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EDITORIAL

Physics and chemistry of water and ice

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Water in its various forms is fascinating to all of us, either when walking on a glacier on high mountains, when swimming in the sea, or simply when looking at clouds. We all know that we must drink water every day, so no explanation is needed for the fact that we need water to stay alive. We learned in school that water is a molecule made up of two hydrogen atoms and one oxygen atom. Since water is important and simple, one would expect that basically everything is known about water, both in its liquid and in its solid form, ice. We certainly know quite a bit about water, but our understanding of its properties, both as a pure substance and as a solvent, is far from complete. It is impossible to cover in just one issue the vast amount of current research on water. In this special issue devoted to the physics and chemistry of water and ice, several examples of ongoing research on water are presented, offering a glimpse on the many questions that remain to be understood about this molecule.

When liquid water is cooled at atmospheric pressure, it usually freezes into ice when the temperature reaches 0 °C. This ice, available in household refrigerators and ubiquitous in the form of snow, is hexagonal ice *I_h*. In ice *I_h*, the molecules of water form an ordered lattice of oxygen atoms while the hydrogens are disordered. But this is not the only solid form of water. In the course of the 20th century 16 different crystal phases

(polymorphs) have been found for water. In this issue, two new types of solids are proposed that may one day be found experimentally: a plastic form at high temperature and pressure (Tanaka and coworkers, DOI: 10.1039/c1cp21871a), and a proton-ordered form related to cubic ice *I_c*, at low temperature (Slater and coworkers, DOI: 10.1039/c1cp22506e).

Under carefully-controlled experimental conditions, water can remain as a liquid below the melting temperature. Under these circumstances, water is metastable with respect to ice, and it is called supercooled water. It is well known that liquid water behaves rather differently from other liquids (for instance, it expands when cooled below 4 °C), and this odd behaviour becomes even more evident in the supercooled regime. In 1976 Speedy and Angell¹ showed that the isothermal compressibility increases markedly when water is supercooled, and they suggested the existence of a divergence at low temperatures. The divergence could not be measured since water freezes “instantaneously” when cooled down to the homogeneous nucleation temperature *T_H*. Since confinement can suppress freezing, insights into the dynamic behaviour of supercooled water can be obtained from experiments on confined water, as reported in the paper by Ricci and coworkers (DOI: 10.1039/c1cp22029b). Nowadays research on water is also done with computers. The advantage of using computer simulations to study supercooled water is that they offer atomic-level length-scale resolution, while accessing time scales long enough for equilibration yet too short for crystallisation. Some results on the dynamics of supercooled water are presented by Jedlovsky and coworkers (DOI: 10.1039/c1cp21850f), and microscopic mechanisms of heat transfer are considered by Bresme and

coworkers (DOI:10.1039/c1cp21895f). In 1992, Poole *et al.*,² using the ST2 model to describe water interactions, proposed the existence of a second critical point in the deeply supercooled region, with two coexisting liquid phases below the critical temperature, high-density and low-density liquids (HDL and LDL, respectively). This scenario is therefore intimately related to the Speedy–Angell divergence. In this issue Sciortino *et al.* (DOI: 10.1039/c1cp22316j) revisit the problem 20 years later, providing further evidence of the existence of the second critical point for the ST2 model. It is interesting to note that the behaviour outside the critical region is also affected by the critical point. In fact, the isothermal compressibility of water exhibits a maximum and the locus of such maxima in response functions has been called the Widom line. The Widom locus becomes a single line only very close to a critical point, the loci of heat capacity and compressibility extrema being distinct sufficiently far away from criticality. Using a geometric criterion, Wikfeldt *et al.* (DOI: 10.1039/c1cp22076d) show that, along the compressibility-based Widom line, the populations of water molecules having HDL- and LDL-like structures are approximately equal. In addition, Huang *et al.* (DOI: 10.1039/c1cp22804h) present experimental results on the structure of liquid water at ambient temperature and pressure which they interpret using the concepts of HDL and LDL. The possibility of determining thermodynamic properties of supercooled water and of testing the second critical point hypothesis is connected to the important question of the time required to nucleate ice, as compared to the time required to equilibrate supercooled water. Ice nucleation is studied here by Molinero and coworkers (DOI: 10.1039/c1cp22022e) and also by Li *et al.*

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(DOI: 10.1039/c1cp22167a), using in both cases the mW coarse-grained water model.

When comparing simulation results to real water it is important to bear in mind that water interactions are only approximately described by models, and different models may lead to different conclusions (that would explain, for instance, the possible differences between the behaviour of ST2 and mW models). Thus the development of water models that attempt to reproduce as closely as possible the properties of real water is an active area of research. The first modern water model was proposed by Bernal and Fowler in 1933 and described water interactions using a Lennard-Jones centre and discrete Coulombic charges.³ Such models have been studied computationally over the past 40 years, and a new model is proposed in this issue by Alejandro *et al.* (DOI: 10.1039/c1cp20858f). The state of the art of rigid non-polarisable water models is discussed in a Perspective paper by Vega and Abascal (DOI: 10.1039/c1cp22168j). More sophisticated ways of describing water interactions can be achieved, either by including polarisation as in the new model proposed by Viererblova and Kolafa (DOI: 10.1039/c1cp22198a), or by using electronic structure calculations, such as density-functional theory (DFT), as shown here in the paper by McGrath *et al.* (DOI: 10.1039/c1cp21890e). Another route is to use very simple potentials to describe water interactions (coarse-grained models) to learn the essence of the physics of water as shown in a perspective article by Nezbeda and Jirsák (DOI: 10.1039/c1cp20903k). Such models use classical statistical mechanics to evaluate the probability distribution of the nuclei. However, nuclei are quantum particles and quantum statistical mechanics should be used to describe their distribution, as shown by Paesani (DOI: 10.1039/c1cp21863h). Nuclear quantum effects would also affect phase transitions, and it is of interest to implement methodologies allowing the calculation of fluid-solid equilibria, as described by Habershon and Manolopoulos (DOI: 10.1039/c1cp21520e).

Not only the fluid–solid transition but also the interfaces of ice are of interest. When ice is exposed to vapour, it typically develops a quasi-liquid layer

even at temperatures below the melting point. The motion of water molecules on the surface of ice is considered here in a contribution by Gladich *et al.* (DOI: 10.1039/c1cp22238d), and the possibility of accumulating protons on the free surface of ice (thus developing surface positive charges) is discussed by Devlin (DOI: 10.1039/c1cp21593k). The adsorption of acetone on the free surface of ice is the subject of the paper by Bluhm and coworkers (DOI: 10.1039/c1cp21493d). The study of the interface of water with other substances is important in order to understand several environmental and climate-related issues. Typically, water can be found as small droplets, aerosols, dispersed in the atmosphere. Quite often these aerosols contain not only water but also other substances. Here, three studies are devoted to aerosols. Darvas *et al.* (DOI: 10.1039/c1cp21901d) studied water on organic aerosols, and Bogdan *et al.* (DOI: 10.1039/c1cp21770d) present experimental results on phase transitions found in small water droplets containing ammonium sulfate. Finally, Alpert *et al.* (DOI: 10.1039/c1cp21844a) investigate the effects of the presence of biogenic cells in small water droplets on ice nucleation.

Since water is the “universal solvent”, it seems relevant to understand the properties of some important water solutions. In this themed issue some interesting examples are considered. The dynamics of water around ions is quite different from that of bulk water, as illustrated for F^- and I^- by Boisson *et al.* (DOI: 10.1039/c1cp21834d), and the same is true for water structure, studied here by Gallo and Rovere (DOI: 10.1039/c1cp22166c). Other substances as P_2O_5 also significantly modify the structure of water, and results are presented in this issue by Corti *et al.* (DOI: 10.1039/c1cp22185j) showing that the structure of P_2O_5 solutions at low temperatures is HDL-like. A very special type of ‘solution’ is that of gas hydrates, in which small molecules such as methane, carbon dioxide, or hydrogen are trapped within crystalline cages of water molecules. The hydrates are formed when the gas at moderate pressure is cooled in the presence of water. Hydrates are present on ocean floors and in permafrost, and they could eventually be used for the storage of hydrogen or for sequestration

of carbon dioxide. Not surprisingly, this issue includes several contributions dealing with hydrates. The properties of hydrates are studied from a microscopic point of view, considering thermodynamic and kinetic aspects (see the papers by Kusalik and coworkers (DOI: 10.1039/c1cp21810g), Walsh *et al.* (DOI: 10.1039/c1cp21899a), Gorman *et al.* (DOI: 10.1039/c1cp21882d) and Finney and Rodger (DOI: 10.1039/c1cp21593k)). A new method to obtain CO_2 hydrates that does not require the application of pressure and which uses amorphous water is reported by Loerting and coworkers (DOI: 10.1039/c1cp21856e) and adhesion forces between hydrates and an organic solvent have been measured by Aman *et al.* (DOI: 10.1039/c1cp21907c).

Last but not least, water is the medium where life takes place, and it is commonly referred to as the matrix of life.⁴ Proteins, which contain hydrophobic and hydrophilic domains, are surrounded by water. Hydrophobicity has been shown to play a key role in determining the structure and phase behaviour of proteins. It is therefore not surprising that several contributions to this themed issue address the subject of hydrophobicity, either by itself, or in the context of the molecules of life. The interaction between amorphous solid water and a hydrophobic substrate (CCl_4) is considered by Smith and coworkers (DOI: 10.1039/c1cp21855g). The properties of water around hydrophobic solutes is studied by Koga (DOI: 10.1039/c1cp22344e). Proteins are used efficiently by several species to avoid the formation of ice, as discussed in a study by Nada and Furakawa (DOI: 10.1039/c1cp21929d). Luzar and coworkers (DOI: 10.1039/c1cp22082a) present results on a simple model to understand capillary evaporation within proteins, a phenomenon that is believed to play an important role in the folding of such molecules. Finally Paschek and Garcia (DOI: 10.1039/c1cp22110h) show that water is not simply a spectator when considering the folding of a protein. The subtle balance of hydrogen bonds between the protein and water plays a key role in determining the folded state. The above examples all involve water at interfaces, the dynamics of which are considered by Stirnemann *et al.*

(DOI: 10.1039/c1cp21916b) from both theoretical and computational perspectives for a range of hydrophilic surfaces.

This issue brings together just a few examples highlighting the many different aspects of contemporary research on the physics and chemistry of water and ice. We hope that the reader will have a flavour of current research and of the many still unsolved problems related to water. We would like to thank all of the authors for their valuable contributions to this issue. We would also like to express our gratitude to Helen Gray of the Royal Society of Chemistry, for her valuable assistance on all editorial matters. A consequence of working on

this issue was that our 2011 summer was slightly shorter than usual (fewer days to enjoy real sea water). We hope that the result will prove to be worthy of the temporary deprivation. In any case, and taking into account that the three guest editors of this theme issue are native Spanish speakers, we would like to finish with the initial sentence of the novel "One Hundred Years of Solitude" by the Nobel Prize winner Gabriel Garcia Marquez: "Muchos años después, frente al pelotón de fusilamiento, el coronel Aureliano Buenda habría de recordar aquella tarde remota en que su padre lo llevó a conocer el hielo". In our case, we can still remember the afternoon when

we became attracted by the physics and chemistry of ice and water, and decided to invest a substantial part of our lives investigating the fascinating properties of this substance. We can only hope that, unlike Colonel Buendía, we will not face the firing squad.

References

- 1 R. J. Speedy and C. A. Angell, *J. Chem. Phys.*, 1976, **65**, 851.
- 2 P. H. Poole, F. Sciortino, U. Essmann and H. E. Stanley, *Nature*, 1992, **360**, 324.
- 3 J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, **1**, 515.
- 4 F. Franks, *Water a Matrix of Life*, RSC Publishing, 2nd edn, 2000.