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Jacob Israelachvili in his famous book *Intermolecular and Surface Forces*[1] writes—commenting on the observed increase in the dielectric constant and in the proton conductivity on freezing—that "to understand the secrets of liquid water one may first have to unravel those of ice." This Special Topic on the "Chemical Physics of Supercooled Water" in *The Journal of Chemical Physics* has been ideated, planned, and realized with the idea that not ice, but supercooled water, holds promises for unravelling the peculiar physics originating from the directionality and the strength of the water-water interaction. It is in supercooled states that the famous thermodynamic anomalies of water show up in full glory. Indeed in water, differently from other liquids and despite the reduction in thermal vibrations, fluctuations in density and enthalpy significantly rise on cooling, as revealed by the temperature dependence of the compressibility and specific heat. Supercooling thus acts as a magnifying lens allowing us to explore the origin of water's peculiar dynamic and thermodynamic behavior. However, the study of supercooled water is often hampered due to its metastability with respect to crystalline ices. Especially, if long measurements are required, it is only possible to study supercooled water down to temperatures of 255 K as in Ref. 2 on D_2O expansivity, or to 235 K as in the study of the O–O radial density functions.[3] Crystallization rates rise so rapidly with decreasing temperature that a boundary for the possibility to study supercooled water has been set, below which noncrystalline water can no longer be studied. This boundary is, however, only a soft limit and depends on the timescale, where typically minutes or seconds are used to set the line. An understanding of nucleation and ice growth is of key importance in this context.[4–7] When beating crystallization through ultrafast cooling of liquid droplets or through vapor-deposition of water on cold substrates, the amorphous solid state can be reached. Such amorphous samples may also crystallize, since crystallization rates rapidly increase upon heating, typically near 150 K. References 8 and 9 go beyond this limit and determine nucleation and crystallization rates in transiently heated films for temperatures up to 230 K.

In order to be able to measure the properties of noncrystalline water in its "no-man's land," quite often, solutes and/or confinement are employed instead of ultrafast experiments. References 10–13 employ salt solutions, Ref. 14 investigates polyalcohol solutions, Ref. 15 studies the monoalcohol methanol, and Ref. 16 studies the cryoprotecting sugar trehalose. References 17–19 study supercooled water in confinement, and Ref. 20 even combines the two strategies, putting confined salt solutions under scrutiny.

While it is appealing to study confinement and aqueous solutions because water rarely occurs in its pure form in nature, care needs to be taken to extrapolate from such studies to the properties of pure H_2O. Certainly, many of water's properties are affected by confinement, and it is even possible to render water unfreezable due to the interaction with its surroundings. This is often the case for hydration water, which is studied in Refs. 16 and 21–23.

In this collection the physical origins behind the increase in the density and enthalpy fluctuations are discussed.[24] The presence of distinct local structures, competing to minimise the Gibbs free energy, characterised by differences in their local density and local potential energy may provide an accurate modelling of water's thermodynamics.[2,25–27] Some of the articles discuss how to identify these structures,[3,28–30] how to distinguish them from ice-like structures,[31] and how to decipher their contribution to the anomalies of water.[32]

Central in this line of research is the detection of correlation between the spatial ordering of these local structures, a correlation that would indicate the possibility of a true phase separation in the no-man's land.[26,33–35] Beside temperature and pressure changes, perturbation of the water network via addition of small solute molecules,[10–12,14,20,36] even active ones,[37] offers an alternative way of shifting the equilibrium between different local structures in a controlled way.

Supercooled water can also be studied in a tiny temperature window above the glass transition temperature, just before crystallization takes place. Below the crystallization line, noncrystalline water can be studied as an amorphous solid or as an ultraviscous liquid in a tiny window above the glass transition temperature. In this low-temperature regime, first-order like transitions occur, where the density changes suddenly by 25%. By contrast, supercooled water above the no-man's land does not experience such a transition, but rather a continuous change. That is, one cannot speak about two distinct types of liquid water above 200 K as pointed out in Ref. 38, but this could be different near 150 K. The reversible interconversion between the low- and high-density amorphous ices is thought to be low temperature proxy of a possible liquid-liquid transition that might take place just below the crystallization line and within the no-man's land.

Several articles in this collection are devoted to the study of water polyamorphic structures and to the connections, if any, of these structures with the liquid state. Amorphous states can be generated by vapor deposition, hyperquenching, pressure amorphization,[39] and interconversion of different amorphous states.[40] Also, in this low-temperature regime, aqueous solutions may be employed to possibly reach higher temperatures without crystallization. The stable crystalline structures are then often clathrate hydrates or even chiral hydrates rather than ice I_h or high-pressure ice phases, and so the study of hydrates and their behavior in comparison with pure ices and supercooled water is of interest.[30,39,41–43] The relation of the sharp polyamorphic transition with a possible first order liquid-liquid transition is tackled in this special topic from quite different angles.[2,10,14,27,40,44,45] Needless to say, the investigation of out-of-equilibrium systems requires novel experimental[41] and theoretical approaches.[44,45]

The investigation of ice,[46] ice nucleation, and ice growth rate[4–9,47] as a function of temperature, pressure, and impurities is another crucial topic discussed in the collection, a topic of relevance for basic science research and climate models, as well as for weather forecasts. In fact, the question whether clouds remain supercooled, crystallize partly or fully, and whether the droplet freezes from the inside outwards or from the outside inwards are crucial for our understanding of their reflective properties, which govern the cooling effect that clouds have on our climate. Indeed, water droplets in the atmosphere are often in metastable conditions. This requires control of the proper order parameters[31] and of several delicate quantities[48] entering in the nucleation rate.

The glassy dynamics of water molecules in supercooled states is also a key feature to understand water's complex behaviour. In fact, thermodynamic and structural modifications that water undergoes upon supercooling in the bulk phase, in confinement and in solutions—including solutions of biomolecules—strongly affect the slow dynamics and the dynamic crossovers observed in water upon decreasing temperature. This topic is here discussed in bulk, under confinement and in solutions,[12,13,15,17,19,49] as well as in the proximity of biomolecules.[16,21–23,50,51] These articles focus on glassy dynamics (both α and secondary relaxations) in pure and in biological-hydration water. Some articles also study the onset of a super-slow relaxation connected to the coupling with the dynamics of the biomolecule. The influence of hydrophobicity on the diffusion of small spheroidal particles is discussed in Ref. 52.

In total, the present collection encompasses 51 articles, testifying the importance of water and aqueous solutions in sciences and our environment, both on Earth and in space. The research described in these articles certainly helps to push the forefront of our understanding of the chemical physics of supercooled water. Nonetheless, more questions than the ones answered still remain open, as pointed out in several concluding sections in this collection. In this sense, this special collection will hopefully be a stimulus for further research and trigger scientific discourse that will bring the field forward.

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