water molecules in such a way that any variation on the nucleation temperature can be exclusively ascribed to the structural mismatch. We find that a one per cent increase of structural mismatch leads to a decrease of approximately 4 K in the nucleation temperature (Fig. 1). We also analyze the effect of the orientation of the substrate with respect to the liquid. The three main ice orientations (basal, primary prism and secondary prism) have a similar ice nucleating ability. We finally assess the effect of lattice flexibility by comparing substrates where molecules are immobile with others where a certain freedom to fluctuate around the lattice positions is allowed. Interestingly, we find that the latter type of substrate is more efficient in nucleating ice because it can adapt its structure to that of ice [1].

[1] M. Camarillo, J. Oller-Iscar, M. M. Conde, J. Ramírez, E. Sanz J. Chem. Phys. 2024.

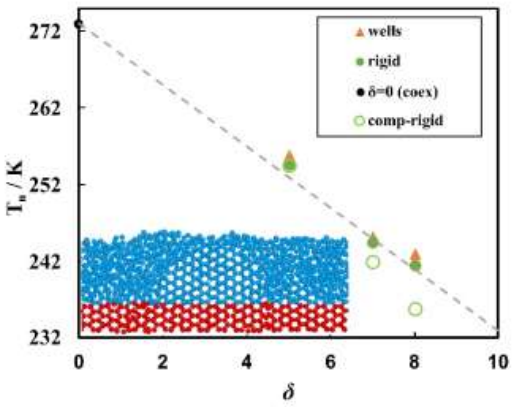

Figure 1 Nucleation temperature dependence on the mismatch between ice and the substrate. Inset: an ice nucleus growing on the substrate.

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Simulations of electrolytes in water

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Modeling electrolytes in water is challenging. Typically force fields for electrolytes are fitted to reproduce free energies of hydration and densities (or ion-water distances). It is not clear which water model to use when modeling electrolytes. Water models can be divided in two families: those reproducing the dielectric constant of water (as OPC for instance) and those not reproducing the dielectric constant of water (as TIP4P/2005). Is it important to reproduce the dielectric constant of water when modeling electrolytes in water ? We shall discuss this issue , and we shall present the current development of the Madrid-2019 force field of electrolytes in water. This force field uses the TIP4P/2005 model of water and scaled charges for the ions. Its current development includes parameters for the cations : Li,Na,K,Rb,Cs,Mg,Ca,Sr,Ba,ammonium and for the anions F,Cl,Br,I, sulfate, nitrate. Results will be presented for densities, structure, viscosities, diffusion coefficients, freezing point depression, and maximum in density. The choice of the value of the scaled charge will be discussed as it will be shown that it is not possible to reproduce all properties with the same value of the scaled charge.

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WaterX@2024 International Workshop May 25 – 30, 2024

Neural Network Potentials Face Ice Nucleation

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We present a novel Neural Network Potential (NNP) with self-trained atomic fingerprints [1] and show how it has been tested on ice nucleation [2]. The novel potential is based on a new set of atomic fingerprints that probe both distances and local orientational order. This new set of atomic fingerprints encapsulates a set of parameters that are trained with the NN weights simultaneously, improving both accuracy and simplicity of use. We found that in the parameter space of this model, an annealing protocol that progressively cycles the learning rate leads to significant improvements in accuracy. We prove the effectiveness of our approach by training an NNP on the mW model of water, a classical three-body potential with known nucleation properties. Our results show that the NNP accurately reproduces the nucleation rates and free energy barriers of the original model, despite being trained only on liquid states, supporting the use of NNPs to study nucleation events [2]. We then train the model on the MBPol potential, presently one of the most accurate but also more computationally expensive potentials. We present the generalization of the one-component NNP model to mixtures as well as preliminary results on water properties accessible by the NNP at the accuracy of the MBPol model.

[1] F. Guidarelli Mattioli, F. Sciortino, and J. Russo, J. Chem. Phys. 158, 104501 (2023)
[2] F. Guidarelli Mattioli, F. Sciortino, and J. Russo, J. Phys. Chem. B 127, 3894 (2023)

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WaterX - Program May 25 - May 30 2024 - La Maddalena (Italy)

time	Saturday May 25
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21:00	Opening Lecture: Pablo Debenedetti

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18:30	Walk to Punta Tegge for Sunset Apero *

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max 10 places available.
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This activity is NOT included in the registration fee. Its cost (lunch included) will be set soon.

CONFINEMENT EFFECTS ON THE NUCLEAR SPIN ISOMERS INTERCONVERSION MECHANISM AND RATES OF H_2O

Thomas Putaud[1,2], Pierre-Alexandre Turgeon[1], Clément Wespiser[1], Jean-Claude Chartrand[1], Jonathan Vermette[1], Yulia Kalugina[1,3], Pierre-Nicholas Roy[3], Xavier Michaud[2], et Patrick Ayotte[1]

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The interconversion between the nuclear spin isomers (NSI) of the water molecule, o-H_2O ↔ p-H_2O, is a highly forbidden process that has been predicted to occur over several billon years under the low temperatures and pressures typical of the interstellar medium. However, spontaneous interconversion occurs readily in water molecules confined to substitutional sites of inert matrices (Ne, Ar, Kr, Xe, p-H_2) or within fullerenes (C_{60}) even for temperatures as low as 4K. The evolution of interconversion rates with temperature (T = 4K - 30K), was investigated for the different isotopologues of H_2O ($H_2{}^AO$, A = 16, 17, and 18), isolated in various confinement media. Using a simple model, describing an asymmetric quantum rotor confined within a 3D isotropic harmonic potential, the rotational and rovibrational spectra of confined water molecules can be satisfactorily retrieved, thereby revealing the topology of the confinement potential. This toy model thus reveals how the coupling between the quantized translational degrees of freedom, arising from extreme confinement conditions experienced by the water molecules, and its intramolecular rotational degrees of freedom, leads to the mixing of very specific rotranslational states within each of the NSI manifolds [2]. While the intricate mixing schemes exhibit strict selection rules, they also admit new NSI interconversion pathways. Confinement effects may elucidate how and why the strict selection rules that govern intramolecular hyperfine couplings that forbid NSI interconversion in isolated water molecules are lifted. A better understanding of confinement effects on the NSI interconversion mechanisms and rates in the water molecule could pave the way to the development of more efficient storage methods to conserve highly enriched samples of o-H_2O [3,4] thereby enabling novel nuclear magnetic resonance spectroscopy and imaging methodologies and their applications to chemical dynamics.

[1] P.-A. Turgeon, et al., J. Phys. Chem. A 2017, 121, 1571 – 1576; [2] T. Putaud., et al., J. Chem. Phys 2022, 156, 074305; C. Wespiser, et al., 2022, 156, 074304; C. Wespiser, et al., Mol. Sim. 2021, 47, 942 – 949; [3] P.-A. Turgeon, et al., Phys. Rev. A 2012, 86, 062710; [4] J. Vermette, et al., J. Phys. Chem. A 2019, 123, 9234 – 9239.

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WaterX@2024 International Workshop May 25 – 30, 2024

Close-packed ices in nanopores

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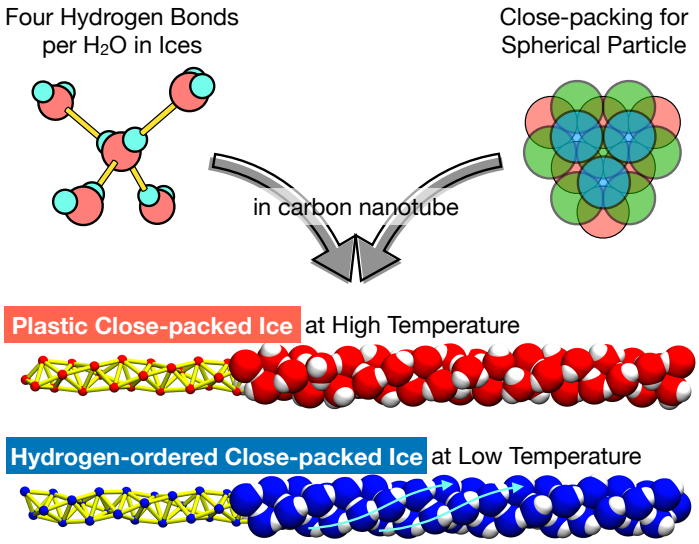
Water molecules in any of the ice polymorphs organize themselves into a perfect four-coordinated hydrogen-bond network at the expense of dense packing. Even at high pressures, there seems to be no way to reconcile the ice rules with the close packing. Here, we report several close-packed ice phases in carbon nanotubes obtained from molecular dynamics simulations. Typically they are in plastic states at high temperatures and are transformed into the hydrogen-ordered ice, keeping their close-packed structures at lower temperatures. The close-packed structures of water molecules in carbon nanotubes are identified with those of spheres in a cylinder. We present design principles of hydrogen-ordered, close-packed structures of ice in nanotubes, which suggest many possible dense ice forms with or without nonzero polarization. In fact, some of the simulated ices are found to exhibit ferroelectric ordering upon cooling.[1]

[1] K. Mochizuki, Y. Adachi, K. Koga, ACS Nano 2024, 18, 347-354



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Very slow nuclear spin conversion of H_2 on porous amorphous solid water below 10 K evidenced by *in situ* infrared experiments

X. Michaut[1], J. Michoud[2], S. Cryan[2], D. Toulouse[1,2], M. Bertin[1], G. Féraud[1], J.-H. Fillion[1], P. Jeseck[1], F. LePetit[2], E. Roueff[2], and E. Bron[2]

1 MONARIS « De la Molécule aux Nano-objets : Réactivité, Interactions et Spectroscopies », UMR8233, Sorbonne Université CNRS, F-75005 Paris, France

2 LERMA, Obs. de Paris, PSL Research University, CNRS, Sorbonne Université, Paris, France

Hydrogenated molecules like H_2 and H_2O exist in several nuclear spin configurations due to the Pauli exclusion principle. These configurations are called *ortho* (parallel proton spins) and *para* (antiparallel proton spins). The *ortho* and *para* populations have been regularly determined by observations in different regions of space in far-UV absorption (Copernicus, FUSE) and in IR and sub-mm emission (ISO, Spitzer, Herschel). The *ortho/para ratio* (OPR) depends on physico-chemical processes in these environments, such as chemical formation, reactive collisions, adsorption and desorption effects of molecules on ice grains, and could be a tracer of molecular history. In order to interpret astronomical observations [1], it is important to compare them with the results of the more comprehensive astrochemical model [1-3]. H_2 is the most abundant molecule in the interstellar medium and is known to be the main reactant involved in the reaction chain to form hydrogenated molecules, so the ortho/para ratio of H_2 plays a role in the chemical evolution of molecules like water [1-3]. The *ortho/para ratio* of H_2 in the gas phase could be affected by the desorption processes of interstellar grains in cold regions [2]. It is therefore necessary to know the characteristic time of equilibration of the nuclear spin states of H_2 on solid water at low temperatures, and the relative abundances of the nuclear spin states during desorption [2]. Measurements reported in the literature on the characteristic time of H_2 nuclear spin conversion on amorphous solid water (ASW) around 10 K have shown wide discrepancies - ranging from a few minutes to hundreds of minutes [4,5]. As H_2 is known to become IR active due to its interaction with dangling OH bonds on surface of the pores of ASW, we developed a new laboratory experiment (COSPINU2) in an ultra-high vacuum chamber to perform *in situ* measurements using Fourier Transform InfraRed (FTIR) spectroscopy. We found that ortho-H_2 species completely transform into para-H_2 species in a few days under experimental conditions. The temporal evolution follows a simple exponential decay with typical long characteristic times between 250 and 1200 minutes much longer than those measured by other methods [4,5]. In this talk, we will present the different methods used to address the question of *ortho-to-para* conversion of H_2 on ASW, the various measurements reported in the literature and their implications for the chemical evolution of the interstellar medium, particularly in the Photon-Dominated Regions (PDR).

[1] T. Putaud et al, Astronomy & Astrophysics 632, A8 (2019)

[2] E. Bron et al, Astronomy & Astrophysics 588, A27 (2016)

[3] P. Hily-Blant et al, MNRAS 477, 4454–4472 (2018)

[4] T. Sugimoto and K. Fukutani, Nature Physics 7, 307 (2011)

[5] M. Chehrouri et al, Physical Chemistry Chemical Physics 13, 2172 (2011)

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The Impact of Alcohol and Ammonium Fluoride on Pressure-Induced Amorphization of Cubic Structure I Clathrate Hydrates

Lilli-Ruth Fidler[1], Paul Posch[1], Johannes Klocker[2], Thomas S. Hofer[2], Thomas Loerting[1]
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We have investigated pressure-induced amorphization (PIA) of an alcohol clathrate hydrate (CH) of cubic structure type I (sI) in the presence of NH_4F utilizing dilatometry, X-ray powder diffraction and molecular dynamics simulations[1]. This unusual CH with ethanol and methanol acting as guests and NH_4F incorporated into the host lattice in the manner of a solid solution has been first synthetized by Shin et al.[2]. It represents a breakthrough in the synthesis of alcohol-containing CHs[2,3], eliminating the requirement of a hydrophobic helper guest.

PIA of this sI CH occurs at 0.98 GPa at 77 K, while other CHs of the same structure type, such as methane hydrates, only amorphize above 2 GPa[4,5]. The amorphized CH in our study also shows a remarkable resistance against crystallization upon decompression. While amorphized sI CHs could not be recovered previously at all, we are able to recover the CH to ambient pressure and characterize it *ex situ*. By contrast to sII CHs the recovery of the amorphized CHs to ambient pressure does not even require a high-pressure annealing step[6,7]. Recovery without any loss of amorphicity is possible at 120 K and below. Further, PIA rather than polymorphic transitions takes place upon compression up to unusually high temperatures of 140 K,wherethe sI CH reaches the highest degree of amorphicity.

Reasons for this unique behavior are suggested from molecular dynamics simulations, which suggest that polar alcoholic guests induce cage deformation at lower pressure than non-polar guests. This is due to the formation of weak hydrogen bonds between guest and host lattice. The substitution of NH_4F into the host-lattice on the other hand stabilizes the collapsed state more than the crystalline state, thereby enhancing the collapse kinetics and lowering the pressure of collapse.

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[3] K. Shin *et al.* CrystEngComm 2014, 16, 7209–7217.
[4] C.A. Tulk, D.D. Klug, J.J. Molaison, A.M. Dos Santos, N. Pradhan, Phys. Rev. B 2012, 86, 1.

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[5] N. Noguchi, Y. Shiraishi, M. Kageyama, Y. Yokoi, S. Kurohama, N. Okada, H. Okamura, Phys. Chem. Chem. Phys. 2023, 25, 22161.
[6] Y. Suzuki, Phys. Rev. B 2004, 70, 1.
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Water's role in the temperature-induced collapse of smart polymers

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In the last forty years, it emerged that several water-soluble polymers, such as poly(N-isopropylacrylamide) [1], poly(N-vinylcaprolactam) [2], polypropylene-oxide [3], undergo a temperature-induced coil-to-globule collapse transition in water and aqueous solutions. These processes are reversible and endothermic, indicating that the driving force is of entropic origin. In several cases T(collapse) is around 30 °C, and so these thermo-responsive polymers have attracted much interest as potential drug carriers in the human body.

Since the polymer chains lose conformational entropy upon collapse, the entropy gain driving the process has to come from water molecules. There is a marked difference in solvent-excluded volume among the conformations belonging to the coil macro-state and those belonging to the globule macro-state, a situation resembling that holding for the unfolded and folded conformations of globular proteins [4]. A decrease in solvent-excluded volume leads to an increase in the volume accessible to water molecules, and so to an increase in their translational entropy. Using classic scaled particle theory, and simple geometric models of the coil and globule macro-states, it is possible to show that the large increase in water translational entropy is due to the very large number density of water that, in turn, has its origin in the strength of H-bonds and the small size of water molecules [5-7].

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[7] G. Graziano, J. Mol. Liq. 2024, 400, 124509.

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Water in biology: moving towards studies of water in more complex biological systems

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A fundamental understanding of the hydration and assembly of nanoscale molecules in aqueous solution is crucial for understanding important molecular mechanisms in biological systems and for the development of novel biomaterials with defined architectures and function. However, accessing self-consistent structural information across multiple length scales is challenging. This limits opportunities to move towards more complex and relevant model systems and to exploit atomic scale interactions to achieve emergent macroscale properties. In this presentation I will share our recent efforts to integrate small-and wide- angle neutron scattering coupled with computational modelling to reveal the multiscale structure of hierarchically self-assembled proteins in aqueous solution[1]. This approach allows us to map out the hydration, assembly and surface properties of a large self-assembled biomolecular structure with atomic resolution. I will share our efforts to dissect the perturbations of a protecting osmolyte and high pressure on water structure[2], and the competing molecular mechanisms of protecting and denaturing osmolytes on a model peptide system in aqueous solution[3]. Finally, I will consider how this approach might be further developed towards the multiscale investigations of more complex proteins in solution and to inform the design of assembled biomolecules for functional biomaterials.

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WaterX@2024 International Workshop May 25 – 30, 2024

Insights into Intermolecular H-Bonding in Aqueous Solutions of Ionic Liquids Using Deep UV Raman Spectroscopy

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Using deep UV Raman spectroscopy (DUVRS), we investigated intermolecular H-bonding in aqueous solutions of a set of imidazolium-based Ionic Liquids (ILs) in the water-rich regime. In this regime, both ionic aggregates and bulk-like water domains coexist. The presence of water molecules, whether added or as contaminants in ILs, can compete for hydrogen bond sites, resulting in significant modifications to the local order of these liquids and the modulation of their physical–chemical properties.

To determine the solute-correlated (SC) spectra, highlighting the spectral modifications induced by the solute on the surrounding water (hydration water), a direct spectral subtraction procedure was employed in the CH and OH stretching spectral region. By combining the analysis of the SC-UV Raman spectra with several diagnostic Raman bands of the imidazolium [MIM] cation, we were able to extract valuable information on the H-bonding features and aggregation of [MIM][X] solutions with different anions ([X] = [Cl], [HSO4], [NO3], [TfO]).

Our findings suggest that for the [NO3]- and [TfO]-based Protic Ionic Liquids (PILs), cation-water (ionic) H-bonds formed by the NH group are stronger than the double-ionic cation–anion ones, indicating a preference for water to hydrate this group. We detected the establishment of H-bonds through the cation C(2)–H and C(4,5)–H ring groups, particularly evident in the case of [MIM][Cl], at increasing IL-molar fraction (starting from ~ 0.05). These double-ionic H-bonds are found to be stronger than the ionic cation-water ones.

Furthermore, the H-bond strength between the anion and hydration water was found to decrease following the order: [Cl] ~ [HSO4] > [NO3] > [TfO].

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Deep (thermo)dynamic alterations upon the water wetting on a solid

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At the liquid/solid interface, the liquid energy is different from that of the bulk due to the imbalance between intermolecular and surface interactions. Similar to external fields such as electric, magnetic, or flow fields, the vicinity of a solid surface can preclude the liquid molecules from relaxing to equilibrium. It is here shown that this non-equilibrium state is also associated to the generation of located temperature gradients in the liquid [1]. This unforeseen thermal effect; i.e. the co-existence of (non-Fourier) thermodynamic states, supports the picture of a correlated liquid state [2] that may be related to a surface induced molecular polarization [3]. We ask now the mirror question: does the wetting also impact the solid?

In a second part of the presentation, we probe the evolution of solid dynamics (atomic (phonon) vibrations) upon wetting, using inelastic X-Ray scattering. We reported significant (>1meV) hardening of the phonons modes of the solid (sapphire crystal) due to wetting for both transverse and longitudinal acoustic phonons at a penetration depth of roughly 150 µm, thus well below the wetted surface [4].

These results may suggest a new definition of the liquid/solid interface as an extended intermediary zone dynamically affected by the presence of the liquid, far beyond the usual interfacial considerations. In essence, the results highlight a possible long range phonon liquid/solid coupling. This is in agreement with the assumption that liquids can propagate shear waves as already suggested by the identification of shear elasticity [2] and thermoelastic effects describable by the Biot theory coupling elasticity to temperature changes [5, 6].

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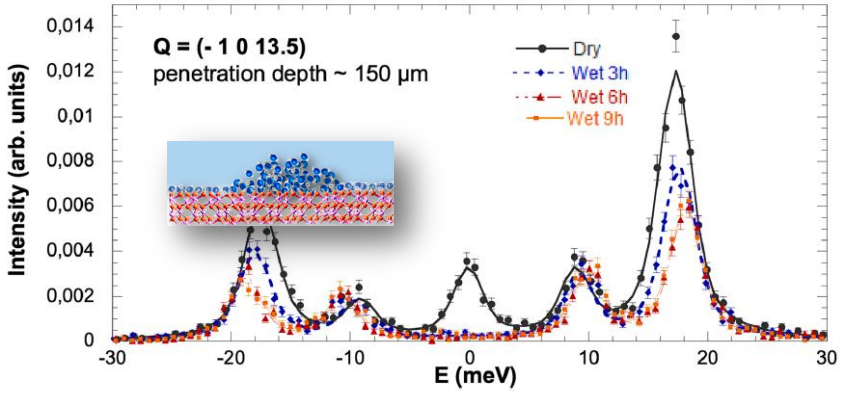

Figure caption: Inelastic X-Ray scattering showing the evolution of the phonon energy at Q = (-1 0 13.5) upon wetting a sapphire crystal with water at room temperature. Black points: Dry α-Al_2O_3, Blue points: H2O wetted after 3hrs, Red points: after 6hrs and Orange points after 9 hrs. The penetration depth is roughly 150µm. A clear change of phonon spectra is observed for the acoustic phonons with inelastic peaks shifting to higher energies (“hardening”) [4]. Measurements carried out on ID28 (ESRF).

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Dilute suspensions of Janus rods: the role of bond and shape anisotropy

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Janus nanoparticles, *i.e.* particles whose tip is functionalised differently from the rest of the particle, have been extensively studied both theoretically, computationally [1], and experimentally [2]. A very rich assembly scenario is unveiled when the anisotropy of the bonding pattern is enhanced by the anisotropy of the particle shape. In the last decades, Janus dumbbells [3], rods [4], and ellipsoids [5] have been widely studied in the context of responsive materials. In this work, we focused on the role of anisotropy and tip functionalisation on the self-assembly behaviour of hard colloidal nanoparticles. In particular, within the variety of assembly behaviours observed in systems of anisotropic Janus colloids, finite clusters have not yet been targeted. Indeed, in contrast to micelles and vesicles made from spherical colloids or colloidal dumbells, stable finite clusters composed of more elongated objects may open up opportunities for their use as storage/delivery nano-devices as well as nanoreactors. We therefore focused on tip-functionalised Janus hard spherocylinders as prototypes of elongated patchy particles and we used Monte Carlo simulations to investigate the self-assembly properties of these units, in particular in the low packing fraction regime. We found that anisotropy plays a crucial role in suppressing phases typical of spherical Janus nanoparticles, while tuning both the range and strength of localised interactions can be used to promote the formation of specific nanostructures, such as spherical or elongated micelles.

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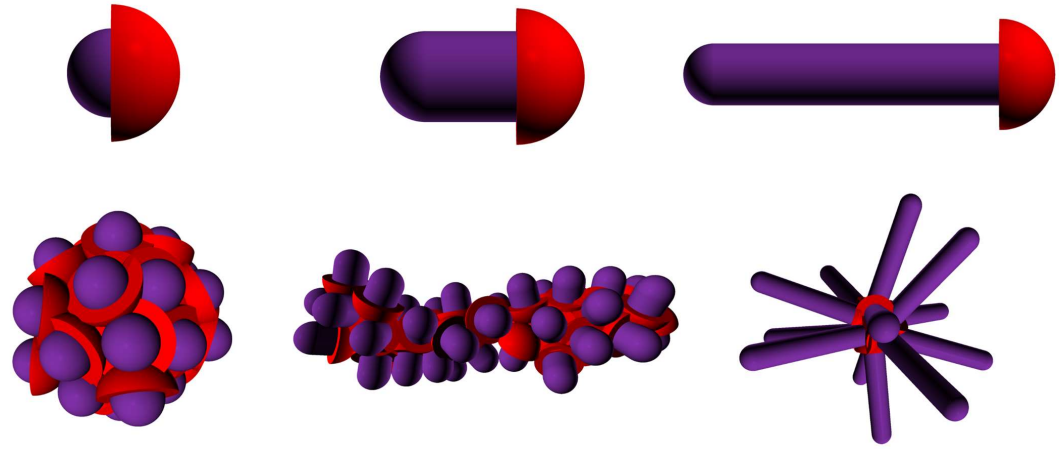

Snapshots of analysed particle types (top) and typical aggregates (bottom), from the left vesicles, elongated micelles, and spherical micelles.

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Unravelling the Mysterious Behaviour of Tetrahedral Liquids: The Topological Nature of the Liquid-Liquid Phase Transition

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It is well known that liquid water behaves anomalously upon cooling, for instance the density of water reaches a maximum at 4°C and ambient pressure.[1] One potential explanation for this weird behaviour is that there is a first-order phase transition line between two liquid phases, which differ in density, terminating at a liquid-liquid critical point (LLCP).[2] The anomalous behaviour of liquid water, along with water polyamorphism, was then suggested to be manifestation of the presence of this liquid-liquid phase transition (LLPT) between a low-density (LDL) and high-density (HDL) liquid. While recent numerical studies have provided strong support to this fascinating hypothesis,[3] experimental evidence of the LLPT has proved elusive due to the rapid formation of ice from the deeply supercooled water around the predicted critical temperature and pressure.[4]

Colloidal patchy particles, due to their synthetic availability[5,6] and their ability to undergo programmed self-assembly, are ideally suited to investigate universal aspects of the LLPT, as well as detailed experimental investigations at single-particle resolution, which is not possible with water. We therefore set out to rationally design a colloidal analog of water constructed from triblock patchy particles.[5,6] The tetrahedrality of the system – key to the uniqueness of water – emerges as the triblock patchy particles undergo two-stage self-assembly upon cooling, with the desired staged-assembly information encoded into the particles *via* the energetics and geometry of the patches.[7] Using extensive isobaric-isothermal Monte Carlo simulations, we show that this colloidal water model possesses the same thermodynamic anomalies as supercooled liquid water. In particular, we show that the model displays a density maximum upon cooling, as well as maxima in its isobaric heat capacity, isothermal compressability and thermal expansion coefficient. Additionally, we find that the colloidal water model does indeed posses a LLCP, and that this critical point is also consistent with the three-dimensional Ising universality class.

Several order parameters, based on geometric or energetic criteria, have been proposed to characterize the LLPT, however, a clear picture for the physical origin of the phenomenon is still lacking. Establishing what features fundamentally distinguish the two liquid networks at the microscopic level should help reveal the physical origins of the LLPT.[8] By introducing a topological order-parameter – the network helicity– we clearly reveal that the LLPT in colloidal water is between two topologically distinct liquid networks, thus addressing a long-standing puzzle in the tale of two liquids: what fundamentally distinguishes the two liquids? Finally, we show that the network helicity is not only able to describe the LLPT for colloidal water, but also for two widely used molecular models of water,[3] thereby establishing the generality of the topological description of the LLPT in tetrahedral liquids. Uncovering the topological distinction between the LDL and HDL networks allows us to understand the physical mechanism underpinning the LLPT from a new perspective that sheds light on its microscopic origin.[9]

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Probing Water Structure around Dissolved Argon by Extended X-Ray Absorption Fine Structure (EXAFS) Spectroscopy

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We use Argon dissolved in water as a probe of lower-density local environments in the liquid through EXAFS at the Argon *K*-edge at 4, 15 and 25 °C. Compared to EXAFS on pure water we find a weaker amplitude and lower frequency in the oscillations, which we ascribe to a longer distance and the lack of protons pointing towards Argon in the hydrophobic cage. We find that simulated EXAFS from MD trajectories give a poor match to the experimental signal and apply the SpecSwap-RMC[1] fitting procedure to elucidate the local structure. We find a somewhat disordered cage with ~20 molecules with structure independent of temperature in the range probed. Argon may be seen as proxy for O_2 and we speculate what such hydrophobic encapsulation entails for the ability of fish to extract similarly dissolved O_2 from water.

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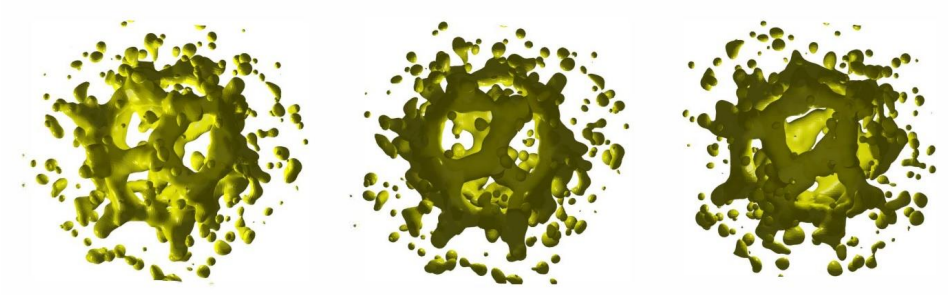

Isosurfaces showing the derived structure of the hydration cavity around the dissolved Argon (not included).

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Short-Range Order in Water and Amorphous Ices – A Molecular Dynamics Study

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Classical Molecular Dynamics (MD) simulations were carried out to study the structural characteristics of water and amorphous ices. The Short-Range Order (SRO) was investigated throughout the Quasi-Crystalline Model (QCM), an approach that aims to reveal the underlying SRO of a given Radial Distribution Function (RDF) by a comparison with a mathematical RDF generated from a reference lattice. This RDF is modelled by a sum of Gaussians representing spherical shells contributions of atoms located at distinct distances from an atom located at the origin. The SRO of the amorphous system is identified with the specific reference lattice producing the best fit for the data. In a previous study [1] we applied the QCM on experimentally derived partial RDFs, and this work aims to compare between the fitting Gaussians of the experimental QCM fit with the MD QCM fit. An example of a successful fit of the partial O-O RDF at ambient conditions is shown in the figure below.

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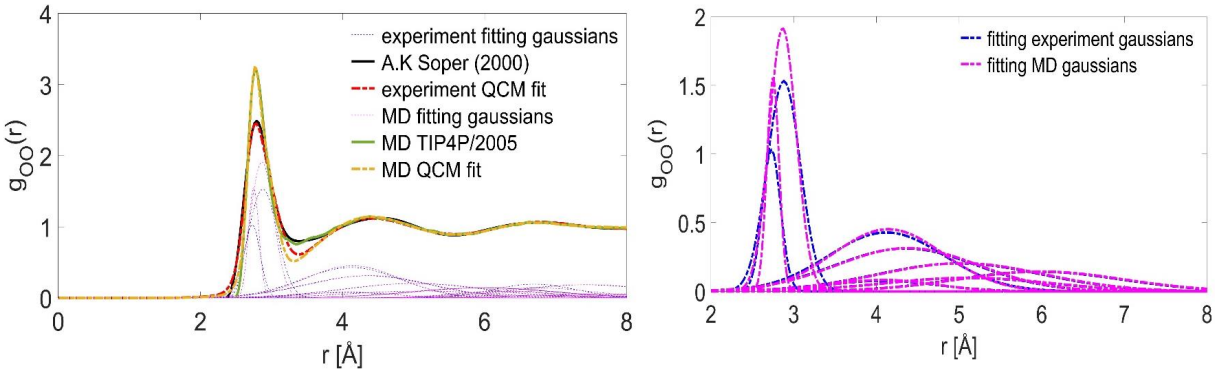

Figure 1. Left: QCM fits to experimental and MD simulation. Right: fitting gaussians comparison

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Water-like Polyamorphism in Hyperquenched Aqueous LiCl Solutions

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In nature, water is exposed to all kinds of solutes. In the two-liquid model of water the question of how solutes impact on the properties of water translates to the question how the solutes impact on the two liquids, low- and high-density liquid water. In our work we have developed the new technique of studying the vitrified and pressurized liquids. Hyperquenching (i.e., cooling micron-sized liquid solution droplets at ~10^6 K/s)[1] produces the low-density amorphous state (LDA) and subsequent pressurization of the vitrified droplets produces the high-density counterpart (HDA). This approach avoids difficulties and caveats previous work on the topic was facing such as phase separation and/or crystallization during sample preparation.[2] Therefore, studies in the past were often limited to rather large mole fractions where water-like behavior tends to disappear[3] or had to deal with complicated phase-segregated systems.[4]

Our new technique[5] allows us to prepare homogeneous LDA- and HDA-like LiCl solutions for any composition between 0 mol% and the eutectic. Our key findings are (i) signatures of a liquid-liquid transition at ambient pressure (see Figure 1), (ii) water-like polyamorphism up to 5.8 mol%, including two glass transitions (one pertaining to LiCl-LDA and LiCl-HDA each), and (iii) a fundamental difference between the electrostrictive effect of LiCl on LDA and HDA. Using this new method it is now possible to fully investigate the effect of solutes on HDA and LDA by analyzing the thermal behavior of the glassy solutions, including both glass transition temperatures at ambient pressure. This has allowed us to identify compositions, in which the range of existence of LDL/HDL is extended much more than in the pure water case, e.g., for a LiCl fraction of 0.03 (see Fig.1), opening the door to many experiments on water structure and dynamics at the liquid-liquid transition that have not been accessible prior to this work.

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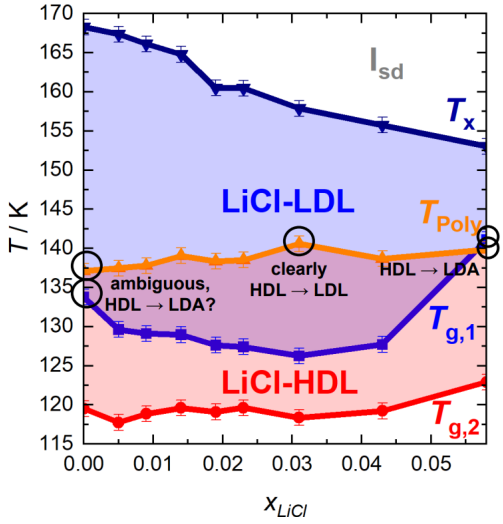

Figure 1: Glass transition onset temperatures of LiCl-HDA ($T_{g,2}$) and LiCl-LDA ($T_{g,1}$), onset temperatures of the polyamorphic transition (T_{poly}) and the crystallization (T_x) upon heating at ambient pressure. Interestingly, LiCl strongly decreases $T_{g,1}$ while having a negligible effect on $T_{g,2}$. This implies that the hydrogen bonded network of LDA is strongly plasticized while the one of HDA seems to withstand the electrostritive forces of the ions. In a certain composition window (around 3.5 mol%), the polyamorphic transition occurs at a temperature where both polyamorphs are observed as liquids (LiCl-HDL and LiCl-LDL), indicating a liquid-liquid transition.

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Poster

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Phase Equilibria and Growth Rates of Gas Hydrates by using Computer Simulations

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Gas hydrates are crystalline structures containing trapped gas molecules, primarily carbon dioxide (CO_2) and methane (CH_4) [1]. Found beneath the ocean floor and in permafrost, they represent a significant reservoir of greenhouse gases [2]. Balancing the challenges and opportunities associated with CO_2 and CH_4 hydrates is crucial for addressing climate change and exploring sustainable energy resources. In this work we begin studying the kinetics of CO_2 and CH_4 by using molecular dynamics simulations, obtaining an excellent agreement with the available experimental results [3]. Subsequently, we explore the three-phase equilibrium for a methane hydrate system in NaCl solutions [4], replicating the conditions found in seawater, and then proceed to investigate more concentrated solutions (see Fig. 1). Our findings demonstrate a strong concordance with experimental phase equilibria. Thus, this computational study offers a comprehensive understanding of gas hydrate kinetics and phase equilibria, providing an accurate portrayal of both aspects.

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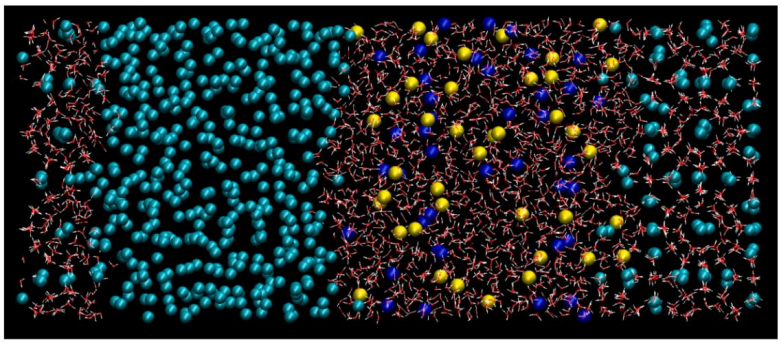

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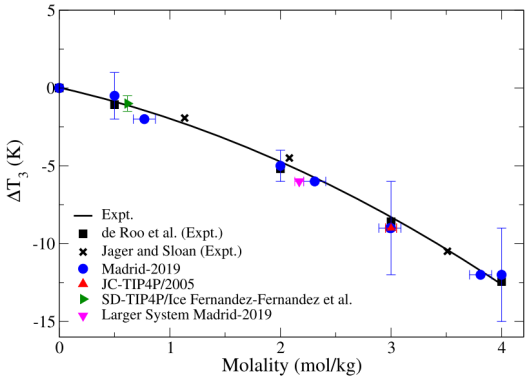

Figure 1. Three-Phase Equilibria of methane hydrate in salt solutions. (a) Initial configuration of the three-phase system formed by a slab of methane hydrate in equilibrium with a NaCl solution and a methane gas phase. (b) Three-phase coexistence line and coexistence point depression for the studied system.

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The role of motility gradients in proliferating active matter

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Certain bacteria have developed helical flagella to move through liquids or across semi-solid surfaces, such as gels, porous media, and tissues. Various motility strategies (swarming) can increase antibiotic resistance [1]. The objective of this study is to identify the reasons for this increase and to comprehend the physical, chemical, and genetic mechanisms that underlie it.

To tackle this issue, we conduct experiments that measure the evolution of bacteria (specifically, *Pseudomonas aeruginosa*) by exposing colonies to antibiotic gradients. Bacteria exhibit complex interactions with both antibiotic discs and sibling colonies, they grow avoiding each other just like they avoid antibiotics, forming distinct demarcation lines (DLs) [2,3,4,5]. Our first goal is to fully understand how bacteria grow without antibiotics and to decipher the phenomenon of DLs. Possible mechanisms that may contribute to this behaviour include food depletion [2], production of inhibitory molecules [3], or deformation of gels [4]. Preliminary experiments suggest that the gel structure may not play a dominant role.

Computational models based on coupled reaction-diffusion equations (Fisher-Kolmogorov equations) can be derived from standard active matter theory (stochastic processes) and population dynamics to simulate our systems. As our bacteria are exposed to an antibiotic gradient, these models must be generalized to space-dependent diffusivity [6]. These models are used to simulate our systems in various situations, such as colonies without antibiotics or a single colony with different antibiotics. By comparing experiments and simulations, we aim to understand how bacteria compete and/or cooperate when growing in the presence of antibiotic gradients and how motility is linked to increased resistance.

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On the solubility and thermal stability of PAmOx in water

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Polyoxazolines (PO) are a class of polymers that are playing an increasingly important role in the development of nanodevices based on smart materials. [1] These systems are easily tunable by ad hoc functionalisation of the chemical groups attached to the amide backbone.
PAmOx is a PO functionalised with a primary amminic group (butanamine moiety), which gives the polymer a hydrophilic and/or cationic character, depending on the operating pH.
Nanoscale lead scavengers have been developed consisting of a paramagnetic core coated with a diblock copolymer made of PAmOx and poly(2-isopropyl-2-)oxazoline (PiPOx), which is also a member of the PO family. The copolymer was attached to the paramagnetic nanoparticle through the PAmOx, while PiPOx remained externalized in the outer shell. When introduced into a water solution contaminated with heavy metal ions, the contaminants penetrate the NPs and the interaction with the polymer branches of PAmOx allows adsorption. Role of PiPOx was controlling the release of the cargo. In fact, PiPOx is a thermoresponsive polymer characterised by a lower critical solution temperature in water, which means that an increase in temperature above a certain threshold renders the polymer insoluble. Therefore, the solubility change with temperature is thus induced to trap the ions within the nanoparticles, and finally the loaded NPs are simply removed from the system using a magnet. [2]

We have recently investigated the thermal behaviour of PiPOx in water [3] and are continuing the study by investigating the solubility and thermal stability of PAmOx. This work originates from a combined experimental/computational approach: from one side, the synthesis of PAmOx was refined ad hoc for the present contribution, and from the other one, molecular dynamics simulations of the polymer in water were carried on. Our study revealed that, while the polymer at almost infinite dilution is water soluble and engages in favorable interactions with water, at finite concentrations relevant aggregation occurs.

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Graph theory based order parameter to gain insights into the structure and dynamics of supercooled water

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Our work focuses on a graph theory based approach applied to the delicate framework of the Liquid-Liquid Phase Transition (LLPT) in supercooled liquid water, simulated via molecular dynamics (MD).

In the LLPT scenario, liquid water exists in two states, the high density liquid (HDL) and the low density liquid (LDL).

Despite the structural, dynamic and thermodynamic differences between the HDL and LDL state, distinguishing them even with computational methods is challenging and, therefore, several order parameters have been introduced to differentiate the two phases.

We recently proposed the Node Total Communicability (NTC) as an order parameter [1], testing its ability to distinguish between HDL/HDL-like molecules and LDL/LDL-like molecules at high pressure[1] where the coexistence line is crossed, and at ambient pressure[2], where the Widom line is crossed.

This descriptor, borrowed from graph theory, yields information about the local connectivity of each water molecule within our simulation box and highlights the influence of the medium-to-long range effects , allowing us to characterize the structural and dynamical behaviour of the system at the microscopic level.

We found in fact that HDL-like forms are not homogeneous but rather characterized by the presence of high connectivity patches composed of molecules with an increased local density and mobility. Small highly connected patches are also found in mainly LDL compositions, and we hypothesize that they could function as initial sites from which the HDL phase starts forming and growing during a phase transition.

Expanding on this hypothesis, we are currently using the NTC to study and characterize the transition of an LDL system to an HDL-like composition (Fig.1) with a spinodal-like decomposition mechanism.

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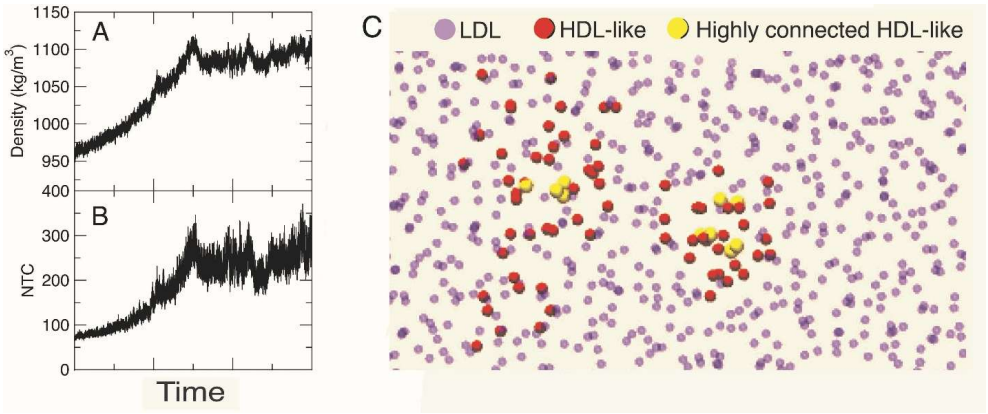

Fig.1: Time evolution of the density during an LDL-to HDL-like transition (A) compared with the time evolution of the NTC (B). Visualization of highly-connected patches and HDL-like patches in an LDL environment (C).

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Beyond the ice: Calorimetric insights into the challenges of biopharmaceutical freezing and thawing processes

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The pharmaceutical industry relies heavily on predictable freezing and thawing (FT) processes for storing and transporting their products. This has become evident during the COVID19 pandemic [1] and will be even more important in the future given the increasingly complex nature of biopharmaceuticals in current development stages [2]. For instance, protein formulations are prone to aggregation during the freezing process where possible reasons include cold-denaturation [3], pH shifts due to freeze concentration [4] or the formation of ice–liquid interfaces [5]. Aggregation may occur as soon as the first ice crystals appear until the freeze concentrated solution immobilizes at the glass transition T_g [6]. However, this range has not been determined for many common buffer and cryoprotectant combinations so far.

We here present an extensive differential scanning calorimetry study on the supercooled region of 13 cryoprotectants in three different buffer systems. The temperature where ice crystals first appear upon cooling ranges from 0°C to -6.4 °C for different buffer and cryoprotectant combinations. All cryoprotectant solutions produce freeze concentrated solutions (FCSs) after complete ice crystallization, regardless of buffer. Upon thawing, most systems experience two glass-to-liquid transitions, which we assign to the devitrification of two FCSs of different concentration, where one corresponds to the maximally-freeze concentrated solution (MFCS). Notably, the T_gs of MFCS are highly sensitive to the choice of cryoprotectant, ranging from -10.3 °C to -74.0 °C. The glass transitions are usually followed by continuous ice melting. However, in some cases we find deviations from this behavior, as in, e.g., D-Mannitol solutions where we observe unwanted cold-crystallization of the cryoprotectant itself.
Ultimately, these findings may improve the current trial-and-error approach of finding a systematic optimization of freezing procedure tailored for individual product formulations while in turn minimizing risks of product degradation during FT cycles.

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NaCl Salty Ice VII: The Search for Planetary Relevant Salty Ice

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A number of years ago, salty ices were discovered [1-3]. These novel structures featured substantial quantities of LiCl and LiBr salts incorporated into the crystalline structure of ice VII under high pressure [4]. The presence of these salt ions within the ice VII lattice led to various changes in its properties. Notably, there was an expansion of the unit cell by 18–20% within the lattice [1], disorder in the orientation of water molecules [2], remarkably high ionic conductivity [1], and prevention of the transition to the ordered ice VIII phase [1,2] and the symmetric ice X phase [3,5] upon decreasing temperature or increasing pressure, respectively. To achieve ion inclusion, the eutectic solution (LiCl: 6.5 D_2O, LiBr: 7 D_2O) was rapidly cooled (>10^3 Ks^{-1}), resulting in the formation of a high-density amorphous structure lacking long-range order. Subsequently, re-crystallization occurred by thermally annealing this amorphous precursor at high temperatures. Under compression, the amorphous precursor adopted a higher coordination configuration around the salt ions, akin to the configuration observed in salty ice VII [6-8]. Consequently, upon raising the temperature, the ions retained their local configurations, but the amorphous structure underwent a transition into an ice VII structure, culminating in the formation of salty ice.

Here we explore the potential inclusion of salts, particularly NaCl, which holds significant importance for planetary modelling. Initial x-ray diffraction data and molecular dynamics (MD) simulations indicate that NaCl-ice VII may exist at pressures exceeding 6 GPa and temperatures above 273 K. The incorporation of NaCl brings about notable changes in lattice volume (5-7%) and thermal properties. Such changes could prove highly significant for modelling the deep interiors of icy moons like Enceladus or Ganymede, where subsurface salty oceans are known to exist [9,10], as well as for understanding the anomalous magnetic fields of "ice giants" Neptune and Uranus.

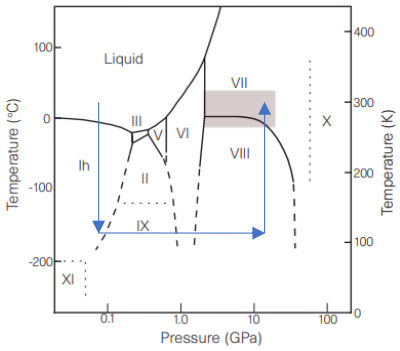

Fig. 1 – Shaded region T > 300K, P > 6GPa is where we are interested in, with the indicated thermodynamic path. Diagram taken from [4].

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On the possible locus of the liquid–liquid critical point in real water from studies of supercooled water using the TIP4P/Ice model

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One of the most accepted hypothesis to explain the anomalous behavior of water is the presence of a critical point between two liquids[1], the liquid–liquid critical point (LLCP), buried within the deep supercooled regime. Unfortunately, such hypothesis is hard to be experimentally confirmed due to fast freezing. Here, we show that the TIP4P/Ice[2] water potential shifted by 400 bar can reproduce with unprecedented accuracy the experimental isothermal compressibility of water and its liquid equation of state for a wide pressure and temperature range. We find, both by extrapolation of response function maxima and by a Maxwell construction, that the location of the model LLCP is consistent with previous calculations[3,4]. According to the pressure shift needed to recover the experimental behavior of supercooled water, we estimate the experimental LLCP to be located around 1250 bar and 195 K. We use the model to estimate the ice nucleation rate (J) in the vicinity of the hypothesized LLCP experimental location and obtain $J=10^{24}$ $m^{-3}s^{-1}$ [5]. Thereby, experiments where the ratio between the cooling rate and the sample volume is equal or larger than the estimated nucleation rate could probe liquid–liquid equilibrium before freezing. Such conditions are not accessible in common experiments with microdroplets cooled at a few kelvin per second[6], but they could be, for instance, using nanodroplets of around 50 nm radius observed in a millisecond timescale.

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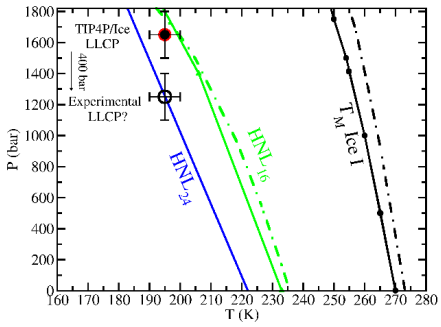
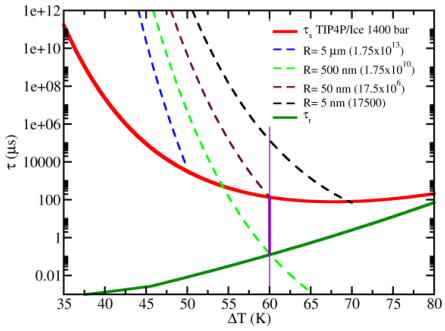


Pressure-temperature location of the experimental (dashed-dotted) versus the TIP4P/Ice (solid) ice Ih melting (black) and homogeneous nucleation (coloured) lines. HNL subscripts indicate the rate (per cubic meter per second) to which the line of interest is associated. Experimental melting and HNL_{16} lines are taken from Refs. [7] and [8] respectively. The simulation HNL_{16} is taken from Refs. [9,10] (except from the 1400 bar point that has been interpolated in this work from those results). The HNL_{24} line (blue, this work) crosses our guess for the experimental LLCP (empty circle) obtained after shifting 400 bar downward the TIP4P/Ice LLCP (solid circle).



Time required for nucleating ice (τ_J) within droplets of different radii as specified in the legend (dashed curves) as a function of supercooling for 1400 bar. The estimated number of water molecules for each droplet size is included in the legend. The crystallization time, τ_x (or the time required for 70 per cent of the volume to crystallize) for 1400 bar as a function of supercooling is depicted by a continuous red curve. The relaxation time (τ_r) is represented by a continuous green curve. Finally, the supercooling at which the LLCP could be found, is depicted by a vertical purple line, which thickest part indicates the time window available to measure 50 nm water drops in the liquid state.

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Glass - and freezing transition of supercooled water confined in mesoporous materials and biological systems

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The behaviour of water confined e.g. in artificial meso- or nanoporous silica materials is intensively discussed in literature. We present the results of Dynamic Mechanical Analysis measurements of water confined in biological systems (foods like e.g. bread, apple, turkey bone, etc.) as a function of temperature and frequency and compare them with results of water confined in artificial mesopores. Two types of cooling/heating protocols were used: slow (2 K/min) cooling/heating runs and quenching the samples from room temperature to 100 K prior to slow heating up to room temperature. We found striking similarities between the behaviour of water confined in mesoporous silica and biological systems, both, in the vicinity of the glass transition as well as in the freezing/melting transition region [1-5]. The obtained results are discussed, using artificial meso- or nanoporous materials as a model system for advancing our understanding of the freezing and glass transition of water confined in foods and other biological systems.

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Experimental observation of a dynamic transition in bulk supercooled water

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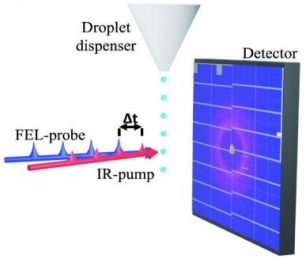
One of the longest standing mysteries of water is the rapid deceleration of dynamic quantities, such as viscosity and diffusivity, upon cooling. [1,2] These quantities are intricately coupled to water's relaxation dynamics, which, when extrapolated, seem to diverge at a temperature around 227 K.[3] In order to retain entropy until the glass transition below 140 K, it has been conjectured, that there is a dynamic transition temperature, below which relaxation dynamics decelerate more gradually with decreasing temperature.[1] The temperature and nature of this transition have however remained elusive to experiment, due to rapid crystallization below the homogeneous nucleation temperature. We have utilized a novel methodology, making it possible to directly probe structural relaxation times in the supercooled regime.[4] 15 μm sized droplets are cooled down to 228 K by evaporative cooling. Temperature jumps on the order of 1 K are induced by an IR-laser. The heating-induced structural relaxation is then probed by wide-angle x-ray scattering of FEL-pulses from SwissFEL. We clearly observe that the dynamics deviate from a power-law decrease below 240 K, indicating a dynamic transition. We show that the results are best explained by gradual interconversion of two structural motifs, rather than by a switch in relaxation mechanism.



Illustrative scheme of the experiment

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WaterX@2024 International Workshop May 25 – 30, 2024

The role of water on the solution behavior of responsive polymers

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Water plays a fundamental role in determining the structure and functionality of macromolecules, such as responsive polymers. In this presentation, I will provide two examples to elucidate the critical nature of the delicate balance between polymer–water and water–water interactions in determining the solution behavior.

First, I will focus on the widely investigated polymer poly(N-isopropylacrylamide) (PNIPAM) to understand the effect of the adopted computational water model on the *in silico* P–T phase diagram. I will discuss a comparative atomistic molecular dynamics simulations study of PNIPAM aqueous solution using two advanced water models: TIP4P/2005 and TIP4P/Ice. I will show that, while both water models can reproduce the temperature-induced coil-to-globule transition at atmospheric pressure and the polymer hydration enhancement that occurs with increasing pressure, the PNIPAM–TIP4P/Ice solution better reproduces the experimental findings [1].

Then, I will further compare the results of the PNIPAM–TIP4P/Ice solution, with those obtained for another thermoresponsive polymer, i.e. poly(N-isopropymethacrylamide) (PNIPMAM) in TIP4P/Ice water. PNIPMAM chemical structure differs from that of PNIPAM solely due to the presence of an additional methyl group, resulting in a higher coil-to-globule transition temperature of approximately 13 K. I will discuss the conformation and hydration properties of the two responsive polymers, highlighting the keys features responsible of the observed increase of the coil-to-globule transition temperature.

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A Numerical Study of the ML-BOP Model

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I will present recent numerical results about the ML-BOP model, a recently proposed machine learning coarse grained models for water [1].
The analysis will focus on the statistical properties of the potential energy landscape in supercooled states, both in the energy and in the enthalpy representation. Deviation from the gaussian distribution of minima in the high density liquid side of the liquid-liquid transition will be reported and discussed.

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