C12-01 Keynote
Water – Structure and Origin of its Anomalous Properties
Lars G.M. Pettersson
FYSKUM, AlbaNova University Center, Stockholm University, S-106 91 Stockholm

I will discuss recent experimental and simulation data from x-ray absorption (XAS), emission (XES) and scattering (XRD and SAXS) of liquid water and the picture of fluctuations between high-density (HD) and low-density (LD) liquid this leads to [1,2]. Such a two-liquid scenario would explain many anomalous properties, but no direct connection has been found to simulations of ambient water. The inherent structure of TIP4P/2005 water shows a strict bimodality in terms of spatially separated HDL- and LDL-like environments at all temperatures and pressures with distributions in agreement with the conclusions from XAS and XES, i.e. 75% HDL and 25% LDL-like at ambient conditions [3]. Structural measurements in “No-Man’s Land” have recently been performed at the x-ray free-electron laser at SLAC by exploiting evaporative cooling in vacuum of micrometer-sized water droplets showing a continuous and accelerated development towards an LD liquid down to at least 227 K [4].


C12-02 Invited
Water from the liquid-vapor critical point to the putative liquid-liquid critical point according to the first principles
Feng Wang
Department of Chemistry and Biochemistry, University of Arkansas

Accurate pair-wise point-charge potentials for water were developed based solely on first principle information using the adaptive force matching method developed in the group. With such potentials, the thermodynamic properties of water were investigated from the liquid-vapor critical point at 647 K to the putative liquid-liquid critical point at 205K. Excellent prediction of heat of vaporization, radial distribution functions, surface tension, dielectric constant, melting temperature, and the temperature of maximum density was achieved with only first principle information as input. The determination of the surface tension and critical point requires proper treatment of long-range dispersion interactions. Water around the liquid-vapor critical point shows the Ising universality class behavior. When combined with the ion-water cross terms also developed with the adaptive force matching approach, good agreement with experimental solvation free energies was obtained.

C12-04 Invited
The melting temperatures of water in the first-principles molecular dynamics simulations and the dynamics of supercooled liquid
Hui Li
Institute of Physics Chinese Academy of Sciences

Along with the developments of the computational hardware and soft packages, the first-principles molecular dynamics simulation (FPMD) within the framework of density functional theory (DFT) has been widely used for simulating the behavior of liquid water, and very different results compared to the empirical water models have been obtained. One important issue is the melting temperature of DFT MD simulation is usually different from the empirical model, leading to anomalous dynamical properties.

In this presentation, I will introduce the measured melting temperatures of liquid water via various widely-used functionals, including the conventional GGA functionals, and Van de Waals corrected DFT-D functionals. It is found most GGA functionals
greatly overestimate the melting temperature of liquid water, and the performance of DFT-D is much better, but the melting point is still much higher than 273K. We also performed the FPMD simulations to intensively study the wetting behavior, diffusion of hydrated ions in bulk and carbon nanotubes, as well as interfacial ice systems at temperatures below (in the case of supercooled liquid) and above (normal water) the melting point. Significant differences in dynamics of supercooled liquid and normal liquid are found, due to the lower hydrogen-bond breaking rate in supercooled water.

C12-05
Freezing of Water Under Shock Wave Loading: A Molecular Dynamics Study
Anupam Neogi1, Nilanjan Mitra2
1Advanced Technology Development Centre, Indian Institute of Technology Kharagpur, Kharagpur-721302, India. 2Department of Civil Engineering, Indian Institute of Technology Kharagpur, Kharagpur-721302, India.

Atomic equilibrium molecular dynamics (EMD) were carried out to investigate phase transition of bulk liquid water at extreme condition when subjected to shock wave loading. Multi-scale shock technique (MSST) was utilized to investigate low (US=2.5 km/s) to strong (US=6.5 km/s) intensity shock response on an extended flexible three point model (SPC/E) up to 100 ns. Freezing of water (partial nucleation of ice VII lattice) was identified at nano-second timescale (~1.5 ns) for the shock velocity of 4.0 and 4.5 km/s without the need of external nucleators (such as quartz, as suggested by previous experiments). The thermodynamic pathway of phase transition from liquid water to ice VII was investigated using temporal variation of thermodynamic state variables, power spectrum analyses of O-H bond vibration along with temporal evolution of pair correlation function, g(r) between O-O, O-H and H-H atoms. Temporal evolution of interpenetration distance of the two SC lattices (distance between first peak to the minor shoulder peak in O-O RDF curve) suggested that nucleated ice VII at US=4.0 km/s is more stable than for the shock velocity of 4.5 km/s.

C12-06 Invited
Molecular-Scale Hydrophilicity and Blockage of Water Flow due to Non-Covalent Interaction between Hydrated Cations and Carbon Structures
Guosheng Shi, Yue Shen, Jian Liu, Jian Liu, Haiping Fang
Devision of interfacial water, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China.

Based on the density-functional theory (DFT) calculations, we have incorporated cation-π interactions into classic all-atoms force fields [Sci. Rep., 3, 3436 (2013)]. In this talk, we will show the molecular-scale hydrophilicity on macroscopic hydrophobic carbon-based surface [Sci. Rep., 4, 6793 (2014)] and blockage of water flow in carbon nanotube (CNT) induced by cation-π interactions between hydrated cations and π electron-rich aromatic rings in carbon-based surfaces. We find a molecular-thick aqueous solution pancake can be formed on the carbon-based surface when the NaCl solutions are removed from the surface under ambient conditions. This indicates the unexpected molecular-scale hydrophilicity of the salt solution on the graphite surfaces, which is different from their macroscopic wetting property of a droplet standing on the surface. The key to the formation of such pancakes is attributed to cation-π interactions between hydrated Na⁺ in the solution and aromatic rings on the graphite surface. It has been further confirmed in the experiment. Further, we show that cations may block the water flow through the CNTs due to the cation-π interactions. Based on the study, we propose the methods to prevent the blocking of the nanotube by cations, including saturating their ends or applying electric fields.

C12-07 Invited
Water wetting and transport at atomistic scale
Sheng Meng

The surface wetting phenomena at the atomic scale might be different from those observed macroscopically. Conventional measure of hydrophilicity, such as contact angles, may not be applicable in such a circumstance. In this talk I will introduce and discuss the concept of atomistic scale wetting, answering questions such as what are the differences and how do we describe them. Insights from molecular dynamics simulations will be presented. Time allowed I will also discuss implications on water transport and water photosplitting. In particular, we investigate the microstructure of water flow through two-dimensional model graphene and graphene membrane containing a variety of nanopores of different size by using molecular dynamics simulations. Our results clearly indicate that the continuum flow transits to discrete molecular flow patterns with decreasing pore sizes. While for pores with a diameter ≥15 Å water flux exhibits a linear dependence on the pore area, a nonlinear relationship between water flux and pore area has been identified for smaller pores. We attribute this deviation from linear behavior to the presence of discrete water flow, which is strongly influenced by the water membrane interaction and hydrogen bonding between water molecules.


C12-08 Invited
Modeling shallow water flows through solid obstacles with windows
Alexander Kurjanov
Mathematics Department, Tulane University, 6823 St. Charles Ave., New Orleans, LA 70115, USA

When floodings occur in urban areas water may flow into houses and other objects through windows. In order to model such situations, we study water flows though solid obstacles with windows. Our goal is to design a highly accurate and robust numerical method for the such flows. We note that in most practical situation when the obstacles are walls of houses or other urban structures, the size of a spatial grid will have to be taken much larger than the width of the walls. We therefore assume that the considered obstacle is infinitely thin.

The flow away from the obstacle is modeled using the Saint-Venant system of shallow water equations. Near the window the single-layer is not valid and we model the flow there using the two-layer shallow water equations: When the water level rises above the upper edge of the window, the upper layer is getting reflected from the solid obstacle, while the lower layer flowing through the window. However, the two-layer shallow water system by itself is incapable of achieving this goal since the layer interface in this model is free and it may get either lower or higher at the window. We therefore develop a special strategy of switching back and force between the single- and two-layer shallow water systems and ensure that at the beginning of each time step the layer interface coincides with the upper edge of the window (obviously, in the case when the water surface level is above the upper edge of the window).

We design both 1-D and 2-D numerical methods for the proposed shallow water model of the flow through obstacles with windows. Our approach is based on the semi-discrete second-order central-upwind scheme scheme, which was originally designed for general hyperbolic systems of conservation and balance laws and then applied to both single- and two-layer shallow water systems. The central-upwind schemes enjoy such important properties as well-balanced (ability to preserve physically relevant steady states like the “lake at rest” ones) and positivity preserving (ability to ensure the water depth to remain nonnegative for all times) properties. We test the designed central-upwind scheme on a number of 1-D and 2-D numerical examples and obtain results that seem to be physically

Beijing National Lab for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
Email: smeng@iphy.ac.cn
relevant. Since to the best of our knowledge no benchmarks are available in the literature, we also conduct a laboratory experiment designed to verify the validity of the proposed model and numerical methods. We compare the experimental and numerical results, which are in a very good agreement.

C12-09 Invited

The Quantum Nature of the Hydrogen Bond

Xin-Zheng Li\textsuperscript{1}, Ji Chen\textsuperscript{1}, Ying Jiang\textsuperscript{1}, Angelos Michaelides\textsuperscript{2}, and Enge Wang\textsuperscript{1}

\textsuperscript{1}ICQM and School of Physics, Peking University, Beijing, P. R. China
\textsuperscript{2}London Centre for Nanotechnology and Department of Chemistry, University College London, London, U. K.

Hydrogen bonds (HBs) are weak, generally intermolecular bonds, which hold much of soft matter together. The small mass of hydrogen means that they are inherently quantum mechanical in nature, though all too often these effects are not considered. As a prominent example, a clear picture for the impact of quantum nuclear effects (QNEs) on the strength of HBs and consequently the structure of hydrogen bonded systems is still absent.

Using ab initio path integral molecular dynamics (PIMD) \cite{1,2}, we show that QNEs weaken weak HBs but strengthen relatively strong ones \cite{1}. This correlation arises from a competition between anharmonic intermolecular bond bending and intramolecular bond stretching. This work rationalizes the influence of QNEs, which can result in either weakening or strengthening of the HBs, and the corresponding structures, across a broad range of hydrogen bonded materials. It provides a rule of thumb to estimate QNEs based on merely classical knowledge, and highlights the need to allow flexible molecules when anharmonic potentials are used in force field-based studies.

\cite{1} X. Z. Li, B. Walker, A. Michaelides, PNAS 108, 6369 (2011)  