

Final report on the workshop:

Modeling and simulation of water at interfaces from ambient to supercooled conditions.

Organizers:

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Summary

The workshop has been devoted to a number of presentations and discussions about the problem of the properties of water when confined and/or at interfaces studied by computer simulation. The workshop has been the occasion for a comparison of different approaches and methodologies. It has been particularly stimulating the possibility of exchanging ideas between people more interested in the statistical mechanics aspects of the phenomenology of water at interfaces, with emphasis on phase transition, conditions for instabilities etc. and people with more interest in reproducing realistic behaviour of water combined with ions, protein surfaces, metallic interfaces. The scientific content was at very high level but at the same time all the talks were suitable for a large audience in particular for young students and post-doc. The programme of the meeting was very intense but the sessions always attracted the vivid attention of the audience with numerous questions and comments at the end of each presentation.

Description of the scientific content

The first session was devoted mainly to general features concerning water and water confined or at interfaces. H. E. Stanley discussed recent progress in understanding the anomalies of water by combining information provided by recent experiments and simulations on water in bulk, nanoconfined, and biological environments. He presented evidences from recent experiments designed to test the hypothesis that liquid water may display "polymorphism" and discussed recent work on water's transport anomalies as well as the unusual behavior of water in biological environments. He added also considerations about the general concept of liquid polymorphism useful in understanding anomalies in other liquids, such as silicon, silica, and carbon, as well as metallic glasses. Stanley in particular focused on the relation between thermodynamical properties and dynamical behaviour of water. An important point in this respect is the phenomenon of the fragile to strong crossover in supercooled water and the presence of maxima in the thermodynamical response functions, that define the so called Widom line.

D. Chandler introduced in the workshop the problem of water in contact with hydrophobic surfaces. He considered the theoretical prediction that liquid water adjacent to sufficiently extended hydrophobic surfaces forms interfaces that are soft and can facilitate with their fluctuations the assembly of hydrated hydrophobic surfaces. He presented recent work done in his group where they explored the validity of this perspective in different contexts through simulations of an assortment of models, some idealized and simple, others detailed and complex.

The problem of how computer simulation can reproduce the properties of water is related of course to the use of appropriate model potentials. R. M. Lynden-Bell talked about an interesting approach to study theoretically the properties of water. She considered modified water models where factors like hydrogen bond, local tetrahedral order are altered in a controlled way. She presented and discussed the changes in liquid properties, anomalies and solvation which result from various modifications.

J. S. Abascal reported a number of calculations by computer simulation of the phase diagram with different potential models. He pointed out that the value of quadrupole moment that comes out from the water model is crucial in determining the melting temperature of hexagonal ice. He presented the results obtained with the new TIP4P/2005 potential. This potential shows good performances for a wide variety of properties and thermodynamic conditions covering a temperature range from 123~K to 573~K and pressures up to 40000~bar. In connection with the previous talk by Stanley, Abascal reported that the simulations with the new model show clearly the existence of peaks in the thermodynamic response functions (thermal expansion coefficient and isothermal compressibility). R. Vallauri discussed the results obtained with a realistic polarizable potential model of water in the supercooled region, close to the liquid-liquid coexistence lines already shown to exist for the considered model. Static and dynamical quantities were investigated in order to characterize the properties of the three low temperature amorphous phases of water.

The thermodynamical and structural properties of water at contact with hydrophobic or hydrophilic solutes has been the subject of a number of talks. The interest ranged from more general studies about the statistical mechanical properties to the more specific applications of interest for chemical and biological processes. D. Corradini investigated the supercooled region of ionic aqueous solutions in order to study the effect of the ions on the liquid-liquid critical point. In some cases where very long computations will be required to look at very general features of phase transitions the potential model for water was reduced to very simplified forms, already introduced by Stanley in his talk. S. Buldyrev examined the behavior of an hard sphere polymer in molecular dynamics simulation in a solvent represented with the Jagla model for water, a spherically symmetric ramp

potential with two characteristic lengths: an impenetrable hard core and a penetrable soft core. He found that Jagla model exhibits water-like solvation properties. The polymer dissolved in the Jagla liquid exhibits swelling upon both cooling and heating. This behavior resembles protein denaturation. G. Franzese reported calculations on lattice models adapted to describe general properties of water at contact with protein surfaces. The results of Monte Carlo and mean field calculations compared with dielectric relaxation experiments on water layers at contact with lysozyme show the presence of two specific heat maxima, corresponding to two dynamics crossover at $T=252$ K and at $T=181$ K. They are attributed to fluctuations in hydrogen bond formation for the higher temperature and at a cooperative rearrangement of the network at lower temperature.

Water confined in solid surfaces was the problem addressed by P. Debenedetti. He pointed out that confining geometries that contain thin water films are ubiquitous in biology, geology, materials science. So understanding the changes in water structure, dynamics and thermodynamics due to interactions with confining surfaces is therefore of interest in a wide variety of scientific problems and technical applications. In his talk Debenedetti reviewed recent computational work of his research group on the structure, dynamics and thermodynamics of water in nano-scale confinement, considering hydrophobic, hydrophilic, patchy, regular, and biological surfaces. P. Gallo presented the results of a computer simulation of water confined in a cylindrical pore of MCM-41 silica material, a system studied in neutron scattering experiments. She calculated by Molecular Dynamics the relaxation time of confined water. The relaxation time of the mobile portion of the confined water was extracted with a layer analysis and its behaviour shows the presence of a fragile to strong dynamic transition at around $T=215$ K with some agreement with experiments. This crossover is confirmed by maxima in the dynamic susceptibility and the specific heat computed in the same simulation. This result is connected to the theory of the liquid-liquid transition exposed by Stanley in his talk. This study evidenced also that experiments on confined water are extremely relevant for the comprehension of low temperature bulk properties.

A more detailed analysis of the structure of water at interface it is needed for studies of interest in biological and chemical applications. From this point of view the talk of P. Jedlovsky introduced a very useful method to determine the intrinsic interface and identifying the molecules located right at the boundary of two phases in a computer simulation. The new method was applied for the analysis of the molecular level structure of the liquid-vapor interface of water, aqueous solutions, liquid liquid interfaces. With the use of the new method it is possible to show that the orientational preferences of the interfacial water molecules depend only on the local curvature of the interface. The vast majority of the truly interfacial water molecules are found to form a strongly percolating two dimensional hydrogen bonded network at the surface, whereas no percolation is observed within any of the following molecular layers.

Very relevant phenomena are expected from the study of water at interfaces with proteins.

A very appropriate introduction to this problem was done by P. Jungwirth in his talk. He started from the consideration that molecular simulations and surface selective spectroscopic techniques show that large polarizable anions and hydronium cations can be found (and even enhanced) at the surface and are involved in chemistry at the air/water interface. He presented recent studies of ions at the water/vapor interface and compared from this perspective more complex aqueous interfaces, such as those of hydrated proteins. Jungwirth found that his results are well explained by considering a local picture of pairing of ions from the solution with charged and polar groups at the protein surface combined with a model for segregation of large soft ions at hydrophobic patches of the protein surface. The role of water in stabilizing proteins was discussed by S. Melchionna.

Metallic interfaces play an important role in many applications and this was the subject of a number of talks and discussions. In particular A. Willard reported molecular dynamics studies of water at

platinum interfaces. Structure and dynamics of water close to 100 and 111 platinum electrodes were considered. A significant dependence on electrode geometry was found. On the same line P. Madden described results from simulations designed to examine the process of electrochemical charge transfer close to a metallic electrode. In the simulations the electrode is treated as an ideally polarizable hydrophilic metal, supporting “image charge” interactions with charged species, and it is maintained at a constant electrical potential with respect to the solution, so that the model is an accurate representation of an electrochemical interface through which no current is passing. He discussed how the simulations can be used to examine the kinetics of electron transfer of redox species close to the surface and the role of absorbed water. The talk of E. Spohr was also related to topic of water in contact with charged surfaces. Spohr discussed the study of the process of the transfer of a proton from aqueous solution to a (charged) metal electrode surface. He reported the results obtained with the use of an empirical valence-bond (EVB) model developed ad hoc. Large scale molecular dynamics simulations for metal/electrolyte solutions including Grotthuss style proton transport were made possible with the EVB model. He presented a systematic study of the the rate of proton discharge on negatively charged surfaces in an extended range of surface charge densities.

Solid nanopores with complex structures as clay and zeolites have also been considered. The confinement of water in such materials is of great relevance in technological applications.

K. Smirnov presented examples of the spatial organization of molecules and of the short and long time dynamical behaviour of water confined in the pores of crystalline aluminosilicates, such as zeolites and clays, and in nanostructured materials, such as imogolite (nanotubes) and allophane (nanospheres). Water in zeolites was also the subject of the contribution of S. Suffritti, who discussed the results of molecular dynamics simulations of water confined in a large variety of zeolites at different temperatures and loadings in connection with experimental data. Rotenberg reported results on the structure and dynamics of water at a clay surface. He analyzed in particular the influence on the H-bond network of the surface oxygens and ions and investigated the surface H-bond formation and dissociation dynamics.

R. Pellenq in his talk considered water confined to pores with different size scale, both cases of disordered and ordered pore were presented with hydrophilic/hydrophobic interaction. Materials taken into account were silicalite and tobermorite, a layered calcio-silicate model of cement at the nanoscale. R. Pellenq from his work took the message that classical simulations of polar molecules such as water in ultra confining environments have to rely on polarizable water potentials in order to capture essential physical features. He discussed also a number of results obtained with Grand Canonical Monte Carlo about adsorption of water in silica slit pores. Results on water confined in Vycor glass show that capillary condensation/evaporation phenomena in this material can be well understood on the basis of a single-pore model.

Water confined on graphene surfaces and carbon nanotubes is a subject particularly relevant for applications. M. C. Gordillo presented results obtained with classical molecular dynamics on structural and dynamical properties considering different geometries of the substrates.

G. Galli in her talk presented a review of the state of the art about the study of confined water by means of *ab initio* molecular dynamics with particular attention to the study of water confined in graphene and carbon nanotubes.

Talks more specific on the properties of water in chemical processes have been presented by Yousung Jung, who discussed theoretical models to explain rate increase observed in a reaction on water, and M. Sulpizi, who reported on recent calculations of the dissociation constant of liquid water with the use of density functional methods and a proton insertion/removal method.

Assessment of the results and impact of the event on the future direction of the field

It was evident during the sessions and in the final discussion of the workshop that the communication between the different communities of researchers active in the computer simulation of water, confined water, water at interfaces is essential for a rapid and fruitful progress in the field. It is well known that water cannot be studied experimentally upon supercooling below the temperature of homogeneous nucleation, but with confinement in porous materials crystallization can be avoided and water properties can be measured well below melting temperature in the approach to the glass transition. From a more fundamental side, computer simulations of confined and/or interfacial water are of relevant interest for testing how different its behaviour is with respect to bulk water. For this type of “statistical mechanics” studies simplified potentials are used, sometimes model system are simulated on lattice in the attempt to catch general properties close to phase transitions. One of the main take home message from the workshop is that the connection between thermodynamics and dynamical behaviour in supercooled water is the key point for the understanding of the anomalies of water. In this respect it is very relevant to clarify the phenomenology of the fragile to strong crossover in water and how it can be modified when water is confined or at contact with different substrates. The studies of the dynamical behaviour must be complemented with analysis of the thermodynamical response functions both in experiments and in simulations. Simulation methods could play an essential role in order to reach a better understanding of the phenomena at molecular level and to connect intermolecular forces to the macroscopic behaviour.

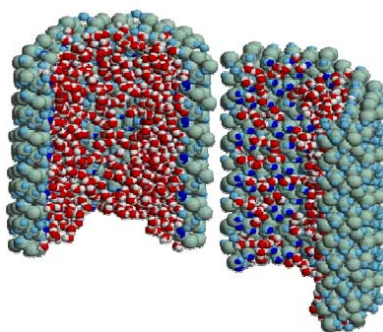
From the point of view of applications the study of hydrophobic effects are essential for understanding a number of phenomena taking place in chemical processes.

In almost all the cases the key point is to understand the different behaviour of water at polar and non-polar interfaces. For instance the complex problem of water-protein interfaces can be studied in first approximation by considering the protein surface as composed of polar and non polar patches. General features of problems connected with hydration in small and large cavities and with the behaviour of water close to hydrophobic solutes are qualitatively understood, however still a large effort is required to make the theoretical approaches predictives. To reproduce real systems it is still unclear whether it is enough to improve empirical models for the water site and water-substrate interactions or it is necessary to include polarizability or eventually perform ab initio calculations. There was a large progress recently in experimental techniques and molecular simulations in this field.

It was evident however that the exchange of information and the comparison between the different methodologies is essential for keeping in mind the general questions involved in the study of water and at the same time for making connection with the applications in biology, chemistry, nanotechnology.

CECAM Workshop

Modeling and Simulation of Water at Interfaces from Ambient to Supercooled Conditions.



Dates :

Jun 29, 2009 - Jul 01, 2009

Location :

CECAM-HQ-EPFL, Lausanne, Switzerland

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1 Details

1.1 Description

This workshop aims to enhance communication among the different communities involved in the study of water when it is confined, in contact with different solutes and/or with biological molecules. In this respect the computer simulation methodology seems at the moment the more appropriate to open the possibility of a more general understanding of the connection between the behaviour of water, and in particular confined water, and the properties of substrates, solutes and biological systems. In computer simulation, in fact, it is possible to take under control different microscopic parameters and study more in details the behaviour of systems at the interfaces. In the same time there is the possibility of looking at both static and dynamical properties upon changing the hydration level and/or the temperature.

The understanding of the behaviour of water in contact with different substrates and/or in solutions is of crucial importance for a wide range of applications and studies of fundamental problems in physics, chemistry, biochemistry. There are a number of relevant topics, that can be mentioned. For instance the mobility of water and hydrated ions in channels or micropores is important in biological systems and in many systems of interest to chemistry and chemical engineering. It is well known that the presence of water plays a fundamental role in the function of the biological macromolecules [1]. The comprehension of the mechanism of solubility would be of great relevance in the studies of many phenomena like mineral dissolution, biomolecular aggregation [2]. How ions affect hydration and hydrophobic interactions is strictly related to the problem of the Hofmeister series. It has also been observed that water in the vicinity of substrates has a low temperature behaviour that differs from that of bulk water. In certain geometrical confinements the water molecules are unable to form a crystalline structure so water remains liquid below 273K. Studies on water confined in different substrates have shown a very rich scenario where the approach to the glass transition and the observation of different polymorphs are easier [3, 4]. Experiments on protein dynamics have evidenced the presence of a dynamical transition as a hydrated protein is heated from low temperature above about 220 K. This temperature is approximately close to the one at which the crossover from Arrhenius to non-Arrhenius would take place in the hydration water, according to recent experimental work on water at contact with lysozyme, DNA and RNA [5].

In the studies of water as a solvent or confined in environments the large variety of phenomena involved, the great range of temperatures to cover, the differences in the type of substrates make difficult to have a clear understanding of the physical mechanisms and parameters which control the behaviour of water in the different cases. Anyway there are key issues that need to be addressed. How the hydrogen bond network is affected by confinement or solutes? When the hydrophobic units are small enough it is expected that water maintains its hydrogen-bond structure in spite of the perturbation of the solute. Instead it has been argued that large hydrophobic species could induce dewetting phenomena at the origin of the attraction between hydrophobic macromolecules [6].

For what concerns ions in water the traditional idea of explaining the Hofmeister series with the presence of structure making and structure breaking type of ions has become to be challenged by experiments and computer simulations. Not different are the questions when water is confined in hydrophobic or hydrophilic media: does water behave in the same way or does the water-confining medium interaction change its behaviour [7,8]?

It is well known that water is characterized by its anomalies [9]: do the anomalies of water change for the presence of substrates? How relevant are those anomalies for the behaviour of the different substrates? Confined water can be experimentally studied also in the supercooled state upon approaching the glass transition temperature and in particular in this framework a crossover from fragile to strong behaviour has been found, as mentioned above, possibly related to the existence of a second critical point [4]. In bulk water this crossover has been related to the anomalies [10].

The first aim of the workshop is to exchange ideas between theorists working with computer simulations on the properties of water in various environments with different methodologies. The common motivation would be the understanding of the mutual influence on the static and dynamical properties of water and

substrates. During the workshop it would be important to identify the main open problems, the possible unifying concepts and to discuss the more appropriate methods to be used in the different cases. An example is the possible interplay between ab initio and classical computer simulation. The final aim is to establish the state of the art and to identify the possible future lines of research in this field to answer questions like the ones proposed above.

2 Key references

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3 Program

Day 1 - June, 29th 2009

Chairman Mauro Rovere

- 09:00 to 09:15 - Welcome
- 09:15 to 10:00 - **H. Eugene Stanley**
LIQUID WATER, THE "MOST COMPLEX" LIQUID: New Results in Bulk, Nanoconfined, and Biological Environments
- 10:00 to 10:45 - **David Chandler**
Liquid water structure and dynamics at hydrophobic surfaces
- 10:45 to 11:15 - Coffee Break
- 11:15 to 12:00 - **Ruth M. Lynden-Bell**
Why is water the way it is? Simulation studies of liquid 'non-waters'.
- 12:00 to 12:30 - **Richard Henchman**
Solution Entropy of Aqueous Noble Gases
- 12:30 to 14:30 - Lunch Break

Chairman Wanda Andreoni

- 14:30 to 15:15 - **Jose LF Abascal**
What phase diagram teaches us about water interactions
- 15:15 to 16:00 - **Renzo Vallauri**
Structural, thermodynamic and dynamical properties of supercooled water close to the liquid-liquid coexistence lines
- 16:00 to 16:30 - **Dario Corradini**
Thermodynamics and liquid-liquid critical point in the supercooled sodium chloride aqueous solution
- 16:30 to 17:00 - Coffee Break
- 17:00 to 17:45 - **Pal Jedlovszky**
A new method for determining the interfacial molecules in computer simulations. Application to liquid-vapor and liquid-liquid interfaces
- 17:45 to 18:30 - **Sergey Buldyrev**
Collapse transition of hydrophobic polymers in a simplified water model.

Day 2 - June, 30th 2009

Chairman Paul Madden

- 09:00 to 09:45 - **Pablo G. Debenedetti**
Structure, dynamics and thermodynamics of water in nano-scale confinement
- 09:45 to 10:30 - **Paola Gallo**

Molecular dynamics studies of the fragile to strong transition in confined water: how similar is it to that of the bulk ?

- 10:30 to 11:00 - Coffee Break
- 11:00 to 11:45 - **Pavel Jungwirth**
Ions at Aqueous Interfaces: From Water Surface to Hydrated Proteins
- 11:45 to 12:30 - **Giancarlo Franzese**
Thermodynamics and dynamics of hydration supercooled water.
- 12:30 to 14:30 - Lunch Break

Chairman Giulia Galli

- 14:30 to 15:00 - **Adam Willard**
Dynamics and structure of liquid water at metal interfaces
- 15:00 to 15:45 - **Paul A. Madden**
Water and ions at an electrochemical interface.
- 15:45 to 16:15 - **Konstantin Smirnov**
Water behaviour in nanoporous aluminosilicates
- 16:15 to 16:45 - Coffee Break
- 16:45 to 17:15 - **Giuseppe B. Suffritti**
The behaviour of water confined in zeolites: molecular dynamics simulations vs. experiment
- 17:15 to 18:00 - **Roland Pellenq**
Water in Nanopores
- 18:00 to 18:30 - **Marialore Sulpizi**
Density functional molecular dynamics calculation of the dissociation constant of liquid water

20.00 Workshop Social Dinner

Day 3 - July, 1st 2009

Chairman Pavel Jungwirth

- 09:00 to 09:45 - **Giulia Galli**
Understanding water at interfaces: recent progress using ab-initio molecular dynamics
- 09:45 to 10:30 - **Eckhard Spohr**
Molecular Dynamics Modeling of Proton Discharge at the Aqueous/Metallic Interface
- 10:30 to 11:00 - Coffee Break
- 11:00 to 11:30 - **Benjamin Rotenberg**
Structure and dynamics of water at a clay surface from molecular dynamics simulation
- 11:30 to 12:15 - **M.C. Gordillo**
Water on graphene surfaces
- 12:15 to 14:30 - Lunch Break

Chairman Paola Gallo

- 15:00 to 15:30 - **Simone Melchionna**
Role of water in the thermal stabilization of biomolecules
- 15:30 to 16:00 - **Yousung Jung**
A striking catalysis of an organic reaction 'on water'
- 16:00 to 16:30 - Coffee Break

16:30 to 17:15 Final considerations on the results presented in the workshop and on future perspectives by David Chandler, Pablo G. Debenedetti and H. Eugene Stanley.

- 17:15 to 18:00 - Discussion
- 18:00 to 18:10 - Closing word

4 Participant List

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5 Abstract list

Role of water in the thermal stabilization of biomolecules

Simone Melchionna

CNR and University of Rome La Sapienza, Rome

Coauthor(s) : F. Sterpone, C. Bertonati, J. Russo, G. Briganti

Abstract

Understanding how water stabilizes proteins is rooted in the multi-faceted behavior of water in proximity of corrugated surfaces, an actively debated, yet elusive, topic. Among the several phenomena related to such chameleonic nature of water, two have attracted our attention.

A first phenomenon regards the formation of nano-bubbles, or nano-cavitation, arising in contact with highly corrugated hydrophobic substrates. A second aspect regards, the distinct behavior of water in proximity of proteins and the role of the hydration layer in stabilizing proteins at high temperature.

In this talk I will describe our recent studies on these topics.

We directly observed the formation of long-lived cavities for water confined in cylindrical pores, and compared our data with the predictions of the Lum-Chandler-Weeks theory.

For the case of thermostabilization, we have undertaken a systematic study of three analogous proteins of different degree of thermal resistance and observed striking correlations between the detailed exposure to the solvent, formation of clustered water layers, and the degree of thermophilicity.

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Water behaviour in nanoporous aluminosilicates

Konstantin Smirnov

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Coauthor(s) : Daniel BOUGEARD

Abstract

The contribution discusses results of molecular dynamics simulation studies of the structure and dynamics of water in the pores of crystalline aluminosilicates, such as zeolites and clays, and of

nanostructured materials, such as imogolite (nanotubes) and allophane (nanospheres). The presented examples concern the spatial organization of water molecules in the voids of the solids, their short- and long-time dynamics and exemplify the relation of the macroscopic behaviour of the systems to their characteristics at the atomic level.

Key References

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Structure, dynamics and thermodynamics of water in nano-scale confinement

Pablo G. Debenedetti

Princeton University, Princeton

Abstract

Confining geometries that contain thin water films are ubiquitous in biology, geology, materials science and engineering practice. Examples include ion channels, mineral inclusions, microfluidic technologies, and mesoscopic surfactant assemblies. Understanding the changes in water structure, dynamics and thermodynamics due to interactions with confining surfaces is therefore of interest in a wide variety of scientific problems and technical applications, such as corrosion inhibition, the design of self-cleaning surfaces, nutrient transport in plants, biological self-assembly, and the development of “lab on a chip” technologies. This talk will review recent computational work in my research group addressing the structure, dynamics and thermodynamics of water in nano-scale confinement by hydrophobic, hydrophilic, patchy, regular, and biological surfaces.

Key References

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Why is water the way it is? Simulation studies of liquid 'non-waters'.

Ruth M. Lynden-Bell

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Abstract

The unusual properties of liquid water have been attributed to factors including hydrogen bonds, the presence of a local tetrahedral network, or the high number density.

Most of the properties of water can be reproduced in simulations using simple potential models with site-site pairwise interactions. Although in real water the factors listed above cannot be separated, one may construct liquids from modified water models ('not-waters') in which these factors are altered independently in a controlled way. With various collaborators I have studied the changes in liquid properties, anomalies and solvation which result from various modifications.

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Structure and dynamics of water at a clay surface from molecular dynamics simulation

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Coauthor(s) : Virginie Marry, Pierre Turq

Abstract

We report a molecular dynamics study of the structure and dynamics of water at a clay surface. The negative charge of the surface and the presence of surface oxygen atoms perturbs water over two to three molecular layers, while the nature of the counterions (Na⁺ or Cs⁺) has only a small effect. In the first molecular layer, approximately half of the water molecules are H-bonded to the surface. We also analyze the H-bond network between surface water molecules. The diffusion of water molecules along the surface is slowed down compared to the bulk case. As far as the orientational order and dynamics of the water dipole are concerned, only the component normal to the clay surface is perturbed. We investigate the surface H-bond formation and dissociation dynamics and their coupling to the release of molecules from the first molecular layer. We introduce a simple kinetic model in the spirit of Luzar and Chandler [Nature, 1996, 379, 55] to allow for a comparison with bulk water dynamics. This model semi-quantitatively reproduces the molecular simulation results and suggests that H-bond formation is faster with the surface than in the bulk, while H-bond dissociation is slower.

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A striking catalysis of an organic reaction 'on water'

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Abstract

A molecular origin of the striking rate increase observed in a reaction on water is studied theoretically. A key aspect of the on-water rate phenomenon is the chemistry between water and reactants that occurs at an oil-water phase boundary. In particular, the structure of water at the oil-water interface of an oil emulsion, in which approximately one in every four interfacial water molecules has a free OH bond that protrudes into the organic phase, plays a key role in catalyzing reactions via the formation of hydrogen bonds. More than a five orders of magnitude enhancement in rate constant was found in a chosen reaction. This structural arrangement is in contrast to the structure of water molecules around a small hydrophobic solute in homogeneous solution, where the water molecules are tangentially oriented. The latter implies that a breaking of an existing hydrogen bond network in homogeneous solution is needed in order to permit a catalytic effect of hydrogen bonds. Thereby, the reaction in homogeneous aqueous reaction is slower than the surface reaction, as observed experimentally. The proposed mechanism of rate acceleration is discussed

in light of other on-water reactions that showed smaller accelerations in rates. To interpret the various results, a method is given for comparing the rate constants of different rate processes, homogeneous, neat and on-water, all of which have different units, by introducing models that reduce them to the same units.

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Y. Jung & R.A. Marcus, JACS 129, 5492 (2007)

Ions at Aqueous Interfaces: From Water Surface to Hydrated Proteins

Pavel Jungwirth

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Abstract

Surfaces of aqueous solutions are traditionally viewed as devoid of inorganic ions. Molecular simulations and surface selective spectroscopic techniques show, however, that large polarizable anions and hydronium cations can be found (and even enhanced) at the surface and are involved in chemistry at the air/water interface. Here, we present recent studies of ions at the water/vapor interface and compare from this perspective more complex aqueous interfaces, such as those of hydrated proteins. We critically examine the suitability of dielectric models for the description of the protein/water interface in analogy to the water/vapor interface. Little correlation is found between these two interfaces in terms of ion segregation. Therefore, a local picture of pairing of ions from the solution with charged and polar groups at the protein surface is advocated and combined with a model for segregation of large soft ions at hydrophobic patches of the protein surface.

Understanding water at interfaces: recent progress using ab-initio molecular dynamics

Giulia Galli

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Abstract

We will report on some progress in understanding the structure and bonding of water at interfaces, using ab-initio molecular dynamics. In particular we will focus on non polar surfaces such as graphene and carbon nanotubes.

What phase diagram teaches us about water interactions

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Abstract

The calculation by computer simulation of the phase diagram involving the solid phases of water has triggered a number of new simulation experiments with somewhat unexpected results.

New behavior not yet observed experimentally is predicted by the simulations: the existence of (metastable) re-entrant behavior in the melting curves of the low density ices.

We have also shown that the phase diagram is a severe test of the potential models. The investigation on the conditions required by a model to give satisfactory predictions of the phase diagram indicates that the magnitude of quadrupole moment of the water model is crucial in determining the melting temperature of hexagonal ice. Moreover, the quality of the predicted phase diagram is strongly dependent on the ratio of dipolar to quadrupolar interactions.

The information provided by the phase diagram calculations together with other usual thermodynamic quantities has allowed the proposal of improved water models. In particular, TIP4P/2005 gives an impressive performance for a wide variety of properties and thermodynamic conditions covering a temperature range from 123~K to 573~K and pressures up to 40000~bar. The model has been recently used to investigate the thermodynamic anomalies of liquid water. It accounts quantitatively for the density maximum and the compressibility minimum and their dependence with pressure. The density results in the supercooled region also agree with the experimental data of water confined in thin pores. The simulations show clearly the existence of a peak in the thermodynamic response functions (thermal expansion coefficient and isothermal compressibility). We have then carried out extensive simulations with the model in order to evaluate the corresponding Widom line.

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PNAS 104, 18387 (2007)

Structural, thermodynamic and dynamical properties of supercooled water close to the liquid-liquid coexistence lines

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Abstract

We discuss results of a computer simulation which makes use of a realistic polarizable potential model of water [1], in the supercooled region, corresponding to the LDA, HDA and VHDA phases. These states are located close to the liquid-liquid coexistence lines already shown to exist for the considered model. Static and dynamical quantities are investigated for the analysis in order to characterize the properties of the three

phases.

Thermodynamic and structural results point out the increasing relevance of the interstitial neighbors, which clearly appear in going from the low to the very high density amorphous phases. The interstitial neighbors are found to be, at the same time, also distant neighbors along the hydrogen bonded network of the molecules. The role of these interstitial neighbors has been discussed in connection with the interpretation of recent neutron scattering measurements [2]. The structural properties of the systems are characterized by looking at the angular distribution of neighboring molecules, volume and face area distribution of the Voronoi polyhedra, and order parameters.

The cumulative analysis of all the corresponding results confirms the assumption that a close similarity between the structural arrangement of molecules in the three explored amorphous phases and that of the ice polymorphs Ih, III and VI exists.

Preliminary results concerning the dynamical quantities such as correlation function of the single molecule velocity, longitudinal and transverse currents are shown and compared with the corresponding data for water at standard conditions.

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Liquid water structure and dynamics at hydrophobic surfaces

David Chandler

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Abstract

According to theory, liquid water adjacent to sufficiently extended hydrophobic surfaces forms interfaces akin to that of liquid-vapor equilibrium. Such interfaces are soft, and their fluctuations can facilitate assembly of hydrated hydrophobic surfaces. Recent work in our group has explored the validity of this perspective in different contexts through simulations of an assortment of models, some idealized and simple, others detailed and complex. One useful tool for analysis is a generally applicable algorithm that identifies liquid interfaces.

Water on graphene surfaces

M.C. Gordillo

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Abstract

In this talk, I will make a brief summary of all the results obtained in our group concerning the behaviour of water close to graphene surfaces in different geometries, basically cylindrical (inside and outside carbon nanotubes) or flat (slit pores or a single graphene sheet). We used classical molecular dynamics simulations to obtain the structural and dynamical (including IR spectra) properties of liquid water in a different conditions, from ambient to supercritical.

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A molecular dynamics study of supercooled Newton black films

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Abstract

A Newton black film consists of a water film in nanometric confinement between two monolayers of adsorbed ionic surfactant that also provide counterions. Newton black films are amphiphilic membranes lying in air, therefore they are unsupported and contain water confined by floppy, fluctuating walls. For this reason they can serve as model systems for studying the water hydrating biological surfaces. They can also serve for testing electrostatics theories for colloids and studying the stability of phases of industrial relevance (e.g. foams and microemulsions). Using molecular dynamics simulations, we investigate the structure and dynamics of Newton black films when subjected to temperatures below the Widom line, understood as the locus of maximum correlation length emanating from the hypothesised liquid-liquid critical point of water.

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The behaviour of water confined in zeolites: molecular dynamics simulations vs. experiment

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Abstract

Zeolites are microporous crystalline aluminosilicates, whose channels and cavities of nanometric dimensions can host many different small molecules, including water. The large variety of the topology, shape and diameter of the micropores gives rise to different kinds of geometric arrangement of the water molecules, such as one-dimensional chains (in Li-ABW and Bikitaite), nano-helices (in Natrolite), worm-like clusters (in Silicalite), ice-like nanotubes (in ALPO4-5 and SSZ-24) and spherical nano-clusters (in Zeolite A).

The structure and the mobility of the adsorbed water depends not only on the features of the micropores, but also on its temperature and concentration (loading), and often may be very different from those of bulk water in similar conditions.

A special characteristics of zeolites is the possible presence of exchangeable cations (usually metallic), which are located on the internal surface of the micropores, which compensate for the charge deficit stemming from the substitution of Al to Si in the SiO₂ crystalline framework. When these cations are present, they are preferentially coordinated by adsorbed water and obviously influence its structure.

Water adsorbed in zeolites is interesting not only from the mineralogical and geophysical points of view, but also for its influence on the practical applications of natural and synthetic zeolites, such as cation exchange (e. g., in detergents and in polluted water remediation), molecular sieving and catalysis.

In order to study the behavior of water in zeolites we developed a sophisticated empirical potential for water, including the full flexibility of the molecule and the correct response to the electric field generated by the cations and by the charged atoms of the aluminosilicate framework. Indeed, one observes experimentally that both the structural parameters and the vibrational frequencies of adsorbed water depend significantly on the electric field to which it is subject.

The use of an empirical potential was needed because first principles molecular dynamics is not yet applicable to follow for nanoseconds the time evolution of hundreds of atoms, as it is needed for the study of water adsorbed in zeolites. However, in the few cases where the comparison is possible, we have shown that the reproduction of experimental data by our potential model is similar or even better than that obtained from the first principles methods.

The results of molecular dynamics simulations of water confined in a large variety of zeolites (see examples above) at different temperatures and loadings (some of them still unpublished) will be reviewed and discussed in connection with the experimental data, whose overall good reproduction encourages to attempt an atomic-scale description of structural and dynamical phenomena occurring in confined water.

Water and ions at an electrochemical interface.

Paul A. Madden

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Abstract

I will describe results from simulations designed to allow an examination of the process of electrochemical charge transfer close to a metallic electrode. The work described (and the presentation) follow on from that described by Willard. In the simulations the electrode behaves as an ideally polarizable hydrophilic metal, supporting “image charge” interactions with charged species, and it is maintained at a constant electrical potential with respect to the solution, so that the model is an accurate representation of an electrochemical interface through which no current is passing. Willard will describe detailed simulation studies of the properties of the water molecules close to a model platinum surface, with the water-platinum interaction described by a three-body potential. He will show how water is strongly attracted to and ordered at the electrode surface. This ordering is different to the structure that might be imagined from continuum models of electrode interfaces. Further, this ordering significantly affects the probability of ions reaching the surface. In my presentation I will build on several aspects of this work. I will show how the simulations can be used to examine, in the context of Marcus Theory, the kinetics of electron transfer of redox species close

to the surface and the role of absorbed water. I will also demonstrate how the electrode-ion interaction potential may be obtained on a first-principles basis. I will present results on the applied potential dependence of the interfacial capacitance obtained from a simulation with such a “realistic” representation of the interactions. The results are affected by a surface phase transition of the absorbed layers.

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Solution Entropy of Aqueous Noble Gases

Richard Henchman

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Abstract

The entropy of a system relates to the number of configurations in which the constituent molecules may arrange themselves. To gain insight into the entropy, it is useful to express the partition function in terms of the system's degrees of freedom. While there is no unique way to carry this out decomposition, here we make a mean-field single-molecule separation whereby each molecule occupies a number of minima of a given size in translational and rotational space. The size of each minimum is quantified by the force magnitude measured for that degree of freedom from the ensemble of equilibrium structures generated in a molecular dynamics simulation. The number of minima depends on the periodicity of the associated degree of freedom. All minima are integrated to give their associated partition functions. Their product equals the system's full partition function whose temperature-derivative leads to the entropy. This approach is applied to examine the entropy of dilute aqueous solutions of noble gases and an examination is made of how the entropy of solvation depends on nature of the solvation process.

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Thermodynamics and liquid-liquid critical point in the supercooled sodium chloride aqueous solution

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Abstract

In the past years several theoretical and experimental studies have led to a picture in which the anomalous

properties of water are due to the presence of a liquid-liquid phase transition in the supercooled region, terminating in a liquid-liquid critical point.

It is thus interesting to investigate the supercooled region of ionic aqueous solutions in order to study the effect of the ions on the liquid-liquid critical point phenomenon.

We report the results of molecular dynamics computer simulations on bulk TIP4P water and on the sodium chloride aqueous solution at three different concentrations ($c = 0.67$ mol/kg, $c = 1.36$ mol/kg and $c = 2.10$ mol/kg), studied upon supercooling. For all systems the temperatures of maximum density line and the limit of mechanical stability line are calculated from the analysis of the thermodynamic planes. We found that although the limit of mechanical stability remains unaltered with respect to bulk water, the temperatures of maximum density line is shifted to lower temperatures and pressures and modified in shape. Signatures of the presence of liquid-liquid coexistence are found for all systems.

In order to locate the position of the liquid-liquid critical point we performed extensive simulations on bulk water and on the $c = 0.67$ mol/kg solution in the low temperature region. The results are presented and discussed.

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Thermodynamic behavior and structural properties of an aqueous sodium chloride solutions upon supercooling
J. Chem. Phys. 128, 244508 (2008).

Dynamics and structure of liquid water at metal interfaces

Adam Willard

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Abstract

We have extended our molecular dynamics studies of water at platinum interfaces[1] to compare structures and dynamics of water molecules adjacent to both the 100 and the 111 surfaces of platinum electrodes. This adsorbed layer of water molecules reorganizes slowly and collectively, and departure of a water molecule from that layer is a rare event. Orientational distributions as well as the relaxation dynamics of the electrode-adsorbed water molecules depend significantly on electrode geometry. This dependence reflects competition between hydrogen bonding and non-hydrogen bonding interactions of electrode adsorbed water molecules, and whether electrode lattice geometry is commensurate with two-dimensional hydrogen bonding patterns of water.

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Molecular dynamics studies of the fragile to strong transition in confined water: how similar is it to that of the bulk ?

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Abstract

Molecular dynamics simulations of deeply supercooled SPC/E water confined in a cylindrical pore of MCM-41 silica material are presented [1] in order to locate the fragile to strong transition recently measured in experiments on water in MCM-41 [2] and in bulk simulations [3].

The alpha-relaxation time of the mobile portion of the confined water is extracted with a layer analysis of the tag-particle density correlators. From examination of the temperature dependent behavior of the relaxation time, the dynamic susceptibility and the specific heat a fragile to strong dynamic transition (FS) at circa $T=215$ K is located. The maximum found in the specific heat at the FS transition also shows evidence that this transition is related to the crossing of the Widom line indicating the presence a low density and high density liquid-liquid coexistence.

This study points out that experiments on confined water are extremely relevant for the comprehension of low temperature bulk properties and gives a strong evidence of a unifying scenario for supercooled water encompassing dynamics and thermodynamics.

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Molecular Dynamics Modeling of Proton Discharge at the Aqueous/Metallic Interface

Eckhard Spohr

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Abstract

An empirical valence-bond (EVB) model is developed in order to describe the transfer of a proton from aqueous solution bulk to a (charged) metal electrode surface. Results of density functional calculations are used for parametrizing the model for the Pt(111) surface. The EVB model makes possible large scale molecular dynamics (MD) simulations for a metal/electrolyte solution including Grotthuss style proton transport [1]. We have systematically studied the rate of proton discharge on negatively charged surfaces in the range of medium to large surface charge densities. The mean rate of transfer was analysed for proton trajectories which were started in the bulk of a water 1 nm adsorbed on the electrode. The results indicate a transition between a reaction-dominated regime at moderate negative charges, where the rate constant increases exponentially, to a diffusion controlled regime where the transfer rate is almost independent of the surface charge density (at more negative surface charge densities) [2].

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Thermodynamics and dynamics of hydration supercooled water.

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Abstract

New experiments for water at the surface of proteins at very low temperature are displaying intriguing dynamics behaviors. The extreme conditions of these experiments make difficult to explore the thermodynamics in order to offer an interpretation of the data, and hinder the thermodynamic equilibrium for detailed simulations for their large slowing down. We show how Monte Carlo simulations and mean field calculations help in this interpretation, revealing new exciting properties of confined supercooled water.

The aqueous proton at hydrophobic nano-scale interfaces

Udo Schmitt

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Abstract

The properties of hydrated protons are strongly influenced by the aqueous solvation phase. To understand in molecular detail how the proton transport properties change at aqueous interfaces we performed molecular dynamics simulations of the hydrated excess proton in hydrophobic confinement using the multistate empirical valence bond model. Specifically, we extract the determinants of proton transport through a coarse-grained hydrophobic nanopore by systematically varying the pore length and pore radius. The effect of the hydrophobic interface on various static and dynamical properties will be reported. The implication of our findings for the design of efficient proton conducting pores will also be discussed.

LIQUID WATER, THE "MOST COMPLEX" LIQUID: New Results in Bulk, Nanoconfined, and Biological Environments

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Coauthor(s) : S. V. Buldyrev, G. Franzese, S. Han, P. Kumar, M. Mazza, L. Xu, Z. Yan, S.-H. Chen and F. Mallamace

Abstract

This talk will introduce some of the 63 anomalies of the most complex of liquids, water. We will demonstrate some recent progress in understanding these anomalies by combining information provided by recent experiments and simulations on water in bulk, nanoconfined, and biological environments. We will interpret evidence from recent experiments designed to test the hypothesis that liquid water may display "polymorphism" in that it can exist in two different phases -- and discuss recent work on water's transport anomalies [1] as well as the unusual behavior of water in biological environments [2]. Finally, we will discuss how the general concept of liquid polymorphism [3] is proving useful in understanding anomalies in other liquids, such as silicon, silica, and carbon, as well as metallic glasses, which have in common that they are characterized by two characteristic length scales in their interactions.

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Collapse transition of hydrophobic polymers in a simplified water model.

Sergey Buldyrev

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Abstract

We examine the behavior of a bead-on-a-string hard sphere polymer in molecular dynamics simulation in a solvent whose particles interact via the Jagla potential, a spherically symmetric ramp potential with two characteristic lengths: an impenetrable hard core and a penetrable soft core. The Jagla fluid has been recently shown to possess water-like structural, dynamic, and thermodynamic anomalies. We find that Jagla

model also exhibits water-like solvation properties. The polymer dissolved in the Jagla liquid exhibits swelling upon both cooling and heating at fixed pressure or upon pressurizing at fixed temperature. This behavior resembles protein denaturation. The swelling at low temperatures happens as a first-order like phase transition associated with complete dewetting of the collapsed polymer globule. The thermodynamics of the swelling transition is compared with the predictions of the theory of hydrophobicity at large scales.

***A new method for determining the interfacial molecules in computer simulations.
Application to liquid-vapor and liquid-liquid interfaces***

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Abstract

Detecting the intrinsic interface and identifying the molecules located right at the interface (i.e., at the boundary of two phases) in a computer simulation, although being a non-trivial task, is a pre-requisite of getting reliable, systematic error-free information on the properties of the interface by simulation methods. Here we present a new method to identify the truly interfacial molecules (ITIM) at fluid/fluid interfaces seen at molecular resolution. In the new method the surface is scanned by moving a probe sphere of a given radius along a large set of test lines that are perpendicular to the plane of the interface. The molecules that are hit by the probe spheres are regarded as interfacial ones, and the position of the test spheres when they are in contact with the interfacial molecules give an estimate of the surface. The dependence of the method on various parameters, in particular, on the size of the probe sphere is discussed in detail. Repeating the entire procedure without the molecules already identified as interfacial ones, the molecules constituting the second (third, etc.) molecular layers beneath the interface can also be identified. The new method is applied for the analysis of the molecular level structure of the liquid-vapor interface of water, aqueous solutions of methanol and acetonitrile, and of the liquid liquid interfaces of water with CCl₄ and CH₂Cl₂. Using the ITIM method allows us to analyze two-dimensional percolation properties, average residence times and orientational preferences of the molecules separately in each of the consecutive molecular layers beneath the surface, as well as to determine the composition, width and molecular scale roughness of these monomolecular layers. As an immediate result of the application of the new method it is shown that the orientational preferences of the interfacial water molecules depend only on the local curvature of the interface, and hence the molecules located at wells of concave curvature of the rippled surface prefer the same orientations as waters located at the surface of small apolar solutes. The vast majority of the truly interfacial water molecules are found to form a strongly percolating two dimensional hydrogen bonded network at the surface, whereas no percolation is observed within any of the following molecular layers. In general, the properties of the first molecular layer turns out to be significantly different from those of the following ones in various respects, whilst the consecutive subsurface layers are found to be practically identical to each other.

Water in Nanopores

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Abstract

In this talk, I shall consider water confined to different types of pores micro/mesopores disordered/ordered, hydrophilic/hydrophobic. First, I will focus on water in microporous porous oxides: silicalite, a silica zeolite with $\varnothing_{\text{pore}} \sim 5 \text{ \AA}$ and tobermorite, a layered calcio-silicate model of cement at the nanoscale with

interlayer spacing $H_{\text{pore}} \sim 5 \text{ \AA}$. Molecular configurations in both environments were first obtained from Grand Canonical Monte-Carlo simulations (GCMC) with empirical water-water and water-substrate potentials and subsequently used in periodic CRYSTAL ab initio calculations. We found that confined water molecules in silicalite have a dipole value $\sim 10\%$ smaller than that in the 3D liquid phase indicating that the environment felt by a confined water molecule in silicalite pores is not equivalent to that in the bulk liquid providing a rationale for explaining the hydrophobic character of all-silica zeolites. By contrast, in the case of tobermorite, the dipole moment of confined water molecules is larger than the bulk values indicating the strong interaction of water molecules with both interlayer calcium ions and charged calcio-silicate lamellae. The general conclusion of this work is that classical simulations of polar molecules such as water in ultra confining environments have to rely on polarizable water potentials in order to capture essential physical features.

The second part of this talk will be devoted to the thermodynamics and dynamics of water in mesopores ($\varnothing_{\text{pore}} \sim$ a few nm). We'll start by considering the water adsorption (and/or) condensation in silica slit pores with pore sizes of 1, 2 and 4 nm at 300K, using a Grand Canonical description with classical water-water and water-substrate potentials. The thermodynamic aspect of this work will be approached by adsorption/desorption isotherms and isosteric heat versus coverage functions. This allows obtaining hints on the role of confinement with respect to adsorption and capillary condensation phenomena. Structural information is obtained from analyzing density and pair distribution functions. The dynamic properties such as self-diffusivities and time correlation functions are obtained from NVT-MD simulations using GCMC configurations. In particular with we can identify three different characteristic times for confined water molecules that depend on pore size and pore filling hence water vapor pressure. Finally, I will consider water confined in vycor, a mesoporous silica glass in order to evaluate the role of textural disorder on water adsorption/condensation thermodynamics. The salient result of this work is the finding that water capillary condensation/evaporation phenomena in vycor can be well understood on the basis of a single-pore model.

Key References

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Density functional molecular dynamics calculation of the dissociation constant of liquid water

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Abstract

Calculation of the dissociation constant (pK_w) of liquid water using all atom density functional theory based molecular dynamics methods is a bench mark test for the computation of acidity constants in more complex aqueous systems. We have performed such a test using a recently developed proton insertion/removal method. Chemical species in this scheme must be explicitly defined by an appropriate classical force field chaperone potential. This enabled us to distinguish between a (hypothetical) Zundel and Eigen form of the solvated proton. The hydroxide anion is treated as a single species. The resulting BLYP estimate of the pK_w values for dissociation in Zundel and Eigen ion are 13.6 and 13.3 respectively. A separate calculation in which the Zundel ion is reversibly transformed into the Eigen ion confirmed that these two forms of the excess proton are practically degenerate in free energy and moreover thermodynamically not stable.

